A dissertation submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

Application of Electro-flotation Method to Agricultural and Livestock Wastewater Treatment

（電気浮遊法の農畜産排水処理への適用）

By

Enjeh Yoland Fobang (19DE061)

Saitama University
埼玉大学

Supervisor: Professor Takeshi Fujino

Graduate School of Science and Engineering

Saitama University

March 2023

DEDICATION

This work is the fruit of countless efforts and sacrifices. Through the researchers' effort, this work is heartily and proudly dedicated to the people who serve as an inspiration. From parents and guardians to classmates and circle of friends who extended their help during problems doing this work. Above all, to our God Almighty who showered us His blessings in our doing this work. Above all, to our God Almighty who showered us His blessings in our everyday lives, especially for the strength, courage, patience, wisdom, time, and guidance in realization of this work.

LIST OF ABBREVIATIONS

$AlCl_3$	Aluminum Chloride
CPAM	Cationic Polyacrylamide
EF	Electroflotation
POME	Palm Oil Mill Effluent
EC	Electrocoagulation
EO	Electrooxidation
COD	Chemical Oxygen Demand
BOD	Biological Oxygen Demand
ζ	Zeta potential (V)
σ	Electrical conductivity (S/m)
F	Faraday’s constant (96,500 C/mol of electrons)
I	Local current (A)
j	Current density (A/m^2)

Abstract of the dissertation

Chapter 1 explains the current situation of palm oil mill effluent (POME) and livestock manure which includes; the huge amount of POME and livestock wastewater produced and are often discharged to the environment as a cheap method of disposal which destroys the ecological resources and functions, endangers aquatic ecosystems, and affects human health. Because of this, the crude palm oil industry and livestock farms are developing several industrial ecosystem practices for waste recycling. Chapter 2, is all about literature review on the diverse ways to solve these wastewaters. The most used treatment processes are gravity separation, hydrocyclone, flotation, coagulation/flocculation, biological treatment, membrane separation, adsorption, and advanced oxidation processes. However, these methods have some limitations. Microorganisms may not be tolerant of aromatics and heavy metals in wastewater for the activated sludge method. High maintenance and energy requirements due to membrane contamination. A chemical treatment that relies on chemical agents is prone to secondary pollution and is more harmful to food and the environment. Cyclone separators cannot separate tiny oil droplets from wastewater shown in. In contrast, electroflotation process is an economical and environmentally friendly method and an attractive alternative, high efficiency in promoting separation of solid from liquid phases or one liquid phase from another, even with the smallest particles separated from a liquid, due to uniform and tiny or micro bubbles of hydrogen and oxygen generated at the electrode's surfaces during electrolysis of an aqueous solution. As a result, electroflotation has become a hot topic for researchers and many oil fields and water treatment plants

In chapter 3, platinized titanium anode and steel cathode were used as electrodes in the electrocoagulation system. Results in chapter 3 showed that, 15 min electrolysis time, current density 0.55A/cm2 could reduce cationic polyacrylamide demand from 120ppm to 80ppm at fixed aluminum chloride 200ppm, showing 99.1% turbidity and 90.7% chemical oxygen demand efficiency removal at the cost of 1.13 yen (0.0078USD). From the electroflotation system, gas bubbles and metallic ions enhanced organic pollutant removal through flotation and coagulation, respectively. Hydrogen and oxygen gas bubbles increased dissolved hydrogen to 257 ppb and dissolved oxygen to 14.47 bppm. Metallic ions increase zeta potential to –13.9 mV. However, in this chapter, the experiment showed by observation, flotation of suspended solid did not occur

when an electrocoagulation system unit was used with a filter paper covering the cathode surface. Instead, flotation occurred without filter paper covering the cathode. Further experiments may be needed for a more practical stage in this chapter.

In chapter 4, dairy manure slurry was treated with aluminum (Al) coagulants, such as polyaluminum chloride (PAC), aluminum chloride (AlCl3), and aluminum sulfate (Al2(SO4)3), PAC combined with the cationic polyacrylamide (CPAM), and PAC and CPAM combined with electrocoagulation (EC). Platinized titanium cathode and stainless-steel anode were used as electrodes in the electro-coagulation system. Results revealed that PAC was the best among the Al coagulants evaluated for the reduction in turbidity in the liquid fraction at a dosage of 100 mg/L. PAC dosage was reduced to 40 mg/L when the treatments were combined with CPAM at a dosage of 40 mg/L, which was further reduced to 30 mg/L when treatments were combined with 5 min EC and 20 mg/L of CPAM dosage

In chapter 5, Platinized titanium anode and stainless-steel cathode were used as electrodes in the electroflotation system. EF treatment at a current density of 5 A/cm^2 achieved 82% of turbidity and 52% of chemical oxygen demand (COD) removal efficiency after 45 min electrolysis time, consuming 0.035 kWh of specific energy for the treatment of one kilogram of COD. When EF combined with 40 mg/L dosage of PAC and 20 mg/L dosage of CPAM, it was noticed that turbidity and COD removal were enhanced to 96 and 54% efficiency, respectively within 15 min electrolysis, subsequently the specific energy consumption was reduced to 0.004 kWh per one kilogram of COD treatment. Results confirmed that the chemical coagulants could increase the POME treatment efficiency and reduce specific energy consumption of EF.

In conclusion, EF and chemical cationic coagulants could be beneficial when used in a hybrid in the treatment of cow manure and POME wastewater. This is because EF shows the benefit of not using chemical coagulant making it an environmentally friendly method and can reduce chemical coagulant in hybrid treatment, however it uses high energy which could be minimized by using it with a limited amount of chemical cationic coagulant.

Table of Content

CHAPTER 1. INTRODUCTION

Increase in global population and industrialization has resulted in an increase in livestock and palm oil production. Livestock wastewater and POME are wastewater produced from livestock farms and palm oil mill industries respectively, which have a high concentration of organic content that can cause environmental pollution. Recently, livestock wastewater and POME environment and health hazards are getting worse, especially in larger farms and rural areas, passively affecting the quality of soil, groundwater, and air, and even threatening public health. On the contrary, livestock wastewater and POME when treated can produce some valuable materials such as fertilizer or energy. Recycling livestock wastewater and POME in agroecosystems to partially substitute synthetic fertilizer can alleviate the environmental degradation, which may also increase food security and reduce greenhouse gas (GHG) emissions. In this chapter the current situation of livestock and palm oil in Asia and Africa, characteristics and composition of livestock wastewater and POME, with their environmental and health hazards and the importance of livestock wastewater and palm oil effluent recycling (POME) will be discussed in detail.

1.1.1 Past, current, and future situation of Livestock in Asia and Africa

According to a recent report, the world population has doubled in the last 40 years and reached 7.7 billion in 2019; with a current growth rate of 1.08% per year the population is estimated to reach 9 billion by 2037 **(Dadrasnia et al.2021**). Undoubtedly, this rapidly growing human population generates pressure on livestock production and subsequent consumption to satisfy the demand for protein. In the last 30 years, it was noticed that the meat consumption in South Asia, Southeast Asia and East Asia combined increased from about 36 to over 125 million tons and milk consumption from 60 to almost 220 million tons, that is by over 250% for both commodities **(Otte et al., 2019).** Currently in developing countries the consumers' demand for meat, milk and eggs has increased considerably and will continue to do so **(Oosting et al., 2014, Hu et al., 2020, Delgado., 2005)** Figure 1.1 and 1.2. Faced with such tremendous consumption, domestic stocking and small-scale livestock farms were incapable of multiplying the production capacity to satisfy the requirements of the population **(Hu et al., 2020).** To improve production ability and efficiency, more concentrated large-scale livestock farms have been set up in large numbers and more products have been produced. For example, large swine farms (> 500 heads) and cattle farms (> 100 heads) have increased from 126,600 and 22,500 in 2008 to 215,500 and 31,500 in 2017, respectively **(Hu et al., 2020).** This has brought about an increasing number of livestock wastewater having large amount of nutrients, heavy metals (HMs), organic matters, xenobiotics, and pathogens to be discharged from farms, and the amount of wastewater released into water bodies has been increasing, passively affect the quality of soil, groundwater, and air, and even threaten public health **(Hu et al., 2020).**

Trend of Livestock production in Asia and Africa

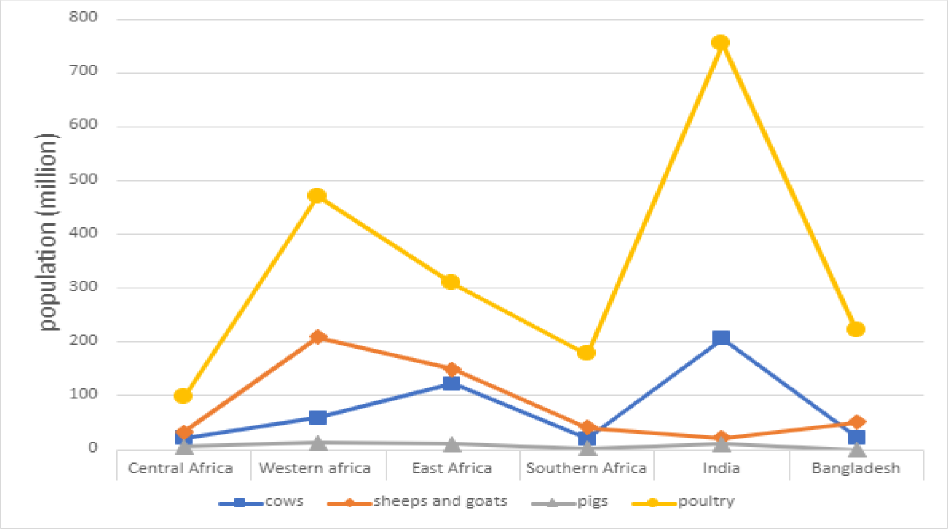

Figure 1.1 livestock population (numbers in millions) in Sub-Saharan Africa and South Asia Source: **(Oosting et al., 2014)**

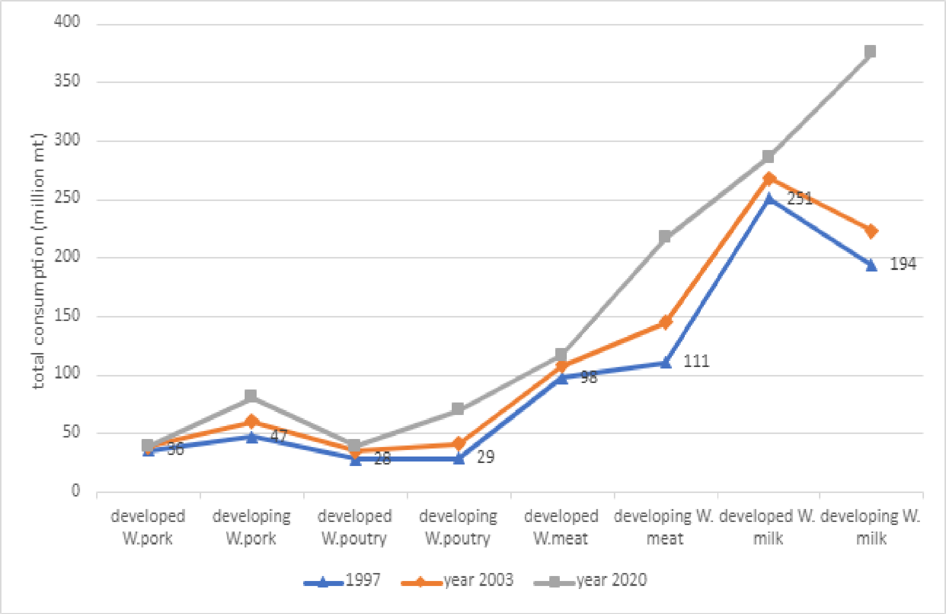

Figure 1.2. Projected food consumption trends of various livestock products Source: **(Delgado., 2005)**

It is currently recorded that Africa's livestock accounts for one-third of the global livestock population and about 40% of agricultural gross domestic product (GDP) in Africa, ranging from 10% to 80% in individual countries **(Mulubrhan et al., 2021)**. Livestock will be increasingly important in the future in sub-Saharan Africa (SSA) because the demand for animal-source food (ASF) is projected to increase due to population growth, increased incomes, and urbanization **(Mulubrhan et al., 2021)**. The predicted expansion of Africa's livestock sector and associated value chains may satisfy consumer demand but, if uncontrolled, could also have negative effects on public health, the environment, and livelihoods **(Otte et al., 2019)**.

1.1.2 Characteristic and composition of livestock wastewater

Livestock wastewater produced by livestock farms is referred to the total name of all excrement or residual excrement, urine, feed residue, washing wastewater, and wastewater generated during the life and production process of workers **(Hu et al., 2020, Musa et al., 2019).** Livestock wastewater is composed of dung and liquid. The liquid is future divided into urine and washed water. Tables 1.2 and 1.3 show the range of dung and urine per kg excreted per animal a day and the amount of water used in waste, respectively.

In general, livestock wastewater includes swine wastewater, poultry wastewater and cattle wastewater. As the quantities of livestock increase around the world, the total amount of livestock wastewater produced also gradually increases. For example, China and India produced more than 430 million cattle as of 2010, which accounted for 26% of the total numbers (1.625 billion) around the world **(Shen et al., 2018).** According to the calculation method of Tang et al. (2008), 6.01 × 107 tons of cattle wastewater could be generated in the world per year. Meanwhile, the worldwide population of swine was 7.09 × 108 heads according to 2018 statistics, and a total of about 2.38 × 106 tons of swine wastewater was generated throughout the year **(Nagarajan et al., 2019)**.

Table 1.2: Dung and Urine production by distinct species. **Source: (Parihar et al.2019)**

Animals	**Quantity of dung (kg/day/animal)**	**Urine (ml/kg bwt/day)**	**Urine (ml/kg bwt/day)**
Animal	Range	Average	Range
horse	9-18	13.50	3-18
cattle	18-30	24.00	17-45
buffalo	25-40	32.50	3-18

Sheep and goat	1-25	1.25	10-40
pigs	3-5	4.00	5-30
Poultry (100 birds)	2.5-3.5	3.00	-

Table 1.3: Water requirement for washing. **Source: (Parihar et al.2019)**

species	**Water requirement for washing (litters)/Animal/Day**
Cattle and buffalo	45-70
horse	36
pigs	25-28

High-concentration solids, volatile, organic matter, nutrients, and fecal coliforms are contained in livestock wastewater due to washing wastewater is the main source of wastewater, which resulted in a high-levels of hazardous contaminants in the effluent **(Cheng et al., 2018)**. As an example, swine wastewater has high total phosphorous (TP) of 100–620 mg/L, total nitrogen (TN) of 200–2100 mg/L, ammonia nitrogen (NH3-N) of 110–1650 mg/L, and chemical oxygen demand (COD) of 3000–30,000 mg/L **(Cheng et al., 2018; Cheng et al., 2019).** The concentrations of COD, NH3-N, and TP of cattle farm wastewater were range from 3000, 150, and 13.2 mg/L to 10500, 665, and 90 mg/ L, respectively **(Lv et al., 2018; Xia, et al., 2020)**. **Musa et al., (2019)** also said that cattle contaminant concentration had high COD (3102 ± 688 mg L−1) suspended solids (SS) (872 ± 178 mg L−1) total Kjeldahl nitrogen (TKN) (186 ± 27 mg (N) L−1), total phosphate (PO3− 4) (76 ± 36 mg L−1) color in Pt-Co 16,426.8 ± 334 and turbidity in formazine attenuation unit (FAU) (12,500 ± 76). In contrast, the concentrations of various pollutants in poultry wastewater are much lower compared with swine wastewater and cattle wastewater. It was reported by **Zheng et al. (2018)** that the concentration range of COD, TN, TP, and BOD5 of poultry wastewater was 320–919, 49–140, 7.6–24.5, and 160–370 mg/L. Such a vast number of pollutants will undoubtedly cause serious detriment to the ecological environment on which people depend.

Apart from organic matter pollutants, cow manure was reported to have been composed of 26% cellulose, 11% hemicellulose, and 11% lignin **(Zulkifli et al., 2018)**. Other researchers have reported that Cow manure has different minerals like nitrogen, potassium, along with trace amounts of Sulphur, iron, magnesium, copper, cobalt, and manganese. Example the indigenous Indian cow holds higher amounts of calcium, phosphorus, and copper than the crossbreed **(Gupta et al., 2016, Parihar et al., 2019)** Table 1.4.

Table 1.4. Cow dung content. Source**: (Parihar et al.2019)**

Cow manure content	**Percentage**
moisture	77%
Organic matter	20%
nitrogen	0.32%
phosphorus	0.14%
potassium	0.30%
calcium	0.40%

Cattle dung have also been reported to harbors a rich microbial diversity with varied species of bacteria (bacillus spp.), protozoa and yeast (Saccharomyces and Candida) **(Gupta et al., 2016),** and many different bacterial genera such as Citrobacter koseri, Enterobacter aerogenes, Escherichia coli, Klebsiella oxytoca, Klebsiella pneumoniae, Kluyvera spp., Morgarella morganii, Pasteurella spp., Providencia alcaligenes, Providencia stuartii and Pseudomonas spp. have been isolated from cow dung **(Gupta et al.2016)**

1.1.3 Environmental and health hazards caused by livestock wastewater

In recent decades, livestock farming activities have been widely increased to accomplish nutritional requirements, which inevitably lead to an increase the wastewater generation. Inappropriate disposal of effluents from livestock farms can create a nutrient surplus in neighboring lands, production of greenhouse gases such as methane (CH4) and cause numerous adverse effects on the environment (Hjorth et al. 2010, Zhang et al. 2022, Dadrasnia et al., 2021).

(a) <u>Environmental hazards</u>

A range of gaseous contaminants such as ammonia, hydrogen sulfide, and volatile acids contained in livestock manure are released together with the storage, treatment, and disposal of livestock waste. Also, greenhouse gases such as carbon dioxide and methane emitted from livestock can exacerbate the global greenhouse effect and seriously affect air quality g 35–40% of methane emissions worldwide. Methane has a 23-fold greater potential for global warming t **(Hu et al., 2020)**. In the third chapter of the FAO, it is estimated that 18% of global greenhouse gas emissions are caused by the livestock industry. The amount of carbon dioxide released into the atmosphere is estimated at approximately 7516 million tons per year. The livestock industry is still the second-largest polluter after the electricity industry, and more polluting than the transportation industry, which contributes approximately 13% **(Dopelt et al., 2019)**. Livestock are also a highly significant source of methane emissions, contributing to carbon dioxide. The U.S. Environmental Protection Agency has shown that in the last 15 years methane emissions from pigs increased by 37% and emissions from cattle increased by 50% **(Dopelt et al., 2019)**.

The livestock industry also leads to great resource waste, particularly water. In the U.S., for example, the amount of water consumed by private residences is approximately 5% of total consumption, while the amount of water consumed by animal agriculture is approximately 55% **(Dopelt et al., 2019)**. The water pollution is caused by animal excreta, antibiotics and hormones, fertilizers and pesticides used in forage production, and rainfall runoff from pasture. The U.S. Department of Agriculture (USDA) declared that animal parts and poultry manure are major sources of water pollution **(Dopelt et al., 2019).**

Livestock dung is an important source of plant nutrients but can cause substantial pollution of ecosystems if managed improperly. Negative environmental consequences of excess nitrogen (N) and phosphorus (P) comprise reduced soil fertility, water eutrophication, contamination of groundwater with nitrates and bio-diversity loss **(Tullo et al.,2019)**. In 2007, the total amount of manure produced by livestock worldwide was estimated at 22.5 billion tons. Globally, the nutrient budget of agriculture is dominated by the rapidly growing livestock sector with its low nutrient recovery. Total nitrogen and phosphorus released into the environment through manure from livestock now exceed global nitrogen and phosphorus applied in fertilizer **(Otte et al.,2019).**

Pathogenic microorganisms, which can cause various forms of gastrointestinal disease in humans and animals, can be considered as elements of soil and water pollution. Animal manure, in addition to nutrients, contains large numbers of microorganisms, which reside in the gastro-intestinal tract and are mostly part of the "normal" gut microbiome. Dairy cows for instance excrete 6 500 billion feeder pigs, 23 billion and layer chicken 1.8 billion coliform bacteria per day **(Otte et al.,2019)**. Some of the excreted organisms may be pathogenic to other livestock species and humans and may be transported to water through surface runoff and erosion or by direct animal access to surface water. Streams and lakes used for drinking water supply and recreational purposes provide the greatest opportunity for transporting these pathogens to humans **(Otte et al.,2019).**

(b) ***Health hazards***

The wide range of contaminants and bioaerosol released into the air, water bodies, and soil from livestock wastewater could significantly affect human health, especially for young children, senior citizens, gravidas, and people who are immunocompromised **(Hu et al., 2020).** Also, ammonia emitted from livestock wastewater will increase the burden on respiratory diseases, and hydrogen sulfide in lagoons may contribute to workers losing consciousness and, in severe cases, to death **(Hu et al., 2020).** Secondly, irregular reuse of livestock wastewater will increase the possibility of pathogens of zoonotic infectious diseases spreading among populations, which can lead to a range of illnesses such as cholera, diarrhea, and typhoid **(Hu et al., 2020).**

1.1.4 Importance of livestock wastewater recycling

The collection and use of livestock wastewater is central to developing a sustainable society. The negative impact on the environment of waste handling can be reduced if increasing amounts of livestock wastewater is to be recycled.

(a) ***Recycling livestock wastewater for agricultural benefits***

Evidence from many studies clearly indicates that the continuous application of chemical fertilizer causes serious environmental problems; such as groundwater pollution, deterioration of soil, and loss of nutrients. The replacement of chemical fertilizers by biowaste-based materials (such as bio fertilizer such as cow manure) has received much attention and is currently known as the green revolution **(Dadrasnia et al., 2021)**. Biofertilizers are rich in organic carbon and valuable nutrients and supply productive microbes to the soil after application. This helps to reduce the ecological disturbance caused during application when compared to chemical fertilizers **(Dadrasnia et al., 2021).**

Research has demonstrated that manure-based fertilization is an alternative to chemical fertilization, not only achieving high crop yields and improved soil quality, but also promoting sustainability and efficiency of agricultural ecosystems in the long term **(Köninger et al., 2021, Zhang et al.,2016)**. The use of chemical fertilizer is prohibited, especially for organic farming. Thus, the application of manure serves as a significant resource to replenish the organic matter content of cultivated soils and supplies plant nutrients **(Dadrasnia et al., 2021, Ndambi et al.,2019)** Figure 1.5.

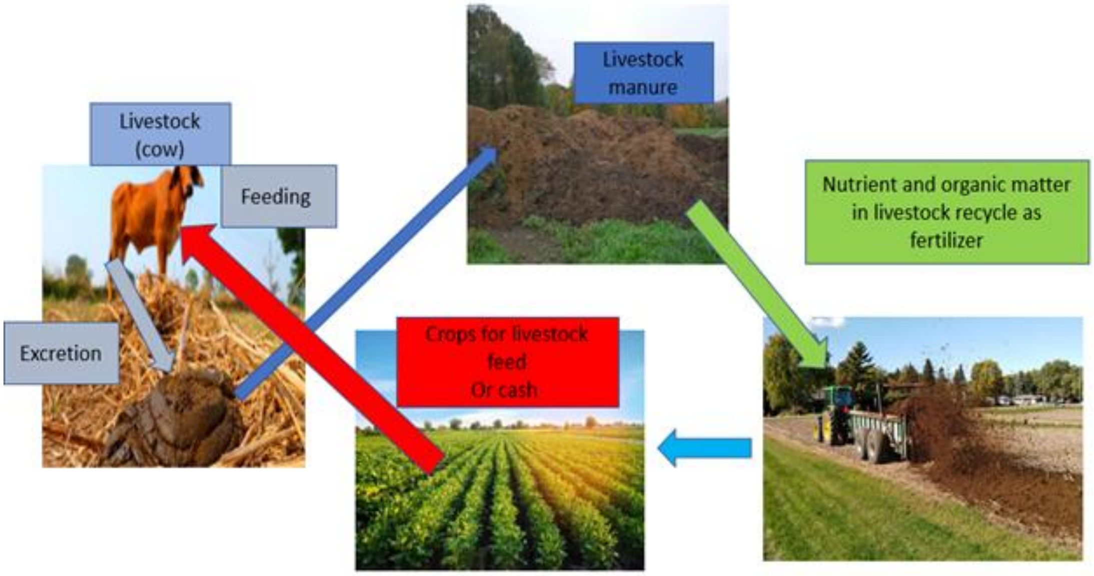

Figure 1.5. Nutrients recycling in crop livestock systems

Source**: (Ndambi et al.2019)**

(b) <u>Recycling livestock wastewater for energy benefits</u>

Human high dependency in fossil fuel sometimes leads to the crude oil price increment, and it is surged more rapidly. It is a huge burden for oil importing countries. In Indonesia, oil and gas is still the main energy source. Continuity in consuming fossil fuel will lead to dwindling of oil reserves. Based on that, renewable energy is needed. One of the renewable energy sources is biogas. These gases are derived from a wide range of organic wastes such as biomass, human, and animal waste through anaerobic digestion, and it can be used as energy. Production of biogas from animal manure, especially cow is very potential and has an advantage, energy derived from it is very environmentally friendly since in addition to utilizing the waste from livestock, left over from the process (biogas slurry) can be used as organic fertilizer that is rich in the elements required by plants. The use of biogas also can reduce atmospheric greenhouse gases and other emissions **(Artanti et al.2012).**

1.2.1 Problems of Oil Palm Processing in Africa.

The African oil palm, Elaeis guineensis, is native to West Africa and in terms of agriculture, it is the world's most important palm species **(Murphy et al.2021, Amugoli et al.2022)**. Oil palm originates from West Africa, in the Niger delta, particularly in the belt between Guinea and North Angola in West and Central Africa (**Amugoli et al.2022)**. It spread widely in the Palm belt of Africa through Sierra Leone, Liberia, the Ivory Coast, Ghana, Togo, Benin, Nigeria, Cameroon, and the Democratic Republic of Congo (formerly Zaire) (**Amugoli et al.2022)**. Through large-scale commercial and small-scale household plantings, oil palm has now been introduced to countries like Burundi, Equatorial Guinea, Ethiopia, Gabon, Gambia, Liberia, Madagascar, Mozambique, Sao tome and Principe, Tanzania, and Uganda where environment and climatic conditions are suitable (**Amugoli et al.2022)**. 2019 data suggests that palm oil production as a percentage of the global output was only about 3% for West Africa and 4% for Africa. The major palm oil production countries in Africa are Nigeria (43%), Cote d'lvoire (17%), Ghana (13%) and Cameroon (11%) (**Awere et al.2022).** During the nineteenth century, oil palm seeds were transported to the Dutch East Indies (modern Indonesia), and to the Malay States (modern Malaysia), as part of colonial ventures to grow newly introduced cash crops in the region. During the twentieth century, more systematic oil palm cultivation on plantations gradually became established in the Malay States **(Murphy et al., 2021).** South-East Asian countries such as Malaysia, Indonesia, and Thailand currently contribute to produce over 85% of global supply **(Lokman et al., 2021).**

Table 1.1 Major centers of global oil palm cultivation in 2020. Source**: (Murphy et al., 2021)**

Rank	**Country**	**Palm oil production Mt**	**Palm oil production %**
1	Indonesia	42.5	58.8
2	Malaysia	18.5	25.6
3	Thailand	2.8	3.9
4	Colombia	1.5	2.1
5	Nigeria	1.0	1.4
Others	Others	5.9	8.2
Total	Total	72.3	

Today, oil palm is crucial to the economies of many countries, especially Indonesia and Malaysia, from which enormous quantities of its products are exported in the form of oil, meal, and other derivatives. More widely, oil palm is now cultivated in plantations across the humid tropics of Asia, Africa, and the Americas, from where its products are exported to global markets Table 1.1 **(Murphy et al., 2021)**. The palm oil production has grown tremendously in recent years. From 1980–2000 production doubled every decade and is continuously rising. Now, worldwide, 75 million metric tons of palm oil are produced annually **(Dirkes et al., 2021)** Figure 1.3. The demand on palm oil is rapidly increased owing to its positive health impacts such as increasing brain health, decreasing the cholesterol level, reducing the oxidative stress, improving hair and skin health, etc. **(Low et al., 2021)**

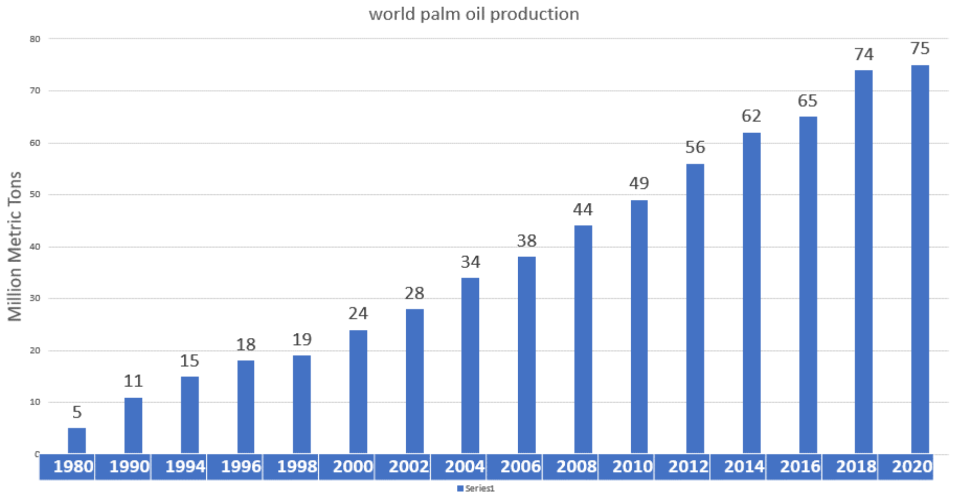

Figure 1.3. Development of world's palm oil production listed from 1960–2020. Data generated from United States Department of Agriculture

Source: **(Dirkes et al., 2021)**

The consumption of palm oil and other palm products is expected to increase in West Africa and in other parts of the continent as the population grows **(Ofosu-Budu and Sarpong. 2013).** In 2013, West Africa's palm oil output was 2.2 million metric tons (MT), and this accounted for only 3.5% of global output. Today, the demand for palm oil in the West African region exceeds its supply, and the region is a net importer of palm oil, with a deficit of between 850,000 to 900,000 tons, per year that is provided for by imports from countries such as Malaysia and Indonesia **(Hassan et al.2016)**. Cote D'Ivoire is the only net exporter in West Africa and exports an estimated 275,000 MT with about 75% of its exports going to West Africa **(Sahel .2015).**

As global demand for palm oil is growing, this crop cultivation serves as a means of livelihood for many rural families, and indeed it is in the farming culture of millions of people in the country. Hence, oil palm is often referred to as a crop of multiple values, which underscores its economic importance **(Ohimain et al.2014).** In Ghana, the processing of oil palm is a major source of income and employment to many women in the rural areas of the forest agroecological zone. By 2015, the palm oil production sector was employing over 2 million people mostly in rural areas (**Awere et al.2022)**.

However, palm oil is an essential multipurpose raw material for both food and non-food industries. It is estimated that for every Nigerian household of five, about two liters of palm oil are consumed weekly for cooking **(Ekine and Onu. 2008).** Data from the 2008 Ghana Demographic and Health Survey shows that one out of every two households (54%) in the country and four out of five (80%) households in the Central Region used palm oil in food preparation (**Awere et al.2022).** Palm oil is used in the manufacturing of margarine, soap candle, base for lipstick, waxes and polish bases in a condense form, confectionary, pharmaceuticals, tin plating, lubricant, biodiesel, fat spread, ice cream, coffee whiteners, whipping creams, fatty acids free formulation, palm-based cheese, micro-encapsulated, filled milk, mayonnaise and sealed dressings, red oil/olefin **(Ohimain et al.2014)**.

Originally from West and Central Africa, oil palm cultivation in sub-Saharan Africa takes place at a variety of scales, from wild harvesting to “smallholder”, non-industrial farms to industrial plantations **(Ordway et al.2017)**. In Cameroon, palm oil contributes to nearly 80% of edible oil demand, 30% of which is estimated to come from non-industrial mills **(Frank et al. 2011).** Before the crude oil boom, Nigeria was the world’s largest producer **(Hassan et al.2016)** but today it’s production accounts for less than 2% of global total; while up to 90 percent of global production occurs in South-East Asia alone, in Indonesia, Malaysia and Thailand **(Hassan et al.2016)**. Many West African countries (and countries in other parts of Africa) have plans to expand and develop oil palm plantations. Buoyed by rising producer prices, strong international demand for vegetable oil and the large demand potential within Africa, as well as demand from biofuel markets, several West Africa countries have formulated national programs to encourage both national and foreign investments in new oil palm plantations **(Ofosu-Budu and Sarpong. 2013)**

There is a serious need for small-scale oil palm production in Africa to increase domestic demand for palm oil since it can create jobs for the teaming unemployed in the country **(Hassan et al.2016)**.

The main objective of this publication is to provide a detailed description of the various processes involved in small-scale palm oil processing, waste produced, and the environmental effect caused by the waste produced.

1.2.2. Small-scale oil palm processing in west and central Africa.

Before the colonizers introduced plantation agriculture to Africa, palm oil production was done with rudimentary tools. This is a very laborious process and in fact the UN Economic Commission for Africa (1983), after studying traditional palm oil production in three African countries namely Cameroon, Cote D'Ivoire and Sierra Leone, qualified the activity as 'long, stressful, and laborious **(Hassan et al.2016)**.

The palm bunches are quartered and left overnight for easy separation of fruits from the spikelet. The fruits are boiled for about 2 hours, pounded in a mortar, or macerated with feet in a canoe-like container or hole dug in the ground. Water is added and well-shoveled up. All nuts are carefully picked out by hand. The fibres are well-shaken over in the sludge until oily foam floats to the surface of the sludge. The foams continue to collect in a container until the operation is completed. This is later boiled in pots for about an hour to evaporate the water from the oil. The clean edible oil then collects on the surface leaving the dirty oil at the bottom of the pot. The surface oil is then scooped off and preserved in containers for sale or domestic consumption while the bottom sludge could be used as animal feed or in soap making. This process will normally have slight variations from one country to another, but the above is a general procedure **(Hassan et al.2016)**.

With the rapid increase in population and a consciousness of industrialization in the continent, came the introduction of simple machines to reduce labor requirements and increase oil yield from a given quantity of fruit. Mechanical devices worth mentioning here include the Duchscher press, the perforated cylindrical metal cage, the Colin expeller, the screw press, the hydraulic press (by Stork of Amsterdam), etc. These presses gained widespread acceptance in all west and central Africa and provided an efficient process (compared to the manual process that existed), for the step of pressing out the oily liquid during oil production. The other unit operations in the crude palm oil processing business, however, remained labor intensive **(Hassan et al.2016)**.

From the simple stand-alone press, small scale palm oil processing has evolved, and attempts have been made to mechanize other unit operations like digesting, threshing and clarification.

Outstanding examples of successful local equipment developed in the region, in this domain are the small-scale palm oil processing equipment (NIFOR-Mini and NIFOR Medium), designed by the Nigerian Institute for Oil Palm Research (NIFOR). Orewa et al **(2009)** reports an increase in processing efficiency by this equipment, from 45-60% to 80-85%. The major advantage of this equipment is that they enable the processing of fresh fruit bunches immediately after harvest. This assures a high quality of the palm oil produced.

Ghana has recorded similar advances by small-scale palm oil producers who use the WACAPOL mini mills which is available in throughputs ranging from 1.0 to 4.0 tonnes FFB per hour. This mill, manufactured in the United Kingdom, has oil extraction efficiency greater than 90% and produces crude palm oil with Free Fatty Acid (FFA) content less than 5.0% **(Hassan et al.2016)**.

Since the introduction of these mechanical devices, the structure of the palm oil industry in the continent has been shaped by the presence of two different markets: home consumption and industrial use in domestic manufacturing **(Hassan et al.2016)**. One of Wacapol’s installations presently run at Weppa farm in Edo state, Nigeria. Hence palm oil processing in the region operates in two sub-sectors which are separate, with each satisfying its own market. Thus, the crude palm oil (CPO) processed is either deemed to be Technical Palm Oil (TPO) or Special Palm Oil (SPO) based on how it is processed and the quantity of free fatty acid. The minimum requirement for SPO is an FFA content of less than 5%. SPO can be consumed or used in products such as creams or further refined for soaps and bleaches. Oil, with FFA greater than 5%, which does not meet the quality grades of SPO characteristics is qualified as TPO and is used for food consumption **(Hassan et al.2016)**. According to recent estimates, Ghana alone counts about 400 small-scale processing units and process about 68% of palm fruits, with a share of 55% on the total palm oil production, though they are characterized by weak milling capacity and low quality of the oil produced **(Hassan et al.2016)**. The World Rainforest Movement **(2010)** records the percentage of African domestic palm oil markets supplied by small scale processors as 50% for Liberia, 58% for Cote D’Ivoire, 80% for Cameroon, Nigeria and Ghana, and up to 83% for Benin Republic; this is enormous.

1.2.3. Waste produced by palm oil processing.

The production of palm oil from FFB of oil palm often results in large waste streams in the form of leaves, empty fruit bunches (EFB), palm kernel shells (PKS), mesocarp fibre (MF), and palm oil mill effluent (POME). These waste streams are solid, liquid, and gaseous emissions.

(a) ***Liquid waste (Palm oil mill effluent (POME))***

Palm oil processing is carried out using enormous quantities of water in mills where oil is extracted from the palm fruits. During the extraction process, about 50% of the water results in palm oil mill effluent. It is estimated that for every 1 tonne of crude palm oil produced, 5-7.5 tonnes of water end up as palm oil effluent (POME) **(Awotoye et al.2011, Ahmad et al., 2003)**. Other Researchers reported, during the industrial processing of every ton of crude palm oil can produce approximately 2.5–3.8 tons of POME **(Lefcourt et al., 2001, Chaudhari et al., 2010)**. Mill owners from Cameroon, results revealed that at least 750 liters of water are needed for processing 220 liters of palm nuts. Therefore, the amount of liquid waste could amount to about 675 liters for processing each drum of fresh fruits **(Ngwelum et al., 2021).**

This effluent contains materials which concentrations are above threshold values Wu et al., **(2009)** and are injurious to the environment. Such soluble materials may be gases such as CH, S0, NH, halogens or soluble liquids or solids which contain ions of either organic or inorganic origin and with their concentration above the threshold value **(Igwe and Onyegbado. 2007)**. It becomes necessary that effluent water should be treated or purified before being discharged into the environment. In Nigeria’s palm oil industry, most of the POME produced by small scale traditional operators undergo little or no treatment and are usually discharged in the surrounding environment. This POME could pollute streams, rivers or surrounding land **(Okwute and Isu, 2007, Yahaya and Lau., 2013).**

POME is generated from various points during processing in an oil mill. These include clarification sludge, hydro cyclone drain-off, various boiler blows down, tank and decanters drain **(Mohammad et al.2021)** Figure 1.4

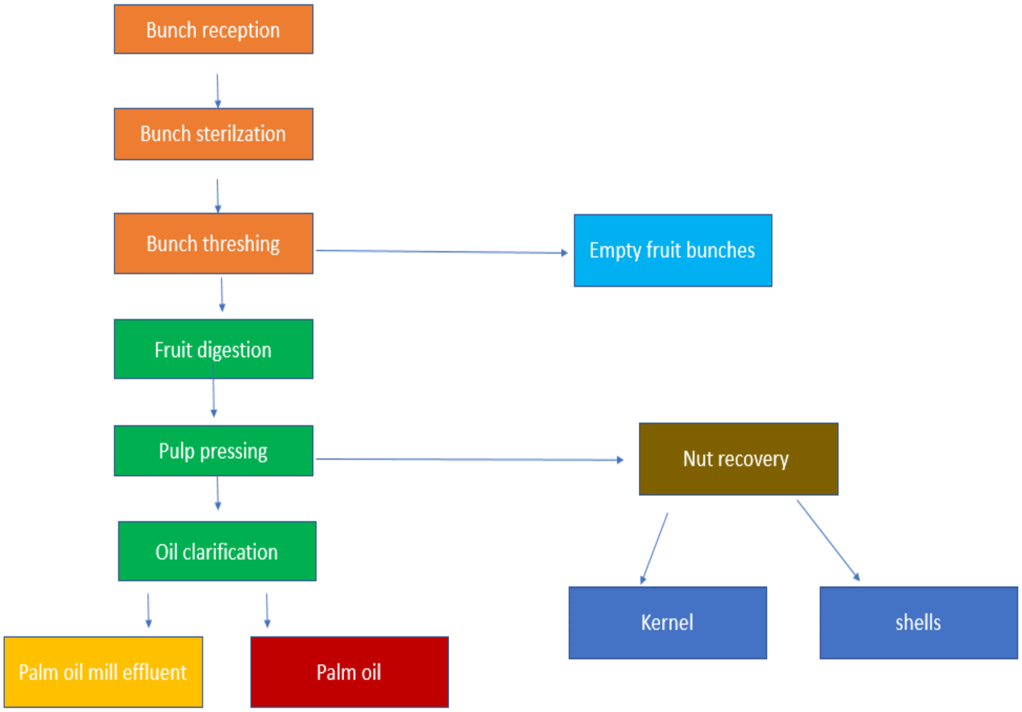

Figure 1.4. Flow Chart to produce Raw Palm Oil Mill Effluent

Source**: (Famurewa and Olarewaju. 2013)**

The composition of the effluent from these various sources is water :93 – 95%, oil: 0.5 – 2%, solids (suspended dissolved) and sand: 3 – 4% (**Igwe and Onyegbado.2007)**. Other researchers reported 95% of water, 4–5% of total solids including 2–4% of suspended solids, 0.6–0.7% of residual oil **(Low et al., 2021, Onyla et al., 2001, Shayandi et al., 2012)**, and sand tables 1.5. **Adam effluent handbook (1992), (Wu et al.2008) and Sutanto (1981).**

Table 1.5. Composition of POME. source**:(Wu et al.2008, Igwe and Onyegbado.2007)**

POME composition	**(Wu et al.2009)**	**Adam (1992)**	**Sutanto (1981)**
water	95-96%	93-95%	95%
solid	4-5%	3-4%	
oil	0.6-0.7%	0.5-2%	1.0%
Suspended solid	2-4%		2.0%
Dissolve solid			2.0%

POME also has a thick brownish color, viscous appearance, high concentration of colloidal suspension, acidic properties with a nuisance odor **(Syahin et al.2020)**. POME includes various liquids, dirties, residual oil and suspended solids. POME in its untreated form is an extremely high strength waste, depending on the operation of the processes, the biological oxygen demand of these wastes' ranges from 225,000 to 35,000mg/l, chemical oxygen demand (53,630 mg/l), oil and grease (8370 mg/l), total solids (43,635 mg/l) and suspended solids (19,020 mg/l) **(Ma,1995)**. The overall characteristics of raw POME and the regulatory discharge limits are presented in Table 1.6 **(Azam et al.2020, Nahrul et al, 2017).**

POME also contains several nutrients including light (nitrogen, potassium, magnesium, phosphorous, sodium) and heavy nutrients/metals (zinc, copper, cadmium, chromium, iron etc) **(Izah et al.2016)**. POME contains arable groups of microorganisms including lipolytic bacteria, methanogens, hydrocarbon degrading bacteria and fungi **(Izah et al.2016)**.

(b) ***Solid waste***

Processing wastes are composed of solid wastes such as wet empty fruit bunches (EFB), wet press palm mesocarp fibre, wet endocarp, palm kernel shell and palm kernel press cake. The liquid waste (wastewater) generated from the extraction of palm oil is known as the palm oil mill effluent (POME) **(Temu et al.2013)**. The milling process generates substantial quantities of solid waste; 0.23 t of EFB, 0.13 t of MF and 0.55 t of kernel shells per ton of FFB **(Osei-Amponsah et al.2012)**. The most common among these by-products is the empty fruit bunch. The empty bunch is a solid waste product of the oil palm milling process and has a high moisture content of 55-65% and high silica content, from 25% of the total palm fruit bunch (**Igwe and Onyegbado.2007).** In developing countries like Nigeria and Cameroon these wastes are seldom used apart from as boilers fuel **(Izah et al.2016, Osei-Amponsah et al.2012)**. These wastes are burnt in the palm oil mills resulting in atmospheric pollution hence they constitute nuisance in the mill **(Izah et al.2016).** Based on these estimates, the quantity of solid wastes that have remained un-utilized in palm oil mills is significantly higher than the level utilized (used as boilers fuel) **(Izah et al.2016)**

(C) Gaseous emission

Oil palm processing waste biomass is often used as boiler fuel in most palm oil mills in developing countries like nation. Whereas the most advanced oil palm producing nation often use electricity to generate steam for sterilization. Conventional diesel is used for digestion activity in Nigeria. These activities release pollutant gases such as carbon monoxide (CO), nitrogen dioxide (NO), ammonia (NH3), sulphur dioxide (SO2), hydrogen sulphide (H2S), volatile organic compounds

(VOCs) and suspended particulate matter (SPM) **(Izah et al.2016)**. This equipment involves drum sometimes known as barrel (used for boiling) and digester connected to diesel powered engine (used for digestion). This is a typical approach employed mostly by smallholder processors which cover about 80% of the Nigerian oil palm industry **(Izah et al.2016).**

1.2.4. Environmental Effect of palm oil processing.

The environmental attendant that emanates from cultivation of oil palm include deforestation (clearing), soil erosion and fertility, water cycle disruption and pollutions associated with fertilizer use, while emissions from combustion, POME discharged, unused solid wastes in the mills also causes pollution. This section evaluates the environmental impacts of oil palm processing in Africa. Like the waste streams, there a three major component of the environment. This includes water (aquatic), soil (land) and air. This section of the paper discusses the impacts of the various waste streams on the environment.

(a) ***Air quality impacts***

Oil palm cultivation has resulted in adverse environmental impacts (such as climate change and greenhouse effects) due to excessive emissions and deforestation. Like other solid wastes, unused biomass is commonly disposed of without treatment in the environment, where they cause environmental impacts together with emissions. Open-air combustion often causes air pollution with the release of CO, smoke, and NO2. Oil palm processing impacts the air quality through odor pollution, and it is seldom reported **(Izah et al.2016)**. The untreated wastewater pollutes the air through odor production as reported **(Awere et al.2022).** Aside from the odor, the degradation of the wastewater could generate biogas with over 60% methane content **(Awere et al.2022, Tchindjang et al.2021)**. Methane gas is considered one of the potent greenhouse gases and contributes 25 times to global warming compared to CO2.

The air pollution from palm oil mills is less in oil palm producing countries like Nigeria. The hazards allied to suspended smoke particles from biomass burning have become a common feature in Malaysia and Indonesia **(Izah et al.2016)**. The air emission from diesel engine has some health implications including cardio-respiratory disorders, pulmonary edema, eye irritation, central nervous system disorders, drowsiness, coughing and other respiratory diseases **(Izah et al.2016)**.

These pollutant gases may be contributing to climate change, which affects biodiversity including vegetation, mammals, reptiles, amphibians, aves, fisheries, arthropods and even microorganisms **(Izah et al.2016)**. Globally, biodiversity contributes to the survival of man in several forms including protein sources, hide and skins (wildlife), pollinator (insects), medicinal plants (vegetation), and employment generation. Due to emission of pollutant gases, the resultant impacts include changes in breeding pattern, spawning, pollination, and encouragement of vector carrier insects **(Izah et al.2016)**.

(b) ***Water quality impacts***

POME causes environmental problems due to voluminous discharge of the wastewater during milling processes. POME is produced in various processing lines including sterilizers, clarifying centrifuges and hydro cyclones (mechanized mills) and boiling, digestion and clarification (traditional/smallholder mills). Most POME produced by the small-scale traditional operators in Nigeria undergoes little or no treatment and is usually discharged into the surrounding environment (**Igwe and Onyegbado.2007, Okwute and Isu, 2007).** In Ghana, the processors dispose of the effluent directly onto the earthen floors of the mills, into nearby streams and farms (86%), thereby polluting surface water **(Osei-Amponsah et al.2012)**. Also, field surveys show that waste oils emanating from SOCAPALM and PAMOL mills flow into rivers and streams close to village dwellings. These rivers and streams remain the most fishing and living places estimated by local populations (consumption, bathing, etc.). Because of this liquid waste, local populations are deprived of much of their fishing resources and exposed to health risks. Another negative aspect is the environmental impact of artisanal mill units whose process is polluting because the discharges are not treated (**Tchindjang et al.2021). These** can cause pollution of waterways due to oxygen depletion, land use and other related effects **(Izah et al.2016, Awere et al.2022).**

During the rainy season, the POME is a breeding habitat for mosquitoes and emits offensive odors. Discharging of POME into aquatic ecosystem turns the water brown, smelly and slimy **(Awotoye et al.2011,** which may adversely affect aquatic life and water quality for domestic purposes **(Toh et al.2014).** POME can alter potable water sources (surface and groundwater).

Awotoye et al., **(2011)** reported that POME which have higher concentration than water quality parameters increase water quality parameters including temperature, pH, total alkalinity, total solid, total dissolved solid, total suspended solid, magnesium, calcium, sodium, potassium, chloride, sulphate, nitrate, phosphate, zinc, iron, manganese, dissolved oxygen, biological oxygen demand in river receiving POME. Similarly, Edward et al., **(2015)** reported POME is having an effect in the physico-chemical properties (i.e., pH, temperature, alkalinity, total suspended solid, dissolved oxygen, biochemical oxygen demand, nitrate, phosphate, potassium, oil, and grease) in Ayanyan River, Ekiti state, Nigeria. In Cameroon water samples were collected upstream, at the spillway and downstream of the palm oil extraction sites in Ngwéi and Ekondo Titi chemical and bacteriological analyses carried out on 9 water samples results revealed contamination and pollution, including even groundwater (**Tchindjang et al.2021)**. In addition, two Ekondo-Titi samples have concentrations of ammonium (NH4 +) ions higher than the recommended value (≤0.50). At the microbiological level, six (06) samples showed concentrations of fecal coliforms not complying with guideline values (0UFC/100 ml) (**Tchindjang et al.2021)**. Concentration above the permissible limit makes the water unfit for domestic consumption. Excess nutrients like nitrate, sulphate, phosphate, etc. in the water could cause eutrophication. High acidic nature of POME causes acidification in water, thereby affecting aquatic life forms or ecosystem **(Izah et al.2016, Tchindjang et al.2021).**

(c) Soil impacts

Vegetation prevents soil erosion. The discharge of POME into soil affects its pH, which is one of the main factors influencing nutrient availability to plants **Okwute and Isu, 2007**. This is because most plants grow and do better within a pH range of 6.5 – 7.5 **(Izah et al.2016)**. POME increases organic carbon, total, nitrogen, phosphate, sulphate, phosphorus, sodium, potassium, calcium, magnesium, aluminum, and hydrogen **Okwute and Isu, 2007**. The availability of nutrients including sodium, phosphorus and potassium enhances plant growth. But high nitrogen, potassium and phosphorus cannot efficiently enhance crop yield if the soil pH is abnormal **Okwute and Isu, 2007**. Organic amendment with POME increased the pH of effluent soils. It has been reported that when raw POME is discharged the pH is acidic but tends towards alkalinity as biodegradation takes place. In a similar study by **Oviasogie and Aghimien (2003),** the results showed an overall increase in the CEC of POME soils especially at the area close to the source of the POME and agree with the observation in this investigation. The results showed that the soils are enriched with phosphorus, nitrogen, calcium, magnesium, sodium and potassium due to the application of POME. In fact, there was a significant increase ($p<0.01$) in phosphorus values of the POME-treated soil over that of non-POME. The available phosphorus in the POME soil leads to high absorption of material. This may lead to a delay effect on the soil due to gradual biodegradation of the POME **Okwute and Isu, 2007**.

The changes in the soil physico-chemical properties and other vital nutrients via POME discharge can affect soil texture and particulate size. POME discharge into the soil increases the soil bulk density, percentage of silt and clay and decreases the percentages of the clay **(Izah et al.2016)**. Again, textural soil class depends on the organic matter content of the soil which POME is discharged into. The POME on soil retains water due to the presence of unrecovered oil and debris from processing. POME changes the soil appearance and some properties including vegetation, color, odor, and constitution **(Izah et al.2016)**. Despite the soil enrichment by POME, it makes the soil lose its vegetation cover, damp with humus. This causes clogging and water logging of the soil spores which could result to death of vegetation on contacts, with the environment being bare **(Chan et al.1980**). Besides that, it also contaminates the land and ecosystem leading to loss of land and resources to local inhabitants such as the soil micro flora and some biodiversity **(Sridhar and Adeoluwa et al.2009)** such as earthworm which play a significant role in soil aeration.

1.2.5. Conclusion and potential options for the processing wastes management

Palm oil production be it by manual traditional small-scale processing methods, which are simple, but tedious and inefficient or advanced large-scale techniques using machinery, generate huge quantities of organic waste. The oil makes up only about 10% of the total biomass produced in the plantation and the remaining 90% consists of liquid and solid wastes **(Temu et al.2013)**. The liquid wastes could contaminate the aquatic ecosystem during runoff leading to acidification and eutrophication in the aquatic ecosystem. The liquid waste POME could lead to loss of biodiversity, mostly vegetation. Waste management is therefore important from the point of view of reducing impact to the environment and sustainable utilization of the waste for production of value-added products **(Temu et al.2013).** The various adverse impacts could be prevented through biotechnological reuse of solid wastes and liquid wastes.

The air emissions can be managed by drying the biomass properly before use as boiler fuel **(Izah et al.2016)**. Valorization is yet another option of utilizing the wastes that is proposed for improved energy efficiency and alternative uses for the wastes and additional income generation while reducing the GHG (greenhouse gas) emissions **(Temu et al.2013).**

- ***Reuse of liquid waste from palm oil production.***

POME can be used to produce organic acids such as acetic and formic acid acids, citric acids, polyhydroxyalkonates, solvents such as actetonebutanol-ethanol, bioinsecticides and antibiotics **(Izah et al.2016)**. Others include biohydrogen and biogas production, using microbial fuel cells technology, composting and vermicomposting and fertilizer production due to ability to enrich the soil phosphorus, nitrogen, and potassium **(Izah et al.2016).**

The concern on the depletion of fossil fuel has led to an increase in research activities on the development of renewable energy such as biogas production from waste for sustainable power generation. POME, being a waste with high organic carbon content, has become a promising source for biogas production and to potentially boosts the renewable energy sector. Biogas production from POME can be done either aerobic or anaerobic. The aerobic digester has a high microbial growth rate that leads to lower retention time during biogas production, while anaerobic treatment process is characterized by slow microbial growth and higher retention time compared to aerobic processes. However, the anaerobic method is considered more effective in terms of cost and conversion into useful products. The biogas produced from POME is known to have a good potential for power generation using the gas engine. Biogas production from POME ranges from (20 to 28) m 3 of CH4 m –3 biogas. About 1 m3 biogas can generate about 1.8 kW h, which is equivalent to 25 % power generation efficiency **(Rajani et al., 2019)**

Composting is a process whereby complex organic residues of plant and animal origins are converted into manure or biofertilizer through the activities of several microbial systems (bacteria, actinomycetes, and fungi). Since POME is of biological origin, its composting can be a good alternative for its sustainable management. It was reported that the utilization of empty fruit bunches (EFB) with POME for composting process can produce acceptable quality compost that can be applied to palm oil plantations as biofertilizer and for soil conditioning **(Salihu et al., 2012) (Truckell et al.2019)** Figure 1.6. Also, biologically treated POME has been widely used in oil palm plantations for irrigation purposes and can be employed as a liquid fertilizer. It is estimated that each 15 million tonnes of POME would have a fertilizer value of RM 95.41 million (Table 1.7) **(Wu et al.2008)**.

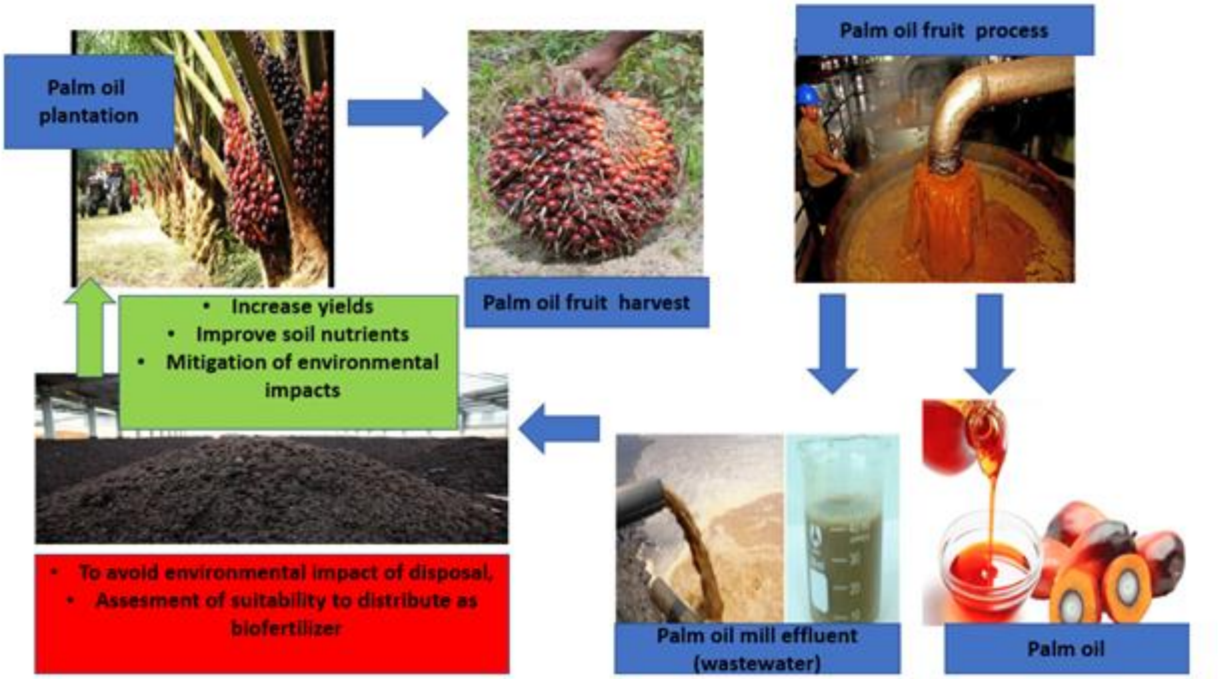

Figure 1.6. POME can be used as an organic fertilizer and avoid environmental impacts. Source: **(Truckell et al.2019).**

Table 1.7. Estimated fertilizer values from POME, which is based on 15 million tonnes of POME. Source: **(Wu et al.2008)**

fertilizer	**Tonnes (*1000)**	**December 2002 price (RM/ton)**	**Fertilizer Value (RM million)**
Ammonium	75.5	580	43.79
Sulphate			
Rock phosphate	19.5	545	10.63
Muriate of potash	68.6	250	17.15
Kieserite	59.6	400	23.84
Total			95.41

An incorporation of POME may help to increase the organic matter in the soil, which may turn into humus after decomposition and become an active soil component. Thus, POME application would result in changes in the chemical properties of the soil. According to **Ferreira and Araujo (2002),** average contents of calcium, magnesium, potassium and phosphorus were found to increase in the soil with an increase in POME dosage, especially at a depth of 0–20 cm but an application of 120 m3 /ha of POME to the soil reduced the aluminum content to zero at a depth of 20 cm after 12 months. Such a reduction of aluminum in the soil would eventually help prevent toxicity and growth hindrance for plants in acid soils **(Matsumoto, 2000; Guo et al., 2007).**

Nevertheless, the use of POME as fertilizer must be carried out with caution because of imbalances in the nutrient composition. A prolonged improper use may cause magnesium to accumulate and thereby inhibit potassium availability **(Onyia et al., 2001)**. Table 1.8 shows the nutrient requirements for the various growth stages of plants and the suitable amount of POME for reuse as fertilizer to avoid soil damage **(Wu et al.2008)**.

Table 1.8. The application of POME (m3/acre/year) as fertilizer for palm plantation**. Source: (Wu et al.2008)**

Crops	**N**	**P**	**K**	**Mg**
Young palms	25-70	27.5-32	5.1-10	12-10
Adult palms	90-128	52.5	10 –18.5	15
Old palms	162	52	18	20

When properly treated and packaged, POME can be used by farmers both in rural and urban areas to improve soil fertility thereby increasing the agricultural productivity for global, national and regional food demands **(Eze et al., 2013).**

- ***Reuse of solid waste from palm oil processing***

The solid wastes can also be converted to a wide range of value-added products that can be clustered into bio-based value-added products and various bioenergy. The potential energy applications include direct power generation, bioelectricity, bioethanol, bio-briquettes, biobutanol, biomethanol, bio-oil, biochar **(Sridhar and Adeoluwa et al.2009),** syngas using various technologies **(Izah et al.2016).** Furthermore, processed palm fronds and kernel meal are used as animal feed and for mushroom cultivation **(Temu et al.2013).** Additionally, PPF and chaff can be used for the cultivation of edible larva/maggot.

Other research stated that oil palm EFB is a lignocellulosic source available as a substrate in cellulase production **(Edoetok.2012)**. The empty fruit bunch can also be used as local fertilizer. The ash produced from empty fruit bunches is sprayed on crops to prevent insects from destroying the crops, it is also used for washing plates and pots **(Edoetok.2012).** The filtrate obtained from the filtration of the mixture of EFB ash and water normally has a brown color and can emulsify oil, thus producing an emulsion with it. It is slippery to touch, giving the impression that it is alkali. In Annang tribe of Akwa Ibom State, Nigeria, this filtrate is used in preparing a local delicacy known as “Otong” which is used in eating meat, drinking of palm wine and can be used to spice soup. Otong, which looks like an emulsion is also slippery to touch just like soap, suggesting that the reaction that produced it may have been a saponification reaction. Saponification is a process that produces soap, usually from fats and lye. In technical terms, saponification involves base (usually caustic soda NaOH) hydrolysis of triglycerides, which are esters of fatty acids, to form the sodium salt of a carboxylate **(Edoetok.2012)**. Traditionally in West Africa, the ash derived from the empty fruit bunch is used in the cooking and production of black soap due to its high potassium content. This soap is advertised as antimicrobial, anti-acne, exfoliating, skin toning, scar fading, and having medicinal properties **(Ogunbiyi and Nkechi.2021).** Through these biotechnological advances, the environmental impact associated with oil palm processing wastes will be reduced **(Izah et al.2016)**.

CHAPTER 2. LITERATURE REVIEW

LIVESTOCK WASTEWATER AND PALM OIL MILL EFFLUENT (POME) TREATMENT TECHNOLOGIES

The direct discharge of POME and livestock wastewater on the land and into waterway causes water depletion, resulting in aquatic pollution with water bodies consequently turning brown with an unpleasant smell, increasing mortality of aquatic organism and depriving local people of the local water sources for domestic uses and fishing. Therefore, the effective techniques for POME treatment are of the uttermost significance. Currently, recycling and recovery of input resources are becoming among the highest concerns for the industry. As a result, the crude palm oil industry and livestock farms are developing several industrial ecosystem practices for waste recycling. In this chapter the application of biological methods, chemical coagulation methods and electrochemical methods will be discussed in detail as the most common method of POME and livestock wastewater treatment. Their advantages and disadvantages will also be elaborated in this chapter.

2.1.1 Legislation in the control of Palm oil mill effluent

The raw POME is a thick brownish color in the viscous and colloidal suspension, which contains high water contents, suspended solids, and oils. POME also exists as an acidic substance with unpleasant odor, high value of COD, and BOD, which can be concomitantly sensitive to environmental issues. Hence, in order to control and minimize the pollution impact towards the environment, the Department of Environment (DOE), Malaysia, had enacted Environmental Quality Act (EQA) 1974 and set standard limits for the discharge of POME into the environment **(Nahrul et al., 2017) (**Table 2.1).

Table 2.1 : POME final discharge with their respective standard discharge limits set by Malaysian Department of Environment (DOE) 2015. **Source: (Nahrul et al, 2017)**

Parameters	**Units**	**Parameter average unit second Schedule**
pH	[Text Wrapping Break]	5-9
Biochemical oxygen demand (BOD 5)	mg/L	100
Chemical oxygen demand (COD)	mg/L	100
Suspended solid	mg/L	400
Color	ADMI	200
Total nitrogen	mg/L	200
Temperature	(°C)	45

2.1.2 Biological treatment (Ponding system or Lagoon system)

Ponding systems (lagoon systems) are a series of one or two pond-like structures designed to treat wastewater for a specified period. Lagoon systems use biological, physical, and chemical processes to treat the wastewater during its storage period before dispersal onto crops, pasture ground or other types of land. Most of the treatment occurs naturally by anaerobic or aerobic bacteria, depending on the design of the lagoon system **(Miller et al., 2011)**. The several types of lagoons and how they work are described below

Ponding systems or land application is the most widely used for palm oil mills for effluent treatment **(Tham., 2015)**. This is due to it being inexpensive, low capital, simplicity, and ease of handling **(Nahrul et al., 2017, Mohammad et al., 2021).** This treatment system requires a vast area to accommodate a series of different facilities such as de-oiling tanks, holding/equalization ponds, acidification ponds, facultative-anaerobic ponds, aerobic ponds, and polishing ponds **(Chou et al., 2016, Low et al., 2021, Harsono et al., 2014)** Figure 2.1.

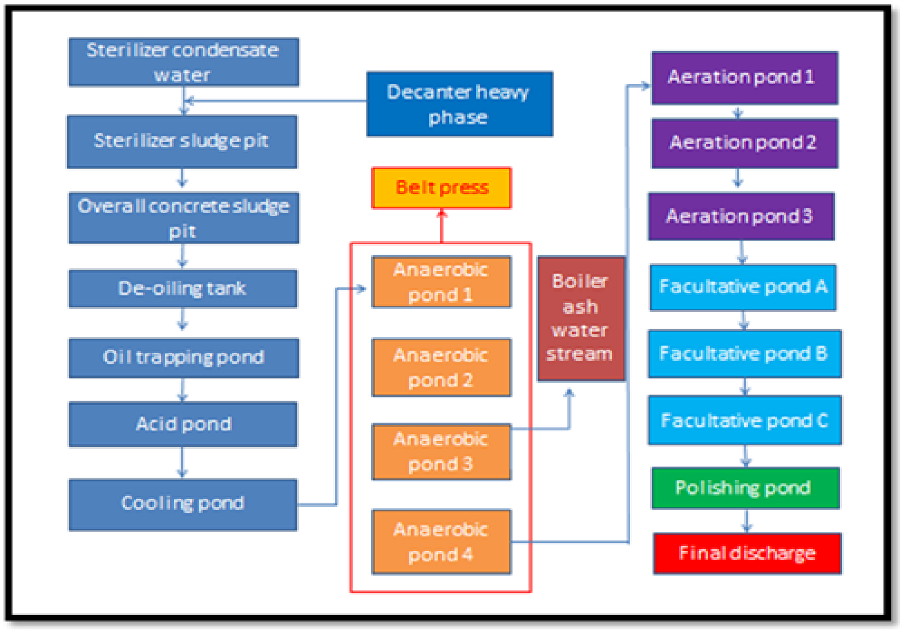

Figure 2.1. Industrial effluent treatment process flow chart

Source**: (Malaysia Unit Palm oil industry)**

2.1.3 Ponding systems (Lagoon systems) and their functions

(a) Anaerobic Lagoons

Anaerobic lagoons use bacteria in the absence of oxygen to treat wastewater. These lagoons are used as a single pond system or as the first pond in a series design. Requiring small design volumes, these lagoons are very deep and work similarly to septic tanks. Over a 20-to-50-day period wastewater solids separate into layers, with oils and floating materials on top and heavy sludge on the bottom. The top layer seals oxygen out of the lagoon system, supplying the anaerobic conditions for bacteria to treat the wastewater. The bottom sludge layer, like a septic tank, must be removed periodically. Wastewater leaving an anaerobic lagoon often requires further treatment either by connected aerobic lagoons or by chemical or physical purification techniques. Odor can be a problem with anaerobic lagoons but can be virtually eliminated with proper management. Anaerobic lagoons are good candidates for methane or biogas capture to run on-farm energy generating plants **(Miller et al., 2011)**.

(b) Aerobic Lagoons.

Aerobics describes dissolved oxygen throughout the lagoon's depth. Aerobic lagoons can be either naturally aerated or mechanically aerated. To allow oxygen to penetrate the entire lagoon, aerobic lagoons tend to be very shallow and so require much more land area than other types of lagoons. However, if professionally designed and kept, an aerobic lagoon can treat wastewater more quickly than all other lagoon types. Aerobic lagoons also produce fewer odors than anaerobic lagoons. Aerobic lagoons are best suited for warm, sunny climates to avoid freezing. Because of the shallow nature of aerobic lagoons, exceptional care needs to be taken to avoid weeds and grass growth on the bottom of the lagoon. Often the bottoms are paved or lined with materials to prevent weed growth. Occasionally the wastewater in an aerobic lagoon needs to be mixed to allow added sunlight and to break up algae clumps that may block the oxygen and sunlight needed for the natural treatment process **(Miller et al., 2011).**

(c) Naturally, Aerobic Lagoons

Naturally, aerobic lagoons do not use a mechanical aeration system, but rather rely on oxygen from the atmosphere or from photosynthesis by algae to keep aerobic conditions. Naturally, aerobic lagoons must be shallow, typically only 1 to 2 feet deep and no more than 5 to 6 feet. The required design volume for a naturally aerobic lagoon is typically four to five times that of an anaerobic lagoon. The land area needed to meet the design volume and shallow depth requirements make naturally aerated lagoons impractical for farm use **(Miller et al., 2011).**

(d) Mechanically Aerated Lagoons

Mechanically aerated lagoons use an aeration system to add oxygen to the lagoon and mix the contents thereby increasing the degree of aeration. A power source is needed to run the aeration system. Some operators use solar or wind power. By aerating a lagoon system one can significantly decrease the amount of land needed for a lagoon and still receive the benefits of a full or partial aerobic lagoon. The required design volume for a mechanically aerated lagoon is about half of an anaerobic lagoon. Depending on the lagoon depth and the extent of aeration, the lagoon can work as a combination of both an anaerobic and an aerobic lagoon **(Miller et al., 2011).**

(e) Facultative Lagoon

Facultative lagoons and aerated lagoons run in an equivalent manner and have many of the same benefits. Facultative lagoons use a combination of aerobic and anaerobic conditions to treat wastewater, but facultative lagoons do not require an aeration system. The top layer, which is exposed to wind agitation, sun, and holds the most oxygen, is the aerobic zone. The middle layer is called the facultative zone where, depending on the climate, both conditions are present. The anaerobic zone is at the bottom of the lagoon and includes the layer of sludge that accumulates there. Since the aerobic layer is on top, facultative lagoons minimize odor emissions produced by the lower layers. Wind and sun are both important for the processes occurring in a facultative lagoon because they supply oxygen, energy for photosynthesis, and affect the hydraulic flow pattern of the wastewater **(Miller et al., 2011).**

2.1.4 Process of POME treatment in Ponding system

The configuration of POME treatment via a pond system is also known as waste stabilization ponds of acidic to final polishing ponds hold an overall HRT of 100–120 days prior to discharge to the environment **(Mohammad et al., 2021).** The raw POME in the oil-trapping pond was pumped into the acidification pond and kept for about 6 days. Then, the POME was pumped into a cooling pond through a cooling tower and kept for another 7 days. Cooling pond reduced the POME temperature to 35–38 °C and stabilised the pH prior to the anaerobic stage. Anaerobic treatment stages are made up of four ponding series with total HRT of 54–60 days **(Mohammad et al., 2021**). Then, anaerobic POME is further treated using a three series of aeration ponds with the floating aerators for about 20 days before being discharged into the facultative ponds. Facultative ponds consisted of three ponding series, which are very crucial to furthermore reduce the organic content in the effluent, prior to discharging to the waterway, as followed the Environmental Quality Act (EQA) 2015, the stipulated regulation for crude palm oil treated effluent discharge **(Mohammad et al., 2021).** The anaerobic ponding system was found to prove impressive performance in treating POME due to reduction of high-level organic properties in POME **(Yaser et al.,2009).** However, 100% decolourization was unable to be achieved using this treatment system **(Tamrin and Yaser., 2017).** Characteristics of POME from different stages of open ponding system are given in table 2.2

Table 2.2 Characteristics of POME from different stages of open ponding system **(Cheng et al.2021)**

Parameter	POME Mean value	Anaerobically treated POME (ANPOME). Mean value	Facultatively treated POME (FPOME) Mean value	Aerobically treated POME (APOME) Mean value
pH	4.45	7.33	6.36	7.55
Temperature	74.75	28.50	-	27.50
Oil and grease	7227	8020	-	16,000
Turbidity	35,889	53.81	-	633
COD	74,118	8660	1300	5079
BOD	28,835	6011	330	602
Total suspended solid (TSS)	22,119	7363	-	1342
Total nitrogen	778.67	249	500	127
Phosphorus	318.35	113.50	-	-
Potassium	935	1737	350	-
Ash	4275	-	-	-
phosphate	19.45	-	-	15.80
sulphate	5	-	-	

2.1.5 Advantages and disadvantages of biological treatment (Ponding or lagoon systems)

(a) Advantage of biological treatment

Among the alternatives to improve manure management, biological processes are often seen as a solution (or a part of) due to their implications in the N, C and P cycles. The biological treatment methods for livestock wastewater treatment can be roughly classified into aerobic reactor, anaerobic lagoons with biogas collection, farm-based biogas units, and centralized biogas plants, and aerobic anaerobic mixing biological treatment **(Bernet and Béline., 2009).** Initially, the works developed on biological treatment of livestock effluents dealt with organic matter degradation, odor reduction and pathogen control **(Bernet and Béline.,2009).**

(c) Disadvantage of biological treatment

Because of the specificities of manures and POME (high nitrogen, chemical oxygen demand (COD) and suspended solid (SS) content, time variability of concentrations), biological treatment such as aerated lagoons and fixed-bed processes have been shown some limitation as not giving satisfying results compared to other systems. Example POME treatment system that is based on conventional biological treatments of anaerobic and aerobic ponding systems stays inefficient due to the high BOD loading, that is the biodegradability of POME less than 0.5, which is a ratio BOD and COD **(Lokman et al., 2021) and** low pH **(Yahaya et al., 2013)**. In addition, the removal of nitrogen from POME is usually unsatisfactory because nitrification is an uncommon phenomenon in the ponding system **(Adlil et al., 2014)**. Another main challenge after the treatment of POME is color which is attributed to the presences of tannin-lignin (which contributes to the brown and yellow color), phenolic, and carotene **(Aziz et al., 2018).** Another limitation is seen in the inflated costs of operation (for aerobic systems), the land area needed for anaerobic lagoons, long retention times (for anaerobic ponds hydraulic retention time ranging from 45 to 60 days **(Othman et al., 2014),** and sludge disposal problems. In addition, anaerobic lagoons liberate high ammonia, methane, and greenhouse gas (GHG) emissions **(Bernet and Béline., 2009)** freely to the atmosphere and this will slowly cause the ozone layer to be thinner and eventually cause a greenhouse effect **(Iskandar et al., 2018, Choi et al., 2013, Hosseini et al., 2015).**

2.2 Chemical treatment (Coagulation-Flocculation)

Chemical treatment of wastewater and water can be done with different coagulants, flocculating and precipitating agents. From their ancient beginnings to the present-day coagulants and flocculants have been used to enhance solid–liquid separation by particle aggregation. Various investigators have carried out investigation on coagulation-flocculation aimed at studying choice of coagulant, flocculants optimization of affecting parameters and combinations with other treatment methods. Choice of coagulating agent, flocculating agent and proper combination of coagulation-flocculation with other physicochemical treatment can lead to highly effective, economical, and efficient solution for wastewater treatment. This review presents and discusses the latest information concerning the role of coagulation and flocculation methods in wastewater treatment.

2.2.1 History of coagulation-flocculation

The process of particle aggregation to assist solid– liquid separation is conventionally described by two mechanisms, and these involve the use of different types of chemicals. Coagulation by coagulants, derived from the Latin word coagulare, meaning to be driven together, involves neutralization of particle surface charge or potential by the action of inorganic counter-ion adsorption or electrostatic screening. Flocculation by flocculants, derived from L. flocculus, meaning a loose fibrous structure pertaining to a tuft of wool, involves the bridging together of particles by long organic polymer chains, where charge neutralization may or may not be involved **(Pearse., 2003)**.

Coagulation is an essential process in water and industrial wastewater treatment. In the area of potable water treatment, clarification of water with coagulating agents has been practiced since ancient times, using a variety of substances, the most notable among them being crushed seeds. The Egyptians, as early as 2000 BC, used almonds smeared around a vessel to clarify river water. The early Romans were also familiar with alum, though it may not have been for water treatment. Nevertheless, its use of a coagulant by the Romans was mentioned in ca. 77 AD. By 1757, alum was used as a coagulant in water treatment in England, and more formally for the treatment of public water supplies in 1881. In modern water treatment, coagulation and flocculation are still essential steps in the treatment processes **(Sahu and Chaudhari., 2013)**.

2.2.2 Contaminants removed by coagulation and flocculation.

Coagulation-flocculation may be broadly described as chemical and physical processes that mix coagulating chemicals and flocculation aids with water. During coagulation-flocculation colloidal particles and other finely divided matter are brought together and agglomerated to form larger particles that can subsequently be removed by the subsequent settling or filtration processes **(Djamel., 2013).**

Coagulation facilitates the removal of both organic and inorganic contaminants in dissolved and suspended forms **(Bhattacharjee et al., 2016).** These contaminants affect the water quality and the water treatment process. The contaminants may be characterized as follows:

a) Particle

Particles found in water vary widely in concentration, origin and size. Soil-weathering and biological processes are the principal sources of most of the particles found in water. Particles of clay, silt and terrestrial detritus are produced by soil weathering; other waterborne biological particles include algae, protozoa, bacteria and other higher microorganisms. Some suspended solids originate from chemical and biological processes within the water source while atmospheric deposition occurs when pollutants, such as dust, soot, ash, pollen spores, algal cells and other airborne particles, are transferred from air to water. The presence of particles in water has a negative effect on water treatment processes, aesthetics and human health. Suspended particles can cause fouling within the water treatment process and have undesired impacts on removal process efficiencies, for example, colloids can shield microorganisms from disinfection. Particles with light scattering properties can increase the water turbidity, giving the water an undesirable cloudy appearance. More importantly, particles such as pathogenic microorganisms affect human health **(Bhattacharjee et al., 2016).**

<u>b) Natural organic matter</u>

Natural organic matter (NOM) originates both from outside the water body (transported into the water body) and within the water body as **(Bhattacharjee et al., 2016).**: Particulate organic matter e.g., algae. Dissolved organic carbon e.g., proteins. Organic matter produced by respiration and decay.

A large portion of the NOM found in polluted water consists of humic substances. Humic substances are derived from soil, chemical and biological processes such as decomposition of vegetation, etc. Humic substances are divided into the more soluble fulvic acid, which is predominant in most waters and the less soluble humic acid. These substances are anionic and of varying molecular weight. The presence of NOM, above its threshold value has the following undesirable effects **(Bhattacharjee et al., 2016).:** Imparts an aesthetically unacceptable color in water., Affects particle stability., Increases alkalinity., Contributes to odor and taste problems., Acts as precursors to disinfection by-products and other by-products., Adversely effects water treatment processes such as chemical dosing., Causes corrosion.

2.2.3 Coagulation

The coagulation-flocculation process is the major physicochemical treatment method used in industrial wastewater treatment, example Aluminum (Al) coagulants were commonly used in the treatment of dairy manure effluent, palm oil mill effluent, and paper and pulp **(Lefcourt et al., 2001, Chaudhari et al., 2010, Malik et al., 2018)**. to reduce colloidal turbidity and suspended solids. Table 2.3. Coagulation is a process where the pollutants, suspended particles lead to the sediment through collision with opposite particles and obtain agglomerate to form an insoluble agglomerate complex **(Megan et al., 2016)**.

In several types of research, coagulant type, coagulant dosage, stirring time and speed, settling time, and pH are the main factors determining the removal of the contaminant in wastewater. These factors will lead to the optimum conditions in the JAR test.

Table 2.3. Different wastewater treated by coagulation technique.

Authors / Coagulant	**wastewater/ Optimum condition**	**Pollutant Efficiency Removal**
Tetteh et al., 2017 aluminum sulfate (Alum), aluminum chloride, ferric sulfate and ferric chloride	Industrial mineral oil wastewater (Alum): 50 mg/L, aluminum chloride: 50 mg/L ferric sulfate: 50 mg/L ferric chloride: 50 mg/L	FC is best at removing turbidity and TSS Alum is best at removing COD and soap oil and grease Increase oil droplet floc size
Kumar et al., 2011 ACL3, PAC and copper sulphat	Pulp and paper PAC=8ml/l AlCl3=5ml/l CuSO4=5ml/l	PAC= COD to 84 % and 92 % AlCl3= 74 % COD and 86 % color CuSO4= 76 % COD reduction and 78 % color
Farajnezhad, and Gharbani., 2012 PAC, FeCl3	Petroleum wastewater PAC :10 mg/L FeCl3 :10 mg/L	PAC= 88% Color FeCl3=78% color
Chaudhari et al., 2007 FeCl3, AlCl3 and PAC	Distillery Industries 60 mM/l AlCl3, 60 mM/l FeCl3 and 30 ml/l of polyaluminium chloride	55, 60 and 72% COD reductions and about 83, 86 and 92% color reductions

2.2.4 Properties of a colloidal system

Colloids are very small particles that have an extremely large surface area. Colloidal particles are larger than atoms and ions but are small enough that they are usually not visible to the naked eye. They range in size from 0.001 to 10 µm resulting in a very small ratio of mass to surface area. Because of their tremendous surface, colloidal particles have the tendency to adsorb various ions from the surrounding medium that impart to the colloids an electrostatic charge relative to the bulk of surrounding water. The developed electrostatic repulsive forces prevent the colloids from coming together and, consequently, contribute to their dispersion and stability **(Djamel., 2013)**.

(a) ***Colloidal structure and stability***

The stability of colloidal particulate matter is dependent on their electrokinetic property. Colloidal particles acquiring similar primary charges develop repulsive forces that keep them apart and prevent their agglomeration. The primary electrical charges could be either negative or positive. However, most colloids that exist in aqueous systems are negatively charged **(Shammas et al.2005).** A colloidal system does not have a net charge. Negative primary charges on colloidal particles are balanced by positive counter-ions near the solid– liquid interface and in the adjoining dispersion medium. In a similar fashion, positively charged particles are counterbalanced by negative ions present in the surrounding water. This natural inclination toward achieving electrical neutrality and counterbalance of charges results in the formation of an electric double layer around colloidal particles. The electric double layer, which comprises the charged particle and surrounding counter-ions, is illustrated in Fig. 2.2.

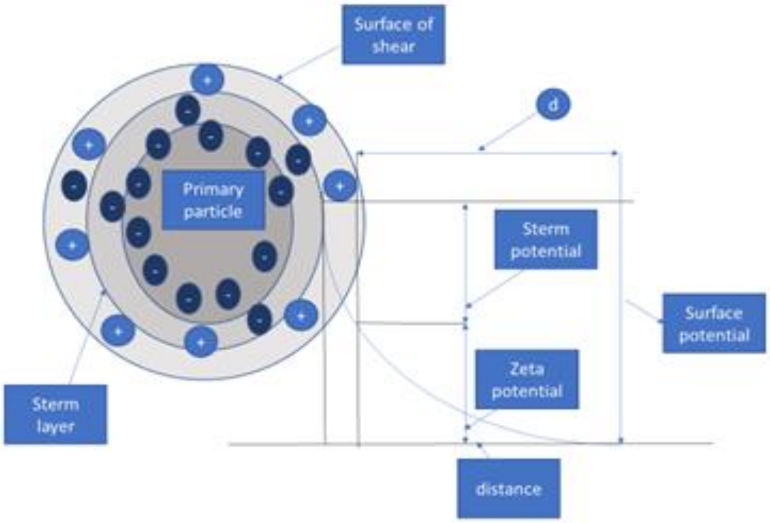

Figure 2.2. The electrical potential of a negatively charged colloidal particle

Source: **(Shammas et al., 2005)**

The total potential at the surface of the primary charged particle is termed the Nernst potential. The dense layer of counter-ions fixed on the surface of the primary particle is called the Stern layer.

The outer limit of this layer is defined by the surface of shear that separates the mobile portion of the colloid from the surrounding mixture of diffuse ions. In an electric field, the ions within the surface of shear will move with the particle as a unit. The concentrated counter-ions within the surface of shear reduce the net charge on the particle by an amount that is usually referred to as the Stern potential. Consequently, the potential is maximum at the surface of the primary particle, the Nernst potential, that decreases rapidly through the Stern layer resulting in a net overall charge on the particle at the surface of shear called the zeta potential (ZP). This potential determines the extent of repulsion between similarly charged particles and is commonly considered the major cause of a colloidal system's stability. Further away from the surface of shear both the concentration and potential gradients continue decreasing, but at a more gradual drop, until the potential approaches the point of electrical neutrality in the surrounding solution **(Shammas et al.2005).** The counter-ions of the Stern layer are concentrated in the interfacial region owing to electrostatic attraction. However, these ions tend to be more loosely attached, as they are located at distances further away from the particle surface because of the potential gradient. Consequently, any thermal agitation may cause these less strongly held ions to diffuse away toward the bulk of the dispersion medium. These two opposite forces, electrostatic attraction, and diffusion, give rise to the distribution of the potential over distance such that the highest concentration of counter-ions occurs at the particle interface and drops gradually with increasing distance. When the dispersion medium contains low concentration of ions (low ionic strength), the diffuse layer will be spread over a wide distance, d, as shown in Fig. 2.3. On the other hand, when the dispersion medium possesses a high ionic strength, the diffuse layer would get compressed, become thinner, and eventually extend far less distance into the bulk of the solution. Detailed analysis of the theory of the double layer and stability of colloids can be found in Verwey and Overbeek [1998], Morel [1982], O’Melia [1990], and Elimelech and O’Melia [1990].

(b) <u>Destabilization of colloidal</u>

When two similar primary charge particles drift toward each other, their diffuse layers start to interact leading to the production of a repulsive electrostatic force. The resulting repulsion between the approaching particles increases as the particles get closer. Such charged particles may not be able to collide at all if their charges are high enough **(O’Melia 1990).** Ultimately, as illustrated in

Fig. 2.3, the colloidal stability depends on the relative strength of the above electrostatic forces of repulsion and the forces of attraction.

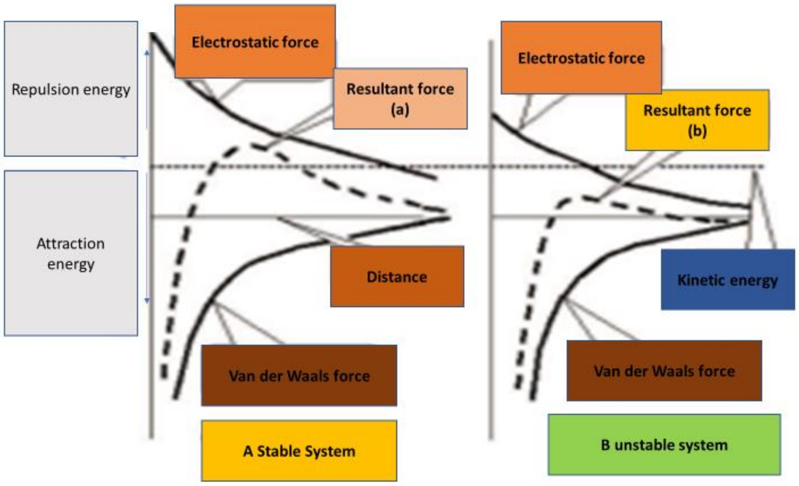

Fig. 2.3 Effect of interparticle forces on the stability of a colloidal system.

Source: **(Shammas et al.2005)**

The forces of attraction are due to van der Waals' forces. All colloidal particles, irrespective of their composition, sign or magnitude of charge, or the composition of the dispersion medium, possess such attractive forces. They arise from the following: Electronegativity of some atoms is higher than for others in the same molecule., Vibration of charges within one atom creates a rapidly fluctuating dipole., Approaching particles induce vibrations in phase with each other **(Shammas et al.2005).** The above phenomena result in an attractive force between the two oppositely oriented dipoles. The magnitude of the force varies inversely with distance between particles, increasing rapidly with decreasing distance (see Fig. 2.2). If particles come close enough for these forces to take over, they will adhere **(Shammas et al.2005)**. The other factor, in addition to van der Waals' attractive forces, tending to destabilize a colloidal system is Brownian movement. This is due to the random motion of colloids brought about by their bombardment by molecules of the dispersion medium. The outcome of the movement is to impart kinetic energy to the colloidal particles. Higher energy particles moving in a random fashion tend to collide eventually **(Shammas et al.2005).** Moreover, Fig. 2.3 illustrates the relationship of forces that exist between colloidal particles as a function of the separation distance. The net resultant force is obtained by the summation of the respective electrostatic repulsive force and van der Waals' attractive force. When the resultant repulsion energy exceeds the kinetic energy (Fig. 2.3A), the particles will not coagulate, and the dispersion is stable. When the kinetic energy is larger than the repulsion energy (Fig. 2.3B), the dispersion is unstable, and the particles will coagulate. Consequently, if it is required to destabilize and coagulate a stable dispersion, then the electrostatic repulsion energy between the particles must be lowered and/or the kinetic energy of the particles must be raised **(Shammas et al.2005)**.

2.2.5 Mechanism of coagulation

Destabilization of colloidal particles is accomplished by coagulation by adding hydrolyzing electrolytes such as metal salts and/or synthetic organic polymers. Upon being added to the water, the action of the metal salt is complex. It undergoes dissolution, the formation of complex highly charged hydrolyzed metal coagulants (hydroxyoxides of metals), interparticle bridging, and the enmeshment of particles into flocs. Polymers work either based on particle destabilization or bridging between the particles **(Kurniawan et al., 2020)**. The destabilization process is achieved by the following four mechanisms of coagulation **(Djamel., 2013)** Figure 2.3: Double-layer compression (DLC)., Adsorption and charge neutralization (CN)., Entrapment of particles in precipitate (sweep coagulation, SC)., Adsorption and bridging between particles.

a*) Double-layer Compression*

The most effective way to remove particulate contaminants through coagulation is by charge neutralization. All coagulant types (under specific conditions) follow this mechanism of coagulation. The concept of charge neutralization is closely related to the electrostatic nature of the colloid or particle. This electrostatic stability is explained by the theory of the electrical double layer. Figure 2.2 shows the various layers surrounding a single colloid or particle in solution. The colloid is negatively charged and attracts positive ions from the solution to its surface to form a tight positive layer called the stern layer. Positive ions are still attracted to the negative colloid but are now repelled by the Stern layer creating a new layer around the Stern layer called the diffuse layer. The diffuse layer has a higher concentration of positive ions closer to the colloid which gradually decreases further away from the colloid until an equilibrium concentration of positive and negative ions is reached **(Megan et al., 2016**).

Zeta potential, usually denoted using the Greek letter zeta (û), is explained using the theory of the electrical double layer as illustrated in Figure 2.2. The slip/shear plane is usually found where the Stern layer and the diffuse layer meet; zeta potential is the potential energy between the dispersion medium (bulk liquid) and the slip/shear plane. Zeta potential is an indicator of a particle's stability and net surface charge. The further away the zeta potential value is from zero (both positive and negative) the more resistant the particles are to aggregation. A negative zeta potential indicates a negative net surface charge **(Megan et al., 2016)**.

When high concentrations of simple electrolytes are introduced into a stabilized colloidal dispersion, the added counter-ions penetrate the diffuse double layer surrounding the particles rendering it denser and hence thinner and smaller in volume. The addition of counterions with higher charges, such as divalent and trivalent ions, will result in even steeper electrostatic potential gradients and a more rapid decrease in charge with distance from the surface of the particles. The net repulsive energy (see Figure 2.3) would become smaller or even would be eliminated, allowing the particles to approach each other and agglomerate **(Djamel., 2013)**.

b) Adsorption and charge neutralization (CN)

The ability of a chemical substance to destabilize and coagulate colloidal particles is the result of a combination of several mechanisms.

(I) Long-chained organic amines

Long-chained organic amines are often mentioned as being typical coagulants that function by adsorption and electrostatic neutralization. The positively charged organic amine molecules (R–NH3 +) are easily and quickly attached to negatively charged colloidal particles. The charge on the particles gets neutralized and the electrostatic repulsion is decreased or eliminated resulting in the destabilization of the colloids and hence their agglomeration. Organic amines are hydrophobic because there is a lack of interaction between the CH2 groups in their R-chain and the surrounding water. As a result, these positively charged ions are driven out of the water and get adsorbed on the particulate interface. An overdose of R–NH3 + counter-ions, however, can lead to charge reversal from negative to positive and the destabilization of the dispersion system **(Djamel., 2013).**

(II) Coagulants such as metal salts

Aluminum (Al)-based, and iron (Fe)-based coagulants are used in wastewater and water treatment **(Ma et al.2019, Wu et al.2019, Ahmad et al.2008).** When coagulants such as metal salts are added to water, they dissociate by yielding metallic ions, which undergo hydrolysis and form positively charged metallic hydroxyoxide complexes. The commonly used coagulants, trivalent salts of aluminum and iron, produce many species because the hydrolysis products polymerize to give polynuclear metallic hydroxides **(Shammas et al.2005).** Examples of aluminum salt polymers are Al6 (OH)15 3+ and Al7 (OH)17 4+ and of iron salt polymers are Fe2 (OH)2 4+ and Fe3 (OH)4 5+. Cationic species absorb the negatively charged particles found in water and neutralize the charge based on the principle of charge neutralization (**Meetiyagoda et al.2022).** When such polyvalent complexes possessing high positive charges get adsorbed on to the surface of the negatively charged colloids, the result is again a neutralization of the charges, decrease in the repulsion energy, and destabilization of the colloids Figure 2.4. In a similar fashion to what occurs with the organic amines, an overdose of metallic salts could reverse the colloidal charge and restabilize the particles **(Djamel., 2013)**. Polyaluminum chloride (PAC) is considered highly efficient than other coagulants owing to the presence of high-charged polymeric forms of Al hydrolysis products **(Wu., 2019, Krupińska. 2020)**. PAC is prepared by partial hydrolysis of acid aluminum chloride (AlCl3) and consists of Al monomers, dimers, and trimers **(Wu., 2019)**. Cationic species absorb the negatively charged particles found in water and neutralize the charge based on the principle of charge neutralization **(Meetiyagoda., 2022)**.

c) **Entrapment of particles in precipitate (Sweep Coagulation (SC))**

When the coagulants alum [Al2 (SO4) 3] or FC (FeCl3) are added in high enough concentration, they will react with water (and hydroxides (OH−)) to form metal hydroxide precipitates, Al (OH)3 or Fe (OH)3 respectively. The colloidal particles get entrapped in the precipitates either during the precipitate formation or just after. This type of coagulation by enmeshment of colloids in precipitates is commonly called SC Figure 2.4. There are three elements that influence this coagulation mechanism **(Djamel., 2013)**:

(I) Oversaturation: The rate of precipitation is a function of oversaturation with the metal hydroxide. To obtain fast precipitation and efficient SC, high concentrations of Al (OH)3 or Fe $(OH)_3$ are required.

(II) <u>Presence of anions:</u> The rate of precipitation is improved by the presence of various anions in water. The most effective anions in this respect are the sulphate ions.

<u>(III) Concentration of colloids</u>: The rate of precipitation is also improved with higher concentration of colloidal particles. The reason for this is that the colloids themselves could act as nuclei for the formation of precipitates. In this case, it can be concluded that lower rather than higher coagulant dosage will be required to coagulate water having higher colloidal particle concentration.

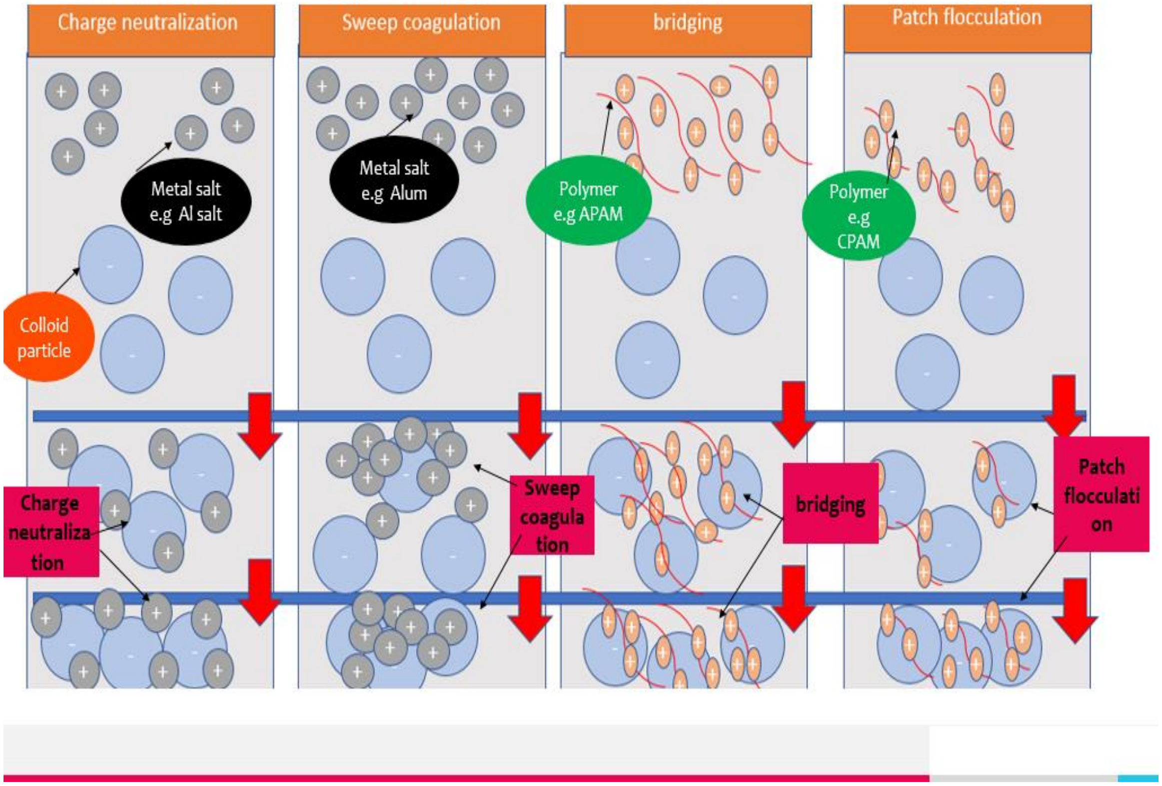

Figure 2.4. Mechanisms of coagulation and flocculation.

Source**:(Kurniawan et al., 2020)**

<u>d) Bridging between particles and Patch flocculation.</u>

<u>(I) Bridging between particles</u>

Bridging between particles occurs when polymers destabilize colloidal particles through the formation of bridges that extend between them. The polymers have reactive groups that bind to specific sites on the surface of the colloidal particles. When a group on a polymer molecule attaches to a colloid, the remainder of the long-chain molecule extends away into the water. Once the extended portion of the polymer gets attached to another colloidal particle, the two particles become tied together or bridged by the polymer. If no other particle is available or if there is an overdose of polymer, the free extended portions of the polymer molecule would wrap around the same original particle, which could effectively bring about the destabilization of the colloid. Destabilization can also occur due to aggressive mixing or extended agitation, which may break the interparticle bridging and allow the folding back of the freed polymer portions around the same original particle **(Djamel., 2013).**

(II) Patch flocculation

In patch flocculation, a polymer or coagulant adsorbs onto an oppositely charged particle surface to give a non-uniform distribution of the surface charge. Direct electrostatic attraction between oppositely charged patches promotes aggregation, and particles with a strong negative zeta potential, such as silica, will aggregate by patch mechanisms in response to polyelectrolytes with a high cationic charge density (>0.15), while a low cationic charge density (<0.15) will favor bridging **(Tripathy & De 2006)**.

2.2.6 Factors affecting coagulation.

Coagulation is affected by the following factors **(Sukmana et al., 2021), (Khazaie., et al.2022)**: Total organic carbon and dissolved organic carbon (color)., Colloid concentration (turbidity)., Temperature., pH. Anions and cations in solution. Electrophoretic mobility or zeta potential. Type of coagulant. Coagulant dosage.

- **Coagulants**

Coagulants could be classified into two types, i.e. chemical and natural coagulants. Both coagulants aim to remove pollutants in the chemical (BOD & COD) or physical (suspended solids & turbidity). Chemical coagulant includes hydrolyzing metallic salts such as ferric chloride, ferric sulphate, magnesium chloride, and alum; pre-hydrolyzing metallic salts such as poly aluminum chloride (PAC), poly ferric chloride (PFC), poly ferrous sulphate (PFS), poly aluminum ferric chloride, and synthetic cationic polymers such as aminomethyl polyacrylamide, polyalkylene, polyethylenimine, polyamine **(Sukmana et al., 2021, Khazaie., et al.2022)**. Natural coagulant contains microorganism substances such as bacterial, microalgae, fungal; animal-based such as chitosan and isinglass and plant-based such as seed and plant extracts, starch and fruit waste

(Sukmana et al., 2021). The low-cost market price is the key factor for choosing coagulants, as given in Table 2.4.

Table 2.4. The market price for bulk sales of coagulants. Source: **(Khazaie., et al.2022)**

Coagulants	**FeCl3**	**Lime**	**Alum**	**PACL**	**Fe2(SO4)3**
Price, €/tonne	250–450	150	175–200	250–400	250–350

2.2.7 Flocculation.

The aggregation of fine particles by polymeric flocculants has been used in wastewater processing Table 2.5. The conventional flocculants widely applied in organic wastewater plant processes are organic polymeric materials. Synthetic polymers can improve flocculation efficiency significantly. The combined usage of metal salts and organic polymers can reduce metal coagulants' dosage and thus the sludge volume Table 2.5. and savings in operational costs such as lower demand for metal salts and the reduction in filter backwash could offset the chemical cost of polymers. Commercial organic flocculants are water-soluble polymers produced by repeating units of different monomers such as acrylamide and acrylic acid. Table 2.6. lists the names and market prices for some of the commercial flocculants, including AN 934, FLOCAN, FO-4350, and FO-4700. These materials are usually derived from oil-based and non-renewable raw materials **(Khazaie., et al.2022).**

Table 2.5. Different wastewater treated by coagulation-flocculation technique.

Authors / flocculants	**Wastewater/ Optimum condition**	**Pollutant Efficiency Removal**
(Sun et al., 2018) cationic polyacrylamide (CPAM) flocculant PADA-3 (cationic degree = 40%, and intrinsic viscosity = 6.30 dL · g−1)	Estrone removal pH = 7, CPAM dosage = 4.0 mg/L Estrone con = 0.75 mg/L	Estrone removal rate: 90.1%, foc size: 18.3 micrometer, focculation kinetics: 22.69 × 10−4 s −1
(Liu et al., 2015) low charge density cationic polyacrylamide (CPAM),	Dairy wastewater CPAM: 50 ppm	About 42.5% Separation efficiency within 1 h) PDCD does not facilitate coagulation of high solid

high charge density cationic polydicyandiamide (PDCD)		but inhibits bacterial pathogens, further lowered solids content manure after CPAM separation
(Li et al., 2017) cationic polyacrylamide	Dyeing mill wastewater CPAM: 30 mg L-1	Turbidity: 4.47 NTU moisture content: 72.2%, COD: 79.2% increasing molecular weight enhances dewatering
(Vanotti et al., 2002) Polyacrylamide	Swine manure PAM: 140 mg/L Screening	TSS 95%, VSS 69%, COD 59% BOD 5 :67%, organic P :92%, organic: 85%
(Chastain et al., 2001) PAM (polyacrylamide)	Dairy manure	Removed 76.1% of the TS,92% of the TSS and 80.8% of the COD.
(Wong et al., 2016) Cationic polyacrylamide Organopol 5415 high molecular weight and low charge density	Paper mill wastewater	95% turbidity removal,98%TSS removal and 93% COD removal.
(Loloei et al.,2014) Alum, Ferrous sulphate, (Polyacrylamide [PAA], polyferric sulphate [PFS]	Dairy wastewater Alum:1000 mg/L, Ferrous sulphate: 1000 mg/L, [PAA]:20 mg/L, PFS]: 20 mg/L	Alum Turbidity: 95% COD: 68% ferrous sulphate turbidity :95% COD:62%
(Kaur et al., 2020) Alum, Chitosan	Pulp and paper mill wastewater Alum: 0.4 g/L. chitosan: 0.3 g/L.	TSS :81%, COD :78%, zeta potential (–1.49 mV), larger floc
(Amuda and Amoo., 2007) Ferric chloride	Beverage industrial wastewater Coagulation only	Coagulation COD: 73%, TP :95%,

Non-ionic polyacrylamide	Ferric chloride: 300 mg/L coagulation/flocculation Optimal pH 9 Ferric chloride :100 mg/L Polyelectrolyte :25 mg/L	TSS: 97% Coagulation/flocculation COD: 91%, TP :99%, TSS: 97% Sludge volume reduction: 60%

Table 2.6. The market price for bulk sales of chemical flocculants. Source:**(Khazaie., et al.2022)**

Coagulant type	**Anionic Flocculants**	**Anionic Flocculants**	**Cationic Flocculants**	**Cationic Flocculants**
Coagulant material	AN 934	FLOCAN	FO-4350	FO-4700
Price, €/tonne	2550	2500	2800	2980

2.2.8 Properties of Polymers

For desirable flocculation results, characteristics of the polymer flocculant such as molecular weight, charge density, and structure have crucial roles. For a specific type of polymeric flocculant, the increase in the molecular weight achieved by increasing the length of the molecular backbone would speed up the sedimentation rate due to improving the bridge-binding of small particles **(Khazaie., et al.2022).** Although increasing the charge density enhances the settling velocity, an excess increase in charge density adversely affects the flocculation process in floc size and floc density **(Khazaie., et al.2022)**. A research experiment investigating the effect of polyacrylamide polymers on floc characteristics showed that increasing the charge density from 10 to 35% increased the adsorption rate by increasing the electrostatic attraction force between the negatively charged kaolinite particles and the positively charged polymer chains. Increasing the absorption rate resulted in decreased floc size by reducing the available sites for bridging **(Nasser and James. 2007).**

(a) Cationic Polymers

The most used polymeric flocculants in wastewater processes are polyacrylamides that can be classified based on their charge types into four categories: Anionic (negatively charged), cationic (positively charged), nonionic (neutral), and amphoteric (contains both anionic and cationic groups). These polymers can vary in molecular weight (low, medium, and high), amount of charge (low, medium, and high), and structure **(Khazaie et al., 2022)**. Polyacrylamide has been also used in the treatment of dairy manure wastewater, paper and pulp wastewater, and beverage wastewater **(Loloei et al., 2014, Kaur et al., 2021, Wong et al., 2006)**.

Cationic polyacrylamides (CPAM) are made by copolymerizing acrylamide with quaternary ammonium derivatives of acrylamide. They include 10 to 80 mol% cationic monomers, with higher molecular weights containing just 10% cationic monomer that may operate as flocculants **(Khazaie et al., 2022)**. Cationic polymers are essential for aggregating suspensions in organic wastewater **(Amuda and Amoo. 2007, Sun et al., 2018, Zhao et al., 2018)** Because they struggle to reach high settling rates, they are not employed in high-throughput applications. CPAM removes pollutants and organic matter by (1) neutralizing the negatively charged colloidal particles, (2) the destabilized colloidal particles are wrapped and connected to form large flocs that dewater easily and quickly settle down under the effect of bridging and sweeping **(Liu et al., 2016, Zhao et al., 2018)**. Cationic degree and relative molecular weight (limiting viscosity) are closely related to electrical neutralization and bridging effect performance, respectively **(Li et al., 2017)**. On the other hand, the CPAM's long-chain operates over a longer distance, resulting in bigger and looser kaolin flocs, lowering the flocculation effectiveness of fine kaolin particles (<10 µm) **(Zhou et al., 2021).**

2.2.9 Interaction Mechanism of Flocculant

According to the Derjaguin and Landau, Verwey, and Overbeek (DLVO) theory, the interaction potential between colloidal particles in aqueous media is controlled by the Van der Waals (attractive) and electrical double layer (repulsive) forces **(Khazaie et al., 2022).** A study carried suggested that the surface charge of particles affects the sedimentation process. Therefore, the low surface charge results in a fast-settling rate and a porous cake with high moisture content. However, the high surface charge results in a slow settling rate, and a compact cake with low moisture content **(Khazaie et al., 2022).** The formation of flocs results from several consecutive steps, including dispersion and diffusion of the flocculants, adsorption of the flocculants on the particles' surfaces, particle collision, formation, and the growth of micro-flocs by consecutive collision and adsorption. The interaction between anionic, cationic, and nonionic flocculants with suspended particles involves several mechanisms, including charge neutralization, polymer bridging, and electrostatic patch, which depend on adsorption of flocculants onto the surface of suspended particles **(Khazaie et al., 2022).** Moreover, the adsorption rate is controlled by the available sites on the surface of particles, and the adsorption rate in flocculated systems typically lies between 0.05 and 0.5 mg/g solids. High molecular weight polymeric flocculants produce large and loose flocs, while low molecular weight polymers create small and compact flocs **(Khazaie et al., 2022).** The optimum flocculant dosage is crucial in a flocculation process before sedimentation and filtration since a low dosage may decrease floc formation rates. In contrast, higher dosage can increase filtration resistance and/or higher moisture content **(Khazaie et al., 2022).**

(a) <u>Interaction Mechanism for Cationic Flocculants</u>

The schematic illustration of flocculation of colloidal particle with cationic flocculants is shown in Figure 2.5. **(Khazaie et al., 2022).** Flocs are formed via two interaction mechanisms in this process, including charge neutralization and electrostatic patch. Charge neutralization occurs where the flocculants and the adsorption sites are of the opposite charge. Since the colloidal particles in organic wastewater carry a negative charge at a neutral to slightly alkaline pH range, the adsorption of cationic flocculants onto their surfaces reduces their surface charge and decreases the repulsive electrical force between suspended areas particles. Thus, van der Waals attraction force becomes dominant, which leads to the formation of micro-flocs **(Khazaie et al., 2022).**

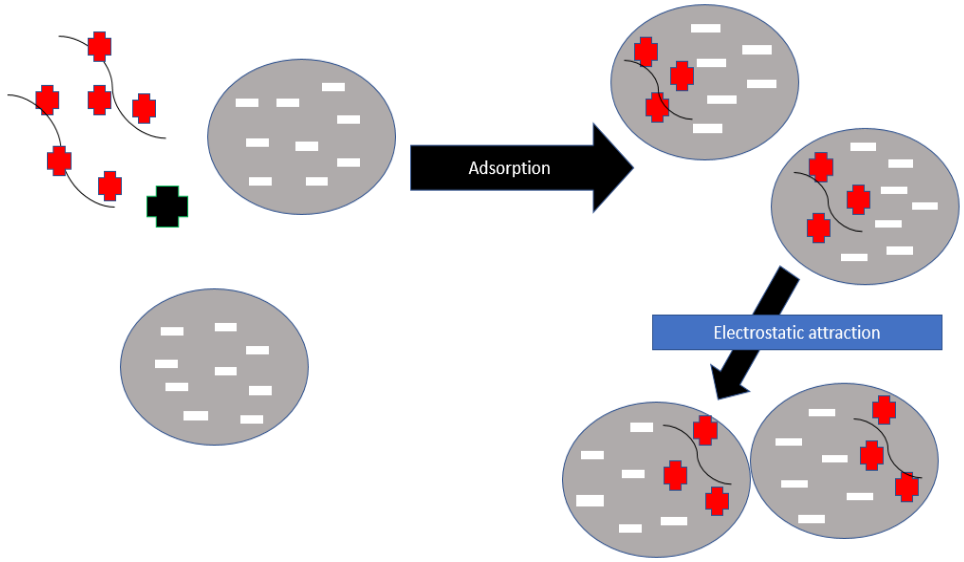

Figure 2.5. Charge-patch mechanism for cationic polymers

Source: **(Khazaie et al., 2022)**

For cationic flocculants with high charge density, an electrostatic patch mechanism called mosaic holding is crucial in flocs formation. When highly charged cationic flocculants adsorb on negatively charged surfaces, they cover exceedingly small parts of them and form cationic patches or islands between uncoated negatively charged surfaces. Under these circumstances, as particles move towards each other, they can be attached via electrostatic attraction between uncoated negative areas of positive islands **(Khazaie et al., 2022)**. Literature reports that the charge patch mechanism forms small flocs with a low settling rate. If too much cationic flocculant is added to the suspension, all the particles become positively charged. Therefore, the electrostatic repulsive forces become dominant, and they will be dispersed again in re-stabilization **(Khazaie et al., 2022)**.

2.2.10 Coagulation-flocculation of palm oil mill effluent (POME)

By adding coagulants and flocculants, coagulation-flocculation induces destabilization and aggregation of colloidal particles in POME, and the sedimentation of the resulting flocs is allowed subsequently to form a separable sludge from clarified POME **(Cheng et al.2021)**. For coagulation-flocculation treatment of POME, multiple procedures can be deployed to predict the main mechanism, viz. population balance model (using interaction energy curve) **(Ahmad et al., 2008)**, zeta potential versus pH curve (predict protonation/deprotonation of functional group from pI) **(Abidin et al., 2017)**, FTIR (from functional group) **(Adnan et al., 2017),** conductometric titration (by charge density) **(Ariffin et al., 2005)**, and pH dependence of metal hydroxide formation (i.e., pH 5–8 for Al(OH)3) **(Huzir et al., 2019).** Table 2.7 summarizes past performance of coagulation-flocculation as POME treatment, which narrates its poor ability in degrading COD and BOD compared to TSS, O&G, turbidity, and colour. During coagulation-flocculation, rapid mixing (50–258 rpm) with short duration (0.08–15 min) is needed to well disperse coagulants and flocculants (may present but not necessary) throughout POME for destabilization (coagulation), then slow mixing (10–40 rpm) with long duration (20–60 min) is crucial to render floc development (flocculation) **(Cheng et al.2021**). Afterwards, the agitation is halted to facilitate sedimentation of heavy flocs with a typical time range of 30–60 min. Since density difference governs sedimentation, denser and larger flocs easier to settle down, thus preferable to shorten total treatment time. Although physical mixing could induce flocculation, trace flocculant with high molecular weight is often added as coagulant aid to promote flocs densification, thereby reduce coagulant dosage **(Chung et al., 2018)**. For POME coagulation, the tested coagulants are classifiable into (i) hydrolysable metal salts [alum/aluminium sulfate, iron (II) sulfate heptahydrate, iron (III) chloride, calcium chloride, magnesium sulfate, calcium lactate, and lime/calcium hydroxide] **(Cheng et al.2021**), (ii) polyelectrolyte [polydiallyldimethyl ammonium chloride (polyDDA) and polyaluminium chloride (PAC)] **(Cheng et al.2021**), (iii) biomass wastes [chickpea seed, dragon fruit foliage, and rice husk ash], biomass extract (from Jatropha curcas seed/press cake), Moringa oleifera, Cassia obtusifolia seed, peanut, Fenugreek seed, and chitosan], biopolymers [chitosan, pectin, and rice starch], and modified coagulants [quaternized C. obtusifolia seed extract and magnetic chitosan] **(Cheng et al.2021**).

For POME flocculation, the evaluated flocculants are commercial flocculants [Profloc 4190, Polyfloc KP 9650, Polyfloc AP 8350, Envifloc 20, Magnafloc LT22, and NALCO 7751], organic flocculants [okra extract, synthetic polymers [cationic/anionic polyacrylamide], and composite [polyacrylamide/magnetic cellulose, and magnetic cellulose] **(Cheng et al.2021**). **Shak and Wu (2014)** noticed the performance of coagulation-flocculation is influenced by initial COD concentration, coagulant/flocculant dosage, pH, sedimentation time, agitation speed, and temperature. Coagulation-flocculation works better for low strength wastewater like the diluted POME with lower COD. High dosage of coagulant/flocculant boosts the treatment efficiencies with more available coagulant/flocculant; withal, surplus amount lessens treatment efficiencies by restabilizing POME suspension. Excess organic coagulant/flocculant could also weaken treatment since their biodegradability augments initial COD **(Cheng et al.2021**). pH can either improve or complicate coagulation-flocculation because (i) acidic pH may protonate functional groups of coagulant/flocculant and induce positive particle surface charge with excess H+ whereas (ii) basic pH may deprotonate the functional groups of coagulant/flocculant and induce negative particle surface charges with excess OH-, wherein the changes are varied with pI. Extreme pH can provoke acid/alkaline hydrolysis of organic coagulant/flocculant. Coagulation-flocculation improved with longer sedimentation time until a plateau **(Cheng et al.2021**). In terms of agitation speed, low speed strengthens flocs development, but high speed resuspends colloid with strong hydrodynamic/ mechanical shear forces **(Cheng et al.2021**).

Table 2.7 Coagulation –flocculation of POME.

Authors / flocculants	**Wastewater/ Optimum condition**	**Pollutant Efficiency Removal (%)**
(Almad et al., 2006b) PAC	POME PAC: 6000mg/L, PH: 4.5	TSS:92.9 Oil and grease :99
(Jagaba et al., 2020) FeCl3	POME FeCl3. 1000mg/L	COD:72, TSS: 99.1 Turbidity: 95.8 Color: 66, Oil and grease: 95.7
(Huzir et al., 2019) Rice husk ash	POME Rice husk ash :6000mg/L PH: 3.6	COD: 52.8%
Zahrim and Dexter (2016) polyDDA 1000	ANPOME polyDDA 1000mg/L PH: 7.95	Color:48
(King et al., 2019) Chitosan	APOME Chitosan 200mg/L	COD:15 TSS: 97, Color :85.8
Som and Wahab (2018) Dragon fruit foliage	POME Dragon fruit foliage 300mg/L PH:2	COD:48.7 TSS:98.8 Color: 99.2
Zinatizadeh et al. (2017) Cationic PAA anionic PAA	POME Cationic PAA:300mg/L anionic PAA: 50mg/L PH:5	COD: 70.9 TSS: 96.4
Ariffin et al. (2005) Cationic PAA	POME Cationic PAA:300mg/L PH :3	COD:54, TSS:98.7 Turbidity: 98

2.2.11 Advantages and disadvantages of coagulation and flocculation.

(a) Coagulation and flocculation advantages.

From a business perspective, one of the main advantages of using inorganic coagulants is that they are often cheaper to use than organic coagulants. Inorganic coagulants are therefore a very cost-effective option across a wide range of industries and applications **(Dotto., et al.2018)**.

The application of polymeric flocculants for industrial purposes has some significant advantages. These include high solubility in aqueous systems, not affecting the pH of the medium, high efficiency at low dosage, and producing large, strong, and stable flocs **(Khazaie et al., 2022)**.

In addition, flocculants are often essential to further improve the performance of coagulation process and reduce the residual Al in treated water **(Zhang et al.2018).**

(b) Limitation of coagulation and flocculation.

Coagulants often need to be used at a higher dosage for polluted wastewater to meet the regulatory goals. This practice generates a large amount of sludge that requires extensive treatment before disposal, which also adds to the overall operating costs **(Teh., et al.2016).**

One of the significant issues related to the coagulation process is the toxicity and health hazard possessed by inorganic coagulants, such as aluminum salt (Alum). The use of conventional coagulant, such as aluminum salt (Alum), has drawn major concern about the increase of Al concentration in the water which may become toxic either to plants, humans or to the aquatic environment **(Chastain., et al.2001)**.

Although the use of high dosages of aluminum salt in the wastewater treatment might reduce COD effectively, it might also result in an increase of aluminum species present in the water which may lead to Alzheimer's disease upon consumption.144 Hence, it is necessary to control the residue Al3+ content in the discharge to be under 200 and 50 μg/L for European and United States of America standards, respectively **(Teh., et al.2016).**

In some cases, it was reported that the coagulation−flocculation process using ferric chloride presented some considerable limitations related to the production of color in the effluent after treatment. For example, in the coagulation treatment of sewage water, the use of ferric chloride resulted in color generation at the end of the treatment, which is unacceptable according to environmental regulation **(Teh., et al.2016)**.

Polymeric flocculants have been reported to cause environmental and health hazards. Since most commercial polymeric flocculants are derived from petroleum-based materials, they are not environmentally acceptable. Most of them are non-biodegradable, and their by-products release monomers that might have carcinogenic effects **(Khazaie et al.,2022)**. However, the reported research experimental results have asserted that the normally used anionic and nonionic polyelectrolytes have a low toxicity rate. Still, cationic types are usually more toxic, especially to aqueous organisms **(Khazaie et al., 2022)**.

Organic polymers are more expensive **(Kinyua et al.,2016),** (around five to ten times more expensive than metal salts). Example, market price for bulk sales of coagulants and flocculants and costs of a studied processes shows that poly-aluminum chloride-PAC and aluminum sulphate costed 0.42 and 0.23 (Euro/Kg) respectively, while anionic polyacrylamide-flocan and anionic polyelectrolyte-Praestol costed 2.32 and 3.10 (Euro/Kg) respectively) **(Pelendridou et al.,2014).**

2.2.12 Manual coagulation/flocculation dose control.

The jar test simulates the coagulation/flocculation process of the water treatment plant to help optimize its performance. The required coagulant dose is determined by laboratory jar testing and is used as the initial set point for the coagulant dosing pump. Further adjustments can be made on the plant coagulant dose until the desired clarifier overflow and/or filtered water turbidity are achieved in the plant **(Megan et al., 2016).**

(a) Jar Tests

Jar tests are used to determine the optimum coagulant dose, which is dependent on several factors, including raw water turbidity, pH, alkalinity, total organic carbon, and ionic strength. A jar test mimics the water treatment process from raw water intake up to and including the clarification process. Beakers containing raw water samples and magnetic stir bars are placed on a multi-position magnetic stirrer unit. Process chemicals are added in the same sequence as they would be added in the plant. One parameter, such as coagulant dose, is varied to achieve the optimum dosages. Jar tests can be used to evaluate **(Megan et al., 2016):** Turbidity and/or color removal., Trihalomethane precursor removal., Iron and manganese removal., Taste and odor of treated water., Process control such as coagulant and dosage selection, optimum pH, mixing energy, coagulant aid selection., Sludge characteristics.

(b) Spectrophotometry

Jar testing can be done with other tests such as spectrophotometry to determine optimum coagulant dose. Spectrophotometry is based on the principle that light from a light source in a spectrophotometer, passing through a water sample in a cell, will be attenuated due to absorption of the incoming light of a specific wavelength by organic compounds in the sample **(Megan et al., 2016).**

(c) Zeta Potential

Zeta potential (electrophoretic mobility) is measured using a zeta meter in a laboratory. A current is applied to the solution inside an electrophoresis cell and the speed and direction of the particles is measured using a stereoscopic microscope. This is known as electrophoretic mobility. Zeta potential is sensitive to changes in ion concentration such as pH. Zeta potential measurements are useful for **(Megan et al., 2016):** Coagulant determination., Optimum pH determination., Chemical dosage., Evaluating dilution and mixing requirements., Turbidity

(d) Turbidity

Turbidity is defined by the American Public Health Association (APHA) as the “expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample”. It occurs due to the presence of suspended and colloidal particles in the water. Turbidity is not affected by certain raw water constituents such as humic acids, which do affect coagulant dosage. This limits the use of a turbidity meter to control primary coagulant dosage **(Megan et al., 2016).**

(e) Fluorescence

Fluorescence is a process whereby light is absorbed by molecules. The absorbed light then excites the particles. The particles emit the absorbed energy when they return to an unexcited state. The wavelength of the realized energy is then measured. There are fluorometers that can measure organics and turbidity. Two online or portable probes can then measure the parameters affecting coagulation dosage for dose control. No case studies have been done for coagulant dosage optimization or control **(Megan et al., 2016).**

2.3 Electrolysis (Electrochemical processes)

Electrolysis is a method in which oxidation and reduction occur due to application of electric current to the electrolytic solution. Electrochemical technology has shown to be a hopeful technique for the destruction of organic pollutants in the wide collection of wastewaters and there is no need for adding additional chemicals. In the 19th century (1889) in London, the electrochemical method was proposed with a well-established plant for sewage treatment. In this process, wastewater was electrolyzed by mixing with sea water. The prime interest of primary stage development of the electrochemical process was to generate chlorine for the removal of odor and disinfection of sewage wastewater. Electrochemical processes include electro-coagulation, electro flotation, electro oxidation, electro-flocculation, electro-disinfection, electro reduction, electro-deposition, etc. **(Bharathet. 2018).**

2.3.1 Electrolysis (electrolysis) process

Electrolysis (electrolysis) process is a process in which an oxidation reaction takes place at the anode and a reduction reaction at the cathode by applying a forced voltage to two electrodes connected to an external power source **(Kim et al., 2013).** In electrolysis, the anode is called an anode in the sense that it is the electrode on which anions react. Similarly, the cathode is called a cathode in the sense that it is the electrode at which cations react. For example, when dilute hydrochloric acid is electrolyzed, chloride ions are oxidized to produce chlorine gas at the anode (Eq. 1), and hydrogen is produced at the cathode through electrolytic reduction of hydrogen ions (Eq. 2).

(anode) $2Cl^{-}(aq) \longrightarrow Cl_2(g) + 2e–$ **Equation 1**

(Cathode) $2e– + 2\,H^{+}(aq) \longrightarrow H2(g)$ **Equation 2**

(Overall reaction) $2H^{+}(aq) + 2\,Cl–(aq) \longrightarrow H_2(g) + Cl_2(g)$ **Equation 3**

Eliminating electrons from equations (1) and (2), we obtain equation (3). In other words, in the electrolysis of dilute hydrochloric acid, the overall reaction that generates hydrogen and chlorine from hydrogen and chloride ions is in progress. From the viewpoint of the overall reaction in Equation (3), the anodic reaction in Equation (1) can be considered to represent only the oxidation reaction and the cathodic reaction in Equation (2) can be considered to represent only the reduction reaction, which is called the half-reaction equation because it constitutes a part of the reaction in Equation (3).

Conductive materials are indispensable for electrolysis because electricity must flow through them. In water treatment by electrolysis, water exists as a medium, but the water itself is not conductive, so an electrolyte such as an ionic substance is necessary. The following is an explanation of the treatment principle and features of electrolysis in water treatment; Process Principle., Electrode reaction.

In an electrolytic process, an oxidation reaction takes place at the anode, where electrons are lost from the material, and a reduction reaction takes place at the cathode, where electrons are given to the material. The reactions of both electrodes always occur in pairs, and it is impossible for only one of them to proceed. In electrochemistry, standard electrode potentials are obtained and organized as thermodynamic parameters for various semi-reaction equations. Table 2.8 shows typical semi-reaction equations used in water treatment and water analysis and their standard electrode potentials. The standard electrode potential is the electromotive force when a battery is constructed using the electrode at which the reaction of interest occurs and a standard hydrogen electrode under standard conditions (a = l, the activity of all chemical species involved in the reaction at 25°C). However, it is a rule to express the electromotive force when the oxidation reaction of hydrogen, shown in equation (4) is taking place at the standard hydrogen electrode.

H_2-$2H^+$+2e- **Equation 4**

Therefore, all half-reaction equations are expressed as reduction reactions (cathodic reactions).

In relation to thermodynamic parameters, the standard electrode potential E°[V] has the following relationship with the standard Gibbs energy change (standard free energy change) ⊿G°[J] in the electrode reaction **(Liu et al., 2004)**.

$\triangle G° = --zFE°$ **Equation 5**

where z is the number of electrons required for the electrode reaction [mol] and F is Faraday constant (=96,485 C/mol).

Table 2.8. Major semi-reactive equations and standard electrode potentials related to water treatment and water quality analysis

semi-reactive	**Standard electrode potential E° [V]**
acidic conditions	
2H++2e~-> H2	0
02+4H++4e_-2H20	1.229
MnO4~+8H++5e_-» Mn2++4H2O	1.51
Cr2072- + 14H++6e--*2Cr3++7H20	1.36
2HCI0 (aq) +2H++2e_- Cl2(g) +2H2O	1.630
03+2H++2e--*02+H20	2.075
Alkaline conditions	
2H20+2e--*20H~+H2	-0.828
O2+2H2O+4e--* 40H-	0.401
MnO4-+2H2O+3e--* MnO2+4OH~	0.60
CIO' + H2O+2e'-> C「+20H-	0.890
03+H20+2e--> O2+2OH-	1.246
Acidic to alkaline	
Ck(aq)+2eJ 2C「	1.396
Fe2++2e~- Fe	-0.44
Fe3++e--* Fe2+	0.771

2.3.2 Required Electrolytic Voltage

When the reactions that proceed at the anode and cathode in an electrolytic reactor are known, the required electrolytic voltage can be determined under standard conditions using the standard electrode potentials. For example, considering the electrolysis of sodium hydroxide solution, oxygen is generated at the anode by oxidation of hydroxide ions and hydrogen and hydroxide ions are generated at the cathode by reduction of water molecules, and the related half-reaction equations and standard electrode potentials are as follows from Table 2.8

$O_2 + 2H_2O + 4 \rightarrow 4O$ E° = 0.401 V **Equation 6**

$2H_2O + 2 \rightarrow H_2 + 2O$ E°= -0.828 V **Equation 7**

To obtain the required electrolytic voltage, the standard electrode potential for the anodic reaction (Equation (6) should be subtracted from the standard electrode potential for the cathodic reaction (Equation (7)). In this example, an electrolytic voltage of 1.229 V is required. Note that the required electrolytic voltage obtained here is for the standard condition. If the electrolysis conditions are different from the standard conditions, it is necessary to correct the standard electrode potential using the Nernst equation and then take the difference between the electrode potentials of the anodic and cathodic reactions. Nernst's equation for the half-reaction equation shown in equation (8) becomes equation (9) **(Liu et al., 2004).**

$Ox + z^* \rightarrow Re$ **Equation 8**

$E_{cell} = E0 – [RT/nF] \ln Q$ **Equation 9**

where E is the electrode potential [V] in Eq. 8, E° is the standard electrode potential [V] in Eq. 8, R is the gas constant (= 8.314 J K-1 mor-1), T is the absolute temperature [K], a Ox is the active volume of the oxidized form (Ox) [mol/L], a Re is the active volume of the reduced form (Re) [mol /L].

(a) Efficiency of Electrolytic Treatment

In electrolytic treatment, redox reactions are carried out by the direct exchange of electrons between the material and the electrode surface. Therefore, the reaction rate in electrolytic treatment depends on the electrolytic current in principle. If only the reaction shown in Equation (8) is taking place on the electrode surface, the reaction rate in Equation (8) is completely proportional to the electrolytic current, and its value is expressed in Equation (11).

- Rate of Reaction Formula

Let’s take a traditional chemical reaction.

$a A + b B \rightarrow p P + q Q$ **Equation 10**

Capital letters (A&B) denote reactants and the (P&Q) denote products, while small letters (a,b,p,q) denote Stoichiometric coefficients

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{p}\frac{d[\mathrm{P}]}{dt} = \frac{1}{q}\frac{d[\mathrm{Q}]}{dt}$$ **Equation 11**

where r is the reaction rate [mol/s] in Eq. 8. I is the current [A], i is the current density [A/m^2], and A is the electrode area [m^2]. It is rare that only the desired reaction proceeds at an electrode, and in general, competing electrode reactions often proceed in parallel.

In this case, the ratio of the amount of electricity (charge) used for the target electrode reaction out of the amount of electricity (charge) supplied for electrolysis is called the current efficiency or Coulomb efficiency ŋ, in Equation (11) **(Yamane et al., 2021).**

Coulombic Efficiency = charge out/charge in **Equation 12**

Thus, electrolytic treatment has the advantage that the reaction rate can be easily controlled by changing the electrolytic current. On the other hand, the current efficiency depends on the current density in general, and in many cases, the reaction rate does not increase as expected even if the current density (or electrolytic current) is increased. Therefore, to operate an electrolytic reactor efficiently, it is important to understand how the current efficiency of the desired electrode reaction depends on the current density.

In addition to current efficiency, energy efficiency is another indicator of the efficiency of electrolytic treatment. The energy efficiency is the reaction rate r divided by the energy (electric power) required to energize the current. In the case of DC electrolysis, the energy required to energize I [A] is expressed by the following equation **(Liu et al., 2004)**

P=VI=I2R **Equation 13.**

where P is the energy (power) required to energize [W], V is the electrolytic voltage [V], and R is the solution resistance [Ω]. As shown in Equation (12), the reaction rate of the electrode reaction is proportional to the current, but Equation (13) shows that the energy required to pass the same current varies with the applied voltage and solution resistance. Therefore, to improve the energy efficiency of the electrolysis process, it is important to improve the current efficiency and at the same time, to reduce the electrolysis voltage.

2.3.3 Direct and Indirect Electrochemical oxidation (electro-oxidation) Treatment

Because physicochemical treatments, including electrolytic treatment, have higher energy costs than biological treatments, contaminants that are difficult to treat with organisms are often the target of treatment. In theory, electrolytic treatment can decompose chemically stable persistent organic pollutants by increasing the electrolytic voltage. In practice, however, since the electrolysis of water as solvent proceeds in parallel, applying a voltage higher than the electrolysis voltage of water leads to a decrease in current efficiency, making it impractical. The potential range where electrolysis of solvent does not occur in the electrolysis process is called the potential window, and the practical electrolysis voltage is limited to the range of the potential window. In other words, it is difficult to directly decompose contaminants that are more chemically stable than water by electrolysis in water treatment by electrolysis. However, it is sometimes possible to decompose and treat chemically stable substances by using indirect reactions with electrode reaction products.

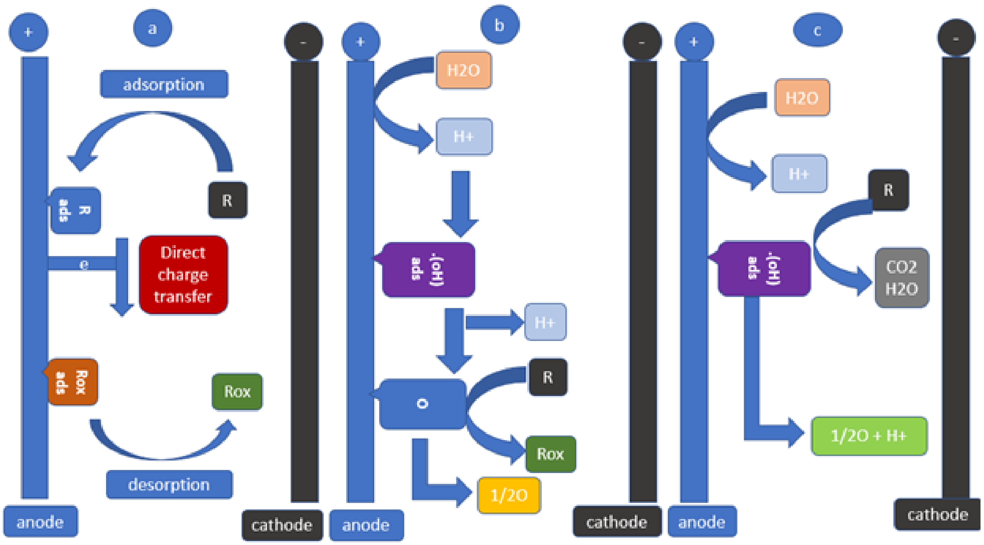

Fig. 2.6 Direct electrochemical oxidation (a) and the mechanism of active oxygen species on the surface of active anode (b) and inactive anode (c) in the electrooxidation system.

Source: **(Qiao and xiong 2021).**

In Fig. 2.6a, direct oxidation means that after organic pollutants are adsorbed on the surface of the anode, they undergo direct charge transfer from the electrode. Therefore, the organic pollutants are oxidized, the molecular chains are broken, and the molecular weight drops rapidly. This process can be expressed as **(Qiao and xiong 2021):**

$R \rightarrow P + e^-$ **Equation 14**

where R and P represent the high-molecular organic pollutants and oxidized matter, respectively. The direct oxidation at the anode has two characteristics

In electrode surface indirect oxidation, 2.6 b and c among the active oxygen species produced by the electrode reaction, ·OH is the main oxidizing species, because it is produced in enormous amounts and has a high oxidation potential (2.8 V). ·OH, is produced by electrolysis of water at the anode (M) as described by Eq. (15):

$M + H_2O \rightarrow M(\cdot OH) + H^+ + e^-$ **Equation 15**

the ·OH produced by the electrolysis of water will react with the active anode, and the anode will bond to the oxygen in ·OH to form a chemically adsorbed MO in the anode lattice. The reaction can be described as follows:

$M(\cdot OH) \rightarrow MO + H+ + e^-$ **Equation 16**

Oxidation of organics to fewer toxic products will follow (equation 16) mediated by the redox couple MO/M, but there will be competition with the side reaction of oxygen evolution via chemical decomposition of the higher oxide species from reaction (equation 17) **(Nurhayati, 2012)**;

$MO + R \rightarrow M + RO$ **Equation 17**

$MO \rightarrow M + (1/2)\ O_2$ **Equation 18**

2.3.4 Electrolytic reactor

The simplest electrolytic reactor is the one-chamber electrolyzer. This is simply a tank filled with treated water in which a pair of electrodes is immersed and is used in both batch and circulation systems. The structure and arrangement of the electrodes may be modified to increase the contact efficiency between the electrodes and the treated water, but because of the simplicity of the equipment structure, it is used in many research and practical equipment.

Along with the one-chamber electrolyzer, the one-chamber electrolytic flow cell is another type of electrolytic reactor that is widely used. This reactor is the same as the one-chamber electrolyzer in that the electrode pairs are immersed in the treated water, but the difference is that the reactor has a flow cell structure figure 2.7. Since electrode reactions are heterogeneous reactions that occur on the electrode surface, the transport of the reacted substance to the electrode surface (mass transfer) is often the rate-limiting factor of the reaction. The mass transfer from the bulk phase to the electrode surface in water is by diffusion transport, and the magnitude of diffusion flux (mass transfer per unit time and unit area) is expressed by Fick's first law as follows **(Liu et al., 2004)**.

$$J = -D\frac{dC}{dx}$$

Equation 19

In an electrolytic reactor, electrolytic oxidation (anodic reaction) and electrolytic reduction (cathodic reaction) proceed simultaneously in a single reactor.

However, depending on the reaction system, the anodic and cathodic reactions may interfere with each other, resulting in a decrease in reaction efficiency. In such cases, a reactor with two electrode chambers is sometimes used. Since conductivity (ion conduction) must be ensured when the electrodes are divided, porous plates made of glass or ceramics, semipermeable membranes, or ion-exchange membranes are often used.

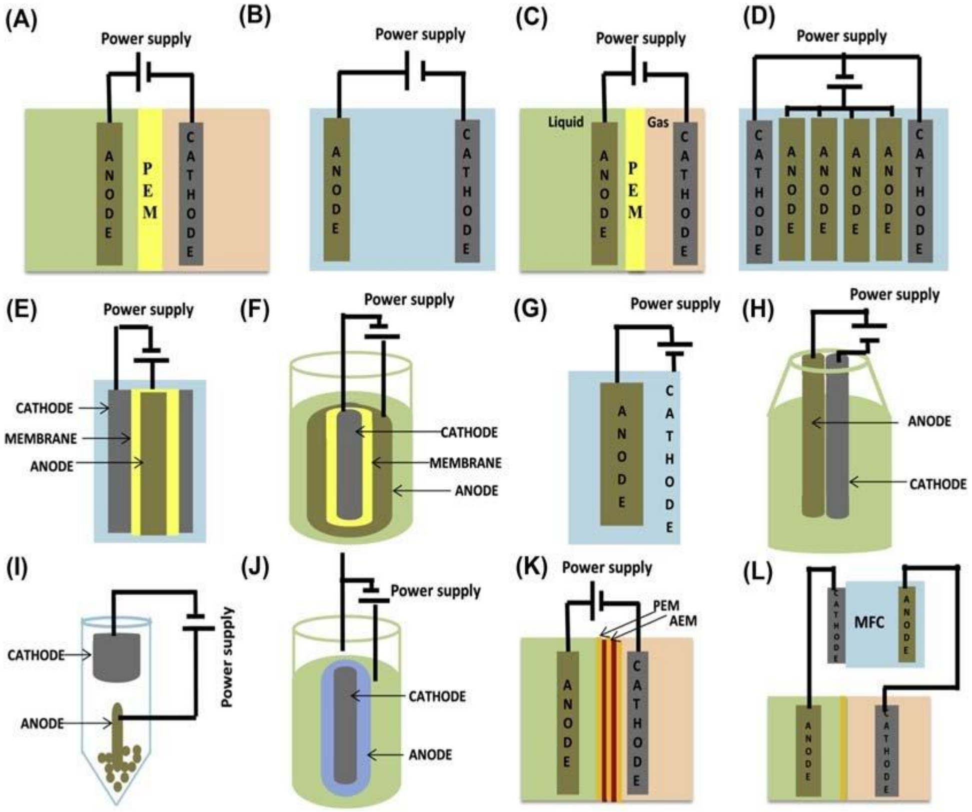

Figure 2.7 Overview of different configurations of MECs (A) two-chamber MEC with ion-exchange membrane; (B) membraneless single-chamber MEC; (C) two-chamber MEC with gaseous cathode; (D) single-chamber MEC with multianode configuration; (E) tubular single-chamber MEC with ion-exchange membrane; (F) cylindrical single-chamber MEC with ion-exchange membrane; (G) SS anaerobic digester modified to MEC by inserting anode inside the reactor while the walls of the reactor serve as cathode; (H) bottle-type membraneless MEC; (I) tubular membraneless MEC; (J) cylindrical membraneless single-chamber MEC; (K) two-chamber MEC with multiple alternate proton-and anion-exchange membranes; (L) an MFC-MECecoupled system where MFC acts as power supply. AEM, anion-exchange membrane; MECs, microbial electrolytic cells; MFC, microbial fuel cell; PEM, proton-exchange membrane

Source: **(varanasi et al., 2019).**

2.3.5 Wastewater treatment using electrolysis technique

Electrolytic processing is widely used in the electrolytic soda industry to produce sodium hydroxide, chlorine, sodium hypochlorite, bleaching powder, hydrochloric acid, and hydrogen. It is also used in the electrolytic refining process for refining metals such as copper, gold, silver, nickel, and platinum. However, there are not necessarily many practical examples in the field of wastewater treatment at present. This is partly since wastewater contains a variety of coexisting substances, which may cause unexpected problems such as scale formation and electrode corrosion, requiring sufficient prior confirmation before application. On the other hand, electrolytic treatment has the advantages of easy automatic control and resistance to load fluctuations, so its application is expected to expand in the future to industrial wastewater treatment where the composition of the wastewater is constant. Here, we introduce some representative examples of electrolytic treatment applied to wastewater treatment at present.

(a) <u>Organic matter decomposition treatment</u>

One application of electrolytic treatment is the electrolytic oxidation of organic pollutants. This is an attempt to decompose and remove organic pollutants from wastewater through direct and indirect anodic electrolysis treatment **(Kim et al., 2013)**. Table 2.9 shows that platinum-coated titanium (Ti/Pt) electrodes are widely used in the treatment of actual wastewater, and there are not necessarily many examples of the use of metal oxide electrodes and boron-doped diamond (BDD) electrodes, which have high 0H radical generation efficiency.

Table 2.9 electrolytic treatment of wastewater

Anode material	**Cathode material**	**Processing target**	**Initial COD [g/L]**	**current efficiency [%]**	**energy efficiency**	**Removal rate [%] (CODcr)**	**Cl in waste water [g/L]**
Ti/Pt	SUS304	Olive oil factory wastewater	178.22		1.27 ～ 4.73kWh/ kg～COD	41-76	24.3
Ti/Pt	SUS304	general sewage	1.047		12.4kWh/ kg～COD	89	8
Ti/Pt	Pt	Chemical factory wastewater	1.361	18		40	
Ti/Pt	Ti/Pt	Leather factory Leather factory	0.093	12		65	1.84

		wastewater (finally treated water) Leather factory					
Ti/Pt	Ti/Pt	Leather factory wastewater (secondary treated water)	0.235～0.458	18.2～25.8		62-64	2.47-2.56
Ti/Pt	Ti/Pt	Leather factory wastewater (raw water)	1.774	6.1～7.4		46-70	2.562
Ti/Pt-lr	Ti/Pt-lr	Leather factoLeather factory wastewater (finally treated water)	0.146	25		57	1.846
Ti/Pt-lr	Ti/Pt-lr	Leather factoLeather factory wastewater (secondary treated water)	0.176	6.9～9.4		19-43	1.935
Ti/Pt-lr	Ti/Pt-lr	Leather factory wastewater (raw water)	1.774	21		11	2.562
Ti/Ta-Pt-lr	SUS316L	Olive oil factory wastewater	1.475		32.2～82.1kWh/kg-COD		1-4
cast iron	cast iron	Tobacco factory wastewater	1.120～1.245		55.6～116kWh/kg-COD	42-60	0.46
Ti/Ru0.3 Ti0.7O2	SUS304	Textile factory wastewater	～0.225		154.0～822.3 kWh/kg-TOC		3.55
Ti/RuO2	SUS304	Olive oil factory wastewater		7～48		17-93	0.8

Ti/RuO2	Ti	distillery wastewater	9.54	7	2.82kWh/ kg-COD	89.62	35.5
Ti/RuO2	Ti	RO membrane for sewage and textile factory wastewater	0.151 ～	15			0.595-0.804
BDD	Ti	ProceProcessing concentrate	0.171	35			
BDD		Automobile factory oil-containing wastewater	2.57	61～95		99	

This is due to the excellent stability of the Ti/Pt electrode, which can be used for both anode and cathode, as well as the accumulation of knowledge over many years. In the treatment of actual wastewater, stability is strongly required to ensure continuous treatment. Because of the presence of various coexisting substances in actual wastewater, electrode polarity reversal is sometimes performed to prevent scale formation and other problems. Considering such actual applications, the Ti/Pt electrode has the advantage of the day. On the other hand, the current efficiency of the BDD electrode is higher than that of the Ti/Pt electrode, indicating the superiority of the electrode with a large overvoltage for oxygen production. Therefore, if the problem of electrode cost is solved, it is expected to be widely used in the future.

2.4.1 Electro-flotation (EF) Method

When oily wastewater like POME or organic pollutant wastewater like livestock wastewater is discharged into the environment, it destroys the ecological resources and functions, endangers aquatic ecosystems, and affects human health. Given the shortage of water resources, severe environmental pollution, and increasingly stringent wastewater discharge standards, dealing with and recycling oily or organic pollutant wastewater has become a crucial problem in environmental engineering fields. There are separate ways to solve these wastewaters. The most used treatment processes are gravity separation, hydrocyclone, flotation, coagulation/flocculation, biological treatment, membrane separation, adsorption, and advanced oxidation process (AOPs) **(Wang et al., 2022)**.

The wastewater treatment system consists of three stages. The first stage of the separation system is treated by gravity separators and other equipment to treat these wastewaters with higher oily or organic pollutant concentrations. At this stage, the organic-rich or oil-rich flow will enter the treatment system for further dehydration and purification, and the water-rich flow will soon enter the secondary treatment, usually hydro cyclone separation, flotation, and membrane microfiltration (MF) or ultrafiltration (UF), which can meet the primary discharge standards. If necessary, it enters the third stage treatment system for organic pollutants or fine oil removals, such as reverse osmosis (RO), nanofiltration (NF), and advanced oxidation methods, so that the treated water meets the discharge recovery and reinjection standard **(Wang et al., 2022)**

Adsorption technology using several types of media (ex-active carbon, fly ash, zeolite) is used in organic polluted wastewater treatment to remove residual oil and suspended and dissolved matters **(Shayandi et al., 2012)**. However, adsorption treatment needs additional pretreatment **(Wahi et al., 2017)**. In case of membrane separation/filtration treatment, high removal of solids can be obtained with excellent quality water output **(Khulbe and Matsuura, et al., 2018).** But those membranes are prone to fouling and these treatment methods required high capital and maintenance cost **(Mahendran et al., 2004, Haji et al., 2017)**. Advance oxidation process is another post treatment method that is a highly effective method in treating POME, which can be used without producing sludge **(Ng and Cheng. 2015)**. However, this is an energy and cost intensive method **(Lokman et al., 2021)**. Electrooxidation (EO) is categorized under advanced oxidation and has recently been given excessive attention owing to its eco-friendly treatment, high efficiency, and compatibility in implementation **(Ganiyo et al., 2018)**. In EO, reactive oxygen species are produced and that can mineralize dissolved organic compounds completely **(Rakhmania et al., 2022).** Nevertheless, EO is inefficient in treating suspended matters **(Baran. 2017).** Coagulation and flocculation process is another cheaper way to treat organic polluted wastewater, but this process only reduces suspended solids, and many coagulants are required **(Sitti Nor et al., 2019)**. Also, chemical treatment that relies on chemical agents is prone to secondary pollution and is more harmful to food and the environment. Electrocoagulation (EC) with sacrificial anodes is another method that can be used to treat organic wastewater as a post-treatment. It is a straightforward process, high removal efficiency can be achieved within minimum time **(Nasrullah et al., 2018, Nasrullah et al., 2019).** But high operating cost due to electrical energy consumption, regular replacement of sacrificial anode, electrode passivation is some of major limitations of EC **(Moussa et al., 2017).** However, in the secondary treatment process, Microorganisms may not be tolerant of aromatics and heavy metals in wastewater for the activated sludge method. High maintenance and energy requirements due to membrane contamination. Cyclone separators cannot separate tiny oil droplets from wastewater shown in Table 10. In contrast, the gas flotation process in electro-flotation is an economical and environmentally friendly method and an attractive alternative, becoming a hot topic for researchers and many oil fields and water treatment plant **(Wang et al., 2022).**

Flotation is a known gravity separation process originated from mineral processing; concerning the used bubble generation method, this could be typically by dispersed-air flotation, dissolved-air flotation or electroflotation. This chapter focuses on applications of electroflotation on waters, oily, heavy metals, biological wastewater. The mechanism of electroflotation were discussed in-depth, like the oil droplet-bubbles and particle-bubble interaction during flotation in pollutant removal in wastewater. Advantages and disadvantages of electroflotation were also discussed.

Table 2.10. Comparison of current technologies for oily and organic wastewater treatment. Source: **(Wang et al., 2022)**.

Technologies	**Working principle**	**Dispersed oil**	**Dissolved oil**	**Advantages**	**Disadvantages**
Corrugated plate separator	Separation of free oil from water under gravity effects enhanced by flocculation on the surface of corrugated plates	yes	no	No energy required, cheaper, effective for bulk oil removal and suspended solid removal, with no moving parts	Inefficient for fine oil particles, the requirement of high retention time, maintenance
API Gravity and enhanced gravity sedimentation	The density differences between heterogeneous phases under the effect of gravity	yes	no	Simple equipment with minimum operating costs and maintenance requirements; Essential pretreatment equipment	Long retention time and low efficiency for fine oil droplets removal.

Hydrocyclone	The density differences between heterogeneous phases under the effect of the swirling flow field	yes	no	Does not require the use of chemicals and energy, and can reduce oil and grease concentrations to 10 ppm	Separation effects are affected by blockage and wear of one or more cyclone tubes; High energy requirement to pressurize inlet
Coagulation/flocculation	reduces the electrostatic repulsion of the electric double layer, allowing the oil droplets to coalesce	yes	no	High feasibility; can improve the efficiency of flotation, filtration, and other physical	Secondary pollution of water for adding chemical agents
Gas floatation	By adhering to oil droplets by microbubbles, the density difference between oil droplets and water is increased, so that oil droplets rise quickly	yes	A part of VOC (benzene)	Efficient removal of fine oil droplets in wastewater	Long retention time, large footprint
Activated sludge	Using oil-degrading microorganisms to degrade contaminants within water.	yes	yes	Cheaper, simple and clean technology	Higher chemical oxygen demand; Sludge waste at the end of the treatment
Membrane separation (MF/UF)	The membrane removes micro-particles from the water under the applied pressure.	yes	yes	Higher recovery of fresh water, compact modules.	High costs and energy consumption; Membranes are easily contaminated,
Adsorption	Porous media adsorbs contaminants from the influent stream	yes	yes	Can achieve nearly 100 % water recovery; Compact packed bed modules, cheaper, efficient	High retention of water; chemical required for regeneration; high operational cost; reliability issue
Membrane separation (RO/NF)	Pure water is squeezed from contaminated water under a pressure differential.	yes	yes	Removes monovalent salts, dissolved contaminants, etc., compact modules.	High-pressure requirements, even trace amounts of oil and grease can cause membrane fouling

2.4.2 Traditional flotation techniques.

Flotation processes are highly effective for separating particles, such as algae and oil, from water. These particles are not easily settled because of their low densities**.** Microbubbles or nanobubbles are injected into the flotation tank through a unique process to attach fine oil droplets or suspended solid for different flotation techniques, which improves the flotation performance and reduces the separation time **(Wang et al., 2022).** According to varying ways of bubbles generation, traditional flotation processes can be divided into three categories: dissolved gas flotation (DGF), induced gas flotation (IGF), Compact flotation units, (CFU) electro-flotation (EF).

(a) Dissolved gas flotation (DGF)

In DGF, fine bubbles are formed by nucleation and growth of gas dissolved in both water and oil phases when the pressure is reduced (Figure 2.8). Nucleation of supersaturated gas could be either hetero- or homogeneous, where heterogeneous is the most efficient mechanism due to the lower energy barriers when existing surfaces are the nucleation sites. Another element to consider in DGF is the higher gas solubility in the oil phase. The gas volume released at pressure reductions will be higher within the oil droplets than in the surrounding water phase. Expansion of gas bubbles in the oil droplets should therefore also be considered during DGF. The generated bubbles are much smaller compared to IGF: 10− 100 µm. Because the size of gas bubbles is smaller, the retention time will also be higher. The gas/oil ratio and hydraulic loading are also important factors to consider in DGF. Recently, attention has been given to nanosized bubbles and their role in DGF. Studies have shown that they can adhere and/or entrain inside oil droplets, generating capillary bridges between the droplets. This improved the hydrophobicity of the droplets and the probability of adhesion to microbubbles and, thereby, increased the overall flotation efficiency **(Piccioli et al., 2020)**

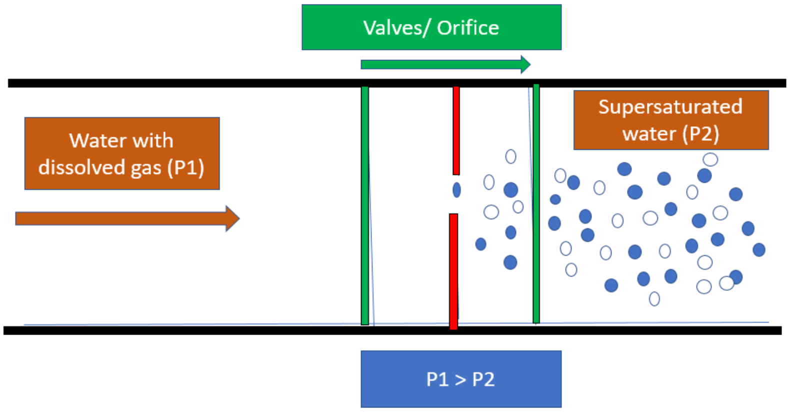

Figure 2.8. Illustration of bubble generation during DGF

Source: **(Piccioli et al., 2020)**

DGF has three basic processes: total inlet water, partial inlet water pressurization, and partial return pressurization. Part of the wastewater is returned to the saturation vessel, and a certain amount of gas is introduced simultaneously, the gas-water mixture is dissolved for some time under pressure conditions, in which the optimal range is 400–600 kPa. The gas dissolved in the water is released instantaneously by the relief valve unit, generating many microbubbles, which enter the gas flotation tank and attach to the oil droplets to achieve efficient oil-water separation. Because of its small bubble production and good oil removal efficiency, the DGF method is widely used to treat oily wastewater after the gravity of hydrocyclone separation **(Wang et al., 2022)**

(b) <u>Induced gas flotation (IGF)</u>

A gas flotation system used should be designed for (i) minimal footprint and weight, (ii) reduced motion sensitivity, (iii) optimal oil removal efficiency, and (iv) simple operation. This led to the development of the CFUs. These are hydraulic units that can use both IGF and DGF advantages to remove oil droplets from wastewater. Performing gas flotation in single mode would result in disadvantages: in IGF systems, the oil droplets much smaller than 100 µm may escape flotation, while in DGF systems, the oil droplets larger than 100 µm cannot be floated. Vertical vessels are usually preferred, because they require less space and are less affected by wave motion. The retention time is typically less than 1 min. The first CFU was introduced to the oil and gas industry at the NCS in 2001. Today, the method has become well-proven and is used worldwide. Modern designs of CFUs have also been developed to maximize performance and minimize the footprint and weight **(Piccioli et al., 2020).**

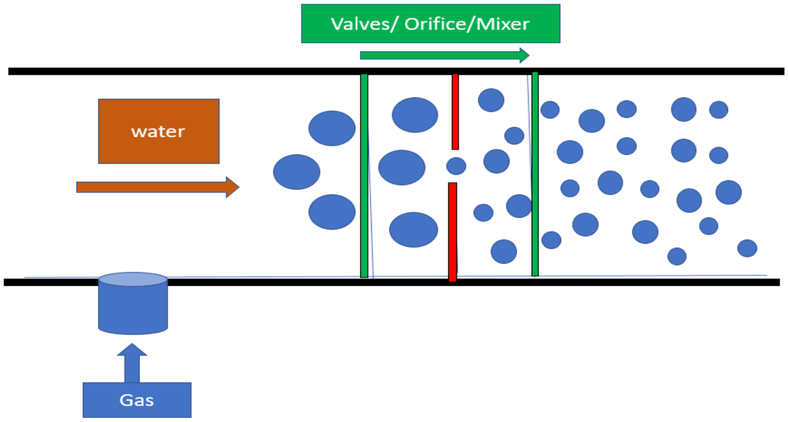

Figure 2.9. Illustration of hydraulic IGF.

Source: **(Piccioli et al., 2020)**.

<u>(c) Compact flotation unit (CFU)</u>

A gas flotation system used should be designed for (i) minimal footprint and weight, (ii) reduced motion sensitivity, (iii) optimal oil removal efficiency, and (iv) simple operation. This led to the development of the CFUs. These are hydraulic units that can use both IGF and DGF advantages to remove oil droplets from wastewater. Performing gas flotation in single mode would result in disadvantages: in IGF systems, the oil droplets much smaller than 100 µm may escape flotation, while in DGF systems, the oil droplets larger than 100 µm cannot be floated. Vertical vessels are usually preferred, because they require less space and are less affected by wave motion. The retention time is typically less than 1 min. The first CFU was introduced to the oil and gas industry at the NCS in 2001. Today, the method has become well-proven and is used worldwide. Modern designs of CFUs have also been developed to maximize performance and minimize the footprint and weight **(Piccioli et al., 2020)**.

2.4.3 Introduction and historical background of electroflotation

Electro flotation development was led by the increasing need to develop technology capable of separating small particles from aqueous effluent, which were not effectively removed with the usual methods applied at the time. In 1904, E. Elmore patented the process of using electrolytic gases as a parting phase during mineral isolation in the flotation enrichment of ores **(Mohtashami and Shang et al.2019).**

Electro flotation shows a high efficiency in promoting separation of solid from liquid phases or one liquid phase from another, even with the smallest particles separated from a liquid, due to uniform and tiny or micro bubbles of hydrogen and oxygen generated at the electrode's surfaces during electrolysis of an aqueous solution, making electrode being considered the heart of an electro flotation unit. In the upcoming sections, various aspects of electroflotation will be presented, including detailed fundamentals of the process, electrode materials and arrangements, design aspects of electroflotation reactor, influential process variables and kinetics of the process.

Table 2.10. compares various technical characteristics of the flotation process and Table 2.11. shows the advanced flotation technologies developed by some companies in this field in recent years, which have proved to be efficient and economical.

Table 2.10. Summary of the characteristics of flotation. Source: **(Wang et al., 2022)**.

Parameter	**DGF**	**IGF**	**EF**	**CFU**
Bubble size (μm)	10–100	10–1000	10–60	20–600
Generation method	Pressure dissolution and decompression release	Velocity-based, entrainment, and dispersion	Chemical electrolysis produces hydrogen and oxygen bubbles	Break outgas, sparge mix method, multiphase pump
Operating condition	Quiescent.	Turbulent and less quiescent conditions	Quiescent.	Strong turbulent.
Retention time (min)	5–15	<5	10–60	<1
Footprint	Large	Compact	Compact	More compact
Advantages	The size of the generated bubbles is small, with high oil removal efficiency	Low energy consumption and large processing capacity	High oil removal efficiency, simple operation, automated	Small footprint, compact structure, large processing capacity
Shortcomings	High energy consumption and large footprint	Large bubbles and poor efficiency	High energy consumption, longer Retention time.	Complex internal structure and challenging to design

Table 2.11. Flotation technology in wastewater treatment

Model name and reference	Technology	Additional remarks
Electroflocculation **(Robinson, 2014)**	Electrolysis, flocculation and flotation	Capacity: handling some pollutant loadings well over 20,000 mg/L without clogging. Removal rates:>99 %
CTOUR PROCESS **(ProSep, 2014)**	Injection of condensate with flotation	Capacity: 300–2000 mg/L Effluent Oil Concentration: <5 mg/L Injection of condensate couple with IGF, or CFU

EPCON Dual CFU **(Gmsthailand, 2016)**	Centrifugal force and flotation	Capacity: 71 m3 /d − 24,000 m3 /d Removal rates:50 % greater oil removal efficiency in the same footprint as conventional technologies
WEMCO® ISF **(Schlumberger, 2016)**	Hydraulically induced gas flotation system	Capacity: 380 m3 /d − 20,670 m3 /d Effluent Oil Concentration: 5–10 mg/L small footprint
RT Series packaged DAF systems **(Evoqua, 2017)**	Dissolved Air Flotation	Capacity: 380 m3 /d − 20,670 m3 /d Effluent Oil Concentration:<100 mg/L

2.4.4 Fundamentals of electroflotation

Electroflotation can be implemented for separation of contaminants present in the industrial effluents by fine hydrogen and oxygen bubble generated from water electrolysis; it involves several physical and electrochemical phenomena. Equations (20–21) show redox reactions, which occurred at the cathode and anode (**Mohtashami and Shang .2019)**. The reduction of water reaction takes place on the cathode resulting in the generation of H_2 and hydroxyl ions (OH^-) (Equation 1); and oxidation of water reaction takes place on the anode resulting in the generation of oxygen gas and hydrogen ions (H^+) (Equation 2) **(Wang et al., 2022, Ghanbari et al., 2014, Kumar and Kangri. 2017):**

At the cathode:

$$2H_2O(l)+2e^- \rightarrow H_2(g)+2OH^-(aq) \qquad (1)$$

At the anode:

$$2H_2O(l) \rightarrow 2H_2(g)+O_2(g) \qquad (2)$$

Overall redox reaction:

$$2H_2O(l) \rightarrow 4H^+(aq)+ O_2(g)+ 4e^-$$

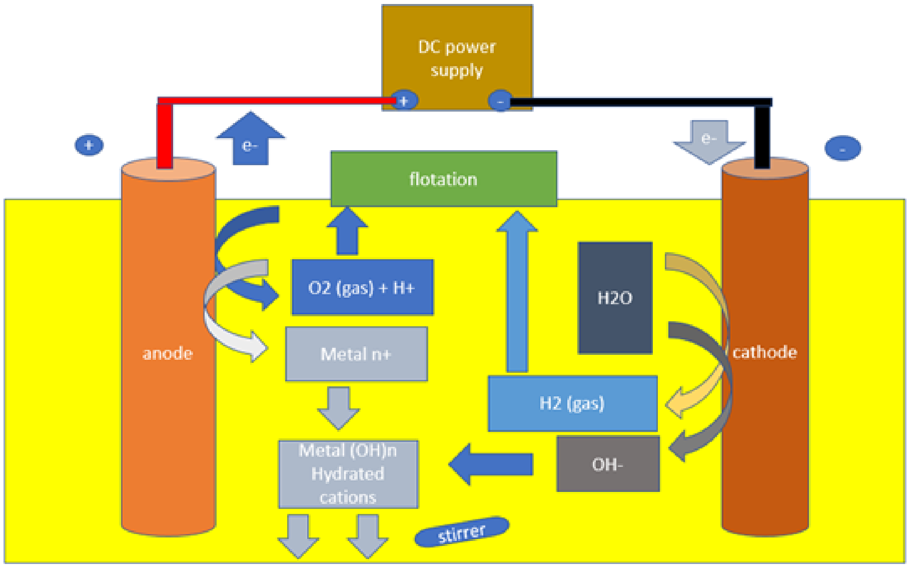

Figure 2.10. Diagrammatic description of an electroflotation process.

Source: **(Jeevanandam et al.2020)**

As schematically depicted in Fig. 2.10, EF will ionize OH− and H+ through the electrolysis of wastewater **(Wang et al., 2022).** So, when direct current electrolysis oily wastewater or organic polluted wastewater, H+ swims to the cathode and produces many hydrogen bubbles at the cathode (Eq. (20)), generally at 10 to 30 μm; OH− swims to the anode,and produce many precipitates oxygen bubbles at the anode about 20–60 μm (Eq. (21)) **(Wang et al., 2022).** The oil droplets or colloidal particles in the wastewater attach to electrolysis's hydrogen and oxygen bubbles **(Wang et al., 2022, Mohtashami and Shang et al.2019)**. In addition, dissolution on the anode generates metallic ions that act as coagulation/flocculation, helping to aggregate oil droplets or colloidal particles in wastewater and achieving automatic floating at the same time, suspended mineral particles accumulate and sink **(Wang et al., 2022, Mohtashami and Shang et al.2019).**

$M\ (s) \rightarrow Mn^{+}\ (aq) + ne^{-}$ **Equation 22**

2.4.5 Bubble evolution dynamics

Electrochemical bubble evolution is defined as the nucleation and growth at, and detachment from, electrodes. Gas bubbles evolving mechanism at the electrode surface, in electrochemical reactors, can be divided into four micro process stages. These stages occur simultaneously at the electrode surface (see Figure 2.11) **(Angulo et al., 2020, Taqieddin et al.2017)**. These phenomena have been studied in batch and flow reactors with the goal of understanding the relationship between the structure of multiphase electrolytes and the performance of electrochemical reactions.

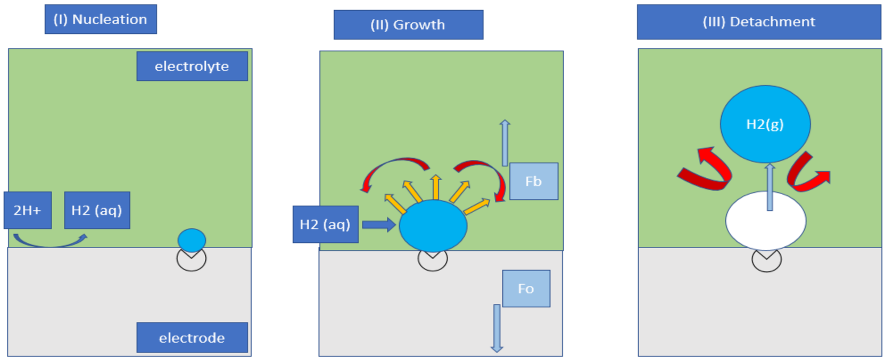

Figure 2.11. The Various Stages of Bubble Evolution The stages of bubble evolution: (1) the nucleation, (2) growth, and (3) detachment of bubbles on a gas evolving electrode surface. Nucleation occurs typically on cracks and crevices in the electrode surface, after which the bubble grows by taking in gas from the dissolved gas boundary layer. Bubbles detach when the buoyancy force overcomes the interfacial tension force. The departing bubble induces convection in the liquid indicated by the spirals. Source: **(Angulo et al., 2020)**.

(a) <u>Bubble Nucleation.</u>

The onset of bubble electro nucleation is marked by the accumulation of dissolved gas on the surface of the electrode until a critical supersaturated concentration is reached, undergoing a physical phase change **(Taqieddin et al.2017)**. Following from supersaturation of a dissolved gas, gas bubble nucleation occurs at the electrode surface. Gas bubbles may nucleate starting from an initial bubble size of zero, as assumed by classical nucleation theory (CNT). On the other hand, bubbles can also form within pre-existing gas pockets trapped on a surface in contact with the supersaturated liquid solution **(Taqieddin et al.2017)**.

(b) <u>Bubble growth</u>

After nucleation, the bubble adhered at the electrode grows due to three causes: diffusion of dissolved gas into the bubble surface, coalescence with other bubbles, due to the high internal pressure. Gas bubbles grow due to continuous electrolysis and the growing bubble may simultaneously slide on the electrode surface to coalescence with another bubble. The large growing bubble acts as a collector and attracts smaller growing bubbles. Bubbles continue to coalesce forming larger bubbles. One of the possible driving mechanisms of bubbles radial coalescence motion on the electrode surface is thermocapillary phenomena. The induced temperature gradient on the electrode surface causes thermocapillary effects. Two main reasons explain the presence of temperature gradient at the electrode surface; first, the reaction overpotential, which happens at the electrode surface, and second, the heat conduction losses because of the electrode material finite resistivity. The dissolved gas concentration determines the supersaturation of dissolved gas, which controls the bubble growth. Moreover, the variation degree of supersaturation depends on interfacial curvature and the surface energy used to build the gas/electrode interface **(Taqieddin et al.2017).**

(c) <u>Bubble detachment (departure)</u>

The bubble detaches from the electrode surface, once the bubble size reaches a critical volume (radius) at which the buoyancy force exceeds the interfacial tension between the gas bubble and the solid electrode surface. After the bubble jumps from the electrode surface, it moves into the bulk flow. At this stage, the detached bubble provides an active vicinity at the electrode surface for new fresh electrolytes to react and regenerate the new bubble. In contrast to equilibrium bubble detachment, it has been found that the bubble which is formed by coalescence of two large bubbles would disassociate from the electrode surface, jump off and sometimes return to the electrode surface **(Taqieddin et al.2017).**

2.4.6 Oil droplets-bubbles and particle-bubble interaction during flotation

The key to the success of effective particle separation by flotation is the efficient capture of hydrophobic particles by air bubbles, which is accomplished in three distinct processes: collision, adhesion, and detachment as shown in Fig. 2.12a and 2.12b. These process terms are explained in Table 3.4, and a detailed description of each process for oil droplets-bubbles interaction is summarized **(Wang et al., 2022)**:

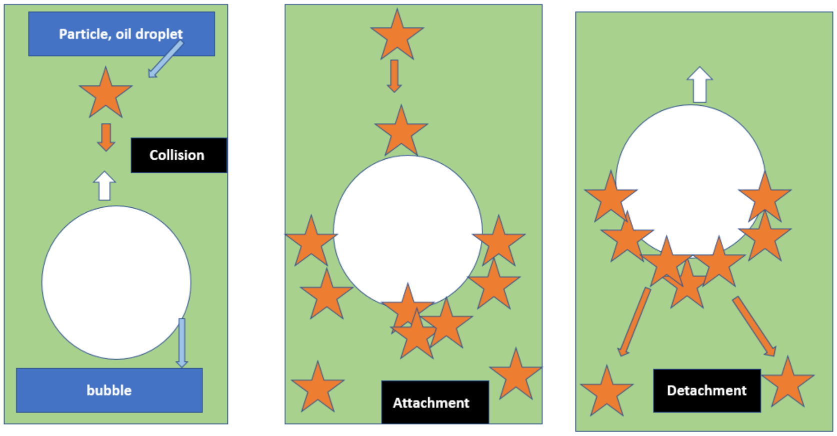

Figure 2.12a. Illustration of three microprocesses in flotation.

Particle separation by flotation depends on the efficiency of collision, adhesion, and detachment processes. Studies showed that tiny bubbles generated by hydrodynamic cavitation were found to change the surface characters of minerals, increasing the contact angle of solids and hence the attachment force, bridging fine particles to form aggregates, minimize slime coating, remove oxidation layers on particle surfaces, and in consequence reduce reagent consumption. Source: **(Wang et al., 2022)**

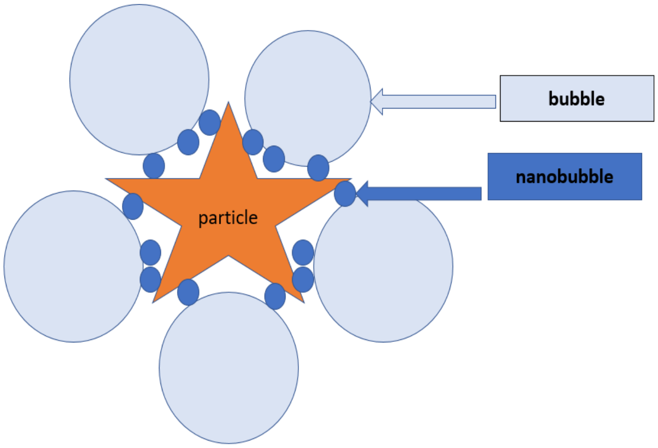

Figure 2.12b. shows schematically that nanobubbles on particle surfaces activate flotation by promoting the attachment of larger bubbles since attachment between nanobubbles or gas nuclei and large bubbles is favored over bubble/solid attachment. Source**: (Wang et al., 2022)**

(a) The collision of oil droplets or particles collides with gas bubbles.

The prepared bubbles are sent into the flotation tank to meet and collide with oil droplets or particle collides because of a sufficiently close encounter **(Wang et al., 2022, Tao., 2004, Miettinen et al., 2010).** A successful collision depends on many factors. Moderate turbulence intensity, good hydrophobicity, and wettability will increase collision probability **(Wang et al., 2022).**

(b) <u>The attachment of oil droplets with gas bubbles includes rupture of the water film and liquid diffusion.</u>

After the oil droplets film ruptures, oil droplets adhere to the surface of the bubbles and gradually drain diffusion figure 2.13. On top of that, the induction time of adhesion (ti , the time when the oil droplets first contact the bubbles to the time when the oil droplets film ruptures) is less than the contact time (tc, the time when the oil droplets first contact the bubbles to the time when the oil droplets adhere to stability), which is necessary to have the attachment possibility **(Wang et al., 2022)**. If a particle is sufficiently hydrophobic, the liquid film between the bubble and the particle thins and ruptures due to the attractive surface forces. This is followed by the establishment of the three-phase line of contact. The oil droplets-bubbles attachment is stable, and the bubbles-oil droplets go up because of buoyancy. When the adhesion of oil droplets and bubbles is stable, the rising rate increases due to the rise in the oil-water density difference of bubbles. At this time, in enough flotation time, the fine oil droplets in wastewater can be successfully flotation to achieve efficient oil-water separation **(Wang et al., 2022).**

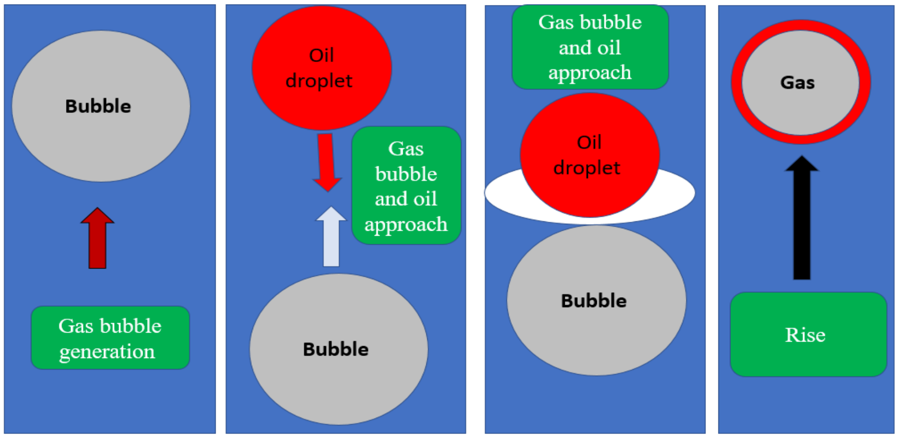

Figure 2.13. The attachment process of oil droplet and micro-bubble Source: **(Huang and Long et al., 2020)**

(c) The attachment of particle collides with gas bubbles includes rupture of the water film and liquid diffusion.

Only those hydrophobic particles whose induction time is smaller than the sliding time can be attached to air bubbles. Obviously, the attachment process is selective and the difference in attachment probability (Pa) of different particles determines the selectivity of flotation. The attachment process is determined by hydrodynamic and surface forces of particles and bubbles **(Tao., 2004).** The probability of attachment is modelled in terms of a contact time and an induction time. Particle–bubble attachment will occur when the bubble–particle contact time is longer than the induction time **(Miettinen et al., 2010)**. Another way to model bubble– particle attachment is to use the energy barrier approach, where for bubble–particle attachment the kinetic energy of a particle must be higher than an energy barrier between the particle and the bubble surface **(Miettinen et al., 2010)**.

(d) Detachment of oil droplets from bubbles.

Even if the bubbles collide with the oil droplets, due to the flow field or its repulsive force, it is highly likely to cause instability and the oil droplets to detach from the bubbles. If point attachment or oil lens is formed during oil droplet and bubble adhesion, such contact is not firm. In the process of rising, the flow disturbance in the flotation cell and gravity desorption will cause adverse effects on flotation **(Wang et al., 2022).**

(e) Detachment of particle from bubbles.

All particles attached to air bubbles do not report to the froth phase. Some of them detach from the bubble surface and drop back into the pulp phase. Particle detachment occurs when detachment forces exceed the maximum adhesive forces. One potential source of excessive forces is bubble oscillations caused by particle – bubble collisions **(Tao., 2004).**

Table 2.12. Oil droplets-bubbles interaction process **(Wang et al., 2022)**

Interaction	**Description**
Collision (contact)	Tiny oil droplets and bubbles contact (collision) in the laminar or turbulent state of the flotation tank

Attachment	Rupture	After oil droplets contact with bubbles, the liquid film of oil droplets ruptures due to hydrophobic action and attaches to the surface of bubbles
	Drainage	After the liquid film of the oil droplet ruptures, the oil droplet gradually spread (drainage) over the bubble
Stabilization		Droplets can spread around the bubbles to form a "perfect" wrap attachment, stay at the bottom of the bubbles (oil lens), or stick to the outer surface of the bubbles to form a point attachment.
Detachment		Flow field or repulsion force is likely to lead to adhesion instability and make the oil droplets detach from the bubbles

.

2.4.7 Bubble Size and bubble charge Influencing Factors.

Electrolysis leads to the formation of uniform, extremely finely or micro dispersed gas bubbles that rise very slowly, producing a slightly undesired convection. The exceptionally fine bubble produced improved the EF process, because the fine particles float easier with small bubbles and the smaller bubbles provide a large surface area for particles attachment. The size and the distribution curve of the desire bubbles, which can be controlled by choosing the electrode material, electrode surface/morphological properties, the curvature, the treatment of the electrode surface, pH, and current density.

(a) Electrode material

Electrode material and its position in the electrochemical cell, which Plays an important role in the size of bubbles. The bubble diameter is proportional to the wire diameter electrode and electrodes with larger diameters generate bubbles with larger diameters. In research done by **Sarkar et al., (2010)**. It was seen that bubble nucleation rate increased with decreased wire diameter, which was thought to be due to smaller detachment diameter of bubble with decreased wire diameter. a smaller diameter bubble detached faster than larger diameter bubble, which took less amount of dissolved hydrogen before detachment. As detachment time is less, more nucleation sites were expected in the case of smaller wire diameter.

(b) Current density

There is a relation between the surface of electrodes and current density of the size of bubbles. For a smooth-surface electrode, the bubble size increased with an increased density, and for rough-surface electrodes the opposite trend was noted **(Sarkar et al., 2010)**. Current density has a significant effect on bubble size. The mean bubble size decreases with the increase in the current density up to a threshold value, with further increase in the current density causing an increase in bubble sizes, which is attributed to the coalescence of free moving bubbles **(Alam et al., 2017).**

(c) pH

pH is also an important parameter for bubble size and bubble charge. Some researchers have tried to explain the effect of pH on bubble size. As **(Mickova., 2015)** said, the smallest hydrogen bubbles are produced at neutral or slightly acidic conditions. pH also influences bubble charge. During the electrolysis of water, due to the excess of OH– ions in the near-cap layer, hydrogen bubbles acquire a negative charge and, thus, are repulsed from the cathode surface. In alkaline media, rapidly growing hydrogen bubbles have a negative charge, and oxygen bubbles do not have a charge due to their neutralization with alkali. In acid media, rapidly growing oxygen bubbles have a positive electric charge, and hydrogen bubbles do not have a charge due to neutralization with acid **(Kolesnikov et al., 2017)**. A study done by a reporter showed that efficiency is highest when bubbles and particles have opposite surface charges and are of similar sizes **(Han et al., 2006)**.

(d) Electrolyte

Electrolytes also influence bubble size, with an increase in ionic strength resulting in a thinner electrical double layer, thus, reducing bubble sizes. The effect of ionic strength (by adding KNO3) on the bubble size was investigated by **(Alarm et al. (2017)** showed a slight decrease in the bubble size with increasing ionic strength. Some researcher suggested that, adding salt would increase the electric repulsive forces between bubbles for their high surface potential, which would also help to avoid collision.in addition, adding salt in the solution increases the viscosity of the electrolyte and hence increases the rigidity of the surface films of the bubbles so that the coalescence is more difficult **(Alam et al., 2017)**.

2.4.8 Electro flotation system

Electroflotation systems do not usually include mechanically moving parts, making the installation, retrofit and maintenance simpler. and more convenient. Also, process adjustments can be readily accomplished by changing applied electric potential/current **(Mohtashami and Shang et al.2019).**

(a) Electrodes

Electrodes are the heart of electroflotation reactors, and therefore, their material and design are crucial for the performance of the system. Electrode materials are divided into two categories, i.e., inert, and active. This is the case especially for anode electrodes. Since cathodes do not corrode in electroflotation, stainless steel and aluminum are the most common and inexpensive cathode materials used in treatment of industrial wastewaters **(Mohtashami and Shang et al.2019).**

Inert anodes are used to produce oxygen gas bubbles in electroflotation. Graphite is used as anodes in electrochemical processes and electroflotation treatment of wastewater. It has a stable condition; however, studies show that graphite deteriorates quickly, and loses its smooth surface, resulting in production of coarse-sized bubbles and reduction of separation efficiency **(Mohtashami and Shang et al.2019)**. Dimensionally stable anodes (DSA) are made of coated metals such as titanium. They were first patented in the US in 1966 for chlorine evolution in form of TiO2-RuO2–coated titanium. Oxides of other metals, e.g., Pb, Sb, Zr and Sn, have been used as coating as well. These electrodes are expensive and have a short service life. In recent years, studies have been performed on production of cheaper DSA electrodes with longer service lives **(Mohtashami and Shang et al.2019)**.

Active anodes, made of metals such as Al and Fe, have also been employed for the treatment of industrial wastewaters. During the process, metal ions are released from the 'sacrificial anodes' and react with hydroxide ions, forming metal hydroxides such as Al(OH)2+, Al(OH)4 − , Fe(OH)3 and polymeric species such as Al2(OH)2 4+, Al6(OH)153+, Fe(H2O)6 3+ and Fe(H2O)5OH2+ . These metal hydroxides act as coagulants and adsorb colloidal particles, form bonds and create aggregates, rise to surface and remove the particles from water **(Mohtashami and Shang et al.2019).**

(b) Electrode Arrangement

Simple electroflotation systems comprise a reactor and electrodes (anode and cathode) connected to a DC power supply. Connection mode of electrodes to DC power supply can be monopolar (parallel or series) or bipolar. While in monopolar-connection mode all electrodes are connected to each other or to DC power supply, only outmost electrodes connect to power supply in bipolar connection mode. Schematics of different electrode connection modes are depicted in Fig. 2.14. **(Mohtashami and Shang et al.2019).** Comparative studies of electrode connection modes have been conducted by different researchers. The monopolar connection mode is proven to be more advantageous than the bipolar mode, in terms of separation efficiency and power consumption **(Mohtashami and Shang et al.2019)**

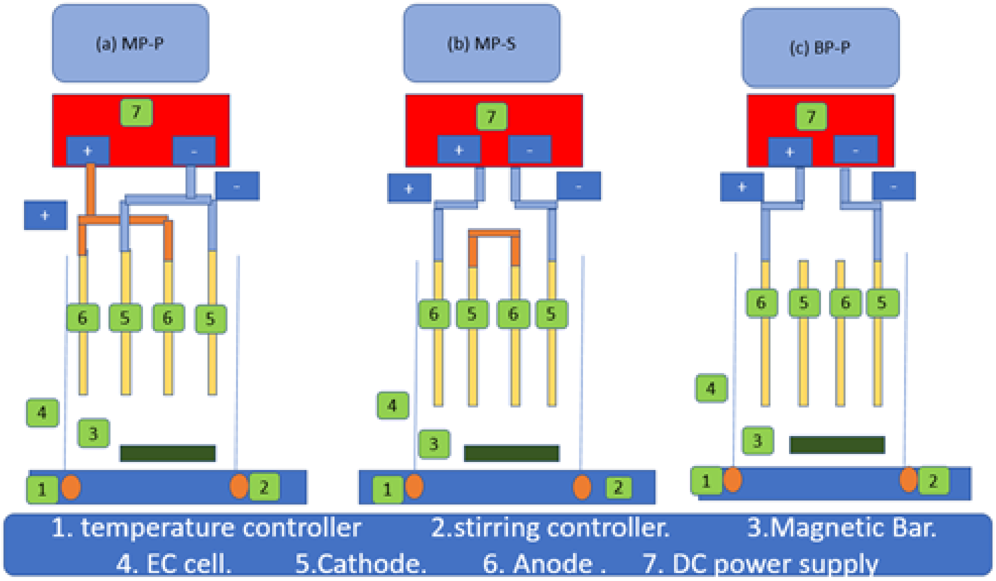

Figure 2.14. Diagrammatic representation of different modes of electrode connection (a) monopolar parallel (b) monopolar series and (c) bipolar parallel Source: **(Bharathet et al.2018)**

<u>(c) Reactor Design</u>

The design of electroflotation reactor includes the electrodes arrangement, reactor shape and flow regime inside the reactor. Most lab/bench-scale electroflotation experiments have been performed in batch-flow processing regime **(Mohtashami and Shang et al.2019).** They usually consist of a small cell as the reactor and a few electrodes. Fig. 2.14 presents a basic and simple design of a batch electroflotation reactor with vertically oriented monopolar electrodes. Other batch reactors have been suggested by researchers as well. Fig. 2.15 shows a cylindrical platinized titanium anode and steel cathode **(Uchibori et al. 2010)**

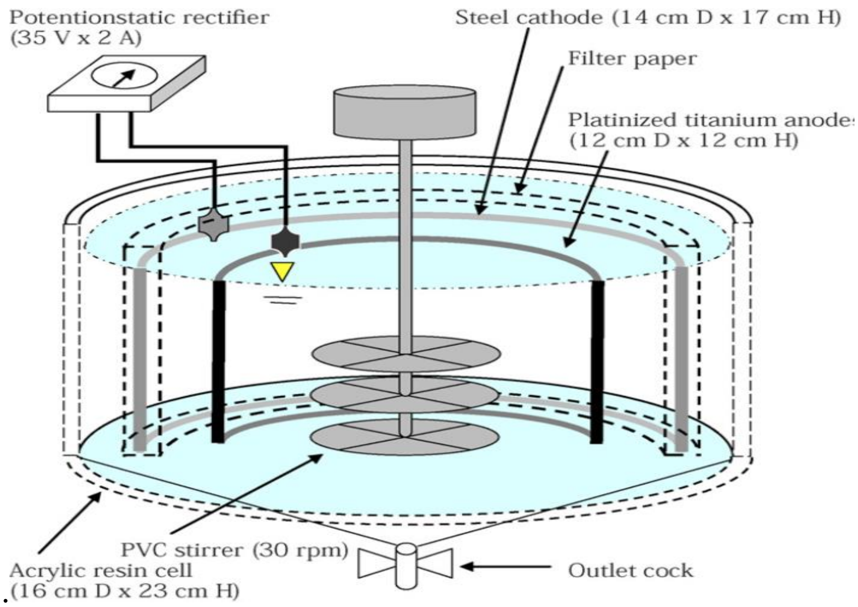

Figure 2.15. A vertical arrangement of tube-shaped electrodes (to increase surface area placed in parallel and in equal distance with a filter paper placed between the electrodes Source**: (Uchibori et al. 2010)**

2.4.9 Electro flocculation Mechanisms

(a) Flotation

During electro flotation treatment of contaminated waters, the pollutants float to the surface of a water body by attaching to the tiny bubbles of hydrogen and oxygen, promoting the separation of small particles (equation 20 and 21) **(Wang et al., 2022, Mohtashami and Shang et al.2019**). In research done by **Sharma et al., (2021)** said, Hydrogen production at the surface of the cathode during the reaction helps the lighter flocs to come up at the surface and due to the continuous Hydrogen bubble formation, there is the accumulation of lighter flocs at the top of the set-up which can be directly observed during the reaction

In addition, the free atomic oxygen generated at the anode can be carried from the anode diffusion layer by convection toward the wastewater and act as an oxidizing agent of organic compounds. Platinized titanium electrodes provide high electrocatalyst activity and by using this electrode, the oxidation process can occur through direct oxidation such as electron exchange between contaminants and electrode surfaces or with indirect processes with active species which have high oxidizing power such as peroxide, O3, and active chlorine **(Ardhianto and Bagastyo. 2019).**

Rumky et al. (2020) also said, among all anodes, TiO2, Pt, IrO2 etc. were considered as extensively used anode in anodic oxidation.

(b) Direct oxidation

Direct oxidation means that after organic pollutants are adsorbed on the surface of the anode, they undergo direct charge transfer from the electrode. Therefore, the organic pollutants are oxidized, the molecular chains are broken, and the molecular weight drops rapidly. This process can be expressed as: Equation 14

where R and P represent the high-molecular organic pollutants and oxidized matter, respectively **(Panizza et al., 2009)** ·OH is chemically adsorbed on the electrode surface. That is, the ·OH produced by the electrolysis of water will react with the active anode, and the anode will bond to the oxygen in ·OH to form a chemically adsorbed MO in the anode lattice. The reaction can be described as follows **(Kapalka et al.,2008)**: Equation 15

Other mechanisms of electrochemical treatment are also possible, such as in the presence of chloride ions, where there is the formation of chlorine gas, hypochlorous acid, and hypochlorite, which are strongly oxidizing species that can oxidize the organic pollutants forming CO2, H2O, and inorganic acids **(Kolesnikov et al.2017).** Equation 16-18.

(c) Electrocoagulation

It is also possible to generate the coagulants in situ by using sacrificial electrodes such as aluminum or iron electrodes that dissolve electrically, forming aluminum or iron ions at the anode (Equation 22). At the cathode, hydrogen gas is generated which favors the flotation of the flocculated particles. The treatment mechanism is therefore an initial electrocoagulation followed by an electro flotation **(Wang et al., 2022, Mohtashami and Shang et al.2019).**

(d) Operating parameters

Electro flotation is easy to operate. Process controls are tailored by electric current and voltage, with low operation voltages making electro flotation operation safe, presenting low energy consumption. Volumetric ratio among bubbles and particles in suspension, electrode (type, amounts, and sizes), electrolyte (type and concentration), current density, pH, and hydrodynamic regimen are important variables that affect electro flotation efficiency.

(e) Electrode Type

Electrode materials are an important part of an electro flotation cell, because production of small and uniform bubbles responsible for treatment efficiency are related to it. Iron, aluminum, and stainless steel are also commonly used **(Mohtashami and Shang et al.2019)**. Stainless steel is more resistant than the electrodes that are typically used and during the electrolytic processes its surface roughness is not easily changed compared to other electrode materials **(Mickova ., 2015).** Modification of Ti with Pt (Pt/Ti) have also been used by some researchers, which improved the electro-catalytic properties of Ti/TiO2 electrodes and increased the nucleation rate because of increased nucleation sites created by the platinizing process **(Sarkar et al.,2010).** Dimensionally stable anodes are used in electro flotation due to their anodically insolubility and they present high electrocatalytic activity for OER **(Mohtashami and Shang et al.2019).**

(f) Bubble size

Bubble size depends on the geometry of the electrode. Bubble diameter increases with increasing thickness of the wire mesh. Some studies have shown that the electrode surface curvature influences the distribution of hydrogen and oxygen bubbles, enabling the control of production ratio and bubble size **(Mohtashami and Shang et al.2019).** In addition, when analyzing the electrode material, comparing bubbles production on stainless steel or titanium as a cathode and platinum as an anode, it was possible to conclude that stainless steel produced smaller bubbles than titanium. In research done by **Mickove., (2015).** It was found that the smallest gas bubbles are produced at the stainless-steel electrodes. Finally, roughness was pointed out to present strong influence on the bubble production, where rougher surface produced more small bubbles, which favors electro-floatation process treatment efficiency (**Sarkar et al. 2010).**

(g) Electrolyte.

Studies have pointed out a linear increase in pollutant removal from various effluent as electrolyte concentration increases. This effect can be associated with an increase in ionic strength resulting in a thinner electrical double layer, thus, reducing bubble sizes; this is known as electronic compression, which favors bubble detachment, decreasing bubble diameter. The effect of ionic strength (by adding KNO3) on the bubble size was investigated by **Alarm et., (2017)** showed a slight decrease in the bubble size with increasing ionic strength. Some researcher suggested that, adding salt would increase the electric repulsive forces between bubbles for their high surface potential, which would also help to avoid collision.in addition, adding salt in the solution increases the viscosity of the electrolyte and hence increases the rigidity of the surface films of the bubbles so that the coalescence is more difficult **(Alam et al.2017).** However, extremely high saline concentrations caused by corrosion and pressure of excessive ions can distribute the electro flotation process, leading to a decrease in the removal rate. These electrolytes, consisting of anions and cations that are contained in the waste to be treated, or added for sufficient conductivity of the medium, can also have appreciable effects on (i) the rate of metal dissolution, (ii) the ohmic drop — and thus on the cell voltage and energy consumption, and (iii) surface phenomena occurring between polluting species and the metal hydroxides **(Jimenez et al.2010). Huang et al. (2020)** said, the addition of electrolytes in wastewater can increase conductivity (i.e., a decrease of the high polarization) and reduce the voltage to achieve energy-saving. NaCl has the highest inactivation efficiency and the lowest energy consumption. The most favorable supporting electrolyte for the treatment of wastewater containing E. coli by electrocoagulation is NaCl **(Ndjomgoue-Yossa et al. 2015)**.

(h) Current Density

Current density, described as ratio of applied electric current to the active surface area of electrodes, is considered as the most important process variable in electroflotation process. According to Faraday's law of electrolysis, Eq. (23), the mass of released gas (H_2 and O_2) or metal ions (e.g., Al and Fe ions) at the electrodes, m (g), is proportional to the applied electrical current, I (A), to system. In this equation, t is the reaction duration (s), MM is the molar mass of released element (g/mol), Z is the number of transferred electrons and F is the Faraday's constant (96486 C/mol) **(Mohtashami and Shang et al.2019)**

$$m = (I*t*M)/Z*F \qquad \textbf{Equation 23}$$

From Eq. (23), the increase of electrical current and current density results in the increase of released bubbles density and/or metal ion coagulants. Consequently, the probability of bubble-particle and/or coagulant-particle collisions and attachments increase, and the separation efficiency grows. This fact has been established in several studies **(Mohtashami and Shang et al.2019).**

However, the current density affects the generated bubble size and the treatment efficiency of electroflotation system. While some authors reported increase of electroflotation bubble size with increasing current density, there are studies suggesting the opposite effects, i.e., bubble size reduction with the increase of current density. Also, neutral influence of applied current density on bubble size has been observed in some experimental studies **(Sarkar et al., 2010)**. In articles presented by **Jiménez et al., (2010) and Alam et al., (2017),** it was stated that the electrolytic bubble size decreased with the increase of current density; but when the applied current density surpassed a threshold, the nucleated small bubbles coalesced, created coarse bubbles, and reduced the treatment efficiency. Therefore, there is an optimum current density, producing the finest bubbles, considering the electrode material and other experimental conditions. Low current densities produce a lower number of bubbles, which does not stimulate ascending flow conditions, favoring sedimentation of the pollutant, however high current densities, favor ascending flow conditions, due to a higher number of bubbles generated, stimulating pollutant flotation. In research done by Holt et al, Operation of the electrocoagulation reactor at higher current densities (27 A m−2) increased the bubble number concentration and concluded, that the combination of increased aggregation and an increased bubble number concentration is the reason for the dominance of flotation as the removal mechanism at high currents in this reactor.

The applied current density affects energy consumption of the treatment system too. Besides, the electrical current as the main process variable, this is also a parameter that can readily be adjusted during the operating phase of treatment system **(Mohtashami and Shang et al.2019).**

(I) Retention Time

In wastewater treatment, hydraulic retention time, HRT (Equation 24), plays a significant role

$$HRT = V/ Q \qquad \textbf{Equation 24}$$

where: HRT is the hydraulic retention time (h); V is the volume of the reactor (m3); and Q is the flowrate entering the reactor (m3/h). In electroflotation process, generation of bubbles, bubble-particle collisions and attachments, aggregates formation, aggregates ascending and skimming, are all time-dependent steps. Therefore, it is important to have adequate retention time **(Kolesnikov et al., 2017).** The retention time in electroflotation reactor is related to the size of treatment facility (capital cost) and electricity consumption (operating cost); hence, the design of reactors should be performed, so that while providing sufficient retention time for treatment process, economy of projects be taken into consideration as well.

(j) pH of the Media.

PH is always highlighted as a strong determinant in treatment efficiency for most electronic processes. By controlling the pH of the electrolyte, formation of determined co-products favored by a certain pH level (either dominant in acid or basic medium) can be controlled. As for electro flotation, pH can determine the ratio of bubble formation, as well as bubble size and bubble charge. Hydrogen bubbles tend to be small in neutral and alkaline pH, while oxygen bubbles gradually increase as pH increases. During the electrolysis of water, due to the excess of OH– ions in the near-cap layer, hydrogen bubbles acquire a negative charge and, thus, are repulsed from the cathode surface. In alkaline media, rapidly growing hydrogen bubbles have a negative charge, and oxygen bubbles do not have a charge due to their neutralization with alkali. In acid media, rapidly growing oxygen bubbles have a positive electric charge, and hydrogen bubbles do not have a charge due to neutralization with acid **(Kolesnikov et al.,2017)**. A study done by a reporter showed that efficiency is highest when bubbles and particles have opposite surface charges and are of similar sizes. Also, solution pH has a fundamental role in electrocoagulation/ electroflotation process when applying sacrificial electrodes, since the solubility of metallic hydroxides formed, which are excellent coagulant agents, is affected. Electro flotation was used in oily wastewater treatment. The optimum reaction conditions were found to be 4.11 mA/cm2, 80 min, pH 7, 1 cm, a NaCl concentration of 150 mg/l, and a chemical oxygen demand concentration (COD) of 4000 mg/l, respectively. The highest chemical oxygen demand removal efficiency was calculated to be 94.6% ± 0.2%, and gas chromatography analysis showed that 97.71% of fatty acids were removed **(Amir et al.2018).**

(k) Pollutant concentration and electrical conductivity.

The removal efficiency of electroflotation system declines with increasing initial pollutant concentration in wastewater, which has been reported in studies of electroflotation treatment of metal finishing effluents **(Khelifa et al., 2005)**. The electrical conductivity, EC, of wastewater is another influencing parameter in electroflotation process. EC is related to the ionic strength of wastewater and impacts energy consumption of electroflotation process. Based on Equation 25, the specific energy consumption is defined as the product of applied electric potential, current and time divided by unit volume of treated wastewater.

$$E = (U*I*T)/V \qquad \textbf{Equation 25.}$$

where: E is the specific energy consumption (W.h/m3); U is the electric potential (V); I is the applied electrical current (A); t is the reactor retention time (h); and V is the reactor volume (m3). With the increase of electrical conductivity of wastewater, the electric current decreases under the same electric potential, i.e., higher electrical conductivity of wastewater leads to less energy consumption and operating cost of electroflotation. Some authors added salt to wastewater to increase the EC and reduce the energy consumption **(Mohtashami and Shang et al.2019).**

(L) Energy consumption

Wastewater treatment plants (WWTPs) are widely implemented to reduce harmful emissions to receiving water bodies. However, most WWTPs were designed to meet certain effluent requirements, without sufficient considerations on energy. However, this situation has been changing in recent years as both water and energy are critical elements **(Gu et al., 2017)**. WWTPs are responsible for 1% of the total national electricity consumption in European countries **(Maktabifard et al. 2018)**. For European countries, the energy intensity for wastewater treatment is similar between Sweden and Germany, which is around 0.42 kWh/m3 **(Gu et al., 2017).** The USA is a typical developed country with unit electricity consumption for WWTPs of 0.52 kWh/m3. The electricity consumption by wastewater treatment is estimated to account for 0.6% of the annual electricity consumption in the USA in 2008 **(Gu et al., 2017).** Compared with USA, Asian countries shows lower energy intensity for wastewater treatment. (0.31 kWh/m3 for China, 0.304 kWh/m3 for Japan and 0.243 for Korea) **(Gu et al., 2017)**. Overall specific energy consumption in Canada and Singapore was 0.3 kWh/m3 and 0.45 kWh/m3, respectively **(Maktabifard et al. 2018)**. Electricity intensity of WWTPs in South Africa varies between 0.079-0.41 kWh/m3 with the most widely used technologies of lagoon and trickling filters **(Gu et al., 2017)**. For given wastewater characteristics and effluent quality, the per volume unit (of inlet wastewater) energy requirements of WWTPs depends on the plant size and type of remediation process **(Siatou et al., 2020)** and most often energy is among the top three most expensive items in a wastewater utility's operation and management budget. Reducing the purchased energy not only benefits lowering the potential costs, but also results in decreasing the carbon footprint and increasing the sustainability of the operations **(Maktabifard et al. 2018).** The energy consumption of flotation technologies for treatment of different industrial wastewaters are presented in Table 2.13 **(Mohtashami and Shang et al.2019)**. It is noted that the energy consumption of electroflotation process (0.1 to 0.5 kWh/m3) is comparable to the established flotation technologies, i.e., dissolved air flotation (0.22 to 0.4 kWh/m3).

Table 2.13: Energy consumption of flotation technologies

Technology	**Wastewater type**	**Energy consumption, kWh/m3**	**references**
Electroflotation	Process and rinsing water	0.1	**Envirochemie (2014)**
Eletroflotation	Electroplating and printed circuit effluents	< 0.5	**Mendeleev University Science Park (2008)**
Dissolved air flotation	Carrier-truck washings effluent	0.4	**Chambers and Cottrell (1976)**
Dissolved air flotation	Petroleum process water	0.33	**Vlasopoulos et al. (2006)**
Dissolved air flotation	Oil and gas operations effluents	0.22	**Ratnayaka et al. (2009)**

Current efficiency is one of the most important parameters considered in industrial applications. Energy consumption depends on reactor project, electrode material, current density, and solution conductivity, among others .Electroflotation is a suitable treatment process for wastewaters with high electrical conductivity (EC), as high EC reduces the power consumption and operating costs of the system. However, electrodes replacement should be considered in the operating costs as well. The review of the literature and commercial systems shows that, by generating a high density of fine bubbles, electroflotation is an efficient and economical method for small to medium-scale operations of treatment of hydrophobic fine suspended particles, where other treatment methods are not successful or are expensive. Also, by choosing effective and proper electrode materials, electroflotation can be implemented for treatment of other types of wastewaters, e.g., wastewaters containing heavy metals. In treatment of wastewaters containing high concentrations of dissolved minerals, e.g., calcium and magnesium, scale build-up might occur on electrodes surface, especially cathode. This issue can be tackled by applying polarity reversal of electrodes and applied electrical current **(Mohtashami and Shang et al.2019).**

2.4.10 Kinetics of Electroflotation

Kinetics is the study of speed (rate) of treatment processes. The term speed or rate of reaction appears in the mass balance equation and based on the theory of mass balance of a closed system (Accumulation = Inflow – Outflow + Change), the following equation can be derived **(Mohtashami and Shang et al.2019)**:

$V*dt/dc = Q*CO - Q*Cef + r*V$ **Equation 26.**

where: V denotes the reactor volume (m3); Q is the wastewater flowrate (m3/h); C is the pollutant concentration in the reactor (g/m3); C0 is the influent pollutant concentration (g/m3); Ceff is the effluent pollutant concentration (g/m3); t is the time (h); and r is the reaction rate (g/m3.h). The rate of reaction, r, is defined by Eq. (27)

$r = -dC/dt = kCn$ **Equation 27**

where: k is the rate constant (h-1 for first order, m3/g.h for second order); and n is the order of reaction. The order of reaction determines how the reaction rate is affected by the concentration of pollutants, e.g., if the order of reaction is zero, the reaction is independent of pollutant concentration. Substituting different rate orders in Eq. (27) and integrating, the following equations for zero-order (Eq. 28), first-order (Eq. 29), and second-order (Eq. 30) kinetic models can be established, where Ct denotes pollutant concentration at time t:

$Ct- Co = -kt$ **Equation 28**

$Ct = Coe-kt$ **Equation 29**

$1/Ct - 1/Co = kt$ **Equation 30**

Researchers defined R and R* parameters as Recovery at time t and final Recovery, respectively; and manipulating Eq. (28) to Eq. (30), the following kinetic models for different reaction orders were presented (**Mohtashami and Shang et al.2019):**

$R = R*(1- e-kt)$ **Equation 31**

$R = R*(kt)/1+kt$ **Equation 32**

R = R*2(kt)/1+ R* kt **Equation 33**

R = R*(1- ((In (1+kt))/ kt) **Equation 34**.

Authors have conducted kinetic study of electroflotation treatment of various types of wastewaters. studied the kinetics of electroflotation treatment of auto paint wastewater and found the second-order kinetics as best fit to electroflotation experimental data. Type and nature of pollutants and duration of experiments affect the order of electroflotation reaction **(Mohtashami and Shang et al.2019)**

2.4.11 Application of Electroflotation for Treatment of Industrial Effluents

Electro flotation can be applied as a preliminary treatment for water used in cooling and washing systems in industrial processes, recovery and separation of minerals, extraction of suspended compounds of heavy and nonferrous metals and emulsions of organic substances, biodiesel wastewater treatment and restaurant wastewater treatment, dairy manure, Palm oil mill Effluent, textile wastewater Figure 2.14. domestic wastewater **(Zhang et al., 2020)**, paper and pulp **(Kalyani et al., 2009).**

Table 2.14. Electroflotation application in wastewater treatment

Wastewater	**Reactor**	**electrode**	**Retention time**	**Applied electricity**	**System performance**	**reference**
Effluent of textile industry in Algeria.	1.5 L batch	aluminum electrode	0-25 min	11.5-91.5 mA/cm2	BOD5 88.9%, COD 79.7%, SS 85.5%, turbidity 76.2%, and color 93%.	**Merzouk et al. (2010)**
Acid Blue 113 Dye Solution	250 mL match	iron anode and stainless-steel cathode	60 min	1–5 A/dm2	91% COD, 95% color	**Saravanan et al. (2010)**
Synthesized dairy wastewater	25.8 L continuous upflow	aluminium electrodes	20 min	0.3-0.7 A/m2	80% COD, 98% phosphate, 100% TSS and 100% turbidity	**Bassala et al. (2017)**

Real dairy wastewater	2 L batch	aluminium electrodes	15-60 min	10-60 V	98.84% COD, 97.95% BOD and 97.75% TSS removal	**Bazrafshan et al. (2012)**
Industrial chrome tanning effluents	1 L batch	Mild steel or Al electrodes	0-90 min	65-98 mA/cm2	More than 90% Cr(III) removal	**Golder et al. (2011)**
Wastewater of leather finishing processing factory	5 L batch	Iron electrodes	0-120 min	43–68 mA/cm2	90–99% turbidity; 30–60% TSS; 40–80% calcium removal	**Espinoza-Quiñones et al. (2009)**
Paper company wastewater in Tunisia	4.2 L continuous	stainless steel cathodes, Ti/RuO2 anode	10-22 min	200 A/m2	95% suspended solids removal	**Mansour et al. (2007)**
Machine-washing effluent of cardboard industry	4.2 L continuous	stainless steel cathodes, Ti/RuO2 anode	28 min optimized	148.7 A/m2 optimized	96% COD, 91% BOD and 96.5% TSS removals	**Mansour and Kesentini (2008)**
Paper and Cardboard effluent in Jordan	6 L continuous	Iron electrode	Up to 90 min	20-80 A/m2	80% TSS and COD removal	**Al-Shannag et al. (2012**
Marine Mediterranean crude oil suspension	0.35 L batch	Stainless steel cathode, Titanium anode	0-60 min	30-180 A/m	70% oil removal at optimum condition	**Mansour and Chalbi (2006)**
Synthetic crude oil solution	2 L batch	perforated aluminium plates	10-50 min	2.5-7.5 V	More than 90% oil removal	**Bande et al. (2008)**
Actual bilge water	4 L continuous	stainless steel cathode and oxidized	Up to 120 min	2-6 A	80% color, 70% turbidity, 50% COD and 40%,	**Carlesi et al. (2015)**

		titanium anode			Pb-Zn removal in 120 min	
Actual poultry chiller water	2.2 L continuous	nonconsumable electrodes	29.3 min	280-1200 coulomb/L charge	82% TSS removal, successful disinfection	**Tsai et al. (2002)**
Poultry slaughterhouse effluent	250 mL batch	Al or Fe electrodes	5-40 min	20-200 A/m2	93% COD, 98% oil and grease removal	**Bayramoglu et al. (2006)**
Olive oil factory effluent	7.5 L continuous	Al anode and RuO2/Ti cathode	5–30 min	5–40 mA/cm2	> 90% COD, TSS, color and oil and grease removal	**Esfandyari et al. (2015)**
Olive pomace oil refinery wastewater	300 mL batch, 4.2 L continuous	Ti/RuO2 anode, stainless steel cathode	25 min optimized	205 A/m2 optimized	> 92% COD and TSS removal	**Hmidi et al. (2017)**
Effluent of vegetable oil refining industry	1 L batch	Ti/RuO_2 anode, stainless steel cathode	30 min	40-260 A/m	Successful removal of turbidity	**Issaoui et al. (2017)**
Palm oil mill effluent (POME)	20 L.	aluminum electrodes		2 to 4 volts	COD and turbidity of POME by 57 and 62%, respectively	**Naustion et al.2011**
Biotreated palm oil mill effluent (BPOME),		aluminium electrodes	15min	160 mA/cm2 (with current 1.75 A)	The optimum Chemical Oxygen Demand (COD) removal of 71.5%	**Tahreen et al.2021**

2.4.12 Advantages and disadvantages of electroflotation technique.

Scientific research, practice, and operational experience have revealed several obvious advantages of the electroflotation method, the main of which are as follows (**Kolesnikov et al., 2017):**

(a) Advantages of electroflotation treatment.

EF is an incredibly useful and a competitive alternative to settling tanks which require large land area **(Nahui et al., 2008)**. Uniform mixing can be achieved due to gas bubble production (kyzas et al., 2016). EF units have small compact that requires lower maintenance and running costs compared to other flotation units **(Nahui et al., 2008)**. Brief time of the process (5–10 min) and high degree of purification (up to 99%). The possibility of simultaneously extracting impurities that have various phase-disperse compositions of 10–100 μm. Low power consumption (0.1–0.3 kW h/m3).

The formation of finely dispersed gas bubbles characterized by high adhesion ability relative to the extracted impurities and efficient coagulation of the dispersed phase. The possibility of the smooth regulation of gas bubble consumption to control the process.The favorable influence of the electrical field on changes in the physicochemical characteristics of the disperse system under treatment, which intensifies the process of coagulation and flocculation.

Electro-flotation (EF) may not only achieve similar performance of coagulation and flocculation but help overcome their drawbacks such as removing pollutants using none, or negligible amount of chemicals **(Bektaş et al., 2014, Can et al., 2006),** use insoluble electrodes and therefore result to absence of secondary water pollution.The additional destruction of dissolved organic impurities and water disinfection due to the oxidation–reduction processes at electrodes and in water volume.

The working volume of flotations is 10–20 times smaller than the volume of the sedimentation tank, while sedimentation and electroflotation times differ by 3–5 times. Obtaining froth products with lower moisture content (90–95%) than that of sediment formed in sedimentation tanks (95–99.8%). The possibility to simultaneously extract dispersed phase and emulsions.

(b) Disadvantages of electroflotation treatment.

On the other hand, the electro flotation process presents the disadvantages of requiring DC power. Effluents need to be conductive. Tank heights must be less than 1m. The electrode material may suffer corrosion or passivation. Poorer performance is obtained with high specific gravity material **(Kolesnikov et al., 2017).**

CHAPTER 3. SEPARATION OF SUSPENDED SOLIDS IN COW MANURE EFFLUENT PARTICLES BY ELECTROCOAGULATION AS A PRE-TREATMENT

Although EF requires electrical energy, raising the overall costs of the process, its application in cow manure effluent treatment for agricultural purposes as fertilizers may be important, because it uses metallic ions and gas bubbles, not chemical coagulants. Hence reducing the use of chemical coagulants and avoiding environmental hazards. This study aims at demonstrating and confirming the hypothesis by applying electrocoagulation method (EC) using platinized titanium and steel anode as an anode and cathode electrode, respectively.

3.1 Methodology

- Sample collection

The cow manure effluent was collected from a discharge point of a dairy farm, Enomoto-Bokujo, located in Ageo-City, Saitama Japan (35o 57’46”N, E139o 32’26”E). A manager translated raw materials into a polyethylene tank and then immediately transported them to Applied Ecological Engineering laboratory in Saitama University (Figure 1). The cow manure effluent was later diluted until the upper limit of measurement and sieved using a 250-micron mesh sieve before experiment (Figure 2). Characteristics of the cow manure effluent are given in Table 1.

Table 3.1: Characteristic of cow manure effluent used in this study.

Component	Value
Turbidity, NTU	4,000
pH	7.2
Zeta potential, mV	-16
ORP, mV	-162
CODcr, mg/L	3,650

where, the turbidity was determined using a turbidimeter (2100N, Hach, USA). The solution pH and ORP were measured with a glass electrode (TOA-DKK, Tokyo, Japan). Zeta potential was measured with Zeta-potential & particle size analyzer (ELSZ-2000 series, Otsuka Electronics Co., Ltd., Tokyo, Japan). CODcr was determined using Spectroquant® COD cell test (Merck KGaA, Darmstadt, Germany).

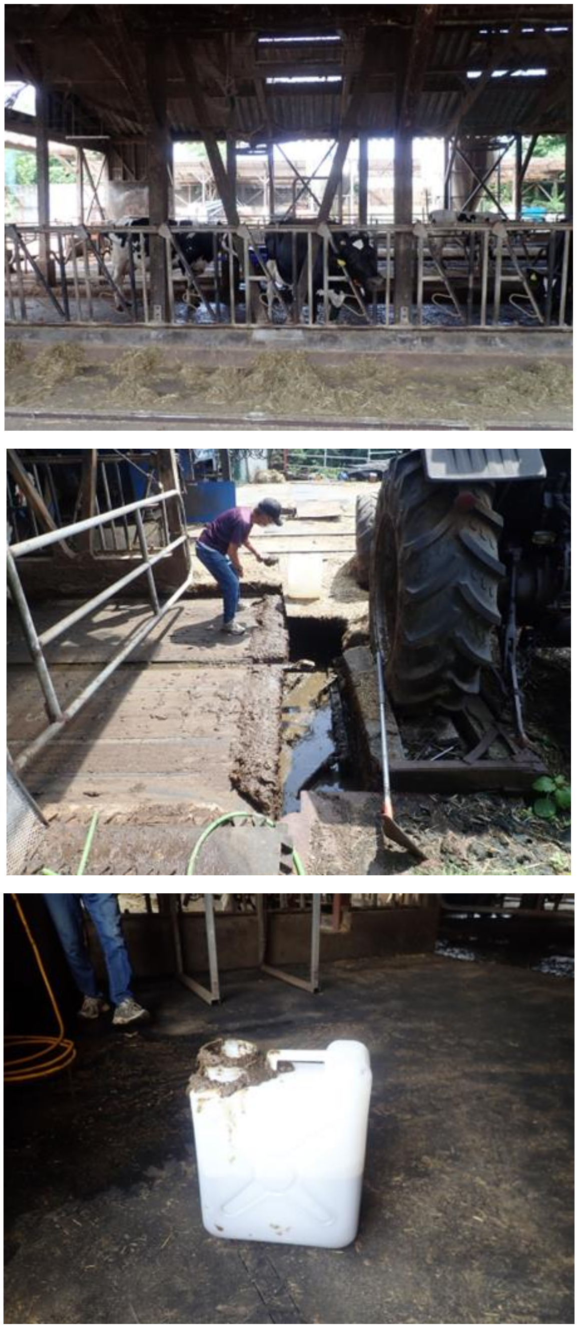

Figure 3.1: Sample collection of cow manure effluent, Enomoto-Bokujo, Ageo-City, Saitama Japan

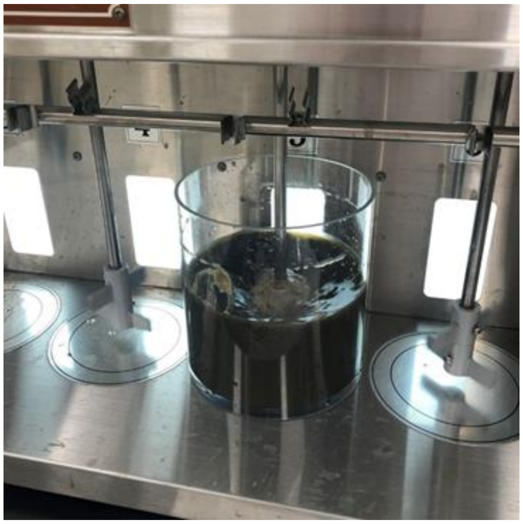

Figure 3.2: Diluted sample for experiment

- **Experimental setup**

A cylindrical platinized titanium anode (12cm diameter x 12cm high) and a cylindrical steel cathode (14cm diameter x 17cm high) were installed in a 3-L cylindrical cell with distances of 1 cm and 2 cm from the lower edge of the anode to the bottom of the cell to ease flowing (Figure 3a and 3b). The cathode surface was covered with 0.2-mm pore size filter paper (ADVANTEC, No.5C, Tokyo, Japan) to retard the diffusion of the catholyte and avoid direct contact with caw manure particles; tiny holes were made at the top of the covered filter paper for effluent hydrogen gas. The anode and cathode were connected to a galvanostatic rectifier of 35V–2A (Kikusui, Yokohama, Japan). For electrolysis, the anode current density was 4–6 mA/cm2 **(Uchibori et al., 2010)**.

- **Coagulant agent**

Coagulation and flocculation experiments were performed on a jar test apparatus (VT-4P, Sugiyamagen Inc., Tokyo, Japan). Aluminum chloride (AlCl3) coagulant and cationic polyacrylamide flocculant (CPAM, commercial name: C-512, MT Aqua Inc., Tokyo Japan) were used as a chemical coagulant. The cationic polyacrylamide polymer was prepared from radical polymerization of acrylamide monomers, with characteristic given in Table 2.

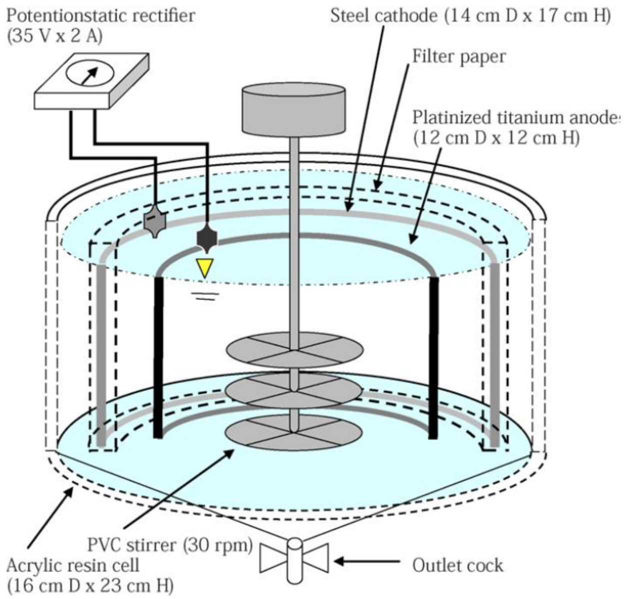

Figure 3.3a: Schematic diagram of the experimental setup for electrolytic treatment

Figure 3.3b: Photo of the experimental setup for electrolytic treatment

Table 3.2: Characteristic of cationic polyacrylamide flocculant (CPAM) used in this study, C-512

Type	Cation
Principal component	Polyacrylic acid ester
Bulk specific gravity	0.65±0.1
pH in water	2.5-5.5
Molecular weight	4,000,000
Viscosity at 0.2%, 25C	230 mPa · s

3.2 Experiment, Procedure and Conditions

- **Case-1: Coagulation method**

Coagulation experiments were performed to determine the effect of AlCl3 in cow manure effluent treatment and optimal AlCl3 concentration. Firstly, predetermined AlCl3 concentration at 50, 100, 200, 400, 600 and 800 ppm were added into 1L of cow manure effluent, respectively and rapidly stirred at 230 rpm for 3 min to fully collide AlCl3 coagulants and suspension particles. Finally, the formed flocs freely settled for 10 mins and the supernatant turbidity, COD and Zeta potential at depth 2 cm below the water surface were analyzed for AlCl3 coagulation performance.

- **Case-2: coagulation -flocculation method**

Coagulation-flocculation experiments were performed to determine optimal CPAM concentration when a fixed amount of AlCl3 concentration is added. Another reason was also to determine the effect and advantage of adding AlCl3 to CPAM. Firstly, 200 ppm AlCl3 coagulant was added into each beaker containing 1L of the cow manure and rapidly stirred for 1 min. Immediately predetermined CPAM concentration at 20, 40, 80, 120, 160 and 200 ppm were added, respectively and continued stirring at 230 rpm for 2 min. Finally, the formed flocs free settled for 10min. Coagulation-flocculation performances were evaluated by analyzing the supernatant turbidity, COD and Zeta potential at depth 2 cm below the water surface.

- **Case-3: EF-coagulation-flocculation method**

EF-coagulation-flocculation experiments were performed to determine optimal CPAM concentration when a fixed amount of AlCl3 concentration and EF operation time is used with it. Another reason was to determine the advantage of using electrocoagulation method in this process. During each run, 1L of cow manure effluent was added to a reactor having platinized titanium anode and steel cathode. The reactors were placed under a jar test stirrer apparatus with the speed held constant at 120 rpm during each electro-flotation run that was performed at 15 mins electrolysis time. Next all electrodes were removed for coagulation-flocculation test which was done with jar test apparatus. Firstly, 200 ppm AlCl3 coagulant concentration was added into each beaker containing 1L of the pretreated cow manure without change of pH and rapidly stirring at 230 rpm for 1 min. Immediately predetermined CPAM concentration at 20, 40, 80, 120, 160 and 200 ppm were added, respectively and continued stirring for 2min at 230 rpm. Finally, the formed flocs could settle free for 10min. EF-coagulation-flocculation performances were evaluated by analyzing the supernatant turbidity, COD and Zeta potential at depth 2 cm below the water surface.

3.3 Results and Discussions

- **<u>Effect of AlCl3 concentration (Case-1)</u>**

From the coagulation experiment, it was observed that increased AlCl3 concentration enhanced pollutant and organic matter removal from cow manure effluent. Figure 4a shows that increased AlCl3 concentration increased turbidity and COD removal. Optimum AlCl3 concentration 800 ppm gave the highest removal rate of turbidity (99.8%) and COD (84.4%), respectively. In relation to pH, increased AlCl3 concentration decreased the cow manure effluent pH to 6.1. Increase pollutant and organic matter removal after the addition of AlCl3 concentration to cow manure effluent was because AlCl3 coagulant hydrolyzed and formed positive charge aluminum ions, which neutralized the negative charges on the colloidal particles resulting to an increase Zeta potential value at -6.8 mV, thus promoting destabilization of the colloid dispersion and agglomeration of the resulting individual colloidal particles (Figure 4b) **(Chaudhari et al., 2010)**.

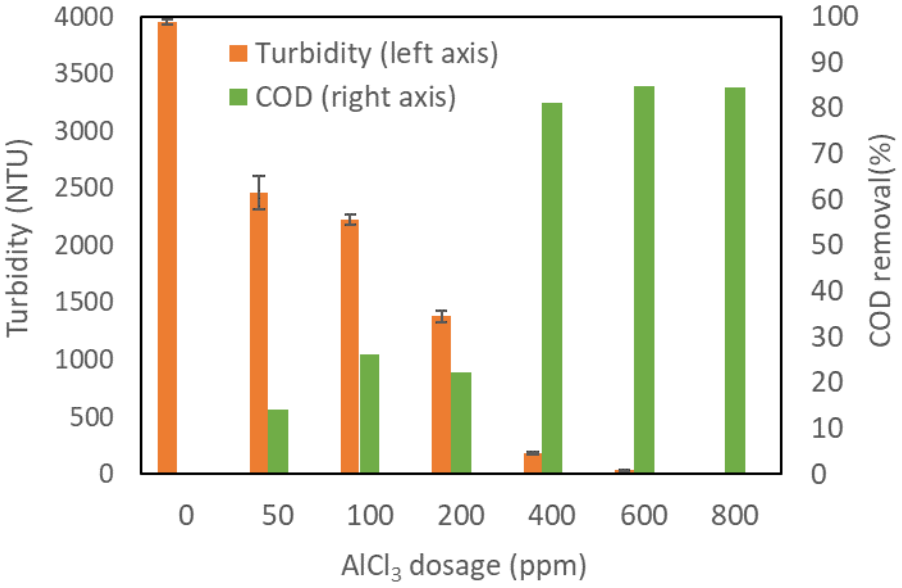

Figure 3.4a: Turbidity and COD removal rate results by adding $AlCl_3$ on cow manure effluent treatment (Case-1)

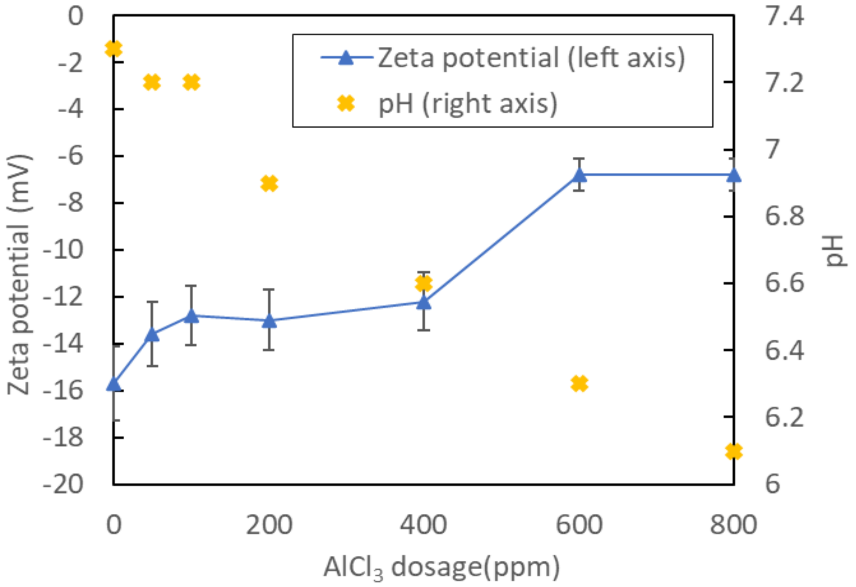

Figure 3.4b: Zeta potential and pH results by adding AlCl$_3$ on cow manure effluent treatment (Case-1)

- **Effect of CPAM concentrations with fixed 200ppm AlCl3 concentration (Case-2)**

Coagulation for Case-1 on cow manure treatment showed that high concentration of AlCl3 was needed to give an appropriate result which could lead to high concentration of Al in the treated wastewater. It may threaten human life, plants, and aquatic environment **(Malik. 2018, Kurniawan et al., 2020)**. Here, 200ppm AlCl3 was applied with CPAM to enhance organic matter removal. Figure 5a shows turbidity and COD removal rate results by adding CPAM on cow manure effluent treatment under 200ppm AlCl3 addition. Optimum CPAM concentration 200 ppm enhanced turbidity and COD removal rate by 99.1% and 91%, respectively. A slight increase in pH due to low AlCl3 addition was also observed. Increase pollutant and organic matter removal after increased CPAM concentration under low AlCl3 addition was because increased CPAM concentration enhanced the neutralization effect and bridging effect by destabilizing, increasing organic matter floc size and removal **(Liu et al., 2016)**. A charge neutralization is modified by both from positive charge Al ions and CPAM increased Zeta potential reached at –5 mV corresponding to 120 ppm of CPAM under 200 ppm of AlCl3 concentration (Figure 5b). Further increase to 200 ppm of CPAM concentration resulted in a much higher zeta potential (+13 mV) and turbidity removal tended to slight decrease.

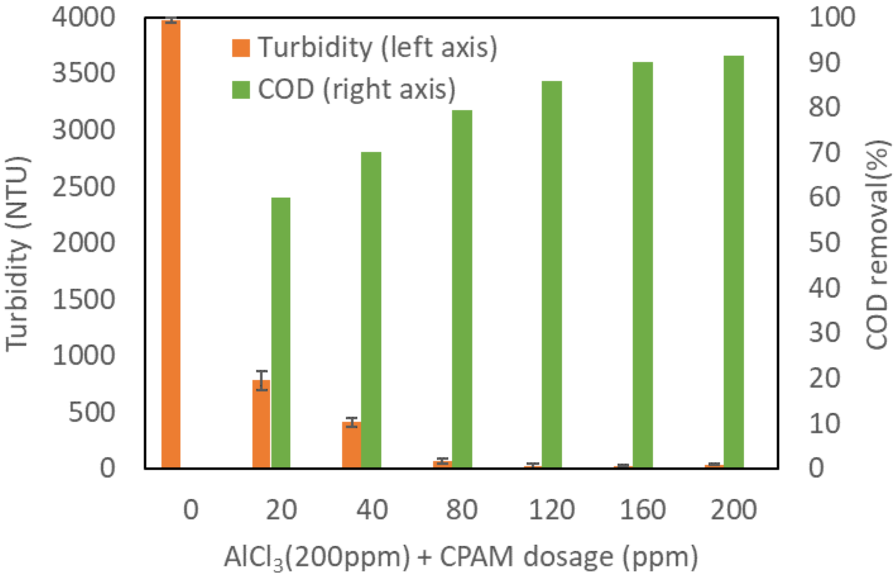

Figure 3.5a: Turbidity and COD removal rate results by adding $AlCl_3$ (200 ppm) and CPAM dosage on cow manure effluent treatment (Case-2)

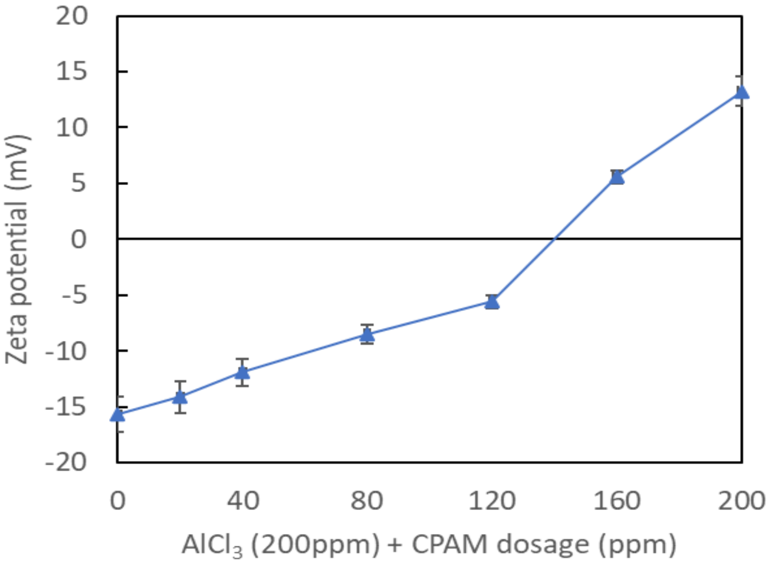

Figure 3.5b: Zeta potential result by adding $AlCl_3$ (200 ppm) and CPAM dosage on cow manure effluent treatment (Case-2)

- **Effect of Electrocoagulation on $AlCl_3$ with CPAM (Case-3)**

From the coagulation-flocculation experiment, it was noticed that fixed 200 ppm of AlCl3 concentration enhanced organic matter removal on cow manure treatment when used with CPAM flocculant. The aim of this process was to enhance pollutant and organic matter removal and reduce chemical coagulant concentration. To achieve this aim, a fixed EC operation time of 15 min was used with fixed 200 ppm of AlCl3 concentration and different concentration of CPAM. Since increased electrocoagulation time results in an increased energy consumption, only 15 min EC operation time was applied **(Shamaei et al., 2018, Kim et al., 2013)**. Figure 6a shows that the optimum CPAM concentration at 80 ppm was noticed which gave 99.1% and 95% of removal rates for turbidity and COD, respectively. The trend is almost same as Case-2 and the difference is lower pH inner anode and aggregation is enhanced in EC system. The positive charge aluminum ion from AlCl3 and CPAM cations increased the Zeta potential at -9.48 mV corresponding to 80 ppm of CPAM concentration (Figure 6b). A further increase to 200 ppm CPAM concentration with 15 min EC operation time resulted in a much higher zeta potential at +11.82 mV. While carrying out the water electrolysis, oxygen gas bubble is generated inner the anode which may play the leading role in the EC process, however, the aggregated sludge did not float (Figure 7a).

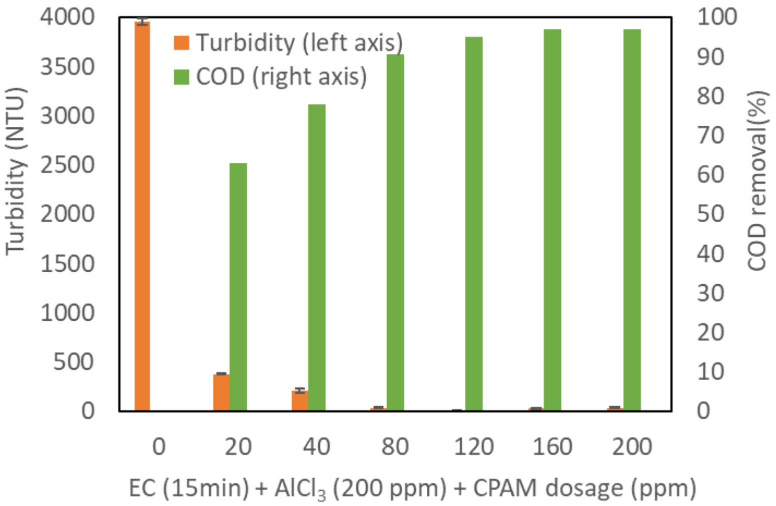

Figure 3.6a: Turbidity and COD removal rate results by electrocoagulation, EC (15 min) as a pre-treatment, and by adding $AlCl_3$ (200 ppm) and CPAM dosage on cow manure effluent treatment (Case-3)

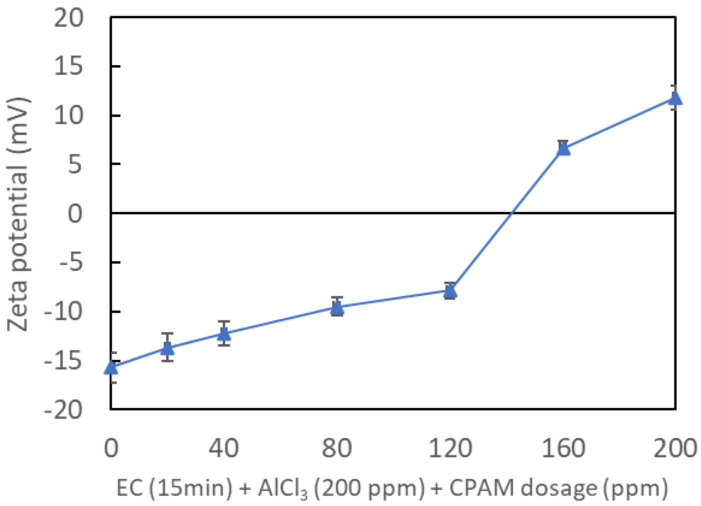

Figure 3.6b: Zeta potential result by electrocoagulation, EC (15 min) as a pre-treatment, and by adding $AlCl_3$ (200 ppm) and CPAM dosage on cow manure effluent treatment (Case-3)

- **Other characters of electrocoagulation method as a pre-treatment: effect of filter paper cover on cathode**

Our study used filter paper cover on cathode to retard the diffusion of the catholyte and avoid direct contact with cow manure particles; tiny holes were made at the top of the covered filter paper for effluent hydrogen gas **(Mohtashami and Shang. 2019)**. Figures 7 a and b show different results between (a) with and (b) without covered filter paper. If we used filter covered, aggregated floc of cow manure sink which is the normal aggregation phenomenon. The pH of inner anode tended to be acids advance for coagulation. If we do not use filter covered, on the other hand, they float due to hydrogen gas mixing produced on the cathode surface and pH was neutral due to mixing. Each final turbidity and COD removal rates were the same. Platinum coated titanium was utilized as an anode electrode and released oxygen gas from the surface. This is a different point from the previous study for dairy wastewater treatment **(Chakchouk et l., 2017).** An electrolysis apparatus is assembled to neutralize the negative charges of cow manure effluent particles owing to an oxidation reaction promoted on a non-consumable anode, by applying a device and surface pre-treatment on a steel cathode to retard the cathodic reduction. This apparatus for particle oxidation prevents contamination of the treated retentate by dissolved metal ions.

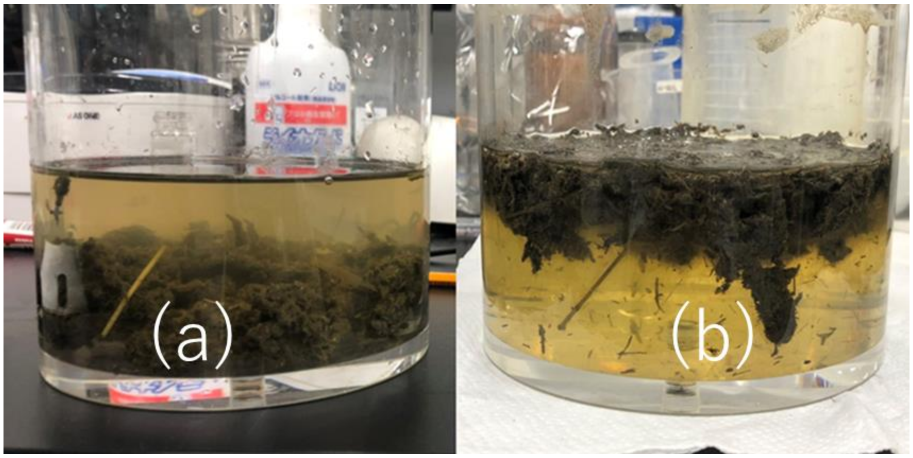

Figure 3.7: Control of aggregated floc of cow manure effluent after electrocoagulation, EC (15 min) as a pre-treatment, and by adding AlCl3 (200 ppm) and CPAM (80 ppm) dosage, (a) with filter paper covered, and (b) without filter paper covered

3.4 Conclusions

We demonstrated electrocoagulation method as pre-treatment of cow manure effluent wastewater. An electrolysis apparatus is assembled to neutralize the negative charges of cow manure effluent particles owing to an oxidation reaction promoted on a nonconsumable anode. This apparatus for particle oxidation prevents contamination of the treated retentate by dissolved metal ions and succeeded in reducing chemical coagulant. Also, it can be used as flotation method if we do not filter paper cover on cathode. Further experiments may be needed for more practical stage.

CHAPTER 4. SOLID –LIQUID SEPARATION OF DAIRY BARN BY ELECTROCOAGULATION WITH CATIONIC POLYMER COAGULANT

This study was aimed at increasing the efficiency of two stage electro- and chemical-coagulation treatment with a minimum chemical dosage for solids–liquid separation in dairy manure slurry for the safe composting of solids and safe discharge of wastewater. We compared three Al coagulants, such as polyaluminum chloride (PAC), aluminum chloride ($AlCl_3$), and aluminum sulfate ($Al_2(SO_4)_3$). The best coagulant was tested with cationic polyacrylamide (CPAM) and EC to improve the separation of solids and liquid from dairy manure slurry and minimize the dosage of Al coagulant

4.1. Material and Methods

Materials and chemicals

Dairy manure was obtained from a dairy farm located in Ageo, Japan. Solid manure was sieved using a 0.5 mm mesh to remove coarse particles and diluted twenty times with deionized water to prepare slurry of dairy manure. The characteristics of slurry are presented in table 1.

Table 4.1. Characteristics of twenty times diluted dairy manure slurry (*n*=3).

Parameter	Average (S.D.)
pH	6.89 (0.17)
Oxidation-reduction potential (ORP) (mV)	−36.5 (6.3)
Electrical conductivity (κ) (μS/cm)	1060 (142)
Dissolved oxygen (DO) (mg/L)	0.11 (0.01)
Turbidity (NTU)	2452 (218)
Suspended solids (SS) (mg/L)	1703.3 (136.7)
Chemical oxygen demand (COD) (mg/L)	6623 (710)

$Al_2(SO_4)_3 \cdot 14–18H_2O$ and $AlCl_3 \cdot 6H_2O$ were purchased from Hayashi Pure Chemical Ind., Ltd., Osaka, Japan. PAC was purchased from Nitto Chemical Industries, Ltd., Kanagawa, Japan. CPAM was obtained from MT Aqua Polymer, Inc., Tokyo, Japan. Table 2 shows the characteristics of CPAM.

Table 4.2. Characteristics of CPAM[a]

Parameter	Description/value
Polyacrylamide polymer type	C-512
Principal component	Polyacrylic acid ester type
Ionic characteristics	Medium/high cationic
Molecular weight	4 million
Viscosity (mPas at 25 °C)	230

(a) Product safety information on ARONFLOC, ACCOFLOC. The revised fertilizers regulation act of special fertilizers.

4.2 . Experimental Methodology

Jar tests were performed to study the effect of Al coagulants and CPAM on solid–liquid separation of dairy manure slurry. Experiments were carried out using a programmable jar testing apparatus (JMD 6E, Miyamoto Riken Ind. Co., Ltd., Osaka, Japan). Each set of experiments was conducted with 1 L of diluted dairy manure slurry samples: addition of Al coagulant is followed by a rapid mixing at 200 rpm for 1 min, addition of CPAM is followed by a moderate mixing at 100 rpm for 3 min, slow mixing at 30 rpm for 5 min, and a 30 min of settling.

Three Al coagulants such as PAC, $AlCl_3$, and $Al_2(SO_4)_3$ were compared in a dosage range of 20 to 800 mg/L on the separation of solid and liquid of twenty times diluted dairy manure slurry. After selecting the best Al coagulant, experiments were carried out with CPAM to reduce the dosage of Al coagulant and find the optimal dosage of CPAM.

Finally, EC treatment was combined with chemical coagulation with PAC and CPAM to investigate the effect of EC on chemical dosage. As shown in figure 1, the EC setup is equipped with a cylindrical shaped steel anode and a platinized titanium cathode at 1 cm. Each set of experiments was performed for 5 min at 35 V under 2 A of direct current.

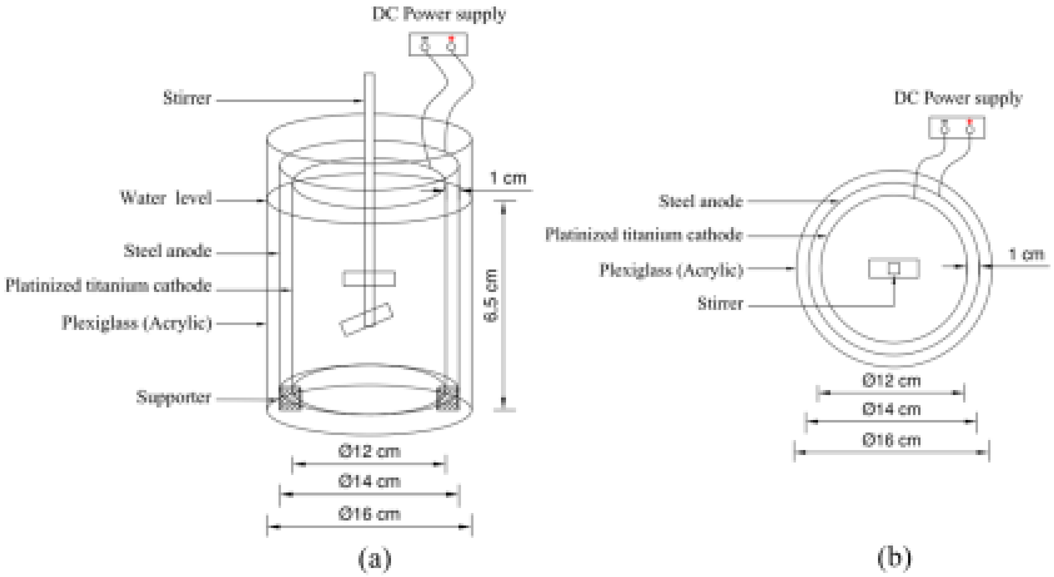

Figure 4.1. Schematic experimental setup for solid and liquid separation in dairy manure slurry. (a) 3D view and (b) plan view.

Analytical methods

Water samples were collected from 5 cm below the water surface after settling. pH (portable digital meter-HM-40P), electrical conductivity (κ) (portable conductivity meter-AS710), oxidation-reduction potential (ORP) (digital ORP meter-MM-41DP), dissolved oxygen (DO) (portable DO meter-HQ30D), zeta potential (zeta potential and particle size analyzer-ELSZ-2000), and turbidity (turbidity meter 2100 N) were analyzed before and after treatment.

Turbidity, COD, and SS were used as the primary parameters to determine the efficiency of solid and liquid separation of dairy manure slurry. The removal efficiency was calculated using equation.

$$\text{Removal efficiency (\%)} = (Ci - C_f / Ci)*100 \qquad (3.1)$$

Where C_i is the concentration of the pollutants before treatment and C_f is the concentration of the pollutants after treatment.

SS were measured by the GFP filtration based on the gravimetric method (Japanese industrial standards). COD of dairy manure slurry was analyzed to identify the removal of organic compounds, which was measured by a method based on catalytic oxidation with coulometric titration using a bench top real-time simplified COD meter (COD-60A).

4.3. Results and Discussion

Comparison of Al coagulants on solid-liquid separation

In this section, three Al coagulants were compared to determine the best coagulant for the separation of solid–liquid in dairy manure slurry. PAC was the best coagulant among the Al coagulants evaluated.

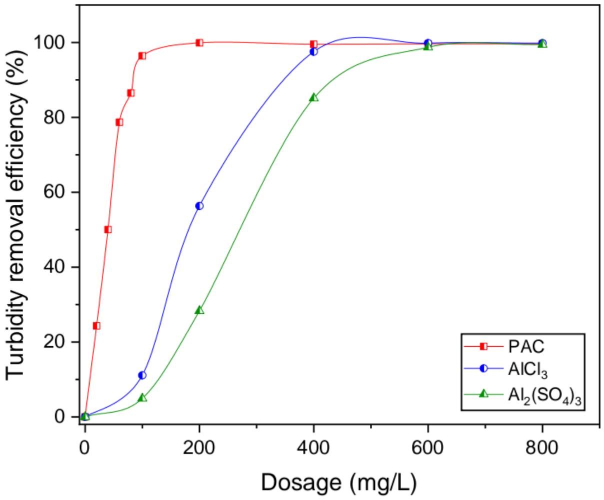

Figure 4.2. Comparison of Al coagulants for solid and liquid separation in dairy manure slurry.

As shown in figure 2, PAC showed the minimum dosage of 100 mg/L to achieve 99% turbidity removal. The optimal dosages of $AlCl_3$ and $Al_2(SO_4)_3$ were 400 and 600, respectively. Therefore, 100 mg/L of PAC was selected as the optimal dosage for further experiments. Table 3 compares the characteristics of treated water at optimal dosages of different Al coagulants. PAC showed the minimum SS of 69 ± 10 mg/L at the optimal dosage compared with $AlCl_3$ and $Al_2(SO_4)_3$.

Table 3. Characteristics of the liquid fraction of dairy manure slurry treated with Al coagulants

		Treated water quality, n=3, average (S.D.)		
Coagulant	Optimum dosage(mg/L)	PH	Turbidity (NTU)	SS (mg/L)
PAC	100	6.26 (0.06)	68.23 (1.56)	69 (10)
$AlCl_3$	400	6.05 (0.07)	31.83 (3.75)	358 (17)
$Al_2(SO_4)_3$.	600	5.92 (0.02)	44.03 (1.46)	200 (50)

PAC was more efficient than $AlCl_3$ or $Al_2(SO_4)_3$. Because PAC is a poly-nuclear form of AlCl3 species and has a high overall positive charge of +7 **(Zouboulis et al.2008, Gao et al.2005),** therefore, adsorption–charge neutralization mechanism is dominant **(Wei et al.2015)** while $AlCl_3$ or $Al_2(SO_4)_3$ show a maximum cationic charge of +3. During the coagulation, numerous monomeric and polymeric are produced by PAC (i.e., $Al_{13}(OH)_{34}^{5+}$, $Al(OH)_{20}^{4+}$, $Al_2(OH)_2^{4+}$, $Al_4(OH)_8^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_3(OH)_4^{5+}$, $Al_{14}(OH)^{8+}$) **(Islam and Mostafa. 2020).** However, $Al_2(SO_4)_3$ and $AlCl_3$ normally form a few species, i.e., Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$, and $Al(OH)_4^{-}$, relying on the pH during hydrolysis **(Nowacka et al.2014).**

The pH of the liquid fraction after treatment was slightly lower than the initial pH at each coagulant. PAC showed the lowest pH reduction than that of other coagulants. This is because PAC contains pre polymerized aluminum species which are less likely affected by pH variation **(Zouboulis et al.2008)**. In the case of AlCl3 and $Al_2(SO_4)_3$, it is important to maintain the pH of the solution below 7. Because $Al(OH)_4^{-}$ are dominant at alkaline pHs and negatively charged coagulants are formed during hydrolysis **(Bojórquez-Quintal et al.2017, Meetiyagoda and Fujino 2022).** These negatively charged precipitates are less efficient in destabilizing the potential repulsion energy between negatively charged colloids in the wastewater **(Sievers et al.1994).** Most importantly, PAC showed less sludge volume than other coagulants used in the study.

Effect of CPAM on PAC dosage

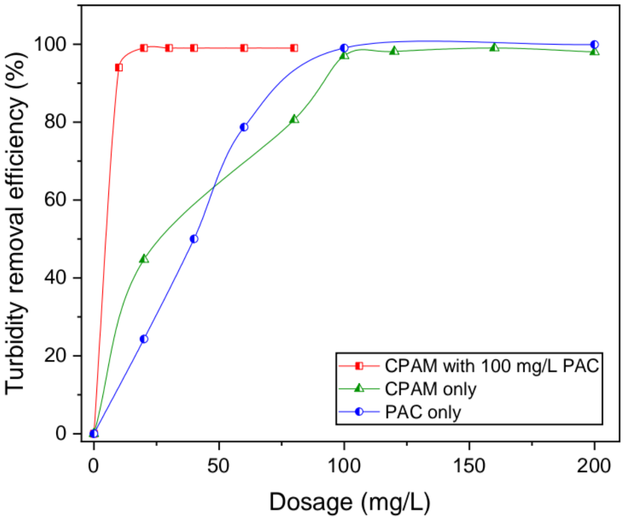

Figure 4.3. Comparison of CPAM and PAC for solid and liquid separation in dairy manure slurry.

PAC and CPAM showed a similar performance when using them separately (Figure 3). The optimal dosage of PAC and CPAM alone was 100 mg/L. However, the CPAM dosage required to achieve the maximum turbidity reduction was significantly decreased when using PAC and CPAM together. We observed that a CPAM dosage of 20 mg/L was sufficient to achieve maximum turbidity reduction when treatments were combined with PAC at a dosage of 100 mg/L. CPAM improved the solid–liquid separation of dairy manure slurry and reduced the PAC dosage. This is because positively charged CPAM neutralizes the negatively charged colloidal particles of dairy manure. The application of cationic polymers would be more beneficial than the application of anionic ones. Because most suspended particles in livestock manure effluents have a negative charge when pH greater than four **(Sievers et al.1994)**. Furthermore, since CPAM and PAC contain a similar polymeric structure, it could enhance their cooperation in the flocculation process **(Luo et al.2018)**.

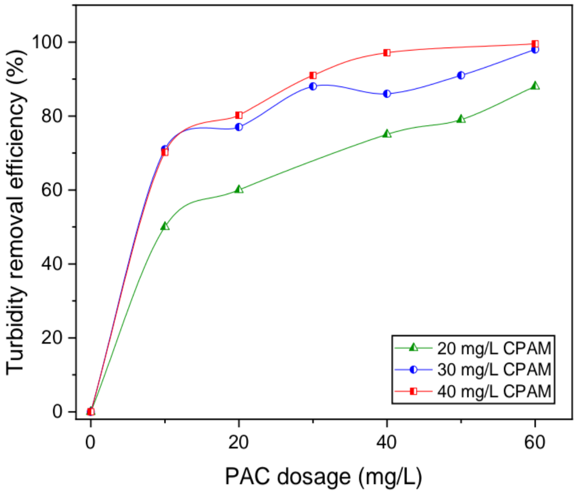

Figure 4.4. Effect of CPAM dosage on PAC dosage for solid and liquid separation in dairy manure slurry.

The effect of CPAM dosage on the variation of PAC dosage was investigated under three different dosing conditions; 20, 30, and 40 mg/L dosages of CPAM. As shown in figure 4, the treatment with a CPAM dosage of 40 mg/L showed the greatest turbidity removal efficiency at the lowest PAC dosage. In other words, CPAM 40 mg/L achieved the highest turbidity removal efficiency of 97% at 40 mg/L of PAC dosage. However, turbidity removal efficiency was 75 and 86% for 20 and 30 mg/L of CPAM, respectively, at 40 mg/L of PAC dosage. Table 4 shows the characteristics of the liquid portion of dairy manure slurry treated with 40 mg/L of PAC and CPAM.

Table 4. Characteristics of the liquid fraction of dairy manure slurry treated with optimal PAC and CPAM dosages (n=3).

Parameter	Average (S.D.)
pH	6.93 (0.02)
ORP (mV)	229.7 (3.7)
κ (µS/cm)	922 (4)
Turbidity (NTU)	55.1 (2.03)
SS (mg/L)	286 (4.7)
COD (mg/L)	1950 (148)\

There was no significant reduction in terms of pH and κ. However, 83 and 71% reductions were observed for SS and COD, respectively. Since PAC and CPAM do not change the pH of the solution, the pH of the treated water was almost neutral under optimal conditions. A slight reduction of κ was observed. This is because the coagulation and flocculation process only remove suspended particles. κ. of the solution may be responsible for dissolved ions. Results showed a highly positive ORP which represents the oxidation-reduction state of the solution **(Pitot. 1996)**.

Effect of EC on PAC dosage

In this section, we investigate the effect of EC treatment on PAC dosage. As shown in figure 5, 98% of turbidity reduction efficiency was observed at a PAC dosage of 30 mg/L when treatments were combined with 5 min EC and 20 mg/L of CPAM.

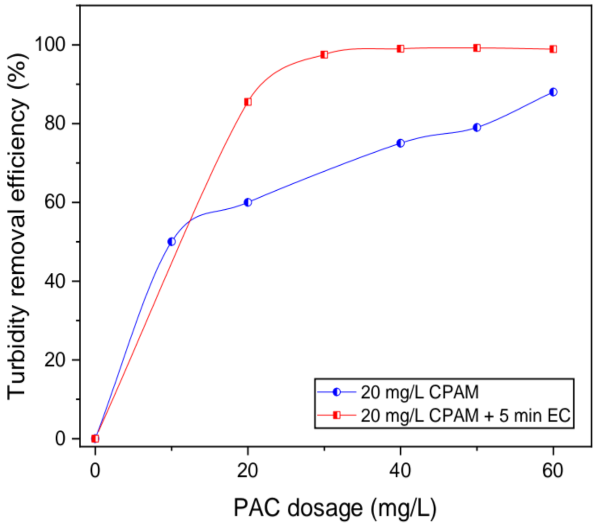

Figure 4.5. Effect of EC on the PAC dosage for solid and liquid separation in dairy manure slurry.

The COD and SS removal efficiencies increased from 71 to 82% and from 83 to 92%, respectively when treatments were combined with EC for 5 min. This is because the Fe^{2+} released from the anode undergoes hydrolysis to produce iron hydroxide compounds that act as coagulants **(Zhang et al.2020)**, thereby increasing the coagulation of dairy manure. However, the color of treated water became green due to the dissolution of Fe^{2+} **(Chen et al.2021)** from the steel anode. 4. Conclusions From this study, we conclude that PAC was the best among Al coagulants evaluated for the reduction in turbidity in the liquid fraction of dairy manure slurry at a dosage of 100 mg/L. The application of positively charged CPAM significantly affected PAC dosage. CPAM at a dosage of 40 mg/L reduced the PAC dosage to 40 mg/L. It was further reduced to 30 mg/L when the treatments were combined with EC owing to the production of iron coagulants. Even though the turbidity removal efficiency achieved was 98%, the residual turbidity of the liquid fraction was 55 NTU, therefore, chemical- and electro-based treatment should be optimized to improve the turbidity and COD removal efficiency and further reduce the chemical dosage.

4.4 . Conclusions

From this study, we conclude that PAC was the best among Al coagulants evaluated for the reduction in turbidity in the liquid fraction of dairy manure slurry at a dosage of 100 mg/L. The application of positively charged CPAM significantly affected PAC dosage. CPAM at a dosage of 40 mg/L reduced the PAC dosage to 40 mg/L. It was further reduced to 30 mg/L when the treatments were combined with EC owing to the production of iron coagulants. Even though the turbidity removal efficiency achieved was 98%, the residual turbidity of the liquid fraction was 55 NTU, therefore, chemical- and electro-based treatment should be optimized to improve the turbidity and COD removal efficiency and further reduce the chemical dosage.

CHAPTER 5. SYNERGETIC EFFECT OF CHEMICAL COAGULATION AND ELECTROFLOTATION ON PALM OIL MILL EFFLUENT TREATMENT.

Since there are no or little information found in combined chemical and EF method as a post treatment method for POME treatment, in this study, we hypothesized that combined chemical coagulation and EF treatment can significantly improve the treatment efficiency by reduce the specific energy consumption by limiting the electrolysis time. We used dimensionally stable electrodes such as platinized titanium anode and a stainless-steel cathode for the EF, which also involve degrading the dissolved organic compounds of POME.

5.1 Materials and Methods

- **<u>Preparation of POME</u>**

POME for the experiments was synthetically prepared using soup palm base which was purchased from Nkulenu Industries Ltd in Ghana. This is a pure and natural soup palm base, free from preservative and coloring, which contained 77% palm fruit pulp, water, and salt. The POME was prepared by adding water to the palm fruit pulp (mesocarp) and boiled at temperature 140 degree Celsius for 30 min. clean palm oil was extracted from the surface while the sludge retained at the bottom was used as POME. This synthetically prepared POME was thick brownish in color and consisted of elevated levels of solid residues and unrecovered oil. The manually made POME was immediately transported to Applied Ecological Engineering laboratory in Saitama University using polyethylene tanks. POME was diluted 10 times before every experiment to reduce the initial concentration to demonstrate the post-treatment influence of POME. The characteristics of POME used in this study are given in table 1.

Table 1. Characteristics of palm oil mill effluent prepared for the experiments.

Parameter	Value (Average, SD)
pH	6.64 ± 0.1
Electrical conductivity	451 ± 20 µS/cm
Oxidation-reduction potential (ORP)	164 ± 10 mV

Turbidity	1431 ± 10 NTU
Dissolved oxygen	8.24 ± 0.2 mg/L
Dissolved hydrogen	<0.001 mg/L
COD	3860 ± 30 mg/L

5.2 Experimental Procedure

Experiments were carried out in three stages: EF treatments, chemical coagulation, and combined EF and chemical coagulation.

- **Electroflotation (EF)**

As shown in Figure 1, a laboratory scale EF setup was made up of plexiglass, circular-shaped electrodes, and other accessories. A cylindrical platinized titanium anode and a cylindrical stainless-steel cathode were connected to an external DC power supply (PMC35-2A, Kikusui, Kanagawa, Japan). Table 2 shows characteristics of EF setup used in this study.

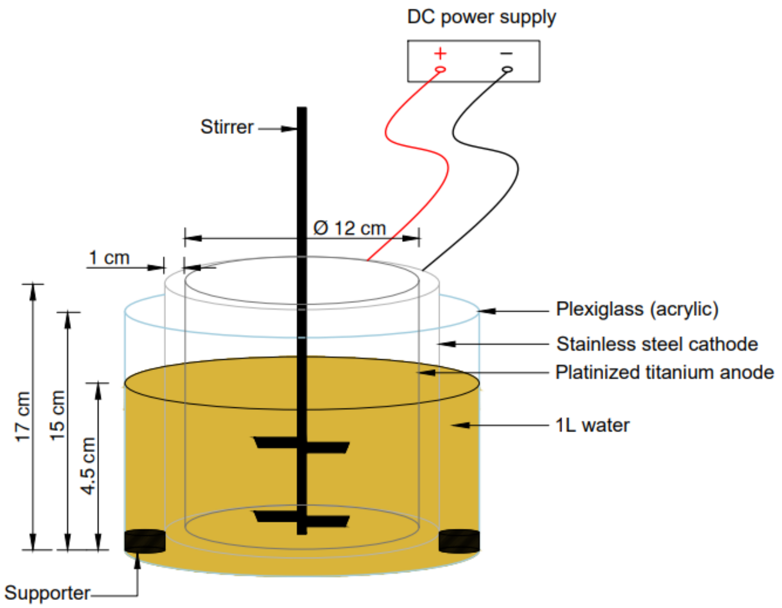

Figure 5.1 Schematic of EF setup for POME treatment. Equipped with cylindrical shaped platinized titanium anode, stainless steel cathode, and a DC power supply.

Table 5.2. Characteristics of EF setup.

Electrode material	Anode: Platinized titanium, Cathode: Stainless steel
Shape	Cylindrical
Effective surface area	Anode: 340 cm2, Cathode: 396 cm2
Inter electrode distance	1 cm
Reactor dimensions	15 cm (Height); 16 cm (Diameter)
Effective volume of the cell	1 L

At the beginning of each EF test, 1 L of POME was fed into the EF cell, respectively. The effect of electrolysis operation time (0 to 45 min) and current intensity (1 A and 2 A) on POME treatment was monitored. Current densities at 1 A and 2 A were 2.5 and 5 mA/cm2, respectively. A continuous stirring was applied at 120 rpm and each set of experiment was performed under the room temperature. Samples were collected at 0, 10, 15, 30, and 45 min. After settling for 10 min, turbidity, COD, zeta potential, DO (dissolved oxygen) and DH (dissolved hydrogen) of the liquid fraction were measured.

- **Chemical coagulation**

PAC and CPAM were used to show chemical coagulation's effect on POME treatment. PAC was purchased from Nitto Chemical Industries, Ltd., Kanagawa, Japan. Commercially available CPAM were supplied by MT Aqua Polymer, Inc., Tokyo, Japan. The CPAM used in this study was prepared from radical polymerization of acrylamide monomers. Characteristics of the CPAM used in this study were as follows; polyacrylamide polymer type was C-512, principal component was polyacrylic acid ester type, ionic characteristic was medium/high cationic, molecular weight was 4 million, and the viscosity was 230 mPas at 25 °C. A 2000 mg/L stock solution was prepared by dissolving 0.4 g of the polymer into 200 mL of distilled water at temperature of 30–50°C. The CPAM stock solutions were agitated at 300 rpm until the polymer particles were completely dissolved.

Laboratory scale chemical coagulation experiments were performed using jar test apparatus (JMD6E, Miyamoto Riken Ind. Co., Ltd., Osaka, Japan) using 1 L POME samples. For the coagulation and flocculation test, different dosages of PAC and CPAM (10, 20, 40, 60, 100 mg/L) were used. For coagulation-flocculation test, after adding 40 mg/L dosage of PAC, POME samples were rapidly stirred for 2 min at 120 rpm followed by slow stirring for 3 min at 20 rpm after adding different dosages of CPAM (10, 20, 40, 60, 100 mg/L). At the end of all the chemical coagulation processes used, the floc settled for about 10 minutes. After settling turbidity, COD, and zeta potential were determined from the supernatant.

- **Combined experiments**

After determining the optimum electrolysis time of EF and current intensity, chemical coagulation and EF were combined. In this test, 15 min electrolysis time with 40 mg/L dosage of PAC, at 1 A was first carried out at 120 rpm, followed by adding different dosage of CPAM (20, 40, 60, 80 100 mg/L) respectively. After 10 min settling, turbidity, COD, and zeta potential were determined from the supernatant.

Analytical methods

Treated water samples were collected after 10 min settling from 5 cm below the surface using a pipette and the physicochemical parameters were analyzed as shown in Table 3.

Table 5.3. Physicochemical parameters and method adopted.

Parameter (Units)	Instrument	Model
pH	Portable digital meter	HM-40P, DKK-TOA
Electrical conductivity (µS/cm)	Portable conductivity meter	AS710
Zeta potential (mV)	Zeta potential and particle size analyzer	ELSZ-2000
DO (mg/L)	Portable DO meter	HQ30D
DH (mg/L)	Portable hydrogen meter	ENH-2000
Turbidity (NTU)	Laboratory turbidity meter	2100 N

COD was measured using the reactor digestion method with 5–80 mg/L range CODCr vials. A 2 mL of homogenized sample was added into individual CODCr test vial and incubated in a COD reactor (45600, HACH, Colorado, USA) for 2 hours at 150 °C. The COD readings were obtained using a photometer (Spectroquant NOVA 60, Merck, Darmstadt, Germany) after cooling to room temperature.

- **Removal efficiency (R%)**

The removal efficiencies (R%) have been calculated with the Equation (5.4):

$$R\% = (C_0 - C_1)/C0 \times 100 \qquad (5.4)$$

Where C_0 and C_1 are concentrations of turbidity and COD before and after treatment, respectively.

- **Specific energy consumption**

The specific energy consumption was calculated using in kWh per unit mass of pollutant treated using Equation 5.5 **(Belkacem et al., 2017, Swain et al., 2020)**.

$$\text{Specific energy consumption} = V*I*t/\ (C_0 - C_t))\ *\forall \qquad (5.5)$$

Where V is the average cell voltage (V), I is the applied current (amp), t is the electrolysis time (h), $\forall$ is the volume of the POME in electrolysis cell units (L), C0 is the initial concentration of the pollutant (mg/L), and Ct is concentration at time t (mg/L).

- **Statistical analysis**

All graphs were produced using OriginLab software 2022 (OriginLab Corporation, Massachusetts, USA). Statistical analyses were carried out using IBM SPSS Statistics 20.0 software. Average turbidity and COD removal efficiencies under different treatments were compared using one-way ANOVA (analysis of variance) post-hoc Tukey HSD (Honestly significant difference) tests to identify the best treatment. All statistical analyses used a significance level of 5% ($p \leq 0.05$).

5.3 Results and Discussions

- **Effect of electroflotation on POME treatment**

As the initial stage, the effect of electrolysis time and current intensity for POME treatment using EF were investigated using turbidity, COD, and zeta potential data. The average initial turbidity and COD were 1431 ± 10 NTU and 3860 ± 30 mg/L, respectively. POME samples were treated using EF separately under 1 A and 2 A current intensities (current densities were 2.5 and 5 mA/cm2, respectively). Figure 5.2 shows the variation of turbidity removal efficiency with the electrolysis time.

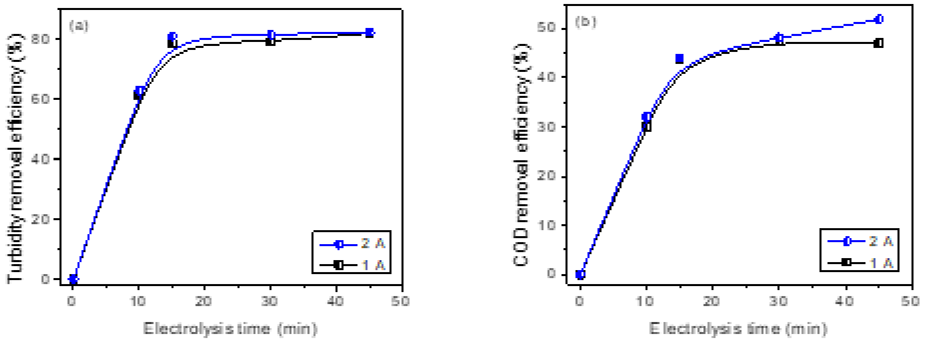

Figure 5.2. Comparison of (a) turbidity and (b) COD removal efficiency between 1 A and 2 A current intensities under EF for POME treatment.

From the results, it could be realized that increasing electrolysis time and current density increased the turbidity and COD removal efficiency. This is because bubble size and their generation rate, and collisions among particles depend on Faraday's law. High electrical current resulted in significant bubble density with smaller in size, which promotes the removal of pollutant in EF treatment **(Ghanbari et al.2014)** through the attachment of suspended pollutants to the charged surface of micro-bubbles **(Poh et al., 2014)**.

In EF treatment, H2 and O2 are produced at the cathode and anode, respectively. Results showed that the DH was increased from <0.001 to 0.24 mg/L after 45 min of electrolysis time at 2 A because of increasing electrolysis time and current density. This was also reported by **Trinke et al. (2017)** and they also noticed that the higher the DH evolution because of increasing applied current density, thus leading to a rising supersaturation of DH. In this study, it was noticed that DO concentration also increases at 2.5 mA/cm2 current density where current intensity was maintained at 1 A, however, later decreased when current density was increased to 5 mA/cm2 at 2 A. The research carried out by **Ben et al. (2007)** also supports this, as it was reported that at higher current densities, a larger amount of O2 was induced into the liquid phase, resulting in more gas bubbles. This increased DO concentration caused an increase in oxygen permeation. Thus, in this study it could be said that increasing electrical current brought about greater bubble generation, which effectively promoted pollutant removal by EF.

Even though the COD removal efficiency continued to increase at 2A, there was no significant variation of turbidity removal efficiency after 15 min either at 1 or 2 A. The turbidity and COD removal efficiency after 15 min electrolysis were 79 and 44% respectively, which was achieved at 1 A current intensity. Comparable results were reported by Ho and Chan **(Ho and Chan. 1986)**. They demonstrated the EF treatment with a lead dioxide–titanium anode and a stainless-steel cathode for POME treatment and achieved about 86% of suspended solids and 40% of COD removal efficiency.

In this study, we observed a gradual increase in COD removal efficiency at 2 A with increasing the electrolysis time. In other words, when current intensity and electrolysis time increased from 1 to 2 A and 15 to 45 min, respectively, the COD removal efficiency increased from 44 to 52%, whereas specific energy consumption increased from 0.01 kWh to 0.035 kWh for the treatment of one kilogram of COD.

Increasing the COD removal efficiency could be a result of production of reactive oxygen species at platinized titanium anode (M) such as hydroxyl radicals (HO°), which mineralize the organic pollutants **(Belkacem et al., 2017)**. This phenomenon is known as EO. In EO process, HO° are produced on the anode surface at high current (Equation 5.6).

$$M + H_2O \rightarrow M(\cdot OH) + H^+ + e- \qquad (5.6)$$

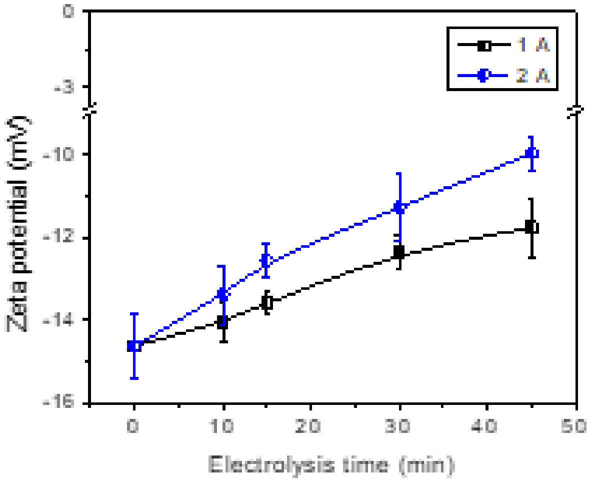

Figure 5.3. Variation of zeta potential with treatment time at different current intensities in EF treatment. Error bars represent the standard deviation (n = 3).

Zeta potential is a crucial and controlling parameter in wastewater treatment studies especially in coagulation and flocculation. Because it measures the magnitude of electrostatic charges of particles in the system. As shown in Figure 3, the average initial zeta potential was –14.62 ± 0.8 mV. The zeta potential was gradually increased with electrolysis time in both current intensities owing to destabilization of suspension caused by particle aggregation due to gas bubble generation **(Mansour et al., 2007)**. However, even after 45 min electrolysis time zeta potential of POME samples treated under 1 A and 2 A current were –12.76 ± 0.7 and –9.97 ± 0.4 mV, respectively. This is because gas bubbles generated between pH 7–8 may have negative zeta potential **(Poh et al., 2014)**. Therefore, application of coagulants could be an appropriate option to improve the zeta potential towards its positive shift.

- **<u>Effect of chemical coagulation on POME treatment</u>**

In section, the effect of PAC and CPAM dosage on POME treatment was investigated using turbidity and COD removal efficiency and variation of zeta potential. Figure 4 shows the turbidity and COD removal efficiency under different chemical treatments. The removal efficiency increased when chemical dosage was increased. Continual addition of PAC dosage until 100 mg/L showed 25 % of COD and 94% of turbidity removal efficiency. The addition of CPAM dosage until 100 mg/L also enhanced turbidity and COD removal efficiency to 96 and 34%, respectively. The optimum turbidity and COD removal efficiencies were 90 and 47%, reported at combined PAC and CPAM treatment at dosage of 20 mg/L PAC and CPAM.

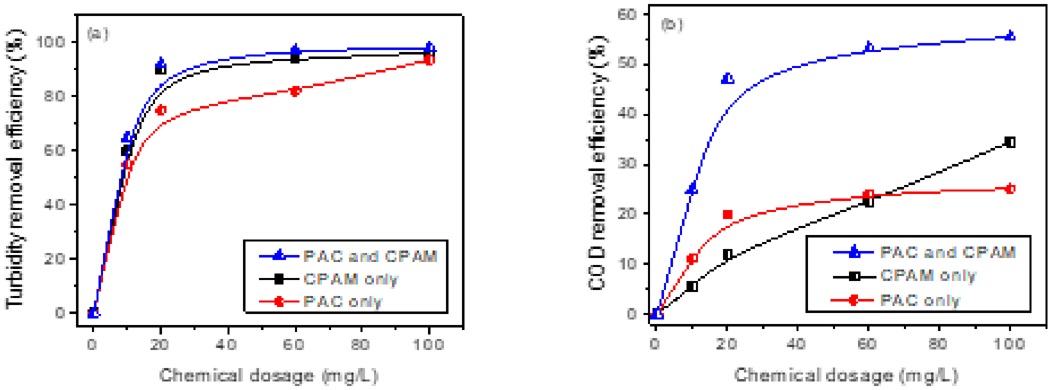

Figure 5.4. Comparison of (a) turbidity and (b) COD removal efficiency at different chemical coagulation methods for POME treatment.

When 40 mg/L of PAC dosage was used with varying dosage of CPAM, organic pollutant removal was higher. The maximum removal efficiencies were seen at 100 mg/L CPAM dosage, which were 55% COD and 98% turbidity removal efficient.

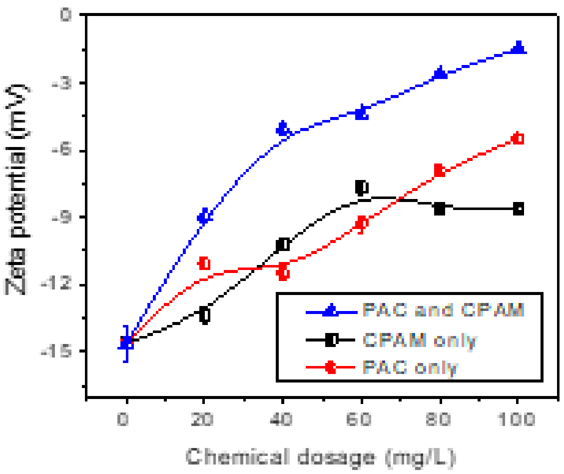

Figure 5.5. Variation of zeta potential with the treatment time at different chemical coagulation methods. Error bars represent the standard deviation (n = 3).

Figure 5.5 shows the variation of zeta potential with chemical dosage at different treatments. At PAC and combined PAC and CPAM treatments, zeta potential was proportionally increased when the chemical dosage was increased. The final average zeta potential of PAC and CPAM treatments were –5.97 ± 0.5 and –8.65 ± 0.6 mV, respectively. In CPAM treatment, zeta potential was slightly increased until 60 mg/L dosage and it was no longer increased after 60 mg/L.

In PAC treatment, highly stable, + 7 charge AlO4 Al12(OH)247+ species is pre-formed and rapidly neutralize negatively charged suspended pollutants in POME, subsequently zeta potential increased **(Zakaria et al., 2020)**. It has also been observed that increasing cationic coagulant dosage increased charge neutralization in the treated water. The final average zeta potential of combined PAC and CPAM treatments was –2.76 ± 0.4 mV. This is because PAC and CPAM both have cationic properties, their combined effect on pollutant removal is enhanced in accordance with the principle of charge neutralization. Increasing CPAM dosage increased the intrinsic viscosity which led to molecular chain growth. In addition, CPAM consists with a special linear structure and abundant functional groups, which help to attract various pollutants **(Wang et al., 2019)**. Furthermore, increasing CPAM dosage also increased the probability of collision among the colloidal particles and favored trapping and bridging of particles **(Guan et al., 2018)**. These changes can be attributed to the increased cationic effect of PAC and CPAM that caused an increase in aggregation and enhanced colloidal organic matter removal in POME treatment.

- **Effect of combined chemical coagulation and electroflotation on POME treatment**

In this section, experiments were carried out using fixed electrolysis time of 15 min and current density of 2.5 A/cm2 at 1 A current in the EF system, fixed dosage of PAC 40 mg/L and varying dosage of CPAM.

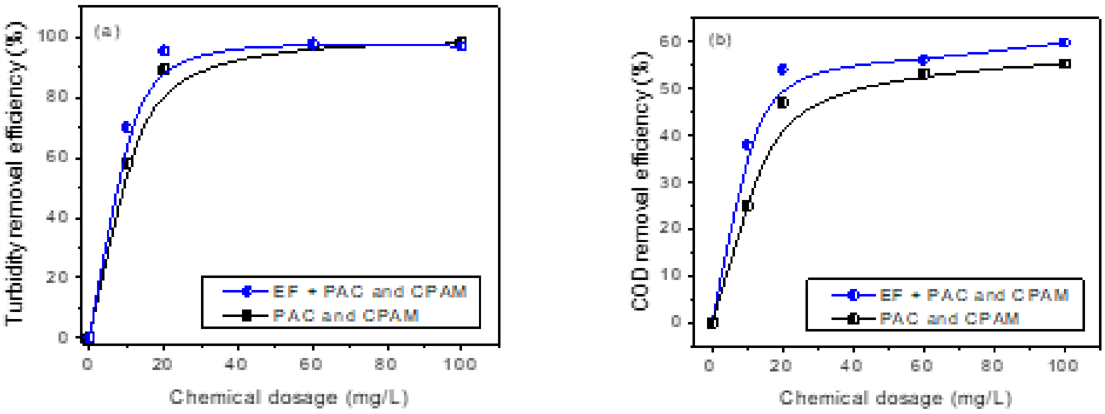

Figure 5.6. Comparison of (a) turbidity and (b) COD removal efficiency between EF and combined EF and chemical coagulation for POME treatment.

When chemical coagulation (PAC and CPAM) combined with EF, COD removal efficiency increased from 55 to 60%. Overall, the highest turbidity and COD removal efficiency of 97 and 60% were noticed when 40 mg/L of PAC and 100 mg/L of CPAM were used with EF. However, there was no significant removal efficiency in terms of turbidity or COD after 20 mg/L of CPAM. Considering the cost and residual impact of chemicals, 20 mg/L was selected as the optimum concentration. Releasing of residual CPAM into the environment might be toxic for aquatic life **(Duggan et al., 2019)**..

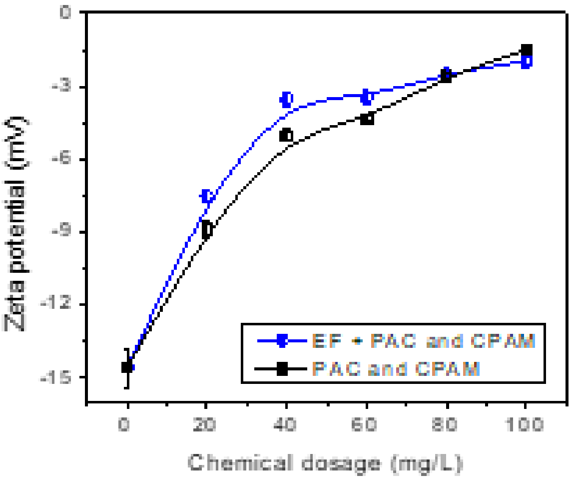

Figure 5.7. Variation of zeta potential with the treatment time at chemical coagulation and combined EF and chemical coagulation. Error bars represent the standard deviation (n = 3).

Both treatments showed an increase in zeta potential when chemical dosage was increased. There was not any significant impact of EF on increasing the zeta potential. At combined chemical and EF treatment improved the zeta potential up to –2.97 ± 0.2 mV, however, it was –12.76 ± 0.7 mV when POME was treated with EF at 1 A.

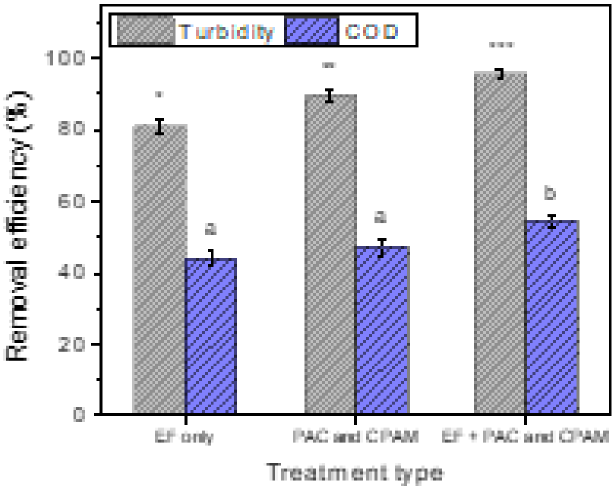

Figure 5.8. Comparison of different treatment types. Error bars represent the standard deviation (n = 3). Different labels of bars for each treatment type indicate the significant difference in turbidity and COD removal efficiency at a significance level of 0.05.

One-way ANOVA results revealed that there was a statistically significant difference in turbidity (F(2,6) = 51.485, p = <0.001) and COD (F(2,6) = 17.007, p = 0.003) removal efficiency among different POME treatments. Tukey's HSD test for multiple comparisons found that the removal efficiency at combined chemical and EF treatment was significantly for turbidity ($p < 0.001$) and COD ($p = 0.003$) higher compared with EF treatments alone. Similarly, treatment efficiency at combined chemical and EF treatment was significantly for turbidity ($p = 0.012$) and COD ($p = 0.018$) higher compared with chemical coagulation treatments alone. Since combined experiments were performed at 1 A for 15 min electrolysis, specific energy consumption reduced to 0.004 kWh for the treatment of one kilogram of COD. These results proved the impact of applying PAC and CPAM on EF treatment to improve the efficiency and reduce the specific energy consumption in POME treatment.

5.4. Conclusion

In this study, we demonstrated that the combined chemical and EF treatment method with a dimensionally stable platinized titanium anode and a stainless-steel cathode can be a viable and efficient option for the post treatment of POME. The production of H2 and O2 at EF promotes the separation of flocs produced by chemical coagulation. This method showed 96 and 54% turbidity and COD reduction of POME within 15 min electrolysis time at 1 A current intensity with 40 mg/L of PAC and 20 mg/L of CPAM dosage. The specific energy consumption was reduced about 10 times when EF combined with chemical coagulation, reducing the current and electrolysis time. However, either treated water turbidity or COD did not meet the discharge water quality standards. Therefore, further studies should be focused on EO for the mineralization of dissolved organic matter to fulfil the discharge water quality standards given by authorities.

CHAPTER 6. CONCLUSIONS and FUTURE STUDY

After applying electrochemical techniques; electrocoagulation, electro-oxidation and electroflotation process, in livestock and palm oil mill effluent wastewater which have high organic pollutants treatment along with chemical coagulants the following conclusions were made;

In chapter 3, the electrolysis apparatus assembled using platinized titanium anode and steel cathode showed a high efficiency in organic pollutant removal by neutralizing the negative charges of cow manure effluent particles owing to an oxidation reaction promoted on a non-consumable anode. When the electrolysis treatment was combined with chemical coagulant AlCl3 and CPAM, EC promoted a high organic removal efficiency with reduced chemical coagulant consumption. The use of EC in this study to treat cow manure with chemical coagulant has been shown to be significant in agriculture as it reduced the dosage of chemical coagulant that was supposed to be applied in separation of solid and liquid waste in cow manure. Because high concentration of Al concentration in solid waste to be use as compose for fertilizer can cause health and environmental problems, EC reducing the chemical coagulant in cow manure effluent will help reduced these health or environmental problems. The design of the reactor used for EC in this treatment can be highly significant especially in Africa because the cost of installation of EC is cheap and EC reactor is easy to control. The electrode use is non consumable therefore the cost of maintaining and stress is reduced. However, EC, also shown some limitation, like high energy consumption for metallic ions or oxygen bubble generation production use in enhancing pollutant removal. From literature review it shows that energy reduction can occur by increasing effluent conductivity, reducing distance between electrode, reducing electrolysis time and current density. Because EC used in this study was an electrolysis process used to treat cow manure, therefore some reduction and oxidation of wastewater might have generated some by production which in some cases might be toxic. Because of fear of generating toxic byproducts after electrolysis of cow manure, the byproducts and their concentration will be analysis for safety use of byproducts from cow manure for compose or discharge of liquid waste into the environment.

In chapter 4, the electrolysis apparatus assembled using platinized titanium cathode and steel anode showed a high efficiency in organic pollutant removal owing to iron 2+ coagulants produced from steel cathode. When EC was used with chemical coagulant CPAM and a highly efficient Al coagulant PAC instead of AlCl3, a much better result was achieved in terms of pollutant removal efficiency, and chemical coagulants reduction. Though the dissolution of steel, which is a consumable anode produces iron 2+ ions which turned the treatment effluent color to green, however this limitation of steel producing iron 2+ ions during dissolution by applying current could be changed to iron 3+ ions which does not produce color by adjusting the pH. Another option to avoid colored effluent is to use platinized titanium anode instead of steel cathode, by doing so, more oxygen bubbles will be produced to increase aggregation of suspended particle by adsorption instead of producing iron 2+ ions to increase aggregation of suspended particles by charge neutralization.

In chapter 5, the combined chemical and EF treatment method using a dimensionally stable platinized titanium anode and a stainless-steel cathode proved to be efficient option for the post treatment of POME, with energy consumption reduced 10 times when EF combined with chemical coagulation, reducing the current and electrolysis time. The production of H_2 and O_2 at EF and chemical coagulants promoted the separation of flocs produced. The treated POME wastewater COD was still high. Because the concentration of the wastewater affects its efficiency, therefore experimenting with different low concentration of effluent could increase the efficiency of the treated effluent. The production of H2 and 02 at EF could increase the efficiency removal of oil and colloidal particle in POME by aggregation and flotation, therefore another way to increase COD removal efficiency in POME is to study factors that will enhance bubble production and size, oil-particle-bubble aggregation, and flotation mechanisms.

From these experimental studies, it can also be said that electro-oxidation, electro-coagulation and electroflotation could be integrates with other chemistry branches such as coagulation and flocculation, for developing new applications which could be useful industrially, and environmentally by providing useful solution for detection of pollution and treatment them, and, other several solutions for energy saving, and water treatment. Electrochemical technologies used in water treatment do not need chemicals but reduce chemical coagulant in a hybrid treatment with it, reducing the environmental effect of the coagulant found in the treated suspended particles to be recycled. Although these electrolysis technologies have advantages, this technology also has limitations like high energy consumption increasing the cost of treatment. In electrocoagulation the need to change anode regularly is needed.

The designed and constructed reactor showed a good efficiency removal performance with high organic matter wastewater; cow manure and POME. This satisfactory performance was facilitated using metallic ions produced from anode and dissolved hydrogen and oxygen gas bubbles produced from cathode and anode. However, in electroflotation process, the dynamic of bubble production and removal mechanism through attachment ("adsorption") of suspended particle to bubble surfaces was not known. Future research will be to carry out theoretical and experimental studies to model this mechanism. Other research will include analyzing the dynamic of bubble production such as factors affecting the design and reactor bubble size and bubble number and the effect of these bubbles size and number on organic pollutant removal mechanism through adsorption.

In electrolysis process, since the electrode anode determines the mechanism, for example steel favours EC, and platinized titanium favours EO and EF removal mechanism which also affects the by product or secondary pollutant of the wastewater produced. In this thesis the type and concentration of by products or waste producted in the wastewater was not analyzed. Future research will also focus on analysis of the factors affecting the waste or by product produced and their concentration after electrolysis or electrochemical process such as EF, EO, EC using this experimental design and reactor.

Since the used energy for the electrochemical process method were high which could affect cost Future research will focus on other factors that can reduced energy such as electrode distance, conductivity of the effluent and coagulant addition to save cost of treatment.

REFERENCES

1. Dadrasnia, Arezoo & Muñoz, Isabella & Hernandez, Eduard & Uald Lamkaddam, Imane & Mora, Mabel & Ponsá, Sergio & Ahmed, Mansour & Argelaguet, Laia & Oatley-Radcliffe, Darren. (2021). Sustainable nutrient recovery from animal manure: A review of current best practice technology and the potential for freeze concentration. Journal of Cleaner Production. 315.
2. Otte J, Pica-Ciamarra U and Morzaria S (2019) A Comparative Overview of the Livestock-Environment Interactions in Asia and Sub-saharan Africa. Front. Vet. Sci. 6:37
3. Oosting, Simon & Udo, H.M.J. & Viets, T.C. (2014). Development of livestock production in the tropics: Farm and farmers' perspectives. Animal: an international journal of animal bioscience. 8. 1-11.
4. Hu, Hao & Li, Xiang & Wu, Shaohua & Yang, Chunping. (2020). Sustainable livestock wastewater treatment via phytoremediation: Current status and future perspectives. Bioresource Technology. 315. 123809
5. Delgado, C.L. 2005. Rising demand for meat and milk in developing countries: implications for grasslands-based livestock production. IN: McGilloway, D.A. (ed.). Grassland: a global resource. Proceedings of the XX International Grassland Congress, Dublin, Ireland, 26-30 June 2005. Wageningen Academic Publishers, The Netherlands. Wageningen (The Netherlands): Wageningen Academic Publishers: 29-39
6. Mulubrhan Balehegn, Ermias Kebreab, Adugna Tolera, Sarah Hunt, Polly Erickson, Todd A Crane, Adegbola T Adesogan, Livestock sustainability research in Africa with a focus on the environment, Animal Frontiers, Volume 11, Issue 4, July 2021, Pages 47–56,
7. Musa MA, Idrus S: Effect of Hydraulic Retention Time on the Treatment of Real Cattle Slaughterhouse Wastewater and Biogas Production from HUASB Reactor. J. Water 12(2), 490, 2020.
8. Parihar SS, KPS Saini, GP Lakhani, A Jain, B Roy, S Ghosh, Bhavna Aharwal. Livestock waste management: A review. J Entomol Zool Stud 2019;7(3):384-393.
9. Shen, Jianguo & Chengxian, Wang & Liu, Yongping & Hu, Chunguang & Xin, Yanjun & Ding, Ning & Su, Shuai. (2017). Effect of ultrasonic pretreatment of dairy manure on the electricity generation of microbial fuel cell. Biochemical Engineering Journal. 129. 44-47
10. Nagarajan D, Kusmayadi A, Yen HW, Dong CD, Lee DJ, Chang JS. 2019.Current advances in biological swine wastewater treatment using microalgae-based processes. Bioresour Technol. 289:121718.
11. Cheng DL, Ngo HH, Guo WS, Liu YW, Zhou JL, Chang SW, Nguyen DD, Bui XT, Zhang XB. Bioprocessing for elimination antibiotics and hormones from swine wastewater. Sci Total Environ. 2018; 621:1664-1682.
12. Cheng DL, Ngo HH, Guo WS, Chang SW, Nguyen DD, Kumar SM. Microalgae biomass from swine wastewater and its conversion to bioenergy. Bioresour Technol. 2019; 275:109-122.
13. Lv J, Liu Y, Feng J, Liu Q, Nan F, Xie S. Nutrients removal from undiluted cattle farm wastewater by the two-stage process of microalgae-based wastewater treatment. Bioresour Technol. 2018; 264:311-318.
14. Ting Xia, Zhenni Liu, Xinxing Pan, Enze Huang, Dan Chen & Zhixing Xiao (2020) Effects of dilution ratio on nutrient removal, sedimentation efficiency, and lipid production by Scenedesmus obliquus in diluted cattle wastewater, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 42:1, 121-130,

15. Zheng, Tianlong & Li, Peng & Ma, Xiaoyu & Sun, Xiaohong & Wu, Chuanfu & Wang, Qunhui & Gao, Ming. (2018). Pilot-scale experiments on multilevel contact oxidation treatment of poultry farm wastewater using saran lock carriers under different operation models. Journal of Environmental Sciences. 77. 10.
16. Zulkifli ZA, Rasit N, Umor NA, Ismail S: The effect of A. Fumigatus SK1 and trichoderma sp. on the biogas production from cow manure. Malaysian J. Fundamental and Applied Sciences., 14(3) 353-359, 2018.
17. Gupta, K.K., Aneja, K.R. & Rana, D. Current status of cow dung as a bioresource for sustainable development. Bioresour. Bioprocess. 3, 28 (2016).
18. Hjorth M, Christensen K V., Christensen M L and Sommer S G 2010 Solid-liquid separation of animal slurry in theory and practice. A review Agron. Sustain. Dev. 30 153–80
19. Zhang X, Liu C, Liao W, Wang S, Zhang W, Xie J and Gao Z 2022 Separation efficiency of different solid-liquid separation technologies for slurry and gas emissions of liquid and solid fractions: A meta-analysis J. Environ. Manage. 310 114777
20. Artanti, D & Saputro, Roy & Budiyono, B. (2012). Biogas Production from Cow Manure. International Journal of Renewable Energy Development (IJRED). 1. 61-64. 10.14710/ijred.1.2.61-64.
21. Murphy, D.J., Goggin, K. Paterson, R.R.M. Oil palm in the 2020s and beyond: challenges and solutions. CABI Agric Biosci 2, 39 (2021).
22. Amugoli, Otuba & Masika, Fred & Asiimwe, Alex & Ddamulira, Gabriel. (2022). Challenges and Opportunities of Oil Palm Production in Uganda. 10.5772/intechopen.108008.
23. Awere, Eric & Bonoli, Alessandra & Obeng, Peter & Pennellini, Sara & Bottausci, Sara & Amanor, William & Akuaku, Emmanuel. (2022). Small-Scale Palm Oil Production in Ghana: Practices, Environmental Problems and Potential Mitigating Measures. 10.5772/intechopen.106174.
24. Lokman, N.A.; Ithnin, A.M.; Yahya, W.J.; Yuzir, M.A. A Brief Review on Biochemical Oxygen Demand (BOD) Treatment Methods for Palm Oil Mill Effluents (POME). Environ. Technol. Innov. 2021, 21, 101258, doi:10.1016/j.eti.2020.101258
25. Dirkes, Rabea & Neubauer, Pia & Rabenhorst, Jürgen. (2021). Pressed sap from oil palm (Elaeis guineensis) trunks: a revolutionary growth medium for the biotechnological industry? Biofuels, Bioproducts and Biorefining. 15.931-944
26. Low, S.S.; Bong, K.X.; Mubashir, M.; Cheng, C.K.; Lam, M.K.; Lim, J.W.; Ho, Y.C.; Lee, K.T.; Munawaroh, H.S.H.; Show, P.L. Microalgae Cultivation in Palm Oil Mill Effluent (POME) Treatment and Biofuel Production. Sustainability 2021, 13, 3247, doi:10.3390/su13063247
27. Ofosu-Budu, K., and D. Sarpong (2013), Oil palm industry growth in Africa: A value chainand smallholders' study for Ghana, In: Rebuilding West Africa’s Food Potential, A. Elbehri (ed.), FAO/IFAD
28. Hassan, Mudathir & Njeshu, Godlove & Raji, Abdulkabir & Zhengwuvi, L.B. & Salisu, Jamilu. (2016). Small-scale Palm oil Processing in West and Central Africa: Development and Challenges. journal of Applied Sciences and Environmental Sustainability. Volume 2.
29. SAHEL Newsletter (2015). Unlocking the Palm Oil Potential in West Africa. Vol 10

30. Ohimain, Elijah & Izah, Sylvester & Dorcas, A. & Cletus, I.. (2014). Small-Scale Palm Oil Processing Business in Nigeria; A Feasibility Study. Greener Journal of Business and Management Studies. 4. 070-082.
31. Ekine, D. I. and Onu, M. E. (2008). Economics of small-scale palm oil processing in Ikwerre and Etche Local Government Areas of Rivers State, Nigeria. Journal of Agriculture and Social Research 8 (2): 1-9
32. Ordway, E.M., Naylor, R.L., Nkongho, R.N., Lambin, E.F. 2017. Oil palm expansion in Cameroon: Insights into sustainability opportunities and challenges in Africa. Global Environmental Change, 47: 190-200
33. Frank, N.E., Albert, M.M., Laverdure, D.E., & Paul, K. Assessment of the quality of crude palm oil from smallholders in Cameroon. Journal of Stored Products and Postharvest Research Vol. 2(3), pp. 52-58, March 2011
34. Awotoye, Olusegun & Dada, Ayokunle & Arawomo, G.A.O. (2011). Impact of Palm Oil Processing Effluent Discharge on the Quality of Receiving Soil and River in South Western Nigeria. Journal of Applied Sciences Research. 7. 111-118.
35. Ahmad AL, Ismail S, Bhatia S. Water recycling from palm oil mill effluent (POME) using membrane technology. Desalination 2003; 157:87–95.
36. Lefcourt AM, Meisinger JJ (2001) Effect of adding alum or zeolite to dairy slurry on ammonia volatilization and chemical composition. J Dairy Sci 84: 1814-1821.
37. Chaudhari PK, Majumdar B, Choudhary R, Yadav DK, Chand S (2010) Treatment of paper and pulp mill effluent by coagulation. Environ Technol 31(4): 357-363.
38. Ngwelum, Chi Chantal, Palm Waste Management and Environmental Sustainability in Sombo Community, Cameroon (July 27, 2021). SSRN: https://ssrn.com/abstract=3894522 or http://dx.doi.org/10.2139/ssrn.3894522.
39. Wu T.Y., A.W. Mohammad, J. Jahim, N. Anuar, 2009. A holistic approach to managing palm oil mill effluent (POME): Biotechnological advances in the sustainable reuse of POME. Biotechnology Advances, 27(1):40-52.
40. Igwe, J.C. and C.C. Onyegbado, 2007. A Review of Palm Oil Mill Effluent (Pome) Water Treatment, Global.Journal of Environmental Research., 1(2): 54-62.
41. Okwute, O.L, N.R Isu, 2007. Impact analysis of palm oil mill effluent on the aerobic bacterial density and ammonium oxidizers in a dumpsite in Anyigba, Kogi State. African Journal of Biotechnology, 6(2): 116 – 119.
42. Madaki, Y.S. & Seng, Lau. (2013). Palm oil mill effluent (POME) from Malaysia palm oil mills: Waste or resource. International Journal of Science, Environment and Technology. 2. 1138-1155.
43. Mohammad, Sharifah & Baidurah, Siti & Kobayashi, Takaomi & Ismail, Norli & Peng, Leh Cheu. (2021). Palm Oil Mill Effluent Treatment Processes-A Review. Processes. 9. 10.3390/pr9050739
44. Famurewa, John Alaba Victor and Akinola Johnson Olarewaju. "INVESTIGATING THE POTENTIAL OF DRIED PALM OIL MILL EFFLUENTS FROM PRESSING AND WATER DISPLACEMENT METHODS FOR ANIMAL FEED." Asian journal of natural and applied sciences 2 (2013): 58-68.
45. Onyla, C.O.; Uyub, A.M.; Akunna, J.C.; Norulaini, N.A.; Omar, A.K.M. Increasing the Fertilizer Value of Palm Oil Mill Sludge: Bioaugmentation in Nitrification. Water Sci. Technol. 2001, 44, 157–162, doi:10.2166/wst.2001.0608.

46. Shavandi, M.A.; Haddadian, Z.; Ismail, M.H.S.; Abdullah, N. Continuous Metal and Residual Oil Removal from Palm Oil Mill Effluent Using Natural Zeolite-Packed Column. J. Taiwan Inst. Chem. Eng. 2012, 43, 934–941, doi:10.1016/J.JTICE.2012.07.001.
47. Adam Palm, Mill, 1992. Palm oil mill Effluent and pollution. Mill paper, pp: 5-11.
48. Wu, Ta & Mohammad, Abdul & Jahim, Jamaliah & Anuar, Nurina. (2008). A holistic approach to managing palm oil mill effluent (POME): Biotechnological advances in the sustainable reuse of POME. Biotechnology advances. 27. 40-52.
49. Sutanto, J., 1981. Solvent Extraction Process to achieve zero-effluent from mill sludge". Paper presented at PORIM workshop on palm oil by product utilization, Khuala Lumpur, Malaysia
50. SYAHIN, M S; W A WAN AB KARIM GHANI and LOH, S K. Decolourisation of Palm Oil Mill Effluent (Pome) Treatment Technologies: A Review. J. Oil Palm Res. 2020, doi:10.21894/jopr.2020.0008.
51. Ma AN. A novel treatment for palm oil mill effluent. Palm Oil Res Instit Malaysia (PORIM) 1995; 29:201–12
52. Akhbari, Azam & Kutty, Prashad & Onn, Chiu & Ibrahim, Shaliza. (2019). A study of palm oil mill processing and environmental assessment of palm oil mill effluent treatment. Environmental Engineering Research. 25(2): 212-221.
53. Nahrul H Z, Nor F J, Ropandi M, Astimar A A (2017). A Review on the Development of Palm Oil Mill Effluent (POME) Final Discharge Polishing Treatments. Journal of Oil Palm Research Vol. 29 (4)
54. Izah, Sylvester & Angaye, Tariwari & Ohimain, Elijah. (2016). Environmental Impacts of Oil Palm Processing in Nigeria. Biotechnological Research. 2. 132-141.
55. Izah, Sylvester & Angaye, Tariwari & Ohimain, Elijah. (2016). Environmental Impacts of Oil Palm Processing in Nigeria. Biotechnological Research. 2. 132-141.
56. Temu, Stella & Mshandete, Anthony & Kivaisi, Amelia. (2013). Tanzania Palm Oil Industry: Auditing and Characterization of Oil Palm Wastes Potential Bio- resource for Valorization. 44. 2249-1929.
57. Osei-Amponsah, Charity & Visser, L.E. & Adjei-Nsiah, Samuel & Struik, Paul & Stomph, Tjeerd Jan. (2012). Processing Practices of small-scale palm oil producers in the Kwaebibirem District, Ghana: A Diagnostic study. NJAS - Wageningen Journal of Life Sciences. 60-63. 49-56.
58. Tchindjang, Mesmin & Iii, Miaro & Mboringong, Fideline & Etoga, Gilles & Eric, Voundi & Ngom, Emmanuel. (2021). Environmental Impacts of the Oil Palm Cultivation in Cameroon. 10.5772/intechopen.97862.
59. FormeluhAbraham Toh et al. Integrated waste management in palm oil mills in south-western Cameroon. International Journal of Current Research Vol. 6, Issue, 12, pp.10927-10932, 2014
60. Edward, J.B., Idowu, E.O. and Oyebola, O.E. (2015). Impact of pam oil mill effluent on physic-chemical parameters of a southwestern River, Ekiti state, Nigeria. Journal of Natural Sciences Research, 4(14): 26 –30
61. Oviasogie, P.O. and A.E. Aghimien, 2003. Macronutrient status and speciation of Cu, Fe, Zn and Pb in soil containing palm oil mill effluent. Global J. Pure Applied Sci., 9: 71-80
62. Chan, K.W., Watson, I. and Lim, K.C. (1980). Use of oil palm waste material for increased production. Paper presented at the Conference on Soil Science and Agricultural development in Malaysia, Kuala Lumpur, Malaysia

63. Sridhar, M.K.C.and AdeOluwa, O.O. (2009). Palm Oil Industry Residue. In: Nigam PS, Pandey A (eds.). Biotechnology for Agroindustrial Residues Utilisation. Springer Science. Pp 341 – 355
64. Rajani, Ahmad & Kusnadi, & Santosa, Alam & Saepudin, A & Gobikrishnan, S & Andriani, D. (2019). Review on biogas from palm oil mill effluent (POME): Challenges and opportunities in Indonesia. IOP Conference Series: Earth and Environmental Science. 293
65. Salihu, Aliyu & Alam, Md. (2012). Palm oil mill effluent: A waste or a raw material?. Journal of Applied Science Research. 8. 466-473.
66. Truckell, I., Shah, S.H., Baillie, I..., Hallett, S.H., & Sakrabani, R. (2019). Soil and transport factors in potential distribution systems for biofertilisers derived from palm oil mill residues in Malaysia. Comput. Electron. Agric., 166.
67. Ferreira WdeA, Araujo SMB. Effect of application of agroindustrial oil palm effluent on chemical characteristics of a yellow alic latosol with medium texture. Bol Pesqui Desenvolv - Embrapa Amazon Orient 2002; 11:26.
68. Matsumoto H. Cell biology of aluminum toxicity and tolerance in higher plants. Int Rev Cytol 2000; 200:1-46
69. Guo TR, Zhang GP, Zhang YH. Physiological changes in barley plants under combined toxicity of aluminum, copper and cadmium. Colloids Surf B 2007; 57:182–8.
70. Eze, V. C., Owunna, N. D. and Avoaja, D. A (2013). Microbiological and physicochemical characteristics of soil receiving palm oil mill effluent in Umuahia, Abia State, Nigeria. Journal of Natural Sciences Research3: 163-169.
71. Udoetok, Inimfon. (2012). Characterization of Ash made from Oil Palm Empty Fruit Bunches (OEFB). International Journal of Environmental Sciences. 3. 518 - 524.
72. Ogunbiyi, Adebola, and Nkechi A Enechukwu. “African black soap: Physiochemical, phytochemical properties, and uses.” Dermatologic therapy vol. 34,3 (2021): e14870. doi:10.1111/dth.14870
73. Miller, Rhonda Ph.D.; Major, Jennifer; and Trinca, Penny, "How a Lagoon Works For Livestock Wastewater Treatment" (2011). Agriculture. Paper 4
74. Tham, M.H. Electro Oxidation of Palm Oil Mill Effluent (Pome): Post Treatment. Univ. Tunku Abdul Rahman 2015, 79.
75. Harsono, S.S.; Grundmann, P.; Soebronto, S. Anaerobic Treatment of Palm Oil Mill Effluents: Potential Contribution to Net Energy Yield and Reduction of Greenhouse Gas Emissions from Biodiesel Production. J. Clean. Prod. 2014, 64, 619–627, doi:10.1016/J.JCLEPRO.2013.07.056.
76. Chou, Kian Weng & Tan, Siew & Morad, Norhashimah & Teng, T.T & Kadir, Mohd & Ismail, Norli. (2016). Aerobic Post-treatment of Different Anaerobically Digested Palm Oil Mill Effluent (POME). International Journal of Environmental Science and Development. 7. 511-515.
77. Yaser, A.; Mansa, R.; Menaka, S.; Su, S.Y.; Melvin, F.; Chan, E.S. Decolorisation of anaerobic palm oil mill effluent via activated sludge-granular activated carbon. World Appl. Sci. J. 2009, 5, 126–129.
78. Tamrin, K.; Yaser, A. Determination of optimum polymeric coagulant in palm oil mill effluent coagulation using multiple-objective optimisation on the basis of ratio analysis (MOORA). Environ. Sci. Pollut. Res. 2017, 24.

79. Cheng, Yoke & Chong, Chi Cheng & Lam, Man & Ayoub, Muhammad & Cheng, Chin & Lim, Jun-Wei & Suzana, Yusup & Tang, Yuanyuan & Bai, Jiaming. (2020). Holistic process evaluation of non-conventional palm oil mill effluent (POME) treatment technologies: A conceptual and comparative review. Journal of Hazardous Materials. 409. 124964.
80. Bernet N, Béline F. Challenges and innovations on biological treatment of livestock effluents. Bioresour Technol. 2009 Nov;100(22):5431-6.
81. Adlil R N, Norhashimah M, Norli I, Wan M, Roziawati M (2014). Reuse of treated palm oil mill effluents (POME) and carbon dioxide emissions for microalgae cultivation: A review. J. Ind. Res. & Technology 4(1), 01-12, 2014
82. Aziz, Hamidi A, Abu A, Salem S.(2018). Advanced Oxidation Processes (AOPs) in Water and Wastewater Treatment
83. Othman, M.R.; Hassan, M.A.; Shirai, Y.; Baharuddin, A.S.; Ali, A.A.M.; Idris, J. Treatment of Effluents from Palm Oil Mill Process to Achieve River Water Quality for Reuse as Recycled Water in a Zero Emission System. J. Clean. Prod. 2014, 67, 58–61, doi:10.1016/J.JCLEPRO.2013.12.004.
84. Iskandar, Muhammad Johan et al. "Palm oil industry in South East Asia and the effluent treatment technology—A review." Environmental Technology and Innovation 9 (2018): 169-185.
85. Choi, W.H.; Shin, C.H.; Son, S.M.; Ghorpade, P.A.; Kim, J.J.; Park, J.Y. Anaerobic Treatment of Palm Oil Mill Effluent Using Combined High-Rate Anaerobic Reactors. Bioresour. Technol. 2013, 141, 138–144, doi:10.1016/J.BIORTECH.2013.02.055.
86. Hosseini, S.E.; Wahid, M.A. Pollutant in Palm Oil Production Process. J. Air Waste Manag. Assoc. 2015, 65, 773–781, doi:10.1080/10962247.2013.873092.
87. Pearse, M.J. (2003). Historical use and future development of chemicals for solid–liquid separation in the mineral processing industry. Minerals Engineering. 16. 103-108.
88. Sahu O. P, Chaudhari P. K. Review on Chem charged ical treatment of Industrial Wastewater J. Appl. Sci. Environ. Manage. June 2013 Vol. 17 (2) 241-257
89. Ghernaout, Djamel. (2014). The Best Available Technology of Water/Wastewater Treatment and Seawater Desalination: Simulation of the Open Sky Seawater Distillation. Green and Sustainable Chemistry. 3. 68-88.
90. Bhattacharjee S. DLS and zeta potential - What they are and what they are not? J Control Release. 2016 Aug 10;235:337-351.
91. Malik, Q.H. Performance of Alum and Assorted Coagulants in Turbidity Removal of Muddy Water. Appl. Water Sci. 2018, 8, 1–4, doi:10.1007/s13201-018-0662-5
92. Schalkwyk, Megan & Rajagopaul, Rachi & Mokonyama, Simon & Thompson, Peter & Water, Umgeni. (2016). EVALUATION AND SELECTION OF AN APPROPRIATE AUTOMATIC COAGULANT DOSE CONTROL SYSTEM FOR WATER TREATMENT PLANTS Water Research Commission.
93. Tetteh E, Rathilal S, Robinson K (2017).Treatment of industrial mineral oil wastewater – effects of coagulant type and dosage. Water Practice and Technology. 12. 139-145. 10.2166/wpt.2017.021

94. Kumar P, Teng TT, Chand S, Kailas L (2011) Wastewater, Treatment of Paper and Pulp Mill Effluent by Coagulation, International Journal of Civil and Environmental Engineering 3, 3
95. Farajnezhad H, Gharbani P (2012). Coagulation treatment of wastewater in the petroleum industry using poly aluminum chloride and ferric chloride. IJRRAS. 13. 306-310.
96. Chaudhari P,Mishra I, Chand S (2007). Decolourization and removal of chemical oxygen demand (COD) with energy recovery: Treatment of biodigester effluent of a molasses-based alcohol distillery using inorganic coagulants. Colloids and Surfaces A-physicochemical and Engineering Aspects - COLLOID SURFACE A. 296. 238-247. 10.1016/j.colsurfa.2006.10.005.
97. Shammas, N.K. (2005). Coagulation and Flocculation. In: Wang, L.K., Hung, YT., Shammas, N.K. (eds) Physicochemical Treatment Processes. Handbook of Environmental Engineering, vol 3. Humana Press. https://doi.org/10.1385/1-59259-820-x:103
98. Kurniawan, Setyo Budi & Abdullah, Siti & Imron, Muhammad & Mohd Said, Nor & Ismail, Nur 'Izzati & Abu Hasan, Hassimi & Othman, Ahmad & Purwanti, Ipung. (2020). Challenges and Opportunities of Biocoagulant/Bioflocculant Application for Drinking Water and Wastewater Treatment and Its Potential for Sludge Recovery. International Journal of Environmental Research and Public Health. 17. 10.3390/ijerph17249312.
99. Ma, B.; Xue, W.; Ding, Y.; Hu, C.; Liu, H.; Qu, J. Removal Characteristics of Microplastics by Fe-Based Coagulants during Drinking Water Treatment. J. Environ. Sci. 2019, 78, 267–275, doi:10.1016/J.JES.2018.10.006.
100. Ahmad, A.L.; Wong, S.S.; Teng, T.T.; Zuhairi, A. Improvement of Alum and PACl Coagulation by Polyacrylamides (PAMs) for the Treatment of Pulp and Paper Mill Wastewater. Chem. Eng. J. 2008, 137, 510–517, doi:10.1016/j.cej.2007.03.088.
101. Wu, Y.; Wang, D.; Liu, X.; Xu, Q.; Chen, Y.; Yang, Q.; Li, H.; Ni, B. Effect of Poly Aluminum Chloride on Dark Fermentative Hydrogen Accumulation from Waste Activated Sludge. Water Res. 2019, 153, 217–228, doi:10.1016/J.WATRES.2019.01.016.
102. Krupińska, I. Aluminium Drinking Water Treatment Residuals and Their Toxic Impact on Human Health. Molecules 2020, 25, doi:10.3390/molecules25030641.
103. Meetiyagoda, T.A.O.K.; Fujino, T. Optimization of Electrocoagulation–Flotation Treatment with an Aluminum Anode to Enhance Microcystis Aeruginosa Cell Removal Efficiency. J. Water Process Eng. 2022, 48, 102871, doi:10.1016/J.JWPE.2022.102871.
104. Tripathy T, De BR (2006) Flocculation: a new way to treat the waste water. J Phys Sci 10:93–127
105. Sukmana H , Naoufal. B, Fernanda. P, Enanda . P, Cecilia. H. Adsorption and coagulation in wastewater treatment – Review Progress in Agricultural Engineering Sciences 17 (2021) 1, 49–68
106. Khazaie, A.; Mazarji, M.; Samali, B.; Osborne, D.; Minkina, T.; Sushkova, S.; Mandzhieva, S.; Soldatov, A. A Review on Coagulation/Flocculation in Dewatering of Coal Slurry. Water 2022, 14, 918.

107. Sun J, Ma X, Li X , Fan J, Chen Q, Liu X, Pan J (2018) Synthesis of a Cationic Polyacrylamide under UV Initiation and Its Flocculation in Estrone Removal. International Journal of Polymer Science. 2018. 1-11. 10.1155/2018/8230965
108. Li X, Zheng H, Zhou W, Sun Y, Tang X, Xu B (2017). Optimized preparation of micro-block CPAM by response surface methodology and evaluation of dewatering performance. RSC Adv.. 7. 208-217. 10.1039/C6RA25245A.
109. Liu Z, Carroll Z, Long S, Gunasekaran S, Runge T (2015) Use of cationic polymers to reduce pathogen levels during dairy manure separation. Journal of environmental management. 166. 260-266. 10.1016/j.jenvman.2015.10.033
110. Vanotti M, Rashash D, Hunt PG (2002). Solid-Liquid Separation of Flushed Swine Manure With PAM: Effect of Wastewater Strength. Transactions of the American Society of Agricultural Engineers. 45. 10.13031/2013.11422. .
111. Wong SS, Teng TT, Ahmad A, Abdullah AZ , Najafpour G (2016) Treatment of pulp and paper mill wastewater by polyacrylamide (PAM) in polymer induced flocculation.Journal of hazardous materials. 135. 378-88. 10.1016/j.jhazmat.2005.11.076.
112. Loloei M, Nekonam G, Alidadi H, Kor Y (2014) Study of the coagulation process in wastewater treatment of dairy industries.International Journal of Environmental Health Engineering. 3. 12. 10.4103/2277-9183.132684.
113. Kaur B, Garg RK, Singh A (2020). Treatment of Wastewater from Pulp and Paper Mill using Coagulation and Flocculation.Journal of Environmental Treatment Techniques , Volume 9, Issue 1, Pages: 158-163
114. Amuda O, Amoo IA (2007). Coagulation/flocculation process and sludge conditioning in beverage industrial wastewater treatment. Journal of hazardous materials. 141. 778-83. 10.1016/j.jhazmat.2006.07.044
115. Nasser, M.; James, A. Effect of polyacrylamide polymers on floc size and rheological behaviour of kaolinite suspensions. Colloids Surf. A: Physicochem. Eng. Asp. 2007, 301, 311–322
116. Zhao, C.; Zheng, H.; Gao, B.; Liu, Y.; Zhai, J.; Zhang, S.; Xu, B. Ultrasound-Initiated Synthesis of Cationic Polyacrylamide for Oily Wastewater Treatment: Enhanced Interaction between the Flocculant and Contaminants. Ultrason. Sonochem. 2018, 42, 31–41, doi:10.1016/J.ULTSONCH.2017.11.006.
117. Zhou, S.; Bu, X.; Alheshibri, M.; Zhan, H.; Xie, G. Floc structure and dewatering performance of kaolin treated with cationic polyacrylamide degraded by hydrodynamic cavitation. Chem. Eng. Commun. 2021, 1–11.
118. Ahmad, A.L., Chong, M.F., Bhatia, S., 2008. Population Balance Model (PBM) for flocculation process: simulation and experimental studies of palm oil mill effluent (POME) pretreatment. Chem. Eng. J. 140 (1), 86–100.
119. Abidin, Z.Z., Madehi, N., Yunus, R., 2017. Coagulative behaviour of Jatropha curcas and its performance in wastewater treatment. Environ. Prog. Sustain. Energy 36 (6), 1709–1718.
120. Adnan, O., Abidin, Z.Z., Idris, A., Kamarudin, S., Al-Qubaisi, M.S., 2017. A novel biocoagulant agent from mushroom chitosan as water and wastewater therapy. Environ. Sci. Pollut. Res. 24 (24), 20104–20112.
121. Ariffin, A., Shatat, R.S.A., Norulaini, A.R.N., Omar, A.K.M., 2005. Synthetic polyelectrolytes of varying charge densities but similar molar mass based on acrylamide and their applications on palm oil mill effluent treatment. Desalination 173 (3), 201–208.

122. Huzir, N.M., Aziz, M.M.A., Ismail, S.B., Mahmood, N.A.N., Umor, N.A., Muhammad, S.A. Fa.S., 2019. Optimization of coagulation-flocculation process for the palm oil mill effluent treatment by using rice husk ash. Ind. Crops Prod. 139, 111482.
123. Ahmad, A.L., Sumathi, S., Hameed, B.H., 2006b. Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. Chem. Eng. J. 118 (1), 99–105.
124. Jagaba, A.H., Kutty, S.R.M., Hayder, G., Latiff, A.A.A., Aziz, N.A.A., Umaru, I., Ghaleb, A. A.S., Abubakar, S., Lawal, I.M., Nasara, M.A., 2020. Sustainable use of natural and chemical coagulants for contaminants removal from palm oil mill effluent: a comparative analysis. Ain Shams Eng. J. 11, 951–960.
125. Zahrim, A.Y., Dexter, Z.D., 2016. Decolourisation of palm oil mill biogas plant wastewater using poly-diallyldimethyl ammonium chloride (polyDADMAC) and other chemical coagulants. IOP Conf. Ser. Earth Environ. Sci. 36, 012025.
126. King, W.G., Lee, M.D., Affam, A.C., Chung, W.C., Swee, W.C., Adebayo, J.O., 2019. Application of hybrid ultrasonic cavitation/adsorption and coagulation for treatment of palm oil mill effluent.
127. Som, A.M., Wahab, A., 2018. Performance study of dragon fruit foliage as a plant-based coagulant for treatment of palm oil mill effluent from three-phase decanters. Bioresources 13.
128. Zinatizadeh, A.A., Ibrahim, S., Aghamohammadi, N., Mohamed, A.R., Zangeneh, H., Mohammadi, P., 2017. Polyacrylamide-induced coagulation process removing suspended solids from palm oil mill effluent. Sep. Sci. Technol. 52 (3), 520–527.
129. Dotto, Juliana & Fagundes-Klen, Márcia & Veit, Márcia & Palácio, Soraya & Bergamasco, Rosângela. (2018). Performance of different coagulants in the coagulation/flocculation process of textile wastewater. Journal of Cleaner Production. 208.
130. Zhang, Z.; Jing, R.; He, S.; Qian, J.; Zhang, K.; Ma, G.; Chang, X.; Zhang, M.; Li, Y. Coagulation of Low Temperature and Low Turbidity Water: Adjusting Basicity of Polyaluminum Chloride (PAC) and Using Chitosan as Coagulant Aid. Sep. Purif. Technol. 2018, 206, 131–139, doi:10.1016/J.SEPPUR.2018.05.051
131. Teh, Chee & Budiman, Pretty & Shak, Katrina & Wu, Ta. (2016). Recent Advancement of Coagulation-Flocculation and Its Application in Wastewater Treatment. Industrial & Engineering Chemistry Research. 55., 4363−4389
132. Chastain J, Vanotti M, Wingfield MM (2001). Effectiveness of liquid-solid separation for treatment of flushed dairy manure: A case study. Applied Engineering in Agriculture. 17. 10.13031/2013.6210
133. Kinyua EM, Mwangi IW, Wanjau RN, Ngila JC (2016) Clarification of colloidal and suspended material in water using triethanolamine modified maize tassels. Environ Sci Pollut Res 23(6): 5214-5221.
134. Pelendridou K, Michailides M, Zagklis D, Tekerlekopoulou A, Paraskeva C, Vayenas D: Treatment of olive mill wastewater using a coagulation–flocculation process either as a single step or as post-treatment after aerobic biological treatment. J.Chemical Technology and Biotechnology., 89(12), 1866-1874, 2014
135. Bharath M, Krishna B M and Manoj Kumar B (2018). A Review of Electrocoagulation Process for Wastewater Treatment. International Journal of ChemTech Research. 11(03): 289-30.

136. Kim, G. & Kim, WooYeol & Yun, ChanYoung & Son, DongJin & Chang, Duk & Bae, HyungSuk & Lee, YongHyun & Sunwoo, Young & Hong, Kiho. (2013). Agro-industrial Wastewater Treatment by Electrolysis Technology. International Journal of Electrochemical Science. 8. 9835-9850.
137. Liu H, Ramnarayanan R, Logan BE. Production of electricity during wastewater treatment using a single chamber microbial fuel cell. Environ Sci Technol. 2004 Apr 1;38(7):2281-5.
138. Yamane, Taiki & Yoshida, Naoko & Sugioka, Mari. (2021). Estimation of total energy requirement for sewage treatment by a microbial fuel cell with a one-meter air-cathode assuming Michaelis–Menten COD degradation. RSC Advances. 11. 20036-20045.
139. Qiao J, Y. Xiong.Electrochemical oxidation technology: A review of its application in high-efficiency treatment of wastewater containing persistent organic pollutants J. Water Process Eng., 44 (2021)
140. Nurhayati, Ervin. (2012). A Brief Review on Electro-generated Hydroxyl Radical for Organic Wastewater Mineralization. Jurnal Sains &Teknologi Lingkungan. 4. 24-31. 10.20885/jstl.vol4.iss1.art3.
141. Varanasi, Jhansi & Veerubhotla, Ramya & Pandit, Soumya & Das, Debabrata. (2019). Biohydrogen Production Using Microbial Electrolysis Cell. 10.1016/B978-0-444-64052-9.00035-2.
142. Wang. C , Lü.Y, Song.C, Zhang. D, Rong. Separation of emulsified crude oil from produced water by gas flotation: A review Science of the Total Environment 845 (2022) 157304
143. Wahi, R.; Chuah Abdullah, L.; Nourouzi Mobarekeh, M.; Ngaini, Z.; Choong Shean Yaw, T. Utilization of Esterified Sago Bark Fibre Waste for Removal of Oil from Palm Oil Mill Effluent. J. Environ. Chem. Eng. 2017, 5, 170–177, doi:10.1016/J.JECE.2016.11.038.
144. Khulbe, K.C.; Matsuura, T. Removal of Heavy Metals and Pollutants by Membrane Adsorption Techniques. Appl. Water Sci. 2018, 8, 1–30, doi:10.1007/s13201-018-0661-6.
145. Mahendran, R.; Malaisamy, R.; Arthanareeswaran, G.; Mohan, D. Cellulose Acetate-Poly(Ether Sulfone) Blend Ultrafiltration Membranes. II. Application Studies. J. Appl. Polym. Sci. 2004, 92, 3659–3665, doi:10.1002/app.20302.
146. Haji Alhaji, M.; Sanaullah, K.; Fong Lim, S.; Ragai Henry Rigit, A.; Hamza, A.; Khan, A. Modeling and Optimization of Photocatalytic Treatment of Pre-Treated Palm Oil Mill Effluent (POME) in a UV/TiO2 System Using Response Surface Methodology (RSM). Cogent Eng. 2017, 4, doi:10.1080/23311916.2017.1382980.
147. Ng, K.H.; Cheng, C.K. A Novel Photomineralization of POME over UV-Responsive TiO2 Photocatalyst: Kinetics of POME Degradation and Gaseous Product Formations. RSC Adv. 2015, 5, 53100–53110, doi:10.1039/c5ra06922j.
148. Ganiyu, S.O.; Zhou, M.; Martínez-Huitle, C.A. Heterogeneous Electro-Fenton and Photoelectro-Fenton Processes: A Critical Review of Fundamental Principles and Application for Water/Wastewater Treatment. Appl. Catal. B Environ. 2018, 235, 103–129, doi:10.1016/J.APCATB.2018.04.044.
149. Rakhmania; Kamyab, H.; Yuzir, M.A.; Riyadi, F.A.; Ostadrahimi, A.; Khademi, T.; Ghfar, A.A.; Kirpichnikova, I. Electrochemical Oxidation of Palm Oil Mill Effluent Using Platinum as Anode: Optimization Using Response Surface Methodology. Environ. Res. 2022, 214, 113993, doi:10.1016/J.ENVRES.2022.113993.

150. Baran Özyurt, Ş.C. Applications of Combined Electrocoagulation and Electrooxidation Treatment to Industrial Wastewaters; 2017;
151. SITI NOR, M.-S.; NUR, M.-Z.; NORZILA, O. A Review of Wastewater Treatment Using Natural Material and Its Potential as Aid and Composite Coagulant. Sains Malaysiana 2019, 48, 155–164.
152. Nasrullah, M.; Singh, L.; Krishnan, S.; Sakinah, M.; Zularisam, A.W. Electrode Design for Electrochemical Cell to Treat Palm Oil Mill Effluent by Electrocoagulation Process. Environ. Technol. Innov. 2018, 9, 323–341, doi:10.1016/J.ETI.2017.10.001.
153. Nasrullah, M.; Zularisam, A.W.; Krishnan, S.; Sakinah, M.; Singh, L.; Fen, Y.W. High Performance Electrocoagulation Process in Treating Palm Oil Mill Effluent Using High Current Intensity Application. Chinese J. Chem. Eng. 2019, 27, 208–217, doi:10.1016/J.CJCHE.2018.07.021.
154. Moussa, D.T.; El-Naas, M.H.; Nasser, M.; Al-Marri, M.J. A Comprehensive Review of Electrocoagulation for Water Treatment: Potentials and Challenges. J. Environ. Manage. 2017, 186, 24–41, doi:10.1016/j.jenvman.2016.10.032.
155. Wang. C , Lü.Y, Song.C, Zhang. D, Rong. Separation of emulsified crude oil from produced water by gas flotation: A review Science of the Total Environment 845 (2022) 157304
156. Piccioli, Martina & Aanesen, Svein & Zhao, He & Dudek, Marcin & Øye, Gisle. (2020). Gas Flotation of Petroleum Produced Water: A Review on Status, Fundamental Aspects, and Perspectives. Energy & Fuels. 34. 15579−15592
157. Mohtashami, R., Shang, J.Q. Electroflotation for Treatment of Industrial Wastewaters: A Focused Review. Environ. Process. 6, 325–353 (2019).
158. Robinson, V., 2014. Wastewater treatment by electroflocculation. In: Kreysa, G., Ota, K., Savinell, R.F. (Eds.), Encyclopedia of Applied Electrochemistry. Springer, New York, NY, pp. 2122–2126
159. ProSep, 2014. CTour process. https://www.prosep.com/products-services/water/ctourprocess/. (Accessed 14 June 2022)
160. Gmsthailand, 2016. EPCON dual CFU. https://www.gmsthailand.com/product/epcon-dualcompact-flotation-unit-cfu/. (Accessed 13 June 2022).
161. Schlumberger, 2016. WEMCO® ISF hydraulically induced gas flotation system. https:// www.slb.com/well-production/processing-and-separation/water-treatment/wemco-isfhydraulically-induced-gas-flotation-system(. (Accessed 13 June 2022).
162. Evoqua, 2017. Dissolved Air Flotation (DAF) systems. https://www.evoqua.com/en/evoqua/ products–services/clarifiers–separators/dissolved-air-flotation-daf-systems/. (Accessed 6 October 2022)
163. Ghanbari, F.; Moradi, M.; Eslami, A.; Emamjomeh, M.M. Electrocoagulation/Flotation of Textile Wastewater with Simultaneous Application of Aluminum and Iron as Anode. Environ. Process. 2014, 1, 447–457, doi:10.1007/s40710-014-0029-3.
164. Kumar, V.; Kangri Vishwavidyalaya, G. A Review on the Feasibility of Electrolytic Treatment of Wastewater: Prospective and Constraints Phytoremediation of Industrial Effluents Using Aquatic Macrophytes View Project Bio-Remediation of Contaminants along with Bio-Energy Production View Project. 2017.

165. Jeevanandam, J.; Harun, M.R.; Lau, S.Y.; Sewu, D.D.; Danquah, M.K. Microalgal Biomass Generation via Electroflotation: A Cost-Effective Dewatering Technology. Appl. Sci. 2020, 10, 9053.
166. Angulo, A., van der Linde, P., Gardeniers, H., Modestino, M., & Fernández Rivas, D. (2020). Influence of Bubbles on the Energy Conversion Efficiency of Electrochemical Reactors. Joule, 4(3), 555-579
167. Taqieddin A, Nazari R, Rajic L, Alshawabkeh A. Review-Physicochemical hydrodynamics of gas bubbles in two phase electrochemical systems. J Electrochem Soc. 2017;164(13):E448-E459.
168. D. Tao (2005). Role of Bubble Size in Flotation of Coarse and Fine Particles—A Review, Separation Science and Technology, 39:4, 741-760,
169. Miettinen, Tatu & Ralston, John & Fornasiero, Daniel. (2010). The Limits of Fine Particle Flotation. Minerals Engineering - MINER ENG. 23. 420-437
170. Huang, Q.; Long, X. Analysis of the Influencing Factors on Oil Removal Efficiency in Large-Scale Flotation Tanks: Experimental Observation and Numerical Simulation. Energies 2020, 13, 927.
171. Sarkar, Md & Evans, Geoffrey & Donne, Scott. (2010). Bubble size measurement in electroflotation. Minerals Engineering. 23. 1058–1065
172. Alam R, Shang JQ, Khan AH. Bubble size distribution in a laboratory-scale electroflotation study. Environ Monit Assess. 2017 Apr;189(4):193. doi: 10.1007/s10661-017-5888-4. Epub 2017 Mar 29. PMID: 28357719.
173. Mickova, I. L. (2015). Advanced Electrochemical Technologies in Wastewater Treatment. Part II: Electro-Flocculation and Electro-Flotation. American Academic Scientific Research Journal for Engineering, Technology, and Sciences, 14(2), 273–294.
174. Kolesnikov, V.A., Il'in, V.I., Brodskiy, V.A. et al. Electroflotation during wastewater treatment and extraction of valuable compounds from liquid technogenic waste: A review. Theor Found Chem Eng 51, 369–383 (2017)
175. Han MY, Kim MK, Ahn HJ. Effects of surface charge, micro-bubble size and particle size on removal efficiency of electro-flotation. Water Sci Technol. 2006;53(7):127-32.
176. Uchibori, T; Fujino, T; Asaeda, T.2010. Turbidity removal effect and surface charge shift for electrochemically treated retentate without coagulant addition. Water Science & Technology—WST | 61.1
177. Sharma, L; Prabhakar, S; Tiwari, V; Dhar, A; Halder, A.2021.Optimization of EC parameters using Fe and Al electrodes for hydrogen production and wastewater treatment. Environmental Advances, Volume 3,100029, ISSN 2666-7657,
178. Ardhianto, Rachmad & Bagastyo, Arseto. (2019). Personal Care Wastewater Treatment with Electro-coagulation and Electro-oxidation. E3S Web of Conferences. 125. 03008. 10.1051/e3sconf/201912503008.
179. Rumky, J., Tang, W.Z. & Sillanpää, M. Statistical Analysis of Anode Efficiency in Electrochemical Treatment of Wastewater and Sludge. Environ. Process. 7, 1041–1064 (2020).
180. M. Panizza.M, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev. 109 (2009) 6541–6569,
181. Kapałka .A, G. Foti, ′ C. Comninellis, Kinetic modelling of the electrochemical mineralization of organic pollutants for wastewater treatment, J. Appl. Electrochem. 38 (2008) 7–16,

182. Jimenez Izquierdo C, Canizares P, Rodrigo MA, Leclerc JP, Valentin G, Lapicque F.2010.Effect of the nature of the supporting electrolyte on the treatment of soluble oils by electrocoagulation,Desalination,Volume 255, Issues 1–3, Pages 15-20, ISSN 0011-9164,
183. Huang, Chien-Hung; Shen, Shan-Yi; Chen, Chiu-Wen; Dong, Cheng-Di; Kumar, Mohanraj; Dakshinamoorthy, Balasubramanian; Chang, Jih-Hsing. 2020. "Effect of Chloride Ions on Electro-Coagulation to Treat Industrial Wastewater Containing Cu and Ni" Sustainability 12, no. 18: 7693.
184. Ndjomgoue-Yossa, A.C., Nanseu-Njiki, C.P., Kengne, I.M. et al. Effect of electrode material and supporting electrolyte on the treatment of water containing Escherichia coli by electrocoagulation. Int. J. Environ. Sci. Technol. 12, 2103–2110 (2015).
185. Amir Mirshafiee, Abbas Rezaee, Rasol Sarraf Mamoory. 2018.A clean production process for edible oil removal from wastewater using an electroflotation with horizontal arrangement of mesh electrodes, Journal of Cleaner Production, Volume 198, Pages 71-79, ISSN 0959-6526,
186. Khelifa A, Aoudj S, Moulay S, Hecini M, De Petris-Wery M (2009) Degradation of EDTA by in-situ electrogenerated active chlorine in an electroflotation cell. Desalination and Water Treatment 7: 119–123
187. Gu, Yifan & Li, Yue & Li, Xuyao & Luo, Pengzhou & Wang, Hongtao & Robinson, Zoe & Wang, Xin & Wu, Jiang & Fengting, Li. (2017). The feasibility and challenges of energy self-sufficient wastewater treatment plants. Applied Energy. 204.
188. Maktabifard, Mojtaba & Zaborowska, Ewa & Makinia, Jacek. (2018). Achieving energy neutrality in wastewater treatment plants through energy savings and enhancing renewable energy production. Reviews in Environmental Science and Bio/Technology. 17
189. Siatou, Alexandra & Manali, Anthoula & Gikas, Petros. (2020). Energy Consumption and Internal Distribution in Activated Sludge Wastewater Treatment Plants of Greece. Water. 12. 1204.
190. EnviroChemie (2014) Product information: Compact electroflotation - an energy-saving and resource-saving alternative for water treatment. https://envirochemie.com/cms/upload/news/20140616gb/Compact_electroflotation.pdf. Accessed 11 January 2018
191. Mendeleev University Science Park (2008) Table.1. Electroflotation system capability. http://enviropark.ru/course/category.php?id=10. Accessed 11 January 2018
192. Chambers DB, Cottrell WRT (1976) Flotation: Two Fresh Ways to Treat Effluents. Chemical Engineering 83:95
193. Vlasopoulos N, Memon FA, Butler D, Murphy R (2006) Life cycle assessment of wastewater treatment technologies treating petroleum process waters. Science of the Total Environment 367:58–70
194. Ratnayaka DD, Brandt MJ, Johnson M (2009) Water Supply. Butterworth-Heinemann, UK
195. Kalyani KP, Balasubramanian N, Srinivasakannan C (2009) Decolorization and COD reduction of paper industrial effluent using electro-coagulation. Chem Eng J 151(1-3): 97-104.
196. Merzouk, B., Madani, K., & Sekki, A. (2010). Using electrocoagulation–electroflotation technology to treat synthetic solution and textile wastewater, two case studies. Desalination, 250(2), 573-577
197. Saravanan, M., Sambhamurthy, N. P., & Sivarajan, M. (2010). Treatment of acid blue 113 dye solution using iron electrocoagulation. CLEAN–Soil, Air, Water, 38(5-6), 565- 571.

198. Bassala, H. D., Dedzo, G. K., Bememba, C. B. N., Seumo, P. M. T., Dazie, J. D., Nanseu-Njiki, C. P., & Ngameni, E. (2017). Investigation of the efficiency of a designed electrocoagulation reactor: Application for dairy effluent treatment. Process Safety and Environmental Protection, 111, 122-127
199. Bazrafshan, E., Moein, H., Kord Mostafapour, F., & Nakhaie, S. (2012). Application of electrocoagulation process for dairy wastewater treatment. Journal of Chemistry, 2013.
200. Golder, A. K., Samanta, A. N., & Ray, S. (2011). Removal of chromium and organic pollutants from industrial chrome tanning effluents by electrocoagulation. Chemical Engineering & Technology, 34(5), 775-783
201. Espinoza-Quiñones, F. R., Fornari, M. M., Módenes, A. N., Palácio, S. M., da Silva Jr, F. G., Szymanski, N., ... & Trigueros, D. E. (2009). Pollutant removal from tannery effluent by electrocoagulation. Chemical engineering journal, 151(1-3), 59-65
202. Mansour, L. B., & Chalbi, S. (2006). Removal of oil from oil/water emulsions using electroflotation process. Journal of Applied Electrochemistry, 36(5), 577-581.
203. Bande, R. M., Prasad, B., Mishra, I. M., & Wasewar, K. L. (2008). Oil field effluent water treatment for safe disposal by electroflotation. Chemical Engineering Journal, 137(3), 503-509
204. Carlesi, C., Guajardo Ramírez, N., Carvajal, D., Cataldo Hernández, M., & Fino, D. (2015). Electrochemical treatment of bilge wastewater. Desalination and Water Treatment, 54(6), 1556-1562
205. Tsai, L. S., Hernlem, B., & Huxsoll, C. C. (2002). Disinfection and solids removal of poultry chiller water by electroflotation. Journal of food science, 67(6), 2160-2164.
206. Bayramoglu, M., Kobya, M., Eyvaz, M., & Senturk, E. (2006). Technical and economic analysis of electrocoagulation for the treatment of poultry slaughterhouse wastewater. Separation and Purification Technology, 51(3), 404-408.
207. Esfandyari, Y., Mahdavi, Y., Seyedsalehi, M., Hoseini, M., Safari, G. H., Ghozikali, M. G., ... & Jaafari, J. (2015). Degradation and biodegradability improvement of the olive mill wastewater by peroxi-electrocoagulation/electrooxidation-electroflotation process with bipolar aluminum electrodes. Environmental Science and Pollution Research, 22(8), 6288-6297.
208. Hmidi, K., Ksentini, I., & Mansour, L. B. (2017). Treatment of olive-pomace oil refinery wastewater using combined coagulation-electroflotation process. Journal of Water Chemistry and Technology, 39(5), 275-280.
209. Issaoui, R., Ksentini, I., Kotti, M., & Mansour, L. B. (2017). Effect of current density and oil concentration on hydrodynamic aspects in electroflotation column during oil/water emulsion treatment. Journal of Water Chemistry and Technology, 39(3), 166-170.
210. Nasution, Muhammad & Yaakob, Zahira & Ali, Ehsan & Tasirin, Siti & Abdullah, Siti. (2011). Electrocoagulation of Palm Oil Mill Effluent as Wastewater Treatment and Hydrogen Production Using Electrode Aluminum. Journal of environmental quality. 40. 1332-9.
211. Tahreen, Amina & Jami, Mohammed & Ali, Fathilah & Farid, Nik & Yasin, Mat & Ngabura, Mohammed. (2021). Promising Potential of Electro-Coagulation Process for Effective Treatment of Biotreated Palm Oil Mill Effluents. Pollution. 7. 617-632.

212. Nahui, F.N.B.; Nascimento, M.R.; Cavalcanti, E.B.; Vilar, E.O. Electroflotation of Emulsified Oil in Industrial Wastes Evaluated with a Full Factorial Design. Brazilian J. Chem. Eng. 2008, 25, 435–442, doi:10.1590/S0104-66322008000300001.
213. Kyzas, G.Z.; Matis, K.A. Electroflotation Process: A Review. J. Mol. Liq. 2016, 220, 657–664, doi:10.1016/J.MOLLIQ.2016.04.128.
214. Bektaş N, Akbulut H, Hatice D (2004) Removal of phosphate from aqueous solutions by electro-coagulation. J Hazard Mater 106: 101-105.
215. Can O, Kobya M, Demirbas E, Bayramoğlu M (2006) Treatment of the textile wastewater by combined electrocoagulation. Chemosphere 62: 181-187.
216. Shamaei L, Khorshidi B, Perdicakis B, Sadrzadeh M (2018) Treatment of oil sands produced water using combined electrocoagulation and chemical coagulation techniques. Sci Total Environ 645: 560-572.
217. Kim GK, Woo YY, Chan YS, Dong JC, Duk B, Hyung SL, Yong HS, Young HK (2013) Agro-industrial wastewater treatment by electrolysis technology. Int J Electrochem Sci 8: 9835-9850.
218. Chakchouk I, Elloumi N, Belaid C, Mseddi S, Chaari L, Kallel M (2017) A combined electrocoagulation-electrooxidation treatment for dairy wastewater. Brazilian J Chem Eng 34: 109-11
219. Gao B Y, Chu Y B, Yue Q Y, Wang B J and Wang S G 2005 Characterization and coagulation of a polyaluminum chloride (PAC) coagulant with high Al13 content J. Environ. Manage. 76 143–7
220. Wei N, Zhang Z, Liu D, Wu Y, Wang J and Wang Q 2015 Coagulation behavior of polyaluminum chloride: Effects of pH and coagulant dosage Chinese J. Chem. Eng. 23 1041–6
221. Islam M R and Mostafa M G 2020 Characterization of textile dyeing effluent and its treatment using polyaluminum chloride Appl. Water Sci. 10 1–10
222. Nowacka A, Włodarczyk-Makuła M and Macherzyński B 2014 Comparison of effectiveness of coagulation with aluminum sulfate and pre-hydrolyzed aluminum coagulants Desalin. Water Treat. 52 3843–51
223. Bojórquez-Quintal E, Escalante-Magaña C, Echevarría-Machado I and Martínez-Estévez M 2017 Aluminum, a Friend or Foe of Higher Plants in Acid Soils Front. Plant Sci. 8 1–18
224. Meetiyagoda T A O K and Fujino T 2022 Optimization of electrocoagulation–flotation treatment with an aluminum anode to enhance Microcystis aeruginosa cell removal efficiency J. Water Process Eng. 48 102871
225. Luo H, Lyu T, Muhmood A, Xue Y, Wu H, Meers E, Dong R and Wu S 2018 Effect of flocculation pre-treatment on membrane nutrient recovery of digested chicken slurry: Mitigating suspended solids and retaining nutrients Chem. Eng. J. 352 855–62
226. Pitot H C 1996 SELECTION OF WATER QUALITY VARIABLES Water Quality Assessments vol 5 (CRC Press) pp 81–148
227. Zhang X, Lin H, Wei W and Hu B 2020 Electrocoagulation of Dairy Manure Using Low Carbon Steel Electrodes for Phosphorus Removal J. Environ. Eng. 146 04020044
228. Chen R F, Wu L, Zhong H T, Liu C X, Qiao W and Wei C H 2021 Evaluation of electrocoagulation process for high-strength swine wastewater pretreatment Sep. Purif. Technol. 272 118900

229. Poh, P.E.; Ong, W.Y.J.; Lau, E. V.; Chong, M.N. Investigation on Micro-Bubble Flotation and Coagulation for the Treatment of Anaerobically Treated Palm Oil Mill Effluent (POME). J. Environ. Chem. Eng. 2014, 2, 1174–1181, doi:10.1016/J.JECE.2014.04.018.
230. Ho, C.C.; Chan, C.Y. The Application of Lead Dioxide-Coated Titanium Anode in the Electroflotation of Palm Oil Mill Effluent. Water Res. 1986, 20, 1523–1527, doi:10.1016/0043-1354(86)90116-8.
231. Trinke, P.; Bensmann, B.; Hanke-Rauschenbach, R. Current Density Effect on Hydrogen Permeation in PEM Water Electrolyzers. Int. J. Hydrogen Energy 2017, 42, 14355–14366, doi:10.1016/J.IJHYDENE.2017.03.231.
232. Ho, C.C.; Chan, C.Y. The Application of Lead Dioxide-Coated Titanium Anode in the Electroflotation of Palm Oil Mill Effluent. Water Res. 1986, 20, 1523–1527, doi:10.1016/0043-1354(86)90116-8.
233. Belkacem, S.; Bouafia, S.; Chabani, M. Study of Oxytetracycline Degradation by Means of Anodic Oxidation Process Using Platinized Titanium (Ti/Pt) Anode and Modeling by Artificial Neural Networks. Process Saf. Environ. Prot. 2017, 111, 170–179, doi:10.1016/J.PSEP.2017.07.007.
234. Mansour, L. Ben; Kolsi, K.; Ksentini, I. Influence of Current Density on Oxygen Transfer in an Electroflotation Cell. J. Appl. Electrochem. 2007, 37, 887–892, doi:10.1007/s10800-007-9326-0.
235. Zakaria, Z.A.; Ahmad, W.A. Organic and Inorganic Matter Removal Using High Polymeric Al13 Containing Polyaluminium Chloride. Water. Air. Soil Pollut. 2020, 231, doi:10.1007/s11270-020-04706-8.
236. Wang, J.; Zhu, M.; Chen, Z.; Chen, Y.; Hayat, T.; Alsaedi, A.; Wang, X. Polyacrylamide Modified Molybdenum Disulfide Composites for Efficient Removal of Graphene Oxide from Aqueous Solutions. Chem. Eng. J. 2019, 361, 651–659, doi:10.1016/J.CEJ.2018.12.123.
237. Guan, Q.; Zhu, G.; Liao, Y.; Xu, J.; Sun, X.; Tian, F.; Xu, J.; Luo, M. Preparation, Characterization, and Sludge Conditioning of Cationic Polyacrylamide Synthesized by a Novel UVA-Initiated System. Processes 2018, 6, doi:10.3390/pr6120233.
238. Duggan, K.L.; Morris, M.; Bhatia, S.K.; Khachan, M.M.; Lewis, K.E. Effects of Cationic Polyacrylamide and Cationic Starch on Aquatic Life. J. Hazardous, Toxic, Radioact. Waste 2019, 23, doi:10.1061/(asce)hz.2153-5515.0000467.

ACKNOWLEDGEMENTS

Chapter 3, in full, is a reprint of the material as it appears in International Journal of Earth and Science 2022. Enjeh, Y.Fobang and Fujino, Takeshi. 2022. The dissertation author was the primary investigator and author of this paper.

Chapter 4, in full, is a reprint of the material as it appears in the IOP Conference Series: Earth and Environmental Science. Toshinori Takahashi, Thenuwara Arachchige Omila Kasun Meetiyagoda, Rasheed Bakare, Enjeh Fobang, Ken Takeda and Takeshi Fujino. The dissertation author was the co- author of this paper

Chapter 5, in full. Enjeh, Y.Fobang; Fujino, Takeshi and Thenuwara Arachchige Omila Kasun Meetiyagoda. The dissertation author was the primary researcher and author of this material.