氏　　　　　名	GAJANAYAKA MUDALIGE PRADEEP KUMARA
博士の専攻分野の名称	博士（学術）
学 位 記 番 号	博理工甲第 1147 号
学位授与年月日	令和元年 9 月 20 日
学位授与の条件	学位規則第 4 条第 1 項該当
学 位 論 文 題 目	Utilization of Construction and Demolition Waste (CDW) and Industrial By-products (IBPs) as Low-cost Adsorbents for Simultaneous Removal of Heavy Metals in Wastewater （汚染水中の複数種重金属同時除去を可能とする低コスト吸着材への建設廃棄物及び産業副産物の活用）
論 文 審 査 委 員	委員長　教　　授　川本　　健
	委　員　准 教 授　浅本　晋吾
	委　員　准 教 授　内村　太郎
	委　員　教　　授　田中　規夫

論文の内容の要旨

A high rate of population growth is increasing per-capita income, industrialization, and urbanization results in the generation of an enormous volume of solid waste, which poses a serious threat to environmental quality and human health. Furthermore, weak institutional framework and low capacities, as well as lack of resources, both human and capital, has put waste management in a very terrible state. Several types of solid wastes are generating due to human activities. Municipal solid waste, industrial waste, construction, and demolition waste (CDW), etc. are the most challenging wastes types, and still, most of the nations are unable to tackle these materials on efficient and productive way, especially developing nations. In this study, we were mainly concerned only on construction demolition waste and some industrial by-products (IBPs), which are the most challenging waste materials in the twenty-first century. According to the statistics on treatment and recycling of CDW and IBPs, developing nations are the most vulnerable as well as suffering from a lot of environmental and social issues due to lack of knowledge and technology for the handling these waste on effective ways. Thus, strengthen the institutional framework and introducing the new policies and laws on proper management of wastes are essential. On the other hand, researchers and scientists have a great challenge to carry out research and to propose new technologies and methods for the appropriate treatment, management and set added values for the CDW and IBPs materials to realize the sustainable development in worldwide.

Contamination of water by toxic heavy metals through the discharge of industrial wastewater is a global environmental problem. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water bodies. Mining, electroplating, metal processing, textile, battery manufacturing, pesticides, and photographic industries are the primary sources of heavy metals contamination. Metals such as lead, cadmium, copper, arsenic, nickel, chromium, zinc and mercury have been recognized as most hazardous heavy metals. As an example, the annual global release of heavy metal reached 22,000 tons (metric tons) for cadmium, 939,000 tons for copper, 783,000 tons for lead and 1,350,000 tons for zinc. These metals are non-biodegradable, and they can be accumulated in living tissues, causing various diseases and disorders. Thus heavy metals must be removed before discharge.

Countless efforts are being made to develop improved and innovative methods of wastewater treatment, such as chemical precipitation, membrane filtration, hydroxide precipitation, reverse osmosis, phytoextraction, ion exchange, electrokinetic remediation, and adsorption. Adsorption is one of the most effective processes of advanced wastewater treatment, which industries employ to reduce hazardous metals present in the effluents. Activated carbon produced by carbonizing organic materials is the most widely used adsorbent. Activated carbon has shown excellent metal ion adsorption capacities. However, the high cost of the activation process limits the utilization of wastewater treatment. Over the last few years, a large number of investigations have been conducted to test the low-cost adsorbents for the removal of heavy metals such as geo and bio sorbents. Adsorption method provides an attractive alternative for the treatment of contaminated water, especially if the adsorbent is inexpensive and does not require an additional pre-treatment step before its application. Also, adsorption is superior compared to the other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation, and insensitivity to toxic pollutants. Then, developing countries, small scale industries are keen to use adsorption technology to treat industrial effluents. However, the adsorption technique sustainability much depends on efficient and abundantly or freely available materials.

Moreover, the literature review in this study revealed that more than 74% of published works on adsorption studies were targeted single or binary metal solutions for the adsorption experiments. But, real industrial wastewater might be a one or mixture of two or several common heavy metals such as Pb^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, etc. Consequently, studies on simultaneous removal of these metals are sensible to increase the effectiveness of adsorption as a method to treat industrial wastewater. The next primary concern is when applying simultaneous removal process by adoption technology, metals like Pb^{2+} and Cu^{2+} always dominating and the other metals (especially Cd^{2+}) are hampering in the system. Thus, the number of researchers have been concluded, simultaneous removal of Cd^{2+} using low-cost adsorbent is impossible. Therefore, it is appreciated to find out low-cost adsorbents which are potential to simultaneous removal of commonly available heavy metals in wastewater. Besides, more than 99% of batch adsorption studies were mainly concerned about the effect of initial concentration (C_i) to study adsorption isotherm/adsorption mechanism rather than the effect of solid:liquid (S:L) ratios. The adsorption efficiency of heavy metals might directly influence it. Generally, for a fixed metal concentration in solution, when increasing the S:L ratio by adding the adsorbent, the amount of metal adsorption is rising due to boosting of the number of adsorption sites. However, S:L ratio directly alternating the characteristics of the adsorbate and adsorbent mixture, and ultimately, it affects for the metal adsorption mechanism which, although not often studied should have a substantial effect on the metal sorption. Thus, main objectives of this study are (i) to set an added value for the selected CDW and IBPs materials as low-cost adsorbents to treat industrial wastewater, (ii) to investigate the metal adsorption mechanism onto selected CDW and IBPs materials, and (iii) to investigate the simultaneous removal potential of Cd^{2+} and Pb^{2+} by the selected CDW and IBPs materials under the batch adsorption condition.

Three CDW (autoclaved aerated light-weight concrete, crushed concrete fines crushed clay bricks), two IBPs (steel slag, municipal solid waste slag) and two reference materials (Japanese zeolite, fine sand) were selected as the low-cost adsorbents to examine the heavy metal adsorption process in this study. First, a series of batch adsorption experiments were carried out using all materials with three different particle sizes to examine the effects of the particle size (<0.105, 0.105-2, 2-4.75 mm), initial metal concentration (0-5000 mg/L), initial pH (3-11), ionic strength (0-0.1), metal desorption, contact time (0-192 h), and competitive metals (binary and multi-metals). Then, based on the materials adsorption capacity of each metal and adsorption mechanism, best-performed materials were selected for the simultaneous removal experiments. In simultaneous experiments, to examine the effect of molar mixed ratios of Cd^{2+} and Pb^{2+} in the binary metal solutions for each metal adsorption, Cd^{2+} to Pb^{2+}, was mixed at metals molar ratios of 1:0, 1:0.25, 1:0.5, 1:0.75, 1:1, 1:2, and 1:5 to investigate the effect of Pb^{2+} concentrations on Cd^{2+} adsorption. Similarly, the same mixing ratios of Pb^{2+} to Cd^{2+} were used to investigate the effect of Cd^{2+} on Pb^{2+} adsorption. To examine the effects of multi-metals solution on Cd^{2+} and Pb^{2+} adsorption onto each adsorbent, C_i of 1,000 mg/L Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+} mixed solutions with metals molar mixed ratios of 1:1:1:1:1 were used. Also, To examine the effect of S:L ratios (adsorption isotherms) and to find out the best S:L ratio/s for simultaneous removal of Cd^{2+} and Pb^{2+} by the selected adsorbents, C_i of 1,000 mg/L binary and multi-metals solutions were used with five different S:L ratios (1:5, 1:10, 1:60, 1:100 and 1:250). The same experiment was carried out with single metal solutions for each adsorbent, and observed results were compared with its binary and multi-metals solutions.

Based on the results in this study, AAC and SS were shown the high capacity to remove harmful heavy metals from wastewater. Noticeably, AAC showed greater affinity with Pb^{2+} (>250 mg/g). In contrast, SS showed greater affinity with Cd^{2+} (>300 mg/g). Importantly, AAC fines (<0.105, 0.105-2 and 2-4.75 mm) were achieved effluent discharge standards (<0.001 mg/L) for Cd^{2+} and Pb^{2+} up to initial concentration of 600 mg/L for Cd^{2+} and 1000 mg/L for Pb^{2+} by the single batch adsorption under carried out experimental conditions, respectively. Also, SS (<0.105, 0.105-2 and 2-4.75 mm) achieved effluent discharge standards for the Cd^{2+} up to initial metal concentration of 800 mg/L by the single batch adsorption process. However, both individual adsorbents were exhibited poor performance on simultaneous removal of Cd^{2+} and Pb^{2+} from binary and multi-metals solution. Therefore, this study introduced three mixtures of AAC and SS fines which are AAC+SS [4:1], AAC+SS [1:1] and AAC+SS [1:4] for the simultaneous removal of Cd^{2+} and Pb^{2+}. Accordingly, serious of batch adsorption experiments were carried out with binary and multi-metals solutions on simultaneous removal of Cd^{2+} and Pb^{2+} from wastewater. Besides, the effect of solid: liquid ratios (S:L ratios) were investigated using binary and multi-metals solutions for the simultaneous removal of Cd^{2+} and Pb^{2+} and, results were compared with its single metal solutions. Results revealed that AAC+SS [1:1] is an effective adsorbent for the simultaneous removal of Cd^{2+} and Pb^{2+} from wastewater than the other tested adsorbents. In the binary metal solutions, AAC+SS [1:1] was capable of removing Cd^{2+} and Pb^{2+} simultaneously, without any effect of metals molar mixed ratios at the S:L ratio of 1:60. Interestingly, AAC+SS [1:1] mixture showed 100 % removal of Cd^{2+} and Pb^{2+} simultaneously, in the multi-metals solution up to S:L ratio of 1:10. Thus, it was able to eliminate the low-cost adsorbents major drawback, which was always Cd^{2+} hampering and Pb^{2+} domination in the multi-metals system. Then, the selectivity sequence of AAC+SS [1:1] mixture was observed as $Cd^{2+} \approx Pb^{2+} \approx Cu^{2+} \approx Zn^{2+} \approx Ni^{2+}$. AAC fines main adoption mechanisms are ion exchange, surface complexation, and surface precipitation. Especially, Ca^{2+} ion exchange on the hydrated adsorbent surface is the dominant adsorption mechanism of Cd^{2+} and Pb^{2+} adsorption for tested AAC fines at the early stage of adsorption. The dominant mechanisms for Cd^{2+} and Pb^{2+} adsorption onto SS are Ca^{2+} ion exchange, surface complexation along with surface precipitation. The solution equilibrium pH mainly controls Pb^{2+} adsorption onto SS fines and its mixtures. At the very high pH (≥12), only Ca^{2+} ion exchange reaction act as the dominant mechanism, but the equilibrium pH<12, surface precipitation playing a significant role to remove Pb^{2+} from the metal system. Thus, it is recommended to pay attention to solid: liquid ratios in batch adsorption studies, which is highly controlling the simultaneous removal of metals from the multi-metals solution. Also, the following facts should be considered in future studies and applications for the sustainable use of low-cost adsorbents like AAC and SS. Along with the metal adsorption process, AAC and SS fines released a relatively high concentration of Ca^{2+}, which should be controlled before the discharge of the treated water into the natural environment. Thus, it is recommended to studies on Ca^{2+} ions control experiments while using the AAC and SS-like low-cost adsorbents on the wastewater treatment process.

論文の審査結果の要旨

当学位論文審査委員会は、令和元年7月30日に論文発表会を開催し、論文内容の発表に続いて質疑と論文内容の審査を行なった。以下に審査結果を要約する。

急激な人口増加とともに急速に都市化・工業化が進行している開発途上国の都市では、廃棄物排出量は増加の一途をたどり、廃棄物の不適切な処理・処分に起因する環境劣化や健康被害の発生が顕在化している。特に、東アジアの都市域や工業地帯では、開発にともなう建設廃棄物や産業副産物の発生量が急増している。これらの建設廃棄物や産業副産物のリサイクルや再資源化に関しては、法制度の未整備やリサイクル支援策の欠如もあり、十分に推進されておらず、回収された建設廃棄物や産業副産物は特定の汚染防止措置を講ずることなく、投棄場での直接埋立もしくは空き地などへの投棄が行われている。一方、建設事業における天然建設資材（バージン材）の無計画な使用は、採取地域の環境破壊や資源枯渇を引き起こすことからも、建設廃棄物や産業廃棄物のリサイクルや再資源化、再生材の積極的な活用は今後益々重要となっている。このような背景のもとに、本学位論文では、建設廃棄物ならびに産業副産物の開発途上国における新規有効利用法の開発を目的とし、特に汚水に含まれる複数種重金属類除去への適用を実験的に検討した。

第1章では、研究の背景や目的、関連する既往の研究について記述している。特に本研究で主要な内容となる、建設廃棄物や産業副産物の重金属類吸着材としての研究事例を整理し、これらの材料がバイオ資材や土質資材と比較しても潜在的に高い重金属除去能を有することを示した。

第2章から第4章にかけては、水中の重金属類としてカドミウムと鉛を対象とし、各種建設廃棄物、産業副産物材料による水中CdやPbの吸着除去能や吸着メカニズム、脱離（不溶化）について詳細な検討を室内実験にて行った。具体的には、第2章では4.75mm以下の粒径に加工した顆粒状軽量気泡コンクリート（AAC）材ならびに比較材料としてのコンクリート細粒分（<4.75mm）、第3章では同粒径の顆粒状粘土レンガ材と一般廃棄物溶融スラグ（0.105-2㎜）、第4章では4.75mm以下の粒径に加工した顆粒状土工用鉄鋼スラグ（SS）材ならびに比較材料としてのゼオライト（0.105-2㎜）を用いている。これらの各種材料を検討した結果、特にAAC材は鉛の吸着除去能力が高く、SS材はカドミウムの吸着除去能力が高いことが示された。両材料とも吸着等温線はラングミュア型を示し、AAC材のカドミウムに対する最大吸着能は250-258mg/g、SS材の鉛に対する最大吸着能は130-313mg/gと極めて高い値を示した。さらに、脱離試験の結果から、これらの吸着重金属は高い不可逆性（固定化）を示すことが明らかとなった。しかし一方、複数種重金属含有水（鉛、カドミウム、銅、亜鉛、ニッケル）に対してこれらの材料を用いて吸着実験を行った結果、これらの材料単独では、複数種の重金属の同時吸着除去には不適であることが示された。つまり、AAC材は鉛に対する吸着能が高いため、カドミウム吸着が著しく阻害され、SS材に関しても鉛吸着がカドミウム吸着を阻害することが明らかとなった。さらに、第2章ではAAC材への重金属吸着メカニズムを重金属吸着に伴うカルシウムイオン溶出分析や吸着前後のpH変化から検討した。その結果、重金属吸着に伴う主要な反応プロセスはカルシウムイオンと重金属のイオン交換であり、同時に表面錯体形成や表面沈殿も一部吸着除去に寄与することが示された。

第5章では、第2-4章で得られた知見（AAC材の鉛に対する強い親和性、SS材のカドミウムに対する強い親和性）をベースに、顆粒状AAC材・SS材の配合比率を変えて混合した材料（AAC-SS混合材）による、水中の複数種重金属の同時除去を詳細に検討した。その結果、配合比率1：1のAAC-SS混合材が水中のカドミウムと鉛の同時除去に最適な材料であり、各種条件（カドウムと鉛の2種混合溶液系、複数種重金属混合溶液系、固液比1:60ならびに1:10）において、カドミウムと鉛の除去率がほぼ100%を示した。また、

AAC-SS 混合材のカドミウムと鉛の同時除去メカニズムは、溶液中の pH 条件により変化し、pH ≧ 12 では AAC 材単独と同様にカルシウムイオンと重金属のイオン交換が主要な反応プロセスであり、pH<12 ではイオン交換と同時に鉛の表面沈殿吸着除去に貢献することが推察された。

第 6 章では、第 2-5 章で検討した吸着材を、実際の重金属吸着除去フィルターシステムに適用するために必要となる透水性評価をカラム試験により行った。既往の研究のレヴュー結果を参考に、処理に用いる水中重金属濃度（汚染負荷）や処理流速を設定し、吸着材の締固め度が透水係数に及ぼす影響を検討した。これらの検討結果は、今後の継続研究に役立つことが期待される。

第 7 章では、第 1 章から第 6 章までに得られた知見をもとに結論を述べるとともに、建設廃棄物ならびに産業副産物を活用した汚染水中の複数種重金属同時除去を可能とする低コスト吸着材の開発に向け、長期性能評価の重要性や原位置適用に向けての課題を挙げるなど、今後の研究展開の方向性を示した。

以上のように、本研究は汚染水中の複数種重金属同時除去を可能とする低コスト吸着材の開発を目的に、各種建設廃棄物ならびに産業副産物の適用可能性を室内実験によって調べた。その成果は、今後、重金属吸着除去フィルターシステムの吸着材選定に直接的に貢献するものであり、開発途上国における環境改善・汚染修復技術の構築に効果的に活用されるものである。このことから、当学位論文審査委員会は、本論文が博士（学術）の学位に相応しい内容であると判断した。

なお、本論文の内容は、第 1 章と第 3 章がそれぞれ国際学術雑誌 International Journal of GEOMATE (2018, 2019) に掲載済み、第 2 章が国際学術雑誌 Journal of Environmental Engineering, ASCE に掲載予定、第 4 章は国際プロシーディングス論文（17th International Waste Management and Landfill Symposium (Sardinia 2019)）にて掲載予定、第 5 章は国際学術雑誌に投稿予定である。