UNIVERSITI PUTRA MALAYSIA

DEVELOPMENT OF EFFECTIVE WATER TREATMENT TECHNIQUE USING CALCEROUS SKELETON STABILIZING AGENT FOR ATTENUATION OF CADMIUM AND LEAD IONS

LIM AI PHING

FPAS 2014 20

DEVELOPMENT OF EFFECTIVE WATER TREATMENT TECHNIQUE USING CALCEROUS SKELETON STABILIZING AGENT FOR ATTENUATION OF CADMIUM AND LEAD IONS

By

LIM AI PHING

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

August 2014

COPYRIGHT

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

DEVELOPMENT OF EFFECTIVE WATER TREATMENT TECHNIQUE USING CALCEROUS SKELETON STABILIZING AGENT FOR ATTENUATION OF CADMIUM AND LEAD IONS

By

LIM AI PHING

August 2014

Chair: Ahmad Zaharin Aris, PhD

Faculty: Environmental Studies

Heavy metal pollution in the environment has become a great public concern globally due to the adverse effects to human health as well as flora and fauna. Various efforts have been taken to reduce the metal contamination level in the environment through controlling and remediation process. Conventional treatment process requires extra procedure to further remove the metal ions in the wastewater in order to produce safe quality of treated water. The thesis discusses on the removal of metal ions; cadmium, Cd (II) and lead ions, Pb (II), by using dead calcerous skeletons (CS) based on batch and column systems. In general, the study aimed to provide potential adsorbent for the removal of metal ions in consideration to the current wastewater treatment techniques. The removal efficiency, adsorption capacity and behaviors of adsorbents were examined during the metals removal process and incorporated with isotherm models. In the batch study, the removal of Cd (II) and Pb (II) ions by CS were evaluated by varying the contact time, adsorbent size, dosage, solution pH, and initial metal concentration. While, for the column study, the factors of adsorbent bed height, influent flow rate and initial concentrations were evaluated to obtain the removal performance of CS in continuous flow system. The results showed that the surface characteristics of CS did not significantly affected the removal efficiency of CS. The dosage requires for optimum removal of Cd (II) and Pb (II) ions in batch system were in minimal amount since the increased of dosage did not show significant increased in removal ($p>0.05$). The acidic solutions were observed to shift to neutral and alkali condition after equilibrated with CS due to the content of calcium carbonate ($CaCO_3$) of CS. The adsorption capacity of CS has increased with high loading of metal ions which reveal that the CS were able to remove high concentration of Cd (II) and Pb (II) ions. Based on the isotherm models, the results demonstrated that the data were more favorable to Freundlich isotherm which indicated the adsorption process occurred in heterogeneous surface rather than monolayer. In the column study, the column with long bed height showed no exhaustion occurred during the continuous flow system as there was no breakthrough of 0.05 C_{eff}/C_o (ratio of effluent concentration to influent concentration). The columns were able to operate more than 24 hours with double dose of CS to the shortest bed height which showed that the ability of CS to withstand high metal ions for long duration of operation. The column models were strongly correlated to the experimental data and well-presented the long bed columns. The PHREEQC model predicted the dissolution of CS which contributed to the increased of pH and calcium ions in the treated solutions. The adsorption and ion-exchange process between the CS and metal ions were also confirm by the formation of otavite and cerussite from Scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis. Thus, this study provides potential materials for application in wastewater treatment system. The outcome of the study also reveals possible application for the treatment of acidic wastewater with high metals loading.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGHASILAN TEKNIK RAWATAN AIR YANG EFEKTIF DENGAN MENGGUNAKAN RANGKA KAPUR SEBAGAI AGEN PENSTABIL DALAM MENYINGKIRKAN ION KADMIUM DAN PLUMBUM

Oleh

LIM AI PHING

Ogos 2014

Pengerusi: Ahmad Zaharin Aris, PhD

Fakulti: Pengajian Alam Sekitar

Pencemaran logam berat di persekitaran telah menjadi perhatian di peringkat global disebabkan kesan-kesan negatifnya terhadap kesihatan manusia serta flora dan fauna. Pelbagai usaha telah dilakukan untuk mengurangkan tahap pencemaran logam di persekitaran melalui proses pengawalan dan pemulihan. Proses rawatan konvensional memerlukan prosedur tambahan untuk menyingkirkan logam ion di dalam air kumbahan bagi menghasilkan air terawat yang berkualiti selamat. Tesis ini membincangkan tentang penyingkiran ion logam; ion kadmium, Cd (II) dan ion plumbum, Pb (II) daripada larutan akueus dengan menggunakan rangka kalkareus mati (CS) berdasarkan sistem kelompok dan kolum. Secara umumnya, matlamat kajian ini adalah untuk menghasilkan bahan penjerap yang berpotensi untuk menyingkirkan ion logam bagi teknik rawatan air kumbahan masa kini. Kecekapan penyingkiran, kapasiti penjerapan dan ciri penjerap telah dikaji sepanjang proses penyingkiran logam dengan menggabungkan model-model isoterma. Dalam kajian kelompok, proses penyingkiran ion Cd (II) dan Pb (II) telah dinilai dari segi masa sentuhan, saiz penjerap, dos, pH larutan, dan kepekatan logam asal. Manakala bagi kajian kolum, faktor ketinggian lapisan penjerap, kadar aliran influen dan kepekatan asal influen dinilai untuk mendapatkan prestasi penyingkiran CS dalam sistem aliran berterusan. Hasil kajian menunjukkan ciri-ciri permukaan CS tidak menjejaskan kecekapan penyingkiran CS secara ketara. Dos CS yang diperlukan untuk menyingkirkan ion Cd (II) dan Pb (II) yang optimum dalam sistem kelompok adalah minimal kerana peningkatan dos tidak menunjukkan peningkatan dalam penyingkiran yang ketara (p>0.05). Larutan yang berasid telah bertukar kepada keadaan neutral dan alkali selepas diseimbangkan dengan CS yang disebabkan oleh kandungan kalsium karbonat ($CaCO_3$) dalam CS. Kapasiti penjerapan CS meningkat dengan pertambahan ion logam. Ini menunjukkan bahawa CS dapat menyingkirkan kepekatan ion Cd (II) and Pb (II) yang tinggi. Berdasarkan keputusan data model-

model isoterma, proses penjerapan kajian ini lebih cenderung kepada isoterma Freundlich, di mana ia berlaku pada permukaan heterogen dan bukan sekadar pada ekalapisan. Dalam kajian kolum, kolumn dengan lapisan penjerap yang tebal tidak menunjukkan sebarang ketepuan dalam sistem aliran berterusan kerana tidak mencapai takat muncul 0.05 C_{eff}/C_o (nisbah kepekatan efluen kepada kepekatan influen). Kolum dapat beroperasi lebih daripada 24 jam apabila dua kali ganda dos CS daripada lapisan yang paling minimum digunakan. Ini menunjukkan bahawa CS berkeupayaan untuk menampung kepekatan ion logam yang tinggi serta masa operasi yang lebih panjang. Model kolum mempunyai korelasi dengan data eksperimen dan ini menunjukkan lapisan kolum yang tebal adalah paling sesuai digunakan. Model PHREEQC telah digunakan untuk meramal kelarutan CS yang menyumbang kepada peningkatan pH dan ion kalsium di dalam larutan terawat.
Proses penjerapan dan pertukaran ion antara CS dan ion logamdibuktikan oleh pembentukan otavit dan serusit daripada analysis mikroskop pengimbas elektron (SEM) dan pembelauan X-ray (XRD). Kesimpulannya, kajian ini menghasilkan bahan yang berpotensi untuk diaplikasikan dalam sistem rawatan air sisa. Hasil kajian ini juga menunjukkan bahawa CS sesuai diaplikasikan bagi merawat air sisa yang berasid dengan kandungan logam berat yang berkepekatan tinggi.

ACKNOWLEDGEMENTS

I would like to offer my sincere thanks to the individuals who have directly and indirectly contributed to the completion of this work. First and foremost, I would like to express my deepest gratitude to my worthy supervisor, Assoc. Prof. Dr. Ahmad Zaharin Aris, for his professional insight, skilful guidance, encouragement, suggestion, time and patience throughout my study period. Thanks a lot for his kind and helpful supervision. I would also extend my sincere appreciation to my co-supervisor, Dr. Hafizan Juahir for this valuable assistance and advice in the whole study. This research was funded by Science Fund, 06-01-04SF1395, from Ministry of Science Technology and Innovation (MOSTI) Malaysia and Research University Grant Scheme (RUGS), 03-01-110142RU, from Universiti Putra Malaysia (UPM). I sincerely acknowledge the support from Graduate Research Fellowship Scholarship awarded by UPM. Part of this thesis is already published. My appreciation is extended to the anonymous reviewers who gave valuables suggestions, comments and positive feedbacks prior to publication. I would also like to thank the faculty and laboratory member, Mr. Zairi Ismail, Looi Ley Juen, Lim Wan Ying, Farhah Amalya Ismail, Noorain Mohd Isa, Nur Aliaa Shafie, Adamu Mustapha, Hazzeman Haris, Farhana Mokhtar, Nordiani Sidi, Mohd Zaimani Ismail and many more for assistance, supports and friendship throughout this study. My heartfelt thanks and love go to my family especially my parents, Lim Soon Lye and Low Soon Ee, for their endless love and strong mental supports throughout the journey of my study. Last but not least, my deepest appreciation to Eric Lim for his sincere encouragement, support, advice and understanding throughout this moment.

I certify that an Examination Committee has met on to conduct the final examination of Lim Ai Phing on her Master Science thesis entitled “Development of Effective Water Treatment Technique Using Calcerous Skeleton Stabilizing Agent for Attenuation of Cadmium and Lead Ions” in accordance with the Universities and University College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U. (A) 106] 15 March 1998. The committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

NORITAH OMAR, PhD
Associate Professor and Deputy Dean
School of Graduate Studies
University Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory committee were as follows:

Ahmad Zaharin Aris, PhD
Associate Professor
Faculty of Environmental Studies
Universiti Putra Malaysia
(Chairman)

Hafizan Juahir, PhD
Senior Lecturer
Faculty of Environmental Studies
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by Graduate Student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universititi Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature:________________________ Date:_____________________

Name and Matric No:____

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature:	___________________	Signature:	___________________
Name of Chairman of Supervisory Committee:	___________________	Name of Member of Supervisory Committee:	___________________

Perakuan Ahli Jawatankuasa Penyeliaan:

Dengan ini, diperakukan bahawa:
- penyelidikan dan penulisan tesis ini adalah di bawah seliaan kami;
- tanggungjawab penyeliaan sebagaimana yang dinyatakan dalam Universiti Putra Malaysia (Pengajian Siswazah) 2003 (Semakan 2012-2013) telah dipatuhi.

Tandatangan: ____________________
Nama Pengerusi
Jawatankuasa
Penyeliaan: ____________________

Tandatangan: ____________________
Nama Ahli
Jawatankuasa
Penyeliaan: ____________________

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Cd	Cadmium
Pb	Lead
Ca	Calcium
APHA	American Public Health Association
CS	Calcerous skeletons
Cu	Copper
Zn	Zinc
Hg	Mercury
As	Arsenic
Cr	Chromium
Ni	Nickel
Fe	Iron
Co	Cobalt
Mn	Manganese
NABC	Needs, Approach, Benefits and Competition
SWOT	Strength, Weakness, Opportunities, Threat
WHO	World Health Organization
USEPA	United States Environmental Protection Agency
UNESCAP	United Nations Economic and Social Commission for Asia Pacific
BET	Brunauer, Emeett and Teller
ICP-MS	Induced-Coupled Plasma Mass Spectrometer
XRD	X-ray diffraction
EDX	Energy Dispersive X-ray
SEM	Scanning electron microscope
SD	Standard deviation

LIST OF UNITS

%	percent
<	less than
>	more than
°C	degree Celcius
µm	micrometer
mm	millimeter
cm	centimeter
g	gram
mL/min	milliliter per minute
rpm	revolution per minute
mg/L	milligram per liter
mg/g	milligram per gram
ppm	parts per million
mg/kg	milligram per kilogram
g/L	gram per liter
m^2/g	square meter per gram
cc/g	cubic centimeter per gram
nm	nanometer

CHAPTER 1

INTRODUCTION

1.1 Background study

The issue on heavy metal pollution in the environment has been emerging over the last decade, affecting the environment and human health. The pollution problems continue to increase with the rapid development in industrial sectors, causing the scarce of clean freshwater supplies in some regions. The heavy metal contamination in the water has lead to the metal accumulation in the aquatic life and presence of trace toxic metal in the water system. The water quality is directly affected by the contamination of heavy metal in the water pathway. The metal pollution presence in high level in the water is found to be caused by the channel of industrial discharge (Nagy et al., 2013; Sewwandi et al., 2014).

Harmful metals especially cadmium and lead are found to be above the detection limit in the water of nearby heavy industrial, agricultural and mining activities (Aziz et al., 2008; Naiya et al., 2009). These metals are usually used in the industries of metal plating, smelting, paints, galvanizing, alloy manufacturing and paints productions (Goel et al., 2005 Naiya et al., 2009; Nagy et al., 2013). The wastewater from these industries is then discharged into the water bodies and caused the metal loading in the river to increase instantaneously. Exposure to these harmful metals effectuates negative impacts in human health. The long-term exposure to the cadmium leads to sickness like renal dysfunction, hypertension, disorder in protein mechanism, reduction of calcium in bones, and kidney failure (Naiya et al., 2009; Vimala and Das, 2011; Nagy et al., 2013). The ingested cadmium ions in the human bodies required a longer time to excrete out. The cadmium ions cause confusion in the body system for its similarity to zinc ions and tend to replace the zinc ions (Hasani and Eisazadeh, 2013). For the lead contamination, the impacts are serious on the children this metals affected the children important organs and central nervous system (Hu et al., 2013; Zhang et al., 2013). The toxicity of Pb (II) causes the decline in the children intelligence quotients (Hu et al., 2013). Figure 1.1 shows the heavy metals contaminations in the environment and the actions that taken to remove the pollution problems.

The efforts to encounter the environmental pollution were sought by scientist to reduce the toxic metals in the surface water. Conventional methods were developed to treat the contaminated effluent in the environment. Generally, the treatment technologies utilized are chemical oxidation and precipitation, ion-exchange, ozone treatment, membrane filtration, flocculation, coagulation and reserve osmosis (Li and Champagne, 2009; Yahaya et al., 2011; Gonte and Balasubramanian, 2013; Grieco and Ramarao, 2013).

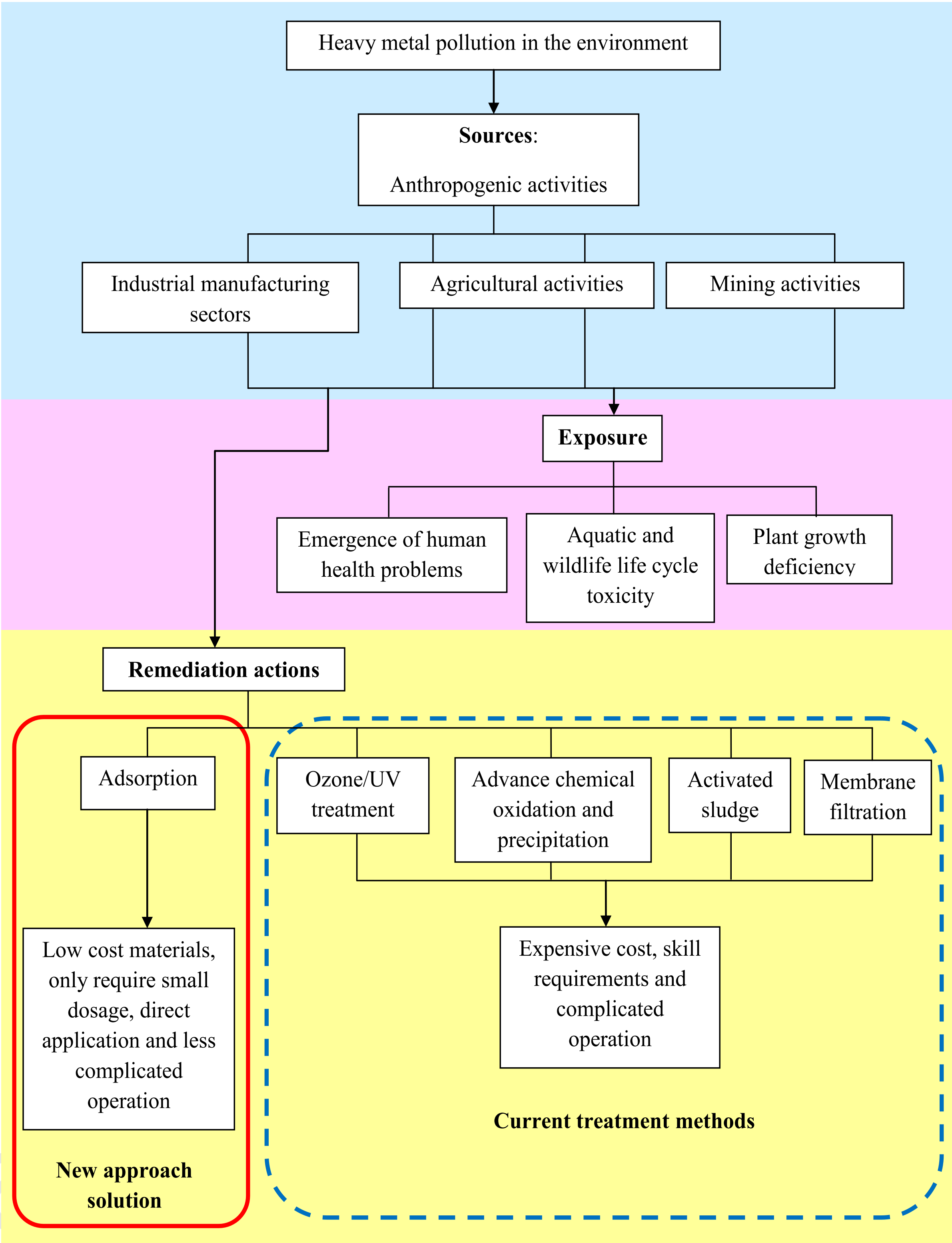

Figure 1.1 Conceptual diagram for the heavy metal pollution in the environment and the efforts conducted to encounter the problems

These methods were known to be effective at certain required factors such as the suitable pH and influent volume. However, the cost of operating these treatment systems are expensive as special requirement need to be achieve to fulfill the requirement of the system and design, such as adding chemicals to adjust pH and control the solutions temperature (Skubal et al., 2002; Hansen et al., 2010). Some of these treatments are not able to particularly too low or high metal concentration and trace metal were still detectable at the treated effluent (Skubal et al., 2002; Liang et al., 2007).

Recently, researches have started to focus on the adsorption process as an alternative way to treat the metal contamination in the water bodies. The outcomes of the metal adsorption are very positive in term of the effectiveness in removing metals and environmental friendly approaches (Pitakpoolsil and Hunsom, 2013; Yu et al., 2013). The advantages of metal adsorption are utilization of waste materials to remove the heavy metals in the environment, the inexpensive cost for treatment procedures, the effective short period and the friendly application (Bailey et al., 1999; Demirbas, 2008; Wang and Chen, 2009). The materials commonly investigated for metal adsorption are agricultural waste, food waste, industrial waste and the minerals available abundantly in the environment (Bailey et al., 1999; Demirbas, 2008; Moon et al., 2011; Wu et al., 2013). These adsorbents are readily available as waste and by reusing these materials; the wastes are revitalized for useful purposes and reduce the cost for waste disposal.

Materials contain of high compound of calcium carbonate ($CaCO_3$) has become one of the popular selection for the metal remediation process. Seafood waste such as the mollusk shells has gained a great attention for the application in removing heavy metals in the water (Tudor et al., 2006; Champagne and Li, 2009; Suteu et al., 2012; Ismail et al., 2013). The aragonite and calcite minerals of $CaCO_3$ on the shell have been reported to be great alternative for metal removal with the high metal removal ability (Prieto et al., 2003; Du et al., 2011; Ismail et al., 2013). These materials contain high level of calcium ions which contributes to the increase of pH in the treated water (Li and Champagne, 2009; Ismail et al., 2013). This criteria has depicted a possible application for pH control in wastewater treatment process instead of using with chemical reagents.

In this study, dead calcerous skeletons were selected as the main material to remove Cd (II) and Pb (II) ions in the aqueous solutions. The constituent dead calcerous skeletons are mainly $CaCO_3$ with the combination mineral of calcite and aragonite (Matthews et al., 2008). The calcerous skeletons were reported to accumulate heavy metals in the seawater and were used as bio-indicator to detect the pollution level in the seawater (Esslemont, 1999; Ali et al., 2010; Mokhtar et al., 2012). The dead calcerous skeletons are harden and break into pieces by the hit of wave and usually washed to the coastal sandy shoreline by strong wave. The dead calcerous skeletons are abundantly available on the sandy beach and clearing is required to prevent the harden skeleton from destroying the live Scleractinian corals. The information of using dead calcerous skeletons as metal adsorbent is still very limited in the literature. Therefore, this study focused on this material as adsorbent to remove the metal ions in aqueous solutions. The study attempts to ascertain the efficiency of the dead calcerous skeletons by evaluating the affecting parameters, adsorbent size, dosage, solution pH, adsorbent bed height, flow rate and initial concentration. The investigations of influence parameters are very important in order to provide optimum performance of the adsorbent for potential application in the real treatment procedures. This works involved analytical analysis as well as integrating the data with mathematical theories and modeling to deliver the output of this study.

1.2 Problem Statement

Utilizing the waste materials for metal removal in the environment has been popularly studied in the recent time. The effectiveness of the waste materials from food, agriculture, and industries have reported to be good metal adsorbents but with respect of suitable factors and conditions apply. The wastes are readily available and abundant in raw conditions. However, the materials from food and agricultural waste especially, required certain steps for cleaning and preparation before use on the metal adsorption procedures (Liu et al., 2012; Liu et al., 2013). The raw materials cannot directly use for the metal removal due to the debris and contaminants from the previous process which can affect metal removal process and interrupt the removal performance (Liu et al., 2013). The searching for materials with criteria of cost-effective, less modification procedure and locally available is still actively conducted.

Many studies have also found that the adsorbent in raw or natural conditions do not high removal efficiency in removing heavy metal and the modification steps are required to further boost the effectiveness of the adsorbents. Modifications are conducted on the adsorbents either physically, chemically or both, depending on the characteristic of the raw adsorbent to improve the adsorption capacity. For the physical modifications, the adsorbents have to undergo process such as heating, encapsulation, reducing the particle size and impregnation to improve the specific surface area of the adsorbents in order to increase the removal efficiency in metal uptake (Chamarthy et al., 2001; Mohan and Pittman Jr, 2006; Randall, 2012; Srivastava et al., 2012). In the chemical modification process, the adsorbents are pre-treated by mixing with chemical reagents such as acid, base solutions and solvents to breakdown the cellulose and tannin to increase the porosity of the materials for better adsorption ability (Chamarthy et al., 2001; Mohan and Pittman Jr, 2006; Xie et al., 2012; Adeogun et al., 2013; Danish et al., 2013). The current adsorbent materials often rely on its specific surface area and the porosity for adsorption, thus, actions were taken to enhance this element (Tseng et al., 2006; Zhang et al., 2013). This explains when the surface is small and pore size is big, the adsorption efficiency of the adsorbents is usually low and need further improvement to increase the efficiency (Liu et al., 2010; Alslaibi et al., 2013; Gautam et al., 2014). All this enhancement procedures has increased the cost of the materials even when the raw materials are from waste, the expenses are invested on the additional chemical reagents, special equipments and techniques for the modification process.

Some of the current adsorbents studied in the literature are often required to control parameters such as pH, adsorbent size and metal initial concentrations. Some metals are pH depended and the adsorbent itself does not able to alter the solution pH to less acidic or neutral condition regarding the required pH value. Therefore, the pH of metal solution need to be adjusted initially to control the H^+ ions and metal species in the solutions before homogenizing with adsorbents (Hashem, 2007; Chaudhuri and Azizan, 2011). Certain adsorbents efficiency depends upon the particle size regarding the specific surface area (Patel, 2012). Thus, the adsorbents need to be prepared in the suitable uniform size ranging from course to clay size through crushing and grinding process. This procedure has lengthened the preparation periods of the adsorbents due to the involvement of extra strength for the workload. Besides, the current adsorbents have limitation to the metal initial concentration. The adsorbents studied in the literature are only able to remove the metal ions at a certain concentration range, extremely high or low concentrations are not successfully removed (Skubal et al., 2002). The dosage of the adsorbent also plays a role in the adsorption performance. The adsorbent dosage needs to be applied in the sufficient amount in order to achieve optimum removal. For some case, high dosage of adsorbent is required and sometimes even the dosage is in excessive amount, the adsorbents still do not able to uptake the high metal concentrations due to agglomeration of particles. Therefore, investigation on adsorbents with high metal removal efficiency and flexible characteristics are strongly needed to encounter the obstacles faced by the current low cost adsorbents in the literature.

Many studies only focus on the advantages of utilizing the inexpensive materials as metal adsorbent but the disadvantages were usually not mentioned in the literature. The area of improvement for using inexpensive materials should be identified to provide sustainable products for water treatment system. The usage perspectives of waste and low-cost materials as metal adsorbents in the recent literature were determined using NABC analysis (Needs, Approach, Benefits, and Competition) as shown in Table 1.1. The NABC analysis evaluated the situations occurred in the literature and provides beneficial strategies for this study to overcome the possible competitions faced by other researches.

Table 1.1 NABC outputs for the current adsorbents used in the recent literature

	Outputs
Needs	• Requirement of low cost and effective materials for metal removal process • Conventional treatment process requires further procedure to remove toxic contaminant • Increasing metal pollution in the environments required fast remediate solutions
Approach	• Simple application for the treatment process by using adsorption approach • Reuse waste materials from the previous production as metal adsorbents
Benefits	• Improvement in treated water quality • Safe water quality • Fast removal results • Alternatives for the treatment techniques
Competitions	• Certain materials require further modification before application • A large amount of materials required for treatment process. • Some materials only available for one-time usage and require frequent replacement

1.3 Objectives

Principally, the main aim of this study was to investigate the potential of dead calcerous skeletons in the removal of Cd (II) and Pb (II) ions from aqueous solution for the employment to the current wastewater treatment techniques. It also provides the information on the behaviors and capabilities of the adsorbent during the metals removal process including the properties of the materials. The research objectives are stated as follows:

i. To determine the optimal condition for the removal of Cd (II) and Pb (II) ions by dead calcerous skeletons under batch mode and continuous flow system
ii. To evaluate the isotherm models and parameters of adsorption process for the removal of Cd (II) and Pb (II) ions by dead calcerous skeletons
iii. To examine the relationship between the dead calcerous skeletons mineralogy and the adsorbed metal ions

1.4 Scopes of study

This study generally covers the area as follows:

i) This study focuses on the removal of Cd (II) and Pb (II) ions in aqueous solutions under batch system at the initial part of this work. The influence parameters on the removal activities were studied by evaluating the adsorbent size, dosage, solution pH, and initial metal concentrations. All this parameters were investigated to determine the adsorbent and metal behavior during the adsorption process.
ii) This study involved the identification of the life-span of the dead calcerous skeletons under continuous flow system with various conditions. The data were combined with related theories and adsorption models to further predict the performance of the adsorbent and the metal ions removal.
iii) This study also narrowed down to evaluate the distinctive characteristic and behavior between the adsorbent and the metal solutions. This study distinguished the extraordinary performance, assessed the weakness faced by the other literature and encountered the problems occurred in the current wastewater treatment methods.

1.5 Significance of study

The current adsorbents studies in the literature still have limitation on the metal removal with the requirement to control working parameters. This study aims to provide the current adsorption technique, a material with flexible and robust characteristics for possible usage in the real treatment process. The findings of this study offer a new alternative and opportunity for the current wastewater treatment technique in respect with the high removal capability and adaptable features. This study is conducted to target the weaknesses encountered in the recent literature for a better future perspectives of using low-cost materials. The outcome of this work serves as a transformation trend towards the utilization of biodegradable materials for the water treatment process. The expected outputs in this study provide metal remediation with harmless and user-friendly techniques as well as to produce green and sustainable water supply management.

Quantitative outputs from this study include: (i) the determination of dead calcerous skeletons removal efficiency as adsorbent for Cd (II) and Pb (II) ions and (ii) the distinctive characteristics of dead calcerous skeletons which opposed with the usual norms of the adsorbents. The performance of dead calcerous skeletons was evaluated in batch and continuous systems to identify the life-span of the adsorbents. The data integrated with mathematical theories and related models will offer further explanation and understanding to the adsorption mechanism present between the metal solutions and the adsorbents.

For the qualitative outputs include: (i) a green approach for application in acidic and high metal loading wastewater treatment (ii) improve the treated effluent quality and also the existing system iii) provide fast solution for metal removal with high removal efficiency. Besides, the findings from this study provide innovative solutions to the current metal adsorption literature and possible upgrade to the current treatment system. Metal adsorption by using eco-friendly materials presented in this study can be introduced to the real separation technologies in the industries as the research field in using low-cost products for metal removal is still actively going-on. This study served as pilot scale demonstration and can be brought to real scale application with the hybrid concept to the current installation.

1.6 Thesis outline

This thesis mainly consists of five chapters which are the Introduction, Literature Review, Materials and Methods, Results and Discussion, and Conclusion to provide information and behaviors of the dead calcerous skeletons as source of metal ions removal. The chapters of this thesis are arranged as the following flow. In the Chapter 1, a brief description was covered on the background study.

In Chapter 2, the extensive background literature related to this study was studies. The information of the toxicity of the metal pollutions was discussed in this chapter. A review was conducted on the materials used in the recent literature to compare the operation criteria and the adsorbents' performance. This chapter has been accepted and published as journal article by "Lim, A.P. and Aris, A.Z. (2014). A review on economically adsorbents on heavy metals removal in water and wastewater. *Reviews in Environmental Science and Bio/Technology*. 13(2): 163-181. (ISSN: 1569-1705) DOI 10.1007/s11157-013-9330-2 (IF 2012: 2.340)"

Chapter 3 consists of the materials and method implemented in this study. The dead calcerous skeletons were the main materials utilized throughout this study. The laboratory analysis applied in this study was divided to batch and column systems. The removal performances of the dead calcerous skeletons were determined by varying the affecting parameters. The date collected from the laboratory samples were analyzed by the related mathematical calculation and applied in modeling analysis. The characteristics of the calcerous skeletons were examined to determine the mechanism occurred between adsorbents and the metal ions.

Chapter 4, 5 and 6 cover the results and discussion obtained from the experimental and data analysis in this study which present in manuscript-style format. Theses chapters also evaluated based on the objectives in this studies. These chapters outlined the physical characteristics of the adsorbent and the influence parameters on the removal of Cd (II) and Pb (II) ions in aqueous solution. The efficiency of the dead calcerous skeletons was discussed by related isotherms and models. The findings in these chapters have been published as journal articles as well as under-reviewed by respective journals, "Lim, A.P. and Aris, A.Z. (2013). A novel approach for the adsorption of cadmium ions in aqueous solution by dead calcareous skeletons. *Desalination and Water Treatment*. 52: 3169-3177. DOI 10.1080/19443994.2013.798843 (ISSN: 1944-3994) (IF 2012: 0.852)", "Lim, A.P. and Aris, A.Z. Removal of lead (II) ions by using dead calcareous skeletons: Experimental studies on sorption performance and influence factors. *Environmental Technology* (Submitted) (ISSN: 1479-487X) (IF 2012: 1.606)", and "Lim, A.P. and Aris, A.Z. (2014). Continuous fixed-bed column study and adsorption modeling: Removal of cadmium (II) and lead (II) ions in aqueous solution by dead calcareous skeletons. *Biochemical Engineering Journal*. 87: 50-61. (ISSN: 1369-703x) (IF 2012: 2.579)".

Chapter 7 concluded the whole findings in this study. It draws a conclusion of the whole chapters and summarized the findings of chapter 4, 5 and 6. The removal efficiency of the dead calcerous in Cd (II) and Pb (II) ions were ascertained. The distinct characteristics of the dead calcerous skeletons were determined from the extensive analysis. SWOT analysis was performed to identify the advantages of this adsorbent and threats that can be avoided. Recommendations were presented in this chapter to provide possible application for the current wastewater treatment process.

REFERENCES

Abdulrasaq, O.O. and Basiru, O.G. (2010). Removal of copper (II), iron (III) and lead (II) ions from mono-component simulated waste effluent by adsorption on coconut husk. *African Journal of Environmental Science and Technology.* 4(6):382-387

Adeogun, A.I., Idowu, M.A., Ofudje, A.E., Kareem, S.O. and Ahmed, S.A. (2013). Comparative biosorption of Mn (II) and Pb (II) ions on raw and oxalic acid modified maize husk: kinetic, thermodynamic and isothermal studies. *Applied Water Science*. 3:167-179.

Ahmad, M., Lee, S.S., Oh, S.-E., Mohan, D., Moon, D.H., Lee, Y.H. and Ok, Y.S. (2013). Modeling adsorption kinetics of trichloroethylene onto biochars derived from soybean stover and peanut shell wastes. *Environmental Science Pollution Research*. DOI: 10.1007/s11356-013-1676-z

Ahmad, M., Usman, A.R.A., Lee, S.S., Kim, S.-C., Joo. J.-H., Yang, J.E. and Ok, Y.S. (2012). Eggshell and coral wastes as low cost adsorbents for the removal of Pb^{2+}, $Cd^{2+}$and Cu^{2+} from aqueous solutions. *Journal of Industrial and Engineering Chemistry.* 18:198-204.

Aksu, Z. and Gönen, F. (2004). Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochemistry*, 39:599-613.

Aksu, Z., Gonen, F. and Demircan, Z. (2002). Biosorption of chromium (VI) ions by Mowital†B30H resin immobilized activated sludge in a packed bed: comparison with granular activated carbon. *Process Biochemistry* 38: 175-186.

Alaerts, G.J., Jitjaturant, V. and Kelderman, P. (1989). Use of coconut shell based activated carbon for chromium (VI) removal. *Water Science and Technology.* 21(12):1701–1704.

Ali, A.A.M., Hames, M.A. and El-Azim, H.A. (2010). Trace metal distribution in the coral reef ecosystems of the Northern Red Sea. *Helgoland Marine Research*. 65 (1):67–80.

Aliabadi, M., Morshedzadeh, K. and Soheyli, H. (2006). Removal of hexavalent chromium from aqueous solution by lignocellulosic solid wastes. *Interntional Journal of Environmental Science and Technology.* 3(3): 321-325.

Almasi, A., Omidi, M., Khodadadian, M., Khamutian, R. and Gholivand, M.B. (2012). Lead (II) and cadmium (II) removal from aqueous using processed walnut shell: kinetic and equilibrium study. *Toxicological & Environmental Chemistry.* 94(4):660-671.

Alshaebi, F.A., Wan Yacoob, W.Z. and Shamsuldin, A.R. (2009). Sorption on zero-valent iron (ZVI) for arsenic removal. *European Journal of Scientific Research.* 33(2):214-219.

Alslaibi, T.M., Abustan, I., Ahmad, M.A. and Foul, A.A. (2013). A review: Production of activated carbon from agricultural byproducts via conventional and microwave heating. *Journal of Chemical Technology and Biotechnology*. 88(7):1183-1190.

Alwash, A.H., Abdullah, A.Z. and Ismail, N. (2012), Zeolite Y encapsulated with Fe-TiO_2 for ultrasound-assisted degradation of amaranth dye in water. *Journal of Hazardous Materials*. 233-234:184-193.

Al-Zboon, K., Al-Harahsheh, M.S., Hani, F.B. (2011). Fly ash-based geopolymer for Pb removal from aqueous solution. *Journal of Hazardous Materials*. 188:414-421.

Amuda, O.S., Giwa, A.A., Bello, I.A. (2007). Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochemical Engineering Journal*. 36:174-181.

APHA (2005) Standard methods for the examination of water and wastewater. 21st Edn. American Water Works Association, Water Environment Federation, Washington.

Apiratikul, R. and Pavasant, P. (2008). Batch and column studies of biosorption of heavy metal by *Caulerpa lentillifera*. *Bioresource Technology* 99: 2766-2777.

Appelo, C.A.J. and Postma, D. (2005). Geochemistry, groundwater and pollution. 2nd Edn. Balkema, Rotterdam.

Aredes, S., Klein, B. and Pawlik, M. (2012). The removal of arsenic from water using natural iron oxide minerals. *Journal of Cleaner Production.* 29-30:208-213.

Arunlertaree, C., Kaewsomboon, W., Kumsopa, A., Pokethitiyook, P. and Panyawathanakit, P. (2007). Removal of lead from battery manufacturing wastewater by egg shell. *Songklanakarin Journal of Science and Technology*. 29(3):857-868.

Asgari, G., Rahmani, A.R., Faradmal, J. and Mohammadi, A.M.S. (2012). Kinetic and isotherm of hexavalent chromium adsorption onto nano hydroxyapatite *Journal of Research in Health Sciences*. 12(1):45-53.

Aziz, H.A., Adlan, M.N. and Ariffin, K.S. (2007). Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr (III)) removal from water in Malaysia: Post treatment by high quality limestone. *Bioresource Technology.* 99: 1578-1583.

Bailey, S.E., Olin, T.J., Bricka, R.M. and Adrian, D.D. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research* 33(11): 2469-2479.

Balasubramanian, R., Perumal, S.V. and Vijayaraghavan, K. (2009). Equilibrium isotherm studies for the multicomponent adsorption of lead, zinc, and cadmium onto Indonesian Peat. *Industrial Engineering Chemical Research* 48:2093-2099.

Basu, A., Mahata, J., Gupta, S. and Giri, A.K. (2001). Genetic toxicology of a paradoxical human carcinogen, arsenic: a review. *Mutation Research.* 488:171–194.

Bhattacharya, P., Banerjee, P., Mallick, K., Ghosh, S., Majumdar, S., Mukhopadhyay, A. and Bandypadhyay, S. (2013). Potential of biosorbent developed from fruit peel of Trewia nudiflora for removal of hexavalent chromium from synthetic and industrial effluent: Analyzing phytotoxicity in germinating Vigna seeds. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering*. 48(7):706-719.

Bhuvaneshwari, S., Sruthi, D., Sivasubramanian, V., Kanthimathy, K. (2012). Regeneration of chitosan after heavy metal sorption. *Journal of Scientific & Industrial Research*. 71:266-269

Biney, C.A. and Ameyibor, E. (1992). Trace metal concentrations in the pink shrimp, Penaeus notialis from the coast of Ghana. *Water, Air, & Soil Pollution.* 63:273-279.

Bothe, J.V. and Brown, P.W. (1999). Arsenic Immobilization by Calcium Arsenate Formation. *Environmental Science and Technology*. 33:3806-3811.

Bueno, B.Y.M., Torem, M.L., Molina, F. and de Mesquita, L.M.S. (2008). Biosorption of lead (II), chromium (III) and copper (II) by *R. opacus*: Equilibrium and kinetic studies. *Minerals Engineering*. 21: 65-75.

Cao, J. and Zhang, W.X. (2006). Stabilization of chromium ore processing residue (COPR) with nanoscale iron particles. *Journal of Hazardous Materials.* 132:213-219.

Chakraborty, S., Chowdhury, S. and Saha, P.D. (2011). Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk. *Carbohydrate Polymers*. 86:1533-1541.

Chakraborty, S., Chowdhury, S. and Saha, P.D. (2012) Batch removal of Crystal Violet from aqueous solution by H_2SO_4 modified sugarcane bagasse: Equilibrium, kinetic, and thermodynamic profile. *Separation Science Technology*. 47(13):1898-1905.

Chamarthy, S., Seo, C.W., Marshall, W.E. (2001), Adsorption of selected toxic metals by modified peanut shells. *Journal of Chemical Technology and Biotechnology*. 76:593-597.

Champagne, P. and Li, C. (2009). Use of Sphagnum peat moss and crushed mollusk shells in fixed bed columns for the treatment of synthetic landfill leachate. *J Mater Cycles Waste Manag*. 11:339–347.

Chang, K.-L., Hsieh, J.-F., Ou, B.-M., Chang, M.-H., Hsieh, W.-Y., Lin, J.-H., Huang, P.-J., Wong, K.-F. and Dr. Chen, S.-T. (2012). Adsorption studies on the removal of an endocrine-disrupting compound (Bisphenol A) using activated carbon from rice straw agricultural waste. *Separation Science and Technology*. 47:1514-1521.

Chaudhuri, M. and Azizan, N.K. (2011). Adsorptive removal of chromium(VI) from aqueous solution by an agricultural waste based activated carbon. *Water, Air & Soil Pollution*. 223(4):1765–1771.

Chaudhuri, M., Mohamed, Kutty, S.R. and Yusop, S.H. (2010). Copper and Cadmium Adsorption by Activated Carbon Prepared from Coconut Coir. *Nature Environment and Pollution Technology*. 9(1):25-28.

Chen, G., Guan, S., Zeng, G., Li, X., Chen, A., Shang, C., Zhou, Y., Li, H. and He, J. (2012). Cadmium removal and 2, 4-dichlorophenol degradation by immobilized Phanerochaete chrysosporium loaded with nitrogen-doped TiO_2 nanoparticles. *Applied Microbiology and Biotechnology*. 97(7):3149-3157.

Chiban, M., Zerbet, M., Carja, G. and Sinan F. (2012). Application of low-cost adsorbents for arsenic removal: A review. *Journal of Environmental Chemistry and Ecotoxicology.* 4(5): 91-102.

Choi, J., Lee, J.Y. and Yang, J.S. (2007). Comparison of Fe and Mn Removal using treatment agents for acid mine drainage. *World Academy of Science, Engineering and Technology*. 28:186-188.

Cimino, G., Passerini, A. and Toscano, G. (2000). Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. *Water Research*. 34(11): 2955-2962.

Dahbi, S., Azzi, M., Saib, N., de la Guardia, M., Faure, R. and Durand, R. (2002). Removal of trivalent chromium from tannery waste waters using bone charcoal. *Analytical and Bioanalytical Chemistry*. 374:540-546.

Danish, M., Hashim, R., Ibrahim, M.N.M. and Sulaiman, O. (2013). Optimized preparation for large surface area activated carbon from date (*Phoenix dactylifera L.*) stone biomass. *Biomass and Bioenergy*. 61:167-178.

Das, D., Chatterjee, A., Mandal, B.K., Samanta, G. and Chakraborty, D. (1995). Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. *Analyst*. 120:917-924.

Dave, P.N., Pandey, N. and Thomas, H. (2012). Adsorption of Cr(VI) from aqueous solutions on tea waste and coconut husk. *Indian Journal of Chemical Technology* .19: 111-117.

Demirbas, A. (2008). Heavy metal adsorption onto agro-based waste materials: a review. *Journal of Hazardous Materials*. 157:220-229.

Demirbas, E., Kobya, M., Oncel, S. and Sencan, S. (2002). Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studie. *Bioresource Technology*. 84:291-293.

Demirbas, E., Kobya, M., Senturk, E. and Ozkan, T. (2004). Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. *Water SA*. 30:533-540.

Djukic´, A., Jovanovic´, U., Tuvic´, T., Andric´, V., Novakovic´, J.G., Ivanovic´, N. and Matovic´, L. (2013). The potential of ball-milled Serbian natural clay for removal of heavy metal contaminants from wastewaters: Simultaneous sorption of Ni, Cr, Cd and Pb ions. *Ceramics International*. 39(6):7138-7178.

Dorado, A.D., Gamisans, X., Valderrama, C., Solé, M. and Lao, C. (2014). Cr (III) removal from aqueous solutions A straightforward model approaching of the adsorption in a fixed-bed column. *Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering* 49(2): 179-186.

Du, Y., Lian, F. and Zhu, L. (2011). Biosorption of divalent Pb, Cd and Zn on aragonite and calcite mollusk shells. *Environmental Pollution* 159: 1763-1768.

Du, Y., Zhu, L. and Shan, G. (2012). Removal Cd^{2+} from contaminated water by nano-sized aragonite mollusk shell and the competition of coexisting metal ions. *Journal of Colloid and Interface Science*. 367:378-382.

Dzikiewicz, M. (2000). Activities in nonpoint pollution control in rural areas of Poland. *Ecological Engineering*. 14:429-434.

Eisazadeh, A., Eisazadeh, H. and Kassim, K.A. (2013). Removal of Pb(II) using polyaniline composites and iron oxide coated natural sand and clay from aqueous solution. *Synthetic Metals*. 171:56-61.

El Kinawy, O.S., El Moneim, N.A. and El Haron, D.E. (2012). The removal of heavy metal ions from wastewater using jojoba oil in a new technique. *Energy Sources, Part A*. 34(13):1169-1177.

El-Eswed, B., Alshaaer, M., Yousef, R.I., Hamadneh, I. and Khalili, F. (2012). Adsorption of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II) onto Kaolin/Zeolite based-geopolymers. *Advances in Materials Physics and Chemistry*. 2(4b):119-125.

Esslemont, G. (1999). Trace metal in corals from Heron Island and Darwin Harbour, Australia. *Marine Pollution Bulletin*. 38 (11):1051–1054.

Farinella, N.V., Matos, G.D. and Arruda, M.A.Z. (2007). Grape bagasse as a potential biosorbent of metals in effluent treatments. *Bioresource Technology*. 98:1940-1946.

Farinella, N.V., Matos, G.D., Lehmann, E.L. and Arruda, M.A.Z. (2008). Grape bagasse as an alternative natural adsorbent of cadmium and lead for effluent treatment. *Journal of Hazardous Materials* 154: 1007–1012.

Ferro-Garcia, M.A., Rivea-Utrilla, J., Rodriguez-Gordillo, J. and Bautista-Tolelo, I. (1988), Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products. *Carbon*. 26(3):363-373.

Foo, K.Y. and Hameed, B.H. (2011). Utilization of rice husks as a feedstock for preparation of activated carbon by microwave induced KOH and K_2CO_3 activation. *Bioresource Technology*. 102:9814-9817.

Friberg, L., Nordberg, G.F. and Vouk, V.B. (1986). Handbook of the toxicology of metals. Vol II, Elsevier, Amsterdam, pp 130-184.

Galendar, M. and Younesi, H. (2013). Biosorption of ternary cadmium, nickel and cobalt ions from aqueous solution onto *Saccharomyces cerevisiae* cells: Batch and column studies. *American Journal of Biochemistry and Biotechnology* 9(1): 47-60.

Gautam, R.K., Mudhoo, A., Lofrano, G. and Chattopadhyaya, M.C. (2014), Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. *Journal of Environmental Chemical Engineering*. 2(1): 239-259.

Gerritse, R.G. (1996). Column-and catchment-scale transport of cadmium: effect of dissolved organic matter. *Journal of Contaminant Hydrology*. 22:145-163.

Gheju, M., Iovi, A. and Balcu, I. (2008). Hexavalent chromium reduction with scrap iron in continuous flow system. Part 1: effect of feed solution pH. *Journal of Hazardous Materials.* 153:655-662.

Glasser, F.P. (1997). Fundamental aspects of cement solidification and stabilization. *Journal of Hazardous Materials*. 52:151-170.

Goel, J., Kadirvelu, K., Rajagopal, C. and Garg, V.K. (2005). Removal of lead (II) by adsorption using treated granular activated carbon: Batch and column studies. *Journal of Hazardous Materials.* B125: 211-220.

Gonte, R. and Balasubramanian, K. (2013). Heavy and toxic metal uptake by mesoporous hypercrosslinked SMA beads: Isotherms and kinetics. *Journal of Saudi Chemical Society*. http://dx.doi.org/10.1016/j.jscs.2013.04.003

Grieco, S.A. and Ramarao, B.V. (2013). Removal of TCEP from aqueous solutions by adsorption with zeolites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. 434:329-338.

Grover, V.A., Hu, J., Engates, K.E. and Shipley, H.J. (2012). Adsorption and desorption of bivalent metals of hematite nanoparticles. *Environmental Toxicology and Chemistry*. 31(1):86-92.

Gupta, V.K. and Suhas (2009). Application of low cost adsorbents for dye removal-A review. *Journal of Environmental Management.* 90:2313-2342.

Hadi, A.G. (2012). Adsorption of Cd(II) ions by synthesize chitosan from fish shells. *British Journal of Science*. 5(2):33-38.

Hamadi, N.K., Chen, X.D., Farid, M.M. and Lu, M.G.Q. (2001). Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tyres and sawdust. *Chemical Engineering Journal*. 84(2):95-105.

Hammond, P.B. and Aronson, A.L. (1964). Lead poisoning in cattle and horses in the vicinity of a smelter. *Annals of New York Academy of Sciences.* 111: 595-611.

Hansen, H.K., Arancibia, F. and Gutiérrez, C, (2010). Adsorption of copper onto agriculture waste. *Journal of Hazardous Materials*. 180: 442-448.

Hasani, T. and Eisazadeh, H. (2013). Removal of Cd (II) by using polypyrrole and its nanocomposites. *Synthetic Metals*. 175:15-20.

Hashem, M.A. (2007), Adsorption of lead ions from aqueous solution by okra wastes. *International Journal of Physical Sciences*. 2(7):178-184.

Hassan, S.S.M., Awwad, N.S. and Aboterika, A.H.A. (2007). Removal of mercury (II) from wastewater using camel bone charcoal. *Journal of Hazardous Materials.* 154:992-997.

Helios-Rybicka, E. and Wójcik, R. (2012). Competitive sorption/desorption of Zn, Cd, Pb, Ni, Cu, and Cr by clay-bearing mining wastes. *Applied Clay Science*. 65-66:6-13.

Hossain, M.A., Ngo, H.H., Guo, W.S. and Nguyen, T.V. (2012). Removal of copper from water by adsorption onto banana peel as bioadsorbent. *International Journal of GEOMATE*. 2(2):227-234.

Hsien, T.-Y. and Liu, Y.-L. (2012). Desorption of cadmium from porous chitosan beads. *Advancing Desalination*. DOI:10.5772/50142.

Hu, Q., Sun, X., Yang, W., Fang, Y., Ma, N., Xin, Z., Fu, J., Liu, X., Mariga, A.M. and Zhu, X. (2013). Concentrations and health risks of lead, cadmium, arsenic, and mercury in rice and edible mushrooms in China. *Food Chemistry*. 147:147-151.

Ideriah, T.J.K., David, O.D. and Ogbonna, D.N. (2012). Removal of heavy metal ions in aqueous solutions using palm fruit fibre as adsorbent. *Journal of Environmental Chemistry and Ecotoxicology*. 4(4):82-90.

Ismail F.A., Aris A.Z. and Latif P.A. (2013). Dynamic behaviour of Cd^{2+} adsorption in equilibrium batch studies by $CaCO_3^-$ -rich Corbicula fluminea shell. *Environmental Science Pollution Research*. 21:344-354.

Issabayeva, G., Aroua, M.K. and Sulaiman N.M. (2010). Study on palm shell activated carbon adsorption capacity to remove copper ions from aqueous solutions. *Desalination*. 262:94-98.

Jain, M., Garg, V.K. and Kadirvelu, K. (2013). Chromium removal from aqueous system and industrial wastewater by agricultural wastes. *Bioremediation Journal*. 17(1):30-39.

Javadi, N., Raygan, S.H. and Seyyed Ebrahimi, S.A. (2012). Production of Nanocrystalline Magnetite for Adsorption of Cr (VI) Ions, 2nd International Conference on Ultrafine Grained Nanostructured Materials (UFGNSM). World Scientific Publishing Company, International Journal of Modern Physics: Conference Series 5:771–783.

Jayakumar, S., Gomathi, T. and Sudha, P.N. (2013). Sorption studies of lead (II) onto cross linked and non cross linked bio polymeric blends. *Biological Macromolecules.* DOI:10.1016/j.ijbiomac.2013.04.031

Jiang, Y.N., Ruan, H.D., Lai, S.Y., Lee, C.H., Yu, C.F., Wu, Z., Chen, X. and He, S. (2013). Recycling of solid waste material in Hong Kong: I. Properties of modified clay mineral waste material and its application for removal of cadmium in water. *Earth Science*. 2(2):40-46.

Jing, C., Korfiatis, G.P. and Meng, X. (2003). Immobilization mechanisms of arsenate in iron hydroxide sludge stabilized with cement. *Environmental Science and Technology*. 37:5050-5056.

Johan, N.A., Kutty, S.R.M., Isa, M.H., Muhamad, N.S. and Hashim, H. (2011). Adsorption of copper by using microwave incinerated rice husk ash (MIRHA). *International Journal of Civil and Environmental Engineering*. 3(3): 211-215.

Kadimpati, K.K., Mondithoka, K.P., Bheemaraju, S. and Challa, V.R.M. (2012). Entrapment of marine microalga, Isochrysis galbana, for biosorption of Cr(III) from aqueous solution: isotherms and spectroscopic characterization. *Applied Water Science*. 3(1):85-92.

Kakalanga, S.J., Jabulani, X.B., Olutoyin, O.B. and Utieyin, O.O. (2012). Screening of agricultural waste for Ni(II) adsorption: Kinetics, equilibrium and thermodynamic studies. *International Journal of the Physical Sciences*. 7(17):2525-2538.

Kannan, N. and Veemaraj, T. (2009). Removal of lead (II) ions by adsorption onto bamboo dust and commercial activated carbons - A comparative study. E-*Journal of Chemistry* 6(2): 247-256.

Karadede, H. and Unlu, E. (1999). Concentrations of some heavy metals in water, sediment and fish species from the Ataturk Dam Lake (Euphrates), Turkey. *Chemosphere*. 41:1371-1376.

Karthikeyan, T., Rajgopal, S. and Miranda, L.R. (2005), Chromium (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. *Journal of Hazardous Materials*. B124:192-199.

Khosravihaftkhany, S., Morad, N., Teng, T.T., Abdullah, A.Z. and Norli, I. (2013). Biosorption of Pb (II) and Fe (III) from aqueous solutions using oil palm biomasses as adsorbents. *Water, Air and Soil Pollution*. 224(1455): 1-14.

Kim, K.-R., Lee, B.-T. and Kim, K.-W. (2011). Arsenic stabilization in mine tailing using nano-sized magnetite and zero valent iron with enhancement of mobility by surface coating. *Journal of Geochemical Explor*ation. 113: 124-129.

Kim., S.A., Kamala-Kannan, S., Lee, K.-J., Park, Y.-J., Shea, P.J., Lee, W.-H., Kim, H.-M. and Oh, B.-T. (2012). Removal of Pb (II) from aqueous solution by a zeolite-nanoscale zero-valent iron composite. *Chemical Engineering Journal*. DOI: http://dx.doi.org/10.1016/j.cej.2012.11.097

Kırbıyık, Ç., Kılıç, M., Çepelioğullar, Ö. and Pütün, A.E. (2012). Use of sesame stalk biomass for the removal of Ni (II) and Zi (II) from aqueous solutions. *Water Science & Technology*. 66.2:231-238.

Kobya, M. (2004). Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. *Bioresource Technology*. 91(3):317-321.

Kobya, M., Demirbas. E., Senturk, E. and Ince, M. (2005). Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresource Technology*. 96:1518–1521.

Kohler, S.J., Cubillas, P., Rodriguez-Blanco, J.D., Bauer, C., Prieto, M. (2007). Removal of cadmium from wastewaters by aragonite shells and the influence of other divalent cations. *Environmental Science and Technology*. 41: 112-118.

Kour, J., Homagai, P.L., Pokhrel, M.R. and Ghimire, K.N. (2012). Adsorptive separation of metal ions with surface modified Desmostachya bipinnata. Nepal *Journal of Science and Technology.* 131(1):101-106.

Krishnan, K.A. and Anirudhan, T.S. (2003). Removal of cadmium (II) from aqueous solutions by steamactivated sulphurised carbon prepared from sugar-cane bagasse pith: Kinetic and equilibrium studies. *Water SA*. 29(2): 147-156.

Kumar, P., Rao, R., Chand, S., Kumar, S., Wasewar K.L. and Yoo, C.K. (2013). Adsorption of lead from aqueous solution onto coir-pith activated carbon. *Desalination and Water Treatment*. 51(13-15): 2529-2535.

Kumar, P.S., Ramalingam, S., Abhinaya, R.V., Kirupha, S.D., Murugesan, M. and Sivanesan, S. (2012). Adsorption of metal ions onto the chemically modified agricultural waste. *Clean – Soil, Air, Water.* 40(2):188–197.

Kumar, U. and Bandyopadhyay, M. (2006). Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource Technology.* 97: 104-109.

Kurniawan, T.A., Chan, G.Y.S., Lo, W.-H. and Babel, S., (2005). Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of Total Environment.* 366: 409-426.

Lee, M.-Y., Park, J.M. and Yang, J.-W. (1997). Micro precipitation of lead on the surface of crab shell particles. *Process Biochemistry* 32(8): 671-677.

Lee, S.M. and Davis, A.P. (2001). Removal of Cu (II) from aqueous solution by seafood processing waste sludge. *Water Research* 35(2): 534-540.

Lee, S.-M., Tiwari, D., Choi, K.-M., Yang, J.-K., Chang, Y.-Y. and Lee, H.-D. (2009). Removal of Mn (II) from aqueous solutions using manganese-coated sand samples. *Journal of Chemical Engineering Data*. 54(6):1823-1828.

Li, C. and Champagne, P. (2009). Fixed-bed column study for the removal of cadmium (II) and nickel (II) ions from aqueous solutions using peat and mollusk shells. *Journal of Hazardous Materials.* 171: 872-878.

Li, Q., Wang, Q., Chai, L. and Qin, W. (2012a). Cadmium (II) adsorption on esterified spent grain: equilibrium modeling and possible mechanisms. *Chemical Engineering Journal*. 197:173-180.

Li, S.J., Li, T.L., Xiu, Z.M. and Jin, Z.H. (2010b). Reduction and immobilization of chromium (VI) by nanoscale Fe^0 particles supported on reproducible PAA/PVDF membrane. *Journal of Environmental Monitoring*. 12:1153-1158.

Li, X.Q., Cao, J. and Zhang, W.X. (2008). Stoichiometry of Cr(VI) immobilization using nanoscale zerovalent iron (nZVI): a study with high-resolution X-ray photoelectron spectroscopy (HR-XPS). *Industrial & Engineering Chemistry Research*. 47:2131-2139.

Li, Y., Jin, Z., Li, T. and Ziu, Z. (2012b). One-step synthesis and characterization of core-shell Fe@SiO_2 nanocomposite for Cr (VI) reduction. *Science of the Total Environment*. 421-422: 260-266.

Li, Y.C., Jin, Z.H., Li, T.L. and Li, S.J. (2011). Removal of hexavalent chromium in soil and groundwater by supported nano zero-valent iron on silica fume. *Water Sci Technol*. 63:2781-2787.

Li, Y.S., Church, J.S., Woodhead, A.L. and Moussa, F. (2010a), Preparation and characterization of silica coated iron oxide magnetic nano-particles. *Spectrochim Acta Part A*. 76:484-489.

Liang, Z.Z., Mei, M.H., Hua, Z.R., Xin, G.Y. and Fu, Z.J. (2007). Removal of cadmium using MnO_2 loaded D301 resin. *Journal of Environmental Sciences*. 19:652-656.

Lim, A.P. and Aris, A.Z. (2013). A novel approach for the adsorption of cadmium ions in aqueous solution by dead calcareous skeletons. *Desalination and Water Treatment*. 52:3169-3177.

Lim, L.B.L., Priyantha, N., Tennakoon, D.T.B. and Dahri, M.K. (2012). Biosorption of cadmium (II) and copper(II) ion from aqueous solution by core of Artocarpus odoratissimus. *Environmental Science and Pollution Research*.19 (8):3250-3256.

Liu, C., Ngo, H.H., Guo, W. and Tung, K. (2012). Optimal conditions for preparation of banana peels, sugarcane bagasse and watermelon rind in removing copper from water. *Bioresource Technology*. 119:349-354.

Liu, Q.-S., Zheng, T., Li, N., Wang, P. and Abulikemu, G. (2010). Modification of bamboo-based activated carbon using microwave radiation and its effects on the adorption of methylene blue. *Applied Surface Science*. 256:3309-3315.

Liu, T.Y., Zhao, L. and Wang, Z.L. (2012). Removal of hexavalent chromium from wastewater by Fe^0-nanoparticles-chitosan composite beads: characterization, kinetics and thermodynamics. *Water Science & Technology*. 66.5:1044-1051.

Liu, T.Y., Zhao, L., Sun, D.S. and Tan, X. (2010a). Entrapment of nanoscale zero-valent iron in chitosan beads for hexavalent chromium removal from wastewater. *Journal of Hazardous Materials*. 184:724-730.

Liu, W., Liu, Y., Tao, Y., Yu, Y., Jiang, H. and Lian, H. (2013). Comparative study of adsorption of Pb (II) on native garlic peel and mercerized garlic peel. *Environmental Science Polluion Research*. 21(3): 2054-2063.

Liu, Y., Sun, C., Xu, J. and Li, Y. (2009), The use of raw and acid-pretreated bivalve mollusk shells to remove metals from aqueous solutions. *Journal of Hazardous Materials*. 168:156-162.

Malkoc, E. and Nuhoglu, Y. (2006). Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed-bed column. *Journal Hazardous Materials*. B135: 328-336.

Manasi, V., Rajesh, A.S.K., Kumar, N. and Rajesh (2013). Biosorption of cadmium using novel bacterium isolated from an electronic industry effluent. *Chemical Engineering Journal*. http://dx.doi.org/10.1016/j.cej.2013.09.016

Martinez-Juarez, V.M., Cardenas-Gonzalez, J.F., Torre-Bouscoulet, M.E. and Acosta-Rodriguez, I. (2012). Biosorption of Mercury(II) from aqueous solutions onto fungal biomass. *Bioinorganic Chemistry and Applications*. DOI:10.1155/2012/156190.

Matthews, K.A., McDonough, W.F. and Grottoli, A.G. (2006). Cadmium measurements in coral skeleton using isotope dilution–inductively coupled plasma–mass spectrometry. *Geochemistry Geophysics Geosystems* 7(11): Q11021. DOI:10.1029/2006GC001352.

Matusik, J. and Bajda, T. (2013). Immobilization and reduction of hexavalent chromium in the interlayer space of positively charged kaolites. *Journal of Colloid and Interface Science.* 398:74-81.

Meunier, N., Laroulandie, J., Blais, J.F. and Tyagi, R.D. (2003). Cocoa shells for heavy metal removal from acidic solutions. *Bioresource Technology.* 90: 255-263.

MOH (2010). National Standard for Drinking Water Quality (NSDWQ). Engineering Services Division, Ministry of Health Malaysia, Kuala Lumpur, Malaysia.

Mohan, D. and Pittman, Jr. C.U. (2006), Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water. *Journal of Hazardous Materials*. B137:762-811.

Mohanty, K., Jha, M., Meikap, V. and Biswas, M.N. (2005). Removal of chromium(VI) from dilute aqueous solutions by activated carbon developed from Terminalia arjuna nuts activated with zinc chloride. *Chemical Engineering Science*. 60(11): 3049-3059.

Mokhtar, M.B., Praveena, S.M., Aris, A.Z., Yong, Q.C. and Lim, A.P. (2012). Trace metal (Cd, Cu, Fe, Mn, Ni and Zn) accumulation in Scleractinian corals: A record for Sabah, Borneo. *Marine Pollution Bulletin* 64(11): 2556-2563.

Moon DH, Wazne M, Yoon I-H, Grubb DG (2008) Assessment of cement kiln dust (CKD) for stabilization/solidification (S/S) of arsenic contaminated soils. Journals of Hazardous Materials 159: 512-518.

Moon, D.H., Kim, K.W., Yoon, I.H., Grubb, D.G., Shin, D.Y., Cheong, K.H., Choi, H.I., Ok, Y.S. and Park, J.H. (2011). Stabilization of arsenic-contaminated mine tailings using natural and calcined oyster shells. *Environmental Earth Sciences.* 64:597–605.

Moreno-Pirajan, J.C. and Giraldo, L. (2012). Heavy metal ions adsorption from wastewater using activated carbon from orange peel. *E-Journal of Chemistry.* 9(2):926-937.

Nagy, B., Măicăneanu, A., Indolean, C., Mânzatu, C., Silaghi-Dumitrescu, L. and Majdik, C. (2013). Comparative study of Cd (II) biosorption on cultivated *Agaricus bisporus* and wild *Lactarius piperatus* based biocomposites. Linear and nonlinear equilibrium modeling and kinetics. *Journal of the Taiwan Institute of Chemical Engineers*. 45(3):921-929.

Naiya, T.K., Bhattacharya, A.K. and Das, S.K. (2009). Adsorption of Cd(II) and Pb(II) from aqueous solutions on activated alumina. *Journal of Colloid and Interface Science*. 333:14-26.

Nomanbhay, S.M. and Palanisamy, K. (2005). Removal of heavy metal from industrial wastewater using chitosan coated oil palm charcoal. *Electronic Journal of Biotechnology of Biotechnology*. 8(1): 43-53.

Ofomaja, A.E. and Naidoo, E.B. (2010). Biosorption of lead (II) onto pine cone powder: Studies on biosorption performance and process design to minimize biosorbent mass. *Carbohydr. Polym*. 82: 1031-1042.

Ok, Y.S., Oh, S.E., Ahmad, M., Hyun, S., Kim, K.R., Moon, D.H., Lee, S.S., Lim, K.J., Jeon, W.T. and Yang, J.E. (2010), Effects of natural and calcined oyster shells on Cd and Pb immobilization in contaminated soils. *Environ Earth Sci.* 61:1301-1308.

Olgun, A., Atar, N. and Wang, S. (2013). Batch and column studies of phosphate and nitrate adsorption on waste solids containing boron impurity. *Chemical Engineering Journal.* 222:108-119.

Olu-owolabi, B.I., Pputu, O.U., Adebowale, K.O., Ogunsolu, O. and Olujimi, O.O. (2012). Biosorption of Cd^{2+} and Pb^{2+} ions onto mango stone and cocoa pod waste: Kinetic and equilibrium studies. *Scientific Research and Essays*. 7(15):1614-1429.

Omri, A. and Benzina, M. (2013). Adsorption characteristics of silver ions onto activated carbon prepared from almond shell. *Desalination and Water Treatment*. 51:2317-2326.

Owlad, M., Aroua, M.K. and Daud, W.M.A.W. (2010). Hexavalent chromium adsorption n impregnated palm shell activated carbon with polyethylenemine. *Bioresource Technology.* 101(14): 5098-5103.

Pal, P., Chakraborty, S. and Roy, M. (2012). Arsenic separation by a membrane-integrated hybrid treatment system: modeling, simulation, and techno-economic evaluation. *Separation Science and Technology*. 47:1091-1101.

Panthi, S.R. and Wareham, D.G. (2011), Removal of arsenic from water using the adsorbent: New Zealand iron-sand. *Journal of Environmental Science and Health, Part A*. 46(13):1533-1538.

Papageorgiou, S.K., Kouvelos, E.P., and Katsaros, F.K. (2008). Calcium alginate beads from Laminaria digitata for the removal of Cu^{2+} and Cd^{2+} from dilute aqueous metal solutions. *Desalination* . 224: 293-306.

Papageorgiou, S.K., Kouvelos, E.P., and Kanellopoulos, N.K. (2009). Prediction of binary adsorption isotherms of Cu^{2+}, Cd^{2+} and Pb^{2+} on calcium alginate beads from single adsorption data. *Journal of Hazardous Materials.* 162:1347-1354.

Park, H.J., Jeong, S.W., Yang, J.K., Kim, B.G. and Lee, S.M. (2007). Removal of heavy metals using waste eggshell. *Journal of Environmental Sciences*. 19: 1436-1441.

Park, S.-J., Jang, Y.-S., Shim, J.-W. and Ryu, S.-K. (2003). Studies on pore structures and surface functional groups of pitch-based activated carbon fibers. *Journal of Colloid and Interface Science*. 260(2): 259-264.

Parkhurst, D.L. and Appelo, C.A.J. (1999).User's Guide to PHREEQC (Version 2)- A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water-Resources Investigations Report 99-4259, U.S. Geological Survey, Denver, Colorado.

Patel, S. (2012). Potential of fruit and vegetable wastes as novel biosorbents: summarizing the recent studies. *Reviews in Environmental Science and Bio/Technology*. 11:365-380.

Patil, Y.B. (2012). Development of a low-cost industrial waste treatment technology for resource conservation-An urban case study with gold-cyanide emanated from SMEs. *Procedia-Social and Behavioral Sciences*. 37:379-388.

Patterson, J.W., Allen, H.E., Scala, J.J. (1977). Carbonate precipitation for heavy metals pollutants. *Journal (Water Pollution Control Federation)*. 49(12):2397-2410.

Periasamy, K. and Namasivayam, C. (1996). Removal of Copper(II) by Adsorption onto peanut hull carbon from water and copper plating industry wastewater. *Chemosphere*. 32(4): 769-789.

Pilli, S.R., Goud, V.V. and Mohanty, K. (2012). Biosorption of Cr (VI) on immobilized Hydrilla verticillata in a continuous up-flow packed bed:prediction of kinetic parameters and breakthrough curves. *Desalination and Water Treatment.* 50(1-3): 115-124.

Pitakpoolsil, W. and Hunsom, M. (2013). Adsorption of pollutants from biodiesel wastewater using chitosan flakes. *Journal of the Taiwan Institute of Chemical Engineers* 44(6):963-971.

Ponder, S.M., Darab, J.G. and Mallouk, T.E. (2000). Remediation of Cr (VI) and Pb (II) aqueous solutions using supported, nanoscale zero-valent iron. *Environ Sci Technol*. 34:2564-2569.

Pontoni, L. and Fabbricino, M. (2012), Use of chitosan and chitosan-derivatives to remove arsenic from aqueous solutions-A mini review. *Carbohydrate Research*. DOI:10.1016/j.carres.2012.03.042.

Praveena, S.M., Aris, A.Z. (2009). A review of groundwater in islands using SWOT analysis. World Review of Science. *Technology and Sustainable Development* 6(2/3/4):186-203.

Prieto, M., Cubillas, P. and Andez-Gonzalez, A.F. (2003). Uptake of dissolved Cd by biogenic and abiogenic aragonite: a comparison with sorption onto calcite. *Geochimica et Cosmochimica Acta* 67(20): 3859-3869.

Prieto-Rodrígue, L., Oller, I., Klamerth, N., Agüera, A., Rodríguez, E.M. and Malato, S. (2013). Application of solar AOPs and ozonation for elimination of micropollutants in municipal wastewater treatment plant effluents. *Water Research*. 47(4): 1521-1528.

Quintela, S., Villaran, M.C., Lopez De Armentia, I. and Elenjalde, E. (2012). Ochratoxin A removal from red wine by several oenological fining agents: bentonite, egg albumin, allergen-free adsorbents, chitin and chitosan. *Food Additives & Contaminants: Part A*. 29(7):1168-1174.

Radnia, H., Ghoreyshi, A.A., Younnesi, H. and Najafpour, G.D. (2012). Adsorption of Fe (II) ions from aqueous phase by chitosan adsorbent: equilibrium, kinetic, and thermodynamic studies. *Desalination and Water Treatment*. 50:348-359.

Radojević, M. and Bashkin, V.N. (2007). Practical environmental analysis. Royal Society of Chemistry, United Kingdom.

Rahman, M.A., Rahman, M.A., Samad, A. and Alam, A.M.S. (2008). Removal of arsenic with oyster shell: Experimental measurements. *Pak J Anal Environ Chem.* 9(2):69-77.

Ramesh, S.T., Rameshbabu, N., Gandhimathi, R., Kumar, M.S. and Nidheesh, P.V. (2013). Adsorption removal of Pb (II) from aqueous solution using nano-sized hydroxyapatite. *Appl. Water Sci*. 3: 105-113.

Randall, P.M. (2012). Arsenic encapsulation using Portland cement with ferrous sulfate/lime and Terra Bond^{TM} technologies-Microcharacterization and leaching studies. *Science of the Total Environment*. 420:300-312.

Reddy, K.J., McDonald, K.J. and King, H. (2013). A novel arsenic removal process for water using cupric oxide nanoparticles. *Journal of Colloid and Interface Science*. 397:96-102.

Rehman, R., Kanwal, F., Anwar, T. and Mahmud, T. (2011). Adsorption studies of cadmium (ii) using novel composites of polyaniline with rice husk and saw dust of eucalyptus camaldulensis. *EJ EAF Che* 10(10):12972-2985.

Reichelt-Brushett, A.J. and McOrist, G. (2003). Trace metals in the living and nonliving components of scleractinian corals. *Marine Pollution Bulletin.* 46: 1573-1582.

Rivera-Utrilla, J., Bautista-Toledo, I., Ferro-Garcia, M.A. and Moreno-Castilla (2001). Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption. *Journal of Chemical, Technology and Biotechnology*. 76:1209-1215.

Saifuddin, M.N. and Kumaran, P. (2005). Removal of heavy metal from industrial waste water using Chitosan coated oil palm shell charcoal. *Environ. Biol.* 8(1): 1-13.

Saka, C., Şahin, Ö., Demir, H. and Kahyaoğlu., M. (2011). Removal of lead (II) from aqueous solutions using pre-boiled and formaldehyde-treated onion skins as a new adsorbent. *Separation Science and Technology*. 46: 507-517.

Saleh, T.A., Gupta, V.K. and Al-Saadi, A.A. (2013). Adsorption of lead ions from aqueous solution using porous carbon derived from rubber tires: Experimental and computational study. *Journal of Colloid and Interface Science*. 396: 264-269.

Sanchez, A.G., Ayuso, E.A. and Blas, J.D. (1999). Sorption f heavy metals from industrial waste water by low-cost mineral silicates. *Clay Minerals*. 34:469-477.

Saravanane, R., Sundararajan, T. and Sivamurthy Reddy, S. (2001), Chemically modified low cost treatment for heavy metal effluent management. *Environmental Management and Health*. 12(2):215-224.

Sarmani, S. (1989), The determination of heavy metals in water, suspended materials and sediments from Langat River, Malaysia. *Hydrobiologia*. 176/177:233-238.

Sdiri, A. and Higashi, T. (2012). Simultaneous removal of heavy metals from aqueous solution by natural limestones. *Applied Water Science*. 3(1):29-39.

Sdiri, A., Higashi, T., Hatta, T., Jamoussi, F. and Tase, N. (2011). Evaluating the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals in aqueous systems. *Chemical Engineering Journal* 172: 37-46.

Seco-Reigosa, N., Peña-Rodríguez, S., Nóvoa-Muñoz, J.C., Arias-Estévez, M., Fernández-Sanjurjo, M.J., Álvarez-Rodríguez, E. and Núñez-Delgado, A. (2012). Arsenic, chromium and mercury removal using mussel Shell ash or a sludge/ashes waste mixture. *Environmental Science and Pollution Research*. 20(4):2670-2678.

Selomulya, C., Meeyoo, V. and Amal, R. (1999). Mechanisms of Cr(VI) removal from water by various types of activated carbons. *Journal of Chemical Technology and Biotechnology*. 74(3):111-122.

Sen, T.K., Mohammod, M., Maitra, S., Dutta, B.K. (2010), Removal of cadmium from aqueous solution using castor seed hull: A kinetic and equilibrium study. *Clean-Soil, Air, Water*. 38(9):850-858.

Sewwandi, B.G.N., Vithanage, M., Wijesekara, S.S.R.M.D.H.R., Mowjood, M.I.M., Hamamoto, S., Kawamoto, K. (2014). Adsorption of Cd (II) and Pb (II) onto humic acis-treated coconut (*Cocos nucifera*) Husk. *Journal of Hazardous, Toxic, and Radioactive Waste*. 18(2):04014001.

Sharma, Y.C., Uma, Singh, S.N., Paras and Goded, F. (2007). Fly ash for the removal of Mn(II) from aqueous solutions and wastewaters. *Chemical Engineering Journal*. 132:319-323.

Singh, D., Gupta, R. and Tiwari, A. (2012). Potential of duckweed (Lemna minor) for removal of lead from wastewater by phytoremediation. *Journal of Pharmacy Research*. 5(3):1578-1582.

Singh, T.S. and Pan, K.K. (2006). Solidification/stabilization of arsenic containing solid wastes using portland cement, fly ash and polymeric materials. *Journal of Hazardous Materials*. B131: 29-36.

Singha, B. and Das, S.K. (2011). Biosoprtion of Cr(VI) from aqueous solutions: Kinetics, equilibrium, thermodynamics and desorption studies. *Colloids and Surfaces B:Biointerfaces*. 84:221-232.

Skubal, L.R., Meshkov, N.K., Rajh, T., Thurnauer, M. (2002), Cadmium removal from water using thiolactic acid-modified titanium dioxide nanoparticles. *Journal of Photochemistry and Photobiology A: Chemistry*. 148: 93-397.

Sreenivas, K.M., Inarkar, M.B., Gokhale, S.V. and Lele, S.S. (2014). Re-utilization of ash gourd (*Benincasa hispida*) peel waste for chromium (VI) biosorption: Equilibrium and column studies. *Journal of Environmental Chemical Engineering*. http://dx.doi.org/10.1016/j.jece.2014.01.017.

Srivastava, V., Weng, C.-H. and Sharma, Y.C. (2012). Application of a thermally modified agrowaste material for an economically viable removal of Cr (VI) from aqueous solutions. *Journal of Hazardous, Toxic, and Radioactive Waste*. 17(2):125-133.

Sud, D., Mahajan, G. and Kaur, M.P. (2008). Agricultural waste materials as potential adsorbent for sequestering heavy metal ions from aqueous solutions-A review. *Bioresource Technology*. 99:6017-6027.

Sugashini, S. and Begum, K.M.M.S. (2013). Optimization using central composite design (CCD) for the biosorption of Cr (VI) ions by cross linked chitosan carbonized rice husk (CCACR). *Clean Technologies and Environmental Policy*. 15:293-302.

Suteu, D., Bilba, D., Aflori, M., Doroftei, F., Lisa, G., Badeanu, M. and Malutan, T. (2012). The Seashell wastes as biosorbent for reactive dye removal from textile effluents. *Clean-Soil, Air, Water*. 40(2):198-205.

Tan, W.T., Ooi, S.T. and Lee, C.K. (1993). Removal of chromium (VI) from solution by coconut husk and palm pressed fibres. *Environmental Technology*. 14(3):277-282.

Tandon, O.K., Shukla, R.C. and Singh, S.B. (2013). Removal of arsenic (III) from water with clay supported zero valent iron nanoparticles synthesized with the help of tea liquor. *Industrial & Engineering Chemistry Research.* DOI:10.1021/ie400702k.

Tang, W., Li, Q., Gao, S. and Shang, J.K. (2011). Arsenic (III, V) removal from aqueous solution by ultrafine α-Fe_2O_3 nanoparticles synthesized from solvent thermal method. *Journal of Hazardous Materials*. 192:131-138.

Thomas, H.C. (1944). Heterogeneous ion exchange in a flowing system. *Journal of the American Chemical Society*. 66(10):1664-1666.

Tomar, V., Prasad, S. and Kumar, D. (2013). Adsorptive removal of fluoride from water samples using Zr-Mn composite material. *Microchemical Journal*. DOI: 10.1016/j.microc.2013.04.007.

Tong, S., Schirnding, Y.E.V., Prapamontol, T., 2000. Environmental lead exposure: a public health problem of global dimensions. *Bulletin of the World Health Organization*. 78(9): 1068-1077.

Tseng, R.L., Tseng, S.K., Wu, F.C. (2006), Preparation of high surface area carbons from corncob with KOH etching plus CO_2 gasification for the adsorption of dyes and phenols from water. *Colloid Surface A: Physicochemical Engineering Aspects*. 279:69–78.

Tudor, H.E.A., Gryte, C.C. and Harri, C.C. (2006), Seashells: Detoxifying agents for metal-contaminated waters. *Water, Air, and Soil Pollution.* 173:209–242.

UNESCAP (1999). Integrating Environmental Consideration into Economic Policy Making Process: Background readings: Vol 1.

UNESCAP (2000). Integrating Environmental Consideration into Economic Policy Making: Institutional Issues.

Unuabonah, E.I., Olu-Owolabi, B.I., Fasuyi, E.I. and Adebowale, K.O. (2010). Modeling of fixed-bed column studies for the adsorption of cadmium onto novel-polymer-clay composite adsorbent. *Journal of Hazardous Materials*. 179:415-423.

USEPA (1998). Toxicological Review of Trivalent Chromium.

USEPA (2012). National Drinking Water Regulations.

Uzun, I. and Güzel, F. (2000). Adsorption of some heavy metal ions from aqueous solution by activated carbon and comparison of percent adsorption results of activated carbon with those of some other adsorbents. *Turkish Journal of Chemistry*. 24:291-297.

Vadahanambi, S., Lee, S.-H., Kim, W.J. and Oh, I.K. (2013). Arsenic removal from contaminated water using three-dimensional grapheme-carbon nanotube-iron oxide nanostructures. *Environmental Science & Technology*. 47(18):10510-10517.

Vázquez, G., Freire, M.S., González-Alvarez, J. and Antorrena, G. (2009), Equilibrium and kinetic modelling of the adsorption of Cd^{2+} ions onto chestnut shell. *Desalination*. 249:855-860.

Vázquez, G., Mosquera, O., Freire, M.S., Antorrena, G. and González-Álvarez, J. (2012). Alkaline pre-treatment of waste chestnut shell from a food industry to enhance cadmium, copper, lead and zinc ions removal. *Chemical Engineering Journal*. 184: 147-155.

Vieira, M.G.A., de Almeida Neto, A.F., Carlos da Silva, M.G., Nobrega, C.C., Melo Filho, A.A. (2012). Characterization and use of *in natura* and calcined rice husks for biosorption of heavy metals ions from aqueous effluents. *Brazilian Journal of Chemical Engineering*. 29(03): 619-633.

Vijayaraghavan, K., Jegan, J., Palanivelu, K. and Velan, M. (2004). Removal of nickel(II) ions from aqueous solution using crab shell particles in a packed bed up-flow column. *Journal of Hazardous Materials* B113: 223-230.

Villaescusa, I., Fiol, N., Martinez, M., Miralles, N., Poch, J. and Serarol, J. (2004). Removal of copper and nikel ions from aqueous solutions by grape stalks wastes. *Water Research*. 38: 992-1002.

Vimala, R. and Das, N. (2011). Mechanism of Cd (II) adsorption by macrofungus *Pleurotus playtypus*. *Journal of Environmental Sciences*. 23:288-293.

Walter, L.M. and Morse, J.W. (1985). The dissolution kinetics of shallow marine carbonates in seawater: A laboratory study. *Geochimica et Cosmochimica Acta.* 49: 1503-1513.

Wan Ngah W.S. and Hanafiah, M.A.K.M. (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology.* 99: 3935-3948.

Wang, F.Y., Wang, H. and Ma, J.W. (2010). Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent-Bamboo charcoal. *Journal of Hazardous Materials.* 177: 300-306.

Wang, J. and Chen, C. (2009). Biosorbents for heavy metal removal and their future. *Biotechnology Advance*. 27:195-226.

Wang, S., Li, L. and Zhu, Z.H. (2007). Solid-state conversion of fly ash to effective adsorbents for Cu removal from wastewater. *Journal of Hazardous Materials.* 139(2): 254-259.

Wang, S., Wei, M. and Huang, Y. (2013). Biosorption of multifold toxic heavy metal ions from aqueous water onto food residues eggshell membrane functionalized with ammonium thioglycolate. *Journal of Agricultural and Food Chemistry*. 61(21): 4988-4996.

Wantala, K., Sthiannopkao, S., Srinameb, B.-O., Grisdanurak, N., Kim, K.-W. and Han, S. (2012), Arsenic Adsorption by Fe Loaded on RH-MCM-41 Synthesized from Rice Husk Silica. *Journal of Environmental Engineering ASCE*. 138: 119-128.

WHO (2011). Cadmium in Drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality.

WHO (2008). Guidelines for drinking-water quality. Recommendations. Incorporating 1st and 2nd Addenda, Vol 1, 3rd edn. World Health Organization (WHO), Geneva.

Wilson, J.A., Pulford, I.D. and Thomas, S. (2003). Sorption of Cu and Zn by bone charcoal. *Environmental Geochemistry and Health.* 25: 51-56.

Woolard, C.D., Petrus, K., Van der Horst, M. (1999). The use of a modified fly ash as an adsorbent for lead. *Water SA*. 26(4): 531-536.

Wu, Y., Yilihan, P., Cao, J. and Jin, Y. (2013). Competitive adsorption of cr (vi) and ni (ii) onto coconut shell activated carbon in single and binary systems. *Water, Air, and Soil Pollution*. 224(9): 1-13.

Xie, R., Wang, H., Chen, Y. and Jiang, W. (2012). Walnut shell-based activated carbon with excellent copper (II) adsorption and lower chromium (VI) removal prepared by acid-base modification. *Environmental Progress & Sustainable Energy*. 23(3): 688-696.

Xu, X., Gao, B., Tan, X., Zhang, X., Yue, Q., Wang, Y. and Li, Q. (2013). Nitrate adsorption by stratified wheat straw resin in lab-scale columns. *Chemical Engineering Journal*. http://dx.doi.org/10.1016/j.cej.2013.04.033

Xu, Y.H. and Zhao, D.Y. (2007). Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. *Water Research*. 4: 2101-2108.

Yadanaparthi, S.K.R., Graybill, D. and Wandruszka, R.V. (2009). Adsorbents for the removal of arsenic, cadmium, and lead from contaminated waters. *Journal of Hazardous Materials*. 171:1-15.

Yahaya, N.K.E.M., Abustan, I., Mohaed Latiff, M.F.P., Bello, O.S. and Ahmad, M.A. (2011). Fixed-bed column study for Cu (II) removal from aqueous solutions using rice husk based activated carbon. *International Journal of engineering & Technology IJET-IJENS*. 11(01):186-190.

Yang, D., Jing, D., Gong, H., Zhou, L. and Yang, X. (2012). Biosorption of aquatic cadmium (II) by unmodified rice straw. *Bioresource Technology.* 114: 20-25.

Yeddou, N. and Bensmaili, A. (2007). Equilibrium and kinetic modeling of iron adsorption by eggshells in a batch system: effect of temperature. *Desalination*. 206: 127-134.

Yoon, G.L., Kim, B.T., Kim, B.O. and Han, S.H. (2003), Chemical-mechanical characteristics of crushed oyster shells. *Waste Management.* 23: 825-834.

Yoon, Y.H. and Nelson, J.H. (1984). Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life. *American Industrial Hygiene Association Journal.* 45(8):509-516.

Yousef, R.I., El-Eswed, B., Alshaaer, M., Khalili, F. and Khoury, H. (2009). The influence of using Jordanian natural zeolite on the adsorption, physical, and mechanical properties of geopolymers products. *Journal of Hazardous Materials*. 165: 379-387.

Yu, X., Tong, S., Ge, M., Wu, L., Zuo, J., Cao, C. and Song, W. (2013). Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals. *Journal of Environmental Sciences*. 25(5):933-943.

Zafar, M.N., Parveen, A. and Nadeem, R. (2013). A pretreated green adsorbent based on Neem leaves biomass for the removal of lead from wastewater. *Desalination and Water Treatment.* DOI:10.1080/19443994.2012.752765

Zahra, N. (2012). Lead Removal from Water by Low Cost Adsorbents: A Review. *Pak. J. Anal. Environ Chem.* 13(1): 01-08.

Zhang, Z., Wang, X., Wang, Y., Xia, S., Chen, L., Zhang, Y. and Zhao, J. (2013). Pb(II) removal from water using Fe-coated bamboo charcoal with the assistance of microwaves. *Journal of Environmental Sciences*. 25(5):1044-1053.

Zhao, Y., Yang, S., Ding, D., Chen, J., Yang, Y., Lei, Z., Feng, C. and Zhang, Z. (2013). Effective adsorption of Cr (VI) from aqueous solution using natural Akadama clay. *Journal of Colloid and Interface Science*. 395: 198-204.

Zhou, Q., Chen, Y., Yang, M., Li, W. and Deng, L. (2013). Enhanced bioremediation of heavy metal from effluent by Sulfate-reducing bacteria with copper-iron bimetallic particles support. *Bioresource Technology*. DOI: http://dx.doi.org/10.1016/j.biortech.2013.03.047

Zhu, B.-L., Xiu, Z.-M., Liu, N., Bi, H.-T. and LV, C.-X. (2012). Adsorption of lead and cadmium ions from aqueous solutions by modified oil shale ash. *Oil Shale*. 29: 266-278.

Zuo, X., Balasubramanian, R., Fu, D. and Li, H. (2012). Biosorption of copper, zinc and cadmium using sodium hydroxide immersed Cymbopogon schoenanthus L. Spreng (lemon grass). *Ecological Engineering*. 49:186-189.