ADSORPTION OF METAL IONS AND DYES FROM AQUEOUS SOLUTIONS USING LALA CLAM (*Paphia textile*) SHELL

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ABSTRACT

This study aimed to evaluate the effectiveness of lala clam shell as an adsorbent for the remediation of water contaminated by metal ions and dyes. Three main studies, namely adsorption, desorption and characterisation, have been conducted. In this study, Cd(II), Cu(II), Pb(II), Congo red (CR), Methylene blue (MB), Rhodamine B (RB) and Methyl orange (MO) were used as contaminants. A systematic evaluation for adsorption process involving several experimental parameters such as solution pH, adsorbent dosage and initial adsorbate concentration was performed. The applicability of lala clam shell to remove metal ions and dyes from aqueous solution was assessed in both single- and mix-system. Hydrochloric acid (HCl) and ethylenediaminetetraacetic acid (EDTA) were used as desorption agents in desorption study. The characterisation study was carried out using Field Emission-Scanning Electron Microscope (FE-SEM), Energy Dispersive X-ray (EDX) Spectrometer and Fourier Transform Infrared (FTIR) Spectrometer. The surface morphology of lala clam shell changed significantly following interaction with metal ions and dyes. The adsorption equilibrium data of metal ions and dyes were correlated with both Langmuir and Freundlich isotherm models. The separation factor (R_L) and Freundlich constant (n) values suggest that the adsorption process was favourable. At an initial metal ion concentration of 200 mg/L, the maximum adsorption capacity (Q_{max}) values of Cd(II), Cu(II) and Pb(II) were 66.66 mg/g, 64.94 mg/g and 100.00 mg/g, respectively. Meanwhile, at an initial dye concentration of 100 mg/L, 15.48 mg/g of CR, 1.50 mg/g of MO, 11.66 mg/g of MB and 0.31 mg/g of RB were adsorbed onto lala clam shell. The adsorption performance of lala clam shell was compared with mangrove stem derived activated carbon (MSAC), a commercial adsorbent for water treatment. In conclusion, the presence of carbonate functional group on lala clam shell enhanced its ability to adsorb metal ions and dyes. The implication of this study is lala clam shell offers an alternative low-cost adsorbent for water treatment particularly in developing countries such as Malaysia and Libya.

PENJERAPAN ION LOGAM DAN PEWARNA DARI LARUTAN AKUEUS MENGGUNAKAN KULIT KERANG LALA (*Paphia textile*)

ABSTRAK

Kajian ini bertujuan untuk menilai keberkesanan kulit kerang lala sebagai suatu penjerap untuk pemulihan air tercemar oleh ion logam dan pewarna. Tiga kajian utama, iaitu penjerapan, penyaherapan dan pencirian, telah dilaksanakan. Dalam kajian ini, Cd(II), Cu(II), Pb(II), Kongo merah (CR), Metilena biru (MB), Rhodamin B (RB) dan Metil oren (MO) telah digunakan sebagai bahan cemar. Satu penilaian yang sistematik untuk proses penjerapan yang melibatkan beberapa parameter eksperimen seperti pH larutan, dos penjerap dan kepekatan awal bahan terjerap telah dilakukan. Kebolehgunaan kulit kerang lala untuk menyingkirkan ion logam dan pewarna daripada larutan akueus telah dinilai dalam kedua-dua sistem tunggal dan campuran. Asid hidroklorik (HCl) dan asid etilenadiaminatetraasetik (EDTA) telah digunakan sebagai ejen penyaherapan dalam kajian penyaherapan. Kajian pencirian telah dijalankan menggunakan Mikroskop Imbasan Elektron – Medan Pemancaran (FE-SEM), Spektrometer Penyebaran Tenaga X-ray (EDX) dan Spektrometer Inframerah Transformasi Fourier (FTIR). Morfologi permukaan kulit kerang lala berubah dengan ketara berikutan interaksi dengan ion logam dan pewarna. Data keseimbangan penjerapan ion logam dan pewarna telah dikaitkan dengan kedua-dua model isoterma Langmuir dan Freundlich. Nilai-nilai faktor pemisahan (R_L) dan pemalar Freundlich (n) mencadangkan bahawa proses penjerapan adalah baik. Pada kepekatan awal ion logam 200 mg/L, nilai maksimum kapasiti perjerapan (Q_{max}) untuk Cd(II), Cu(II) dan Pb(II) ialah 66.66 mg/g, 64.94 mg/g dan 100 mg/g, masing-masing. Manakala, pada kepekatan awal pewarna 100 mg/L, 15.48 mg/g CR, 1.50 mg/g MO, 11.66 mg/g MB dan 0.31 mg/g RB telah dijerap ke atas kulit kerang lala. Prestasi penjerapan kulit kerang lala telah dibandingkan dengan karbon teraktif daripada batang pokok bakau (MSAC), suatu penjerap komersial untuk rawatan air. Kesimpulannya, kehadiran kumpulan berfungsi karbonat pada kulit kerang lala meningkatkan keupayaannya untuk menjerap ion logam dan pewarna. Implikasi kajian ini adalah kulit kerang lala menawarkan alternatif penjerap kos rendah untuk rawatan air terutamanya di negara-negara membangun seperti Malaysia dan Libya.

TABLE OF CONTENTS

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

LIST OF TABLES

LIST OF FIGURES

05-4506832 pustaka.upsi.edu.my Perpustakaan Tuanku Bainun Kampus Sultan Abdul Jalil Shah PustakaTBainun ptbupsi

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
AC	Activated Carbon
Annual O&M	Annual Operation and Maintenance
ATSDR	Agency for Toxic Substances and Disease Registry
BET	Brunauer-Emmett-Teller
BJH	Barrett, Joyner and Halenda
COD	Chemical Oxygen Demand
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray
EU	European Union
FAO	Food and Agriculture Organization
FTIR	Fourier Transform Infrared
FESEM	Field Emission Scanning Microscope Electron
IQ	Intelligence quotients
MCL	Maximum contaminant levels
MF	Microfiltration
MGD	Million Gallons per Day
MSDS	Material Safety Data Sheet
NF	Nanofiltration
RO	Reverse Osmosis

RSC	Royal Society of Chemistry
TDS	Total Dissolved Solid
UF	Ultrafiltration
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

1.1 Water Contamination

Water contamination is a phenomenon that can be defined as the deterioration of the quality of water, which has cause a serious threat to the living things. Water contamination has becoming an immense problem worldwide due to rapid industrial growth, environmental pollution and exhausted water resource among others (Salpekar, 2008; Vapnek, Aylward, & Popp, 2009; Lee & Park, 2013). Many human activities increase water pollution by contaminating natural water sources from several industries such as mining, agriculture, textile, tanneries and transportation both in developing and industrialised countries (Salpekar, 2008; Qu, Alvarez, & Li, 2013). The main sources of water pollution are wastewaters from household, agricultural and industrial activities (Chiu et al., 2015). It has been estimated that about 2 million tonnes of industrial sludge and waste are discharged into water environment daily, worldwide (Jabeen, Huang, & Aamir, 2015).

Globally, the presence of hazardous and toxic pollutants such as heavy metals and organic compounds in industrial wastewater is one of the most challenging problems threatening to human health and the environment (Kyzas & Kostoglou, 2014; Malik, Jain, & Yadav, 2016). Due to this, organic and inorganic substances with a non-biodegradable characteristic can lead to be accumulated in the environment. Through bioaccumulation, their concentration increases in the food chain and consequently they can be very harmful to human health, causing various diseases and disorders (Inyinbor, Adekola, & Olatunji, 2016).

According to Carmona, Soprani, and Sberveglieri (2017), around 1.1 billion of world population has crucial access to clean water supplies and half of the developing world's population are suffering from infections and diseases due to water contamination. Water contamination has caused around 5 million of world's population died, every year (WHO, 2002; Jabeen et al., 2015). Contagious diseases are the main diseases that may affect and kill kids under 5 years old. Schistosomiasis is a major disease in sub-Saharan Africa and it affected more than 160 million of world population every year (Jabeen et al., 2015; Tchuente, Rolinson, Stothard, & Molyneux, 2017). Another infectious disease is commonly found in Sub-Saharan Africa and Southeast Asia is ascariasis (highest prevalent in warm tropical and sub-tropical atmospheres), which affect almost 900 million over population throughout the world. As indicates in Figure 1.1, Wright and Mundial (1997) stated that due to lack of enough precautions in sanitation facilities has led to various diseases in the worldwide. In 2002, nearly 2.1 million world's population died due to diarrheal diseases (WHO, 2002) and the numbers of death reached to 4 billion in 2005 (WHO, 2005; Firdhouse & Lalitha, 2016).

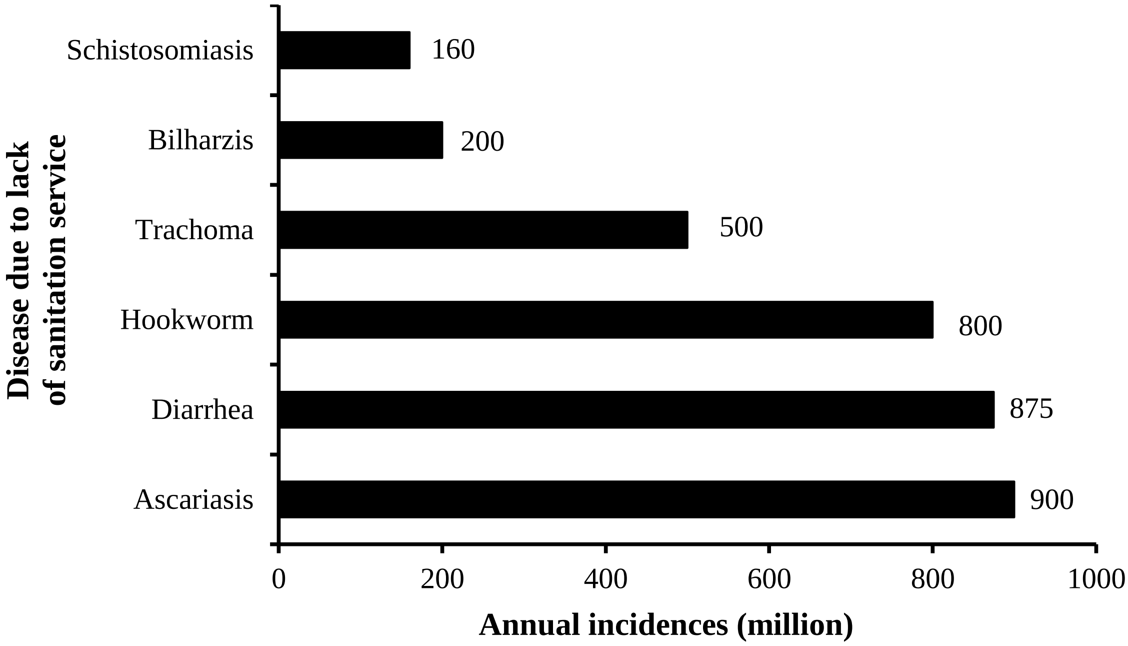

Figure 1.1. The Ranking of Annual Incidences of Diseases Due to the Lack of Sanitation Source: Wright and Mundial (1997); Massoud, Tarhini, and Nasr (2009); Jabeen et al. (2015)

Wastewater treatment is the procedure whereby these pollutants are eliminated from wastewater before discharge into water environment. Overall the cost for water treatment is very expensive. Table 1.1 summarises the techniques used to treat water pollution by heavy metals and dyes. This table involves summary notions for the technologies, nature of the polluter, effectiveness (%) and cost (USD).

Table 1.1

A Summary of Treatment Technologies for Water Pollution by Heavy Metals and Dyes

Technology	Description	Pollutant	Operation	System Limitations	Cost	Effectiveness	References
Adsorption using lala clam shell	Adsorption is accumulation / adhesion of molecules at the surface of a solid material. In contact with water phase.	Metal ions and dyes	Preparation of a water solution contaminated by metal ions or dyes, the need for pH adjustment before adds the adsorbent and filtration.	Dependent on the pH	Lala clam shells are readily available at no cost.	Results from this study indicated that lala clam shell can beneficial and efficient alternative to expensive adsorbents for water treatment.	Present study
Activated carbon (AC)	Innovative technology using powder activated carbon obtained from rubber-seed shell.	Metal ions	Properties of using rubber-seed shell based on AC to remove Cu^{2+} and Zn^{2+} ions from single metal aqueous solution.	Dependent on the temperature	The global market for activated carbon totalled USD 1.9 billion in 2013, driven primarily by Asia-Pacific and North American region for applications in water treatment and then reached USD 2.1 billion, in 2014	Borhan, Abdullah, Rashidi, and Taha (2016) reported that the effectiveness of Cu(II) and Zn(II) are 99%.	Borhan et al. (2016); USEPA (2014); Ceskaa (2015)
Coagulation and flocculation	In this technology is destabilising the solute in the solution to form agglomerates by agitation that settle down under gravity.	Metal ions and dyes	Dependent on material coagulants, examples of chemical treat coagulants include aluminium, iron salts and polyelectrolytes.	At natural pH	Equipment cost is about USD 11.7 million.	Sami et al. (2017) performed coagulation and flocculation, and obtained about 90% dye removal as a result of the activity of the starch chitosan nanocomposite	USEPA (2014); Sami et al. (2017); and Banchon Castillo and Posligua (2017)

(*Continue*)

Table 1.1 (*Continued*)

Electro-coagulation	In this process, water is remedied using electrolysis with graphite or stainless steel cathodes in conjunction with a metal anode. When a voltage is applied across the electrodes, insoluble precipitates are formed from ions the metal present in the water.	Metal ions and dyes	Water was pre-treated using lime neutralization and sedimentation followed by electrocoagulation. After electrocoagulation, water was filtered using a microfiltration flat sheet ceramic membrane. Dependent on the composition of the wastewater is selected anode materials.	The conductivity of the polluted water must be high and it is necessary to replace the electrodes regularly	For some applications, operating costs, including electric power, replacement of electrodes, pump maintenance and labour, can be less than USD 1.53 per thousand gallons.	Heavy metals in water such as arsenic, cadmium, lead and zinc are generally reduced by 95 to 99%. As for colour, using iron electrode only 15.70% removed from wastewater at natural pH.	USEPA (2014); Truttim and Sohsalam (2016)
Ion exchange	Ion exchange is the reversible exchange of pollutant ions from a process stream with more desirable ions of a similar charge adsorbed to solid surfaces known as ion exchange resins. This process provides desalination, alkalinity removal, radioactive waste removal, ammonia removal and metals expulsion.	Metal ions	Important considerations include type of resin, the volume and type of regenerant, the need for pre-filtration of solids, the column configuration, the need for pH adjustment before and after ion exchange, and the cycle length.	Organics, strong oxidants and high temperatures can degrade the resin. Resins may need to be disposed of if they cannot be regenerated, meaning high disposal costs	Equipment cost is USD 4.3 million. About USD 168,993 are estimated annual costs for one site, the Soudan Mine.	Commonly greater than 90% recovery rates, given resin specificity for target constituent and regenerant requirements.	Braun et al. (2002); Oehmen et al. (2014); and USEPA (2014)

(*Continue*)

Table 1.1 (*Continued*)

Nanofiltration (NF)	Nanofiltration is a form of filtration that uses a semi-permeable membrane.	Metal ions and dyes	Requires small space and allows for modular construction. However, due to larger pore size, it is generally less effective.	To meet membrane durability requires pressure, temperature and pH	For a 1 MGD system, total installed cost is estimated at USD 42.9 million. Annual O&M costs are estimated at USD 3.2 million.	Al-Alawy and Salih (2017) reported that the percentage removal of Zn(II) was 97.4% using NF.	Al-Alawy and Salih (2017); and USEPA (2014)
Reverse Osmosis (RO)	Reverse osmosis is the pressure-driven separation through a semi-permeable membrane that allows water to pass through while rejecting contaminants.	Metal ions	The influence of various parameters such as feed pressure (136–544 kPa), feed flow rate (0.25–1.172 L/min), feed concentration (30–100 mg/L) and pH (8, 10, and 11).	Require temperature control to minimize viscosity effects and adjust operating pressure	Equipment cost is USD 1.35 million. Annual costs are estimated at USD 3.2 million at the Kennecott South site for addressing the total dissolved solid (TDS) and sulphate in high pressure.	High efficiency for removal of Cr(II) 99.9% and Cu(II) 99.3% from electroplating wastewater was observed by Al-Alawy and Salih (2017).	Khazaali, Kargari and Rokhsaran, (2014); Codday et al. (2014); and USEPA (2014); Al-Alawy and Salih (2017)

6

Like other developing countries, Malaysia and Libya are committed in finding cost-effective method to treat low concentrations of heavy metals and dyes in a large volume of contaminated water especially for drink and household use. This research is developed for response to the increased water contamination by heavy metals and dyes.

1.2 Contribution of Industrial Activities to Water Pollution

Various industrial processes may utilise water for cooling and large amount of wastewater often has been discharged into streams or lakes, thus cause water pollution. All these chemicals of industrial wastes are toxic and may cause damage or death to different living life of the aquatic fauna and flora. The types of industrial activities contribution to water pollution are shown in Table 1.2.

Table 1.2

Types of Industrial Activities Related to Water Pollution

Type of industrial	Statistics	Pollutant	References
Mining	In 2014, 2531.67 million tonnes of industrial wastewater was discharged by the mining industry in china.	Heavy metals, sulphuric acid hydrogen sulphide.	Xue et al. (2017); Li et al. (2017).
Iron and steel	The biggest producer of steel by far is China (1607 million metric tonnes in 2013), followed by the EU (165), Japan (110), USA (87) and India (81).The three major sources of iron are China (23%), Australia (18%) and Brazil (18%).	Organic such as, oil phenol and naphtha and inorganic as copper, lead, chromium, cadmium and mercury.	Tiwari et al. (2016).
Textile	The country with the highest amount of emissions of organic water pollutants in the world is China, with an impressive value of (9,428,874 kg/day). It is followed by USA (1,850,753 kg/day).	Dyes, sulphates and chromium.	Paraschiv et al (2015); Dey and Islam, (2015).
Paper and pulp	47.4% percentage pollution in Bangladesh.	Sulphides bleaching and cellulose fibres.	Faisal et al. (2001)

1.2.1 Heavy Metals Industry

Heavy metals are the elements which are having atomic weight between 63.5 - 200.6 g/mol, and a specific gravity is greater than five times that of water (Fu & Wang, 2011). These metallic elements can be divided into two groups; namely those that are essential for growth, such as iron and calcium, and those that are nonessential or toxic, such as cadmium and lead. Unlike organic compounds, heavy metals are non-biodegradable and can be accumulated in living tissues, can lead to causing various diseases and disorders or serious health threats up to death (Wang, Chen, Hung, & Shammas, 2009; Vafakhah, Bahroloom, Bazarganlari, & Saeedikhani, 2014).

Therefore, the exposure of human to heavy metals can cause joint diseases such as rheumatoid arthritis, kidneys related diseases, circulatory system, nervous system and damaging of the fetal brain (Nguyen et al., 2013; Kumar, Saravanan, Rajan, & Yashwanthraj, 2016). For example, cadmium a possible carcinogen since its persistent exposure leads to renal dysfunction and death respectively (Fu & Wang, 2011; Wang et al., 2012). Nickel can cause several diseases such as dermatitis, myocarditis, encephalopathy, vomiting, chest pain, rapid respiration etc. (Singh & Gupta, 2016). Excessive dosages of some heavy metal ions replace or displace essential ions from biomolecules and obstruct the functional groups of significant biomolecules such as enzymes thereby altering enzymes' structure as well as inactivating them (Kieu, Müller, & Horn, 2011; Sunitha et al., 2013). Wastewater regulations are established to minimise human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The maximum contaminant levels (MCL) standards and health effects of various toxic metals, established by the United States Environmental Protection Agency (USEPA) are given in Table 1.3.

Table 1.3

The Maximum Contaminant Levels (MCL) for the Most Common Heavy Metals

Heavy metal	Toxicities	MCL (mg/L)
Arsenic (As)	Skin manifestation, visceral cancers, vascular disease.	0.05
Cadmium (Cd)	Kidney damage, renal disorder, human carcinogen.	0.01
Chromium (Cr)	Headache, diarrhea, nausea, vomiting, carcinogenic.	0.05
Copper (Cu)	Liver damage, Wilson disease, insomnia.	0.25
Nickel (Ni)	Dermatitis, nausea, chronic asthma, coughing.	0.20
Zinc (Zn)	Depression, lethargy, neurological signs, increased thirst.	0.80
Lead (Pb)	Damage the fetal brain, diseases of the kidneys.	0.006
Mercury (Hg)	Rheumatoid arthritis and diseases of the kineys.	0.001

Source: USEPA (2000); Barakat (2011); Nguyen et al. (2013); Gautam et al. (2014).

1.2.2 Dyes Industry

The textile, dyestuffs, paper, leather, cosmetic, pharmaceutical, rubber, plastics and food industries frequently used a significant amount of dyes for their various products (Rangabhashiyam, Aun, & Selvaraju, 2013; Boudechiche, Mokaddem, Sadaoui, & Trari, 2016). Consequently, dyes and pigments used in the textile industry considered as one of the most important group of pollutants that get mixed in wastewater (Hosseini et al., 2011; Vieira, Cestari, Carvalho, Oliveira, & Chagas, 2012).

The number of dyes and pigments presently used in textile industry is about 10,000 tonnes, with worldwide annual production of over 7 x 10^5 tonnes (Sharma &