EVALUATION OF RAZOR CLAM (*Ensis directus*) SHELL AS AN ADSORBENT FOR THE REMOVAL OF HEAVY METALS AND DYES FROM AQUEOUS SOLUTION

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ABSTRACT

This research aimed to evaluate the potential of razor clam (*Ensis directus*) shell, a fishery waste material, as an adsorbent for the removal of heavy metals and dyes from aqueous solution. This research is divided into three parts, namely characterisation studies, adsorption studies and desorption studies. Several analytical instruments such as scanning electron microscope (SEM), energy dispersive x-ray (EDX) spectrometer and Fourier transform infrared (FTIR) spectrometer were used to characterise the adsorbent. In this study, three metal ions (Cd(II), Cu(II) and Pb(II)) and four dyes (Congo red (CR), methylene blue (MB), Rhodamine B (RB) and methyl orange (MO)) were used as contaminants. A series of adsorption tests were carried out as a function of solution pH, adsorbent dosage and initial adsorbate concentration. The adsorption capacity of razor clam shell for metal ions and dyes from aqueous solutions was evaluated in both single and mix systems. The desorption study was performed using hydrochloric acid, acetic acid and sodium hydroxide as desorption agents. The adsorption efficiency of the proposed adsorbent was compared with olive tree derived activated carbon, a commercial adsorbent for water treatment in Libya. Research findings showed that the surface morphology of razor clam shell changed after metal ions and dyes uptake, indicate a relevant adsorbate-adsorbent interaction. With an exception of MB, the adsorption of contaminants studied was more favourable at acidic pH media. The Freundlich and Langmuir isotherm models were employed to correlate the adsorption equilibrium data. Based on Langmuir isotherm model, the maximum adsorption capacities of razor clam shell were calculated as 103 mg/g, 98 mg/g and 357 mg/g for Cd(II), Cu(II) and Pb(II) ions, respectively. Meanwhile, the maximum adsorption capacities for CR, MB, MO and RB were determined as 115 mg/g, 24 mg/g, 9 mg/g and 1.16 mg/g, respectively. In conclusion, the presence of carbonate functional group on the surface of razor clam shell was beneficial for adsorption mechanism. In implication, the application of razor clam shell as a low-cost adsorbent could reduce the operational cost for water treatment in developing countries.

PENILAIAN KULIT SIPUT BULUH (*Ensis directus*) SEBAGAI SUATU PENJERAP UNTUK PENYINGKIRAN LOGAM BERAT DAN PEWARNA DARI LARUTAN AKUEUS

ABSTRAK

Kajian ini bertujuan menilai keupayaan kulit siput buluh (*Ensis directus*), suatu bahan sisa perikanan, sebagai penjerap untuk penyingkiran logam berat dan pewarna daripada larutan akueus. Kajian ini dibahagikan kepada tiga bahagian, iaitu kajian pencirian, kajian penjerapan dan kajian penyaherapan. Beberapa alatan analisis seperti mikroskop imbasan elektron (SEM), spektrometer penyebaran tenaga x-ray (EDX) dan spektrometer inframerah transformasi Fourier (FTIR) telah digunakan untuk mencirikan penjerap. Dalam kajian ini, tiga ion logam (Cd(II), Cu(II) dan Pb(II)) dan empat pewarna (merah Kongo (CR), biru metilena (MB), Rhodamin B (RB) dan oren metil (MO)) telah digunakan sebagai bahan pencemar. Satu siri ujian penjerapan telah dijalankan sebagai suatu fungsi pH larutan, dos penjerap dan kepekatan awal bahan terjerap. Kapasiti penjerapan kulit siput buluh untuk ion logam dan pewarna dari larutan akueus telah dinilai dalam kedua-dua sistem tunggal dan campuran. Kajian penyaherapan telah dilakukan menggunakan asid hidroklorik, asid asetik dan natrium hidroksida sebagai ejen penyaherapan. Kecekapan penjerapan bahan penjerap yang dicadangkan telah dibandingkan dengan karbon teraktif daripada pokok zaitun, suatu penjerap komersial untuk rawatan air di Libya. Dapatan kajian menunjukkan bahawa morfologi permukaan kulit siput buluh berubah selepas penjerapan ion logam dan pewarna, menandakan interaksi bahan terjerap-penjerap yang relevan. Dengan pengecualian untuk MB, penjerapan bahan cemar yang dikaji adalah lebih baik pada media pH berasid. Model isoterma Freundlich dan Langmuir telah digunakan untuk mengaitkan data keseimbangan penjerapan. Berdasarkan model isoterma Langmuir, kapasiti penjerapan maksimum untuk kulit siput buluh telah dikira masing-masing sebagai 103 mg/g, 98 mg/g dan 357 mg/g untuk ion Cd(II), Cu(II) dan Pb(II). Manakala, kapasiti penjerapan maksimum untuk CR, MB, MO and RB telah ditentukan masing-masing sebagai 115 mg/g, 24 mg/g, 9 mg/g dan 1.16 mg/g. Kesimpulannya, kehadiran kumpulan berfungsi karbonat pada permukaan kulit siput buluh adalah berfaedah untuk mekanisme penjerapan. Implikasinya, penggunaan kulit siput buluh sebagai suatu penjerap kos rendah mampu mengurangkan kos operasi perawatan air di negara membangun.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
APHA	American Public Health Association
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BET	Brunauer-Emmett-Teller
BFS	Blast Furnace Slag
BJH	Barrett-Joyner-Halenda
CAC	Commercial Activated Carbon
COD	Chemical Oxygen Demand
d	Diameter of pore
DOE	Department of Environment
EDTA	Ethylenediaminetetraacetic acid
EDX	Energy Dispersive X-ray
EU	European Union
FA	Fly Ash
FS	Fish Scale
FTIR	Fourier Transform Infrared
IUPAC	International Union of Pure and Applied Chemistry
NF	Nano-Filtration
OECD	Organisation for Economic Co-operation and Development

OS	Oyster Shell
RCS	Razor Clam Shell
RH	Rice Husk
RM	Red Mud
RO	Reverse Osmosis
SB	Sugarcane Bagasse
SD	Sawdust
SEM	Scanning Electron Microscope
UF	Ultrafiltration
USA	United States of America
USD	United States Dollar
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet Visible
WHO	World Health Organization

CHAPTER 1

INTRODUCTION

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1.1 Water

Water is one of the most ubiquitous natural resources. It is considered as the most precious resource in the world since without it life cannot exist on Earth. It is equally important to human, flora and fauna species. More than 70 % of human mass and 50-90 % of plants and animals' weight are made up of water (Sahoo, Mahananda & Seth, 2016; Sharma, 2015; Sharma & Sanghi, 2012).

Approximately three-fourths of the Earth's surface is covered with water in the form of either gas, solid or liquid (Fianko et al., 2013; Sharma & Sanghi, 2012). Only 2.53 % of the water available on earth is freshwater while the remaining 97 % forms the ocean (Rajasulochana & Preethy, 2016; Ramachandra & Solanki, 2007).

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Water resource can be classified as (Vallée, Margat & Eliasso 2003):

i. Renewable water resource, which comprises surface water (rivers) and groundwater.

ii. Non-renewable water resource which is available as groundwater bodies (deep aquifers).

In Arab countries such as Libya, the main source of water supply is groundwater; up to 97 % of the water used for various purpose is obtained from this source. Groundwater in Libya is classified as a renewable resource while underground water is classified as non-renewable resource (Saad, Shariff & Gairola, 2011). On the contrary, the main source of withdrawn water in Egypt is surface water, with the Nile River forming more than 90 % of the water resource in the Nile basin (Ali, Sabae, Fayez, Monib & Hegazi, 2011). In Malaysia, 97 % of the total water used is surface water, while the remaining 3 % is sourced from groundwater (Prasanna, Praveena, Chidambaram, Nagarajan & Elayaraja, 2012).

Water is essentially a polar inorganic compound made up of two positively-charged hydrogen atoms and one negatively-charged oxygen atom linked together by hydrogen bonds. These bonds give water a molecule electrical balance called ‘polarity’, which means that it has a unique property as a good solvent capable of dissolving more substances than other liquids (Asrari, 2014). It has maximum density at 4 °C, and as a result the solid phase has a lower density than the liquid phase. Water is amphoteric, which means that it is both an acid and a base due to the self-ionisation which occurs in water. It has no colour and no odour, and boils at 100 °C and freezes at 0 °C (Suthersan, Horst, Schnobrich, Welty & McDonough, 2017).

Water is used for different purposes in sectors such as domestic, industry, irrigation, animal husbandry, power generation, navigation, waste transportation, etc. (Sperling, 2007). In general terms, the highest demand for water is from the domestic and industrial sectors. For instance, in 2016, the total fresh water consumption by the industry is 2597 billion m^3 in China, 1112 billion m^3 in the USA, and 308.9 billion m^3 in Malaysia. However, the total water consumption (rainwater, surface water, and groundwater) in the USA is estimated to be 2800 billion m^3 in 2016 (Ono, Kim & Itsubo, 2017).

1.2 Research Background - Water Pollution

1.2.1 Overview

The rapid industrialisation and technological advances over the last several decades have brought prosperity and urbanisation to many countries (Umpuch & Jutarat, 2013). Each form of anthropogenic activity, however, is a potential source of pollution (atmosphere, hydrosphere, geosphere) (Yacout & Hassouna, 2016). Environmental pollution is generally defined as any perturbation or any undesirable alteration in the physical, chemical or biological characteristics of any component of the environment by substances which have harmful effects on human beings and the ecosystem (Rai, 2012). These harmful and poisonous substances are called pollutants (Manahan, 2005). Pollution of the environment by organic and inorganic industrial discharges is of utmost concern. This is especially so with regard to water pollution since industrial discharge is an important cause of water degradation due to its level of toxicity and harmful effects on humans and the environment (Bozbas & Boz, 2016; Subbaiah & Kim, 2016). The release of various types of industrial runoffs into water bodies (groundwater, rivers, lakes, etc.) have caused much worry because of the potential threat to health that are related to the entry of noxious constituents into the food chains of humans and animals (Devi, Saraswathi & Makeswari, 2016).

The sharp increase in the use of toxic chemical by many industries have ultimately resulted in increased production of waste and wastewater effluents (Liu, Li, Wang, Gou & Duan, 2015; Visa, Bogatu & Duta, 2010). For example, more than 400 factories continuously discharge more than 2.5 million m^3 wastewater each day into Egypt's water resources (Ali, Sabae, Fayez, Monib & Hegazi, 2011). According to the Department of Environment (DOE), Malaysia produced 2,854,516.78 metric tonnes wastewater (scheduled wastes) in 2012, and in 2013 the volume increased to 2,965,611.65 metric tonnes (Jamin & Mahmood, 2015). Industrial wastewater poses a serious threat to the environment and is among the major sources of water pollution. Bahadori Clark and Boyd (2013) noted that 10 countries are currently facing serious water pollution problems. Brazil, the USA, China, Japan and Indonesia have the highest level of water pollution (Bahadori, Clark & Boyd, 2013). It is estimated that about 600,000 fields were affected by polluted water and wastewater effluent in the USA (lone, 2008).

Water pollution is a compelling and important issue since it is one of the most crucial public health concerns in modern societies (Khaniabadi, Heydari, Nourmoradi, Basiri & Basiri, 2016). The World Bank contended that in India 21 % of the transmittable diseases are water-borne. One of them, diarrhea, is believed to have caused about 535,000 deaths in 2004 (Rajasulochana & Preethy, 2016). In addition, up to 90 % of the cities in China are facing problems related to polluted water as estimated in 2005 (Bhuiyan et al., 2013). Undoubtedly, increased consumption of polluted water will result in increased threat to human health.

1.2.2 Water pollution in Libya

Libya is an Arab country with a population of 5-6 million according to the most recent population census (ELabbar, 2008). Approximately 94.5 % of the country is desert and the supply of fresh water is very scarce. Libya relies mainly on groundwater to meet the needs of various sectors, such as domestic, agriculture, industry, etc. Surface water makes up only a small percentage of the total water supply. Libya is estimated to have 0.8 km^3 renewable water resource (Bindra, Abulifa, Hamid, Al-Reiani & Abdalla, 2013).

Pollution of water is a serious ecological issue faced by Libya, and the pollution is due to a combination of problems related to sewage, oil by-products, industrial wastes, and agricultural run-off (Bindra, Abulifa, Hamid, Al Reiani & Abdalla, 2013). Industrial waste has the greatest potential for polluting surface water and groundwater (Abbas, Murtaza & Munir, 2011; Bindra, Muntasser, El-Khweldi & El-Khwedi, 2003). Groundwater pollution by heavy metals and organic compounds could occur naturally due to natural factors, such as soil erosion and volcanic activities, or it could be caused by substances produced through anthropogenic activities (Akpor, Ohiobor & Olaolu, 2014; Uwamaria, 2013). Nour (2015) examined the concentration of several metals in the groundwater of Al-Jamel well in the northwest of Libya. The average concentration of heavy metals present in the samples was evaluated based on the quality standards set by the World Health Organization (WHO). Table 1.1 presents the mean concentration of metals detected in the groundwater samples and the levels set by WHO.

Results show that the concentration of Cd, Mn, Ni, Pb in the samples exceed the permitted levels set by WHO. Table 1.1 shows that the metal with highest concentration in the groundwater sample is Mn (0.92 mg/L), followed by Pb (0.15 mg/L), Ni (0.11 mg/L), and Cd (0.083 mg/L). Additionally, the amounts of these heavy metals exceed the levels permitted by the Libyan standard. Conversely, Cu shows the lowest level of concentration in the sample; in fact, its level is lower than levels permitted by the Libyan and WHO standard. The presence of Cu in groundwater is due to weathering and erosion of parent rocks (natural sources) (Nour, 2015).

Table 1.1 also shows a comparison of the level permitted in the Libyan and international (WHO) standards. There is no big differences between the values set by both standards. The Libyan standard allows for a higher values of Cd and Pb than that set by WHO, while the levels for Cu, Mn and Fe allowed by the Libyan standard are lower than those set by the WHO standard.

Table 1.1

Comparison of Mean Concentration of Heavy Metals in Groundwater Samples with the Levels Set by the Libyan and WHO Standards for Drinking Water.

Metal	Heavy metal in groundwater[a] (mg/L)	Libyan standard[b] (mg/L)	WHO Standard[c] (mg/L)
Cd	0.083	0.005	0.003
Cr	-	0.05	0.05
Cu	0.30	1.00	2.00
Mn	0.92	0.05	0.40
Ni	0.11	0.02	0.02
Pb	0.15	0.05	0.01
Fe	-	0.10	0.30

Note. Adapted from *Alhibshi, Albriky & Bushita*, 2014[b]; *Nour*, 2015[a]; *WHO*, 2008[c].

The rapid industrialisation in Libya has led to an increase in water demand by the industry. Industrial water consumption is expected to increase to 425 m^3 in 2020 compared to the 145 m^3 consumed by the industry in 1995 (Bindra, Muntasser, El-Khweldi & El-Khwedi, 2003). Table 1.2 lists some of Libyan manufacturing sectors and their respective water consumption in 2002.

Table 1.2

Water Consumption by Libyan Industry.

Industry	Actual production (tonne per year)	Water consumption (Litre per tonne)
Pulp and paper	-	4000
Cement	4298	440
Pipe	40,400	61
Iron and steel	905,000	2200
Glass	30,000	3300

Note. Adapted from *Bindra, Muntasser, El-Khweldi & El-Khwedi*, 2003.

Pulp and paper, cement, iron and steel, and glass are some of the industries operating in Libya. The iron and steel company is one of the largest companies in Libya. As can be seen in Table 1.2, iron and steel has the highest production rate compared to other industries. Bindra, Muntasser, El-Khweldi and El-Khwedi (2003) reported that about 905,000 tonnes iron and steel were produced in 2002. Its production increase to 1,324,000 tonnes in 2010 (Abugeddida, 2014). The pipe industry has the second highest rate of production and recorded a production of 40,400 tonnes of pipes; this is followed by the glass and cement industries (Bindra, Muntasser, El-Khweldi & El-Khwedi, 2003). However, the industry with higher water consumption is pulp and paper, followed by glass, and iron and steel. The pipe industry requires the smallest volume of water, where only 1 litre of water is needed to manufacture one a ton of pipes (Bindra, Muntasser, El-Khweldi & El-Khwedi, 2003).

Heavy metals and dyes are widely used by the industry and are considered as one of the major causes of water pollution in Libya. Hamad, Agll, Hamad and Sheffield (2014) and Gebril, Omran, Pakir and Aziz (2010) highlighted that the overall generation of industrial waste in Libya is approximately 1,248,000 tonnes per year, which contributes significantly to water pollution. Alajtal, Edwards and Elbagermi (2013) analysed the concentration of heavy metals in the Tawargah Pond in Misurata city, which is one of the industrial centres in Libya. The results were compared with the permitted heavy metals limit set by the American Public Health Association (APHA). Results show that the concentrations of Fe and Pb in the sample are 0.55 and 0.68 mg/L, respectively. The values for Fe and Pb are found to be higher than the 0.30 and 0.05 mg/L set by the APHA, respectively. The heavy metals detected in the Tawargah Pond is from the discharge of industrial wastes (Alajtal, Edwards & Elbagermi, 2013).

In light of these facts, polluted water is considered to be one of the main reasons for the prevalence of serious diseases among the Libyans. The past several years have witnessed increasing incidences of intestinal, dermatological, and chest diseases, in addition to cirrhosis of the liver, kidney failure, and poisoning, which are all related to water pollution. For example, approximately 27 % of the residents in the city of Derna (northeast of Libya), have contracted diseases, with the majority of them contracting intestinal diseases (Jumma, Toriman & Hashim, 2012). In fact, the problem of water pollution in Libya has been receiving special attention since the past several years and it has also been recognised to be a worldwide environmental problem.

1.3 Contribution of Industrial Activities to Water Pollution

Pollutants in the aquatic system of urban countries come from complex and diverse sources (Devi, Saraswathi & Makeswari, 2016). The identification and understanding of these sources and their properties are crucial in the study of water quality (WHO, 2006). Two primary sources which contribute to the accumulation of pollutants in aquatic environment are the heavy metal and dye industries.

1.3.1 Heavy metal industry

From a historical perspective, heavy metals are commonly used in most industrial activities. The level of heavy metals usage has increase as civilisations thrive, especially in the electroplating, extractive metallurgy, battery manufacturing, agriculture, metal mining, and plating industries (Samiey, Cheng & Wu, 2014; Saravanan, Kumar & Mugilan, 2016). Among the most frequently used heavy metals in the industrial sector are As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn (El-Baz et al., 2015). Some of these heavy metals have been used for thousands of years. For example, Cu and Au have been used for more than 6,000 years to produce brass and bronze, electrical equipment, plumbing pipes, glass and pigments (Alloway, 2013; Chen, Wang, Wang, Hung & Shammas, 2016). Table 1.3 presents the data for selected heavy metals and metalloids mined for the period from 1985 to 2010.