ADSORPTION OF LEAD (II) FROM AQUEOUS SOLUTION USING NANO-PAPAYA PEEL

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To my love, Nima, for his devoting love, and supports through every step of life

To my mom, Saeideh, for her everlasting love and encouragement

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ABSTRACT

The presence of toxic heavy metals like lead (Pb(II)) in water resources due to industrialization is known to be a major environmental concern in many communities. Agro-waste has been the focus of studies as a reliable source of sustainable adsorbents for heavy metal removal from aqueous solutions. In this study, papaya peel has been introduced as a new source of agro-waste. The high annual papaya production in Malaysia potentially provides a good base to use its waste to develop an inexpensive adsorbent. Most of previous studies only consider the raw or carbon-active form of bioadsorbents. The present study aims to develop potential adsorption media for the removal of Pb(II) from contaminated water. While raw and carbon-activated adsorbents from papaya peel agro-waste are considered, a new nano adsorbent has been developed and evaluated in this research. The equilibrium sorptions of Pb(II) from an aqueous solution using synthesized adsorbents of activated carbon papaya peel (AC-PP) and nano-papaya peel (Nano-PP) were investigated. The synthesized adsorbents were characterized using Fourier transform infrared spectroscopy, scanning electron microscopy, field emission scanning electron microscopy, x-ray diffractometery and x-ray photoelectron spectroscopy. The batch experiments were carried out considering various Pb(II) concentrations of 10, 20, 50, 100, 200, and 400 mg/L, by changing variables of pH, adsorbent dosage, initial metal concentration, and temperature and contact time. The removal efficiency of the adsorbed amount of metal ions was considered relative to the equilibrium parameters. Desorption and regeneration studies were additionally conducted to evaluate reusability. The developed adsorbents showed excellent performance. Pb(II) was removed after 2 h of agitation, reaching optimal removal percentages of 82.6% using AC-PP (100 mg dosage) and 99.39 % using Nano-PP (50 mg dosage) after 3 h, at pH=5, in ambient condition. Equilibrium adsorption isotherms and kinetics were reviewed using the different isotherm models of Langmuir, Freundlich, and Temkin and kinetic models of the pseudo-first order, pseudo-second order, and intra-particle diffusion. The adsorption processes of Pb(II) onto Nano-PP and AC-PP were better described by the Langmuir isotherm model indicating monolayer Pb(II) adsorption onto the surface of the developed adsorbents and the adsorption kinetics was well fitted with the pseudo second-order kinetic model. Additionally, thermodynamic results confirmed the spontaneous adsorption processes with exothermic and endothermic nature onto surface of AC-PP and Nano-PP, respectively. The results obtained, especially for Nano-PP, confirm the capability of papaya peel adsorbents as a new, low-cost, efficient and environmentally friendly alternative for Pb(II) removal from contaminated water.

ABSTRAK

Kehadiran logam berat bertoksik seperti plumbum (Pb(II)) di dalam sumber air yang disebabkan oleh perindustrian telah diketahui sebagai salah satu pencemaran alam sekitar yang utama oleh kebanyakan masyarakat. Sisa pertanian telah menjadi fokus kajian sebagai satu sumber bahan penjerap lestari yang dipercayai boleh menyingkirkan logam berat daripada larutan berair. Dalam kajian ini, kulit betik telah diperkenalkan sebagai sumber sisa pertanian yang baru. Pengeluaran tahunan betik yang tinggi di Malaysia mempunyai potensi yang baik untuk menggunakan sisanya sebagai asas menghasilkan bahan penjerap yang murah. Kebanyakan kajian terdahulu mempertimbangkan bahan mentah atau bentuk karbon aktif daripada bahan penjerap-bio sahaja. Kajian ini bertujuan untuk menghasilkan media bahan penjerap yang berpotensi bagi menyingkirkan Pb(II) daripada air tercemar. Sementara bahan mentah dan bahan penjerap karbon aktif dipertimbangkan, satu bahan penjerap nano telah dihasilkan dan dinilai dalam penyelidikan ini. Keseimbangan jerapan Pb(II) daripada larutan berair menggunakan bahan penjerap sintesis karbon aktif kulit betik (AC-PP) dan nano kulit betik (Nano-PP) telah disiasat. Bahan penjerap sintesis telah diciri menggunakan spektroskopi inframerah transformasi Fourier, mikroskopi elektron penskanan, mikroskop elektron pengimbas pancaran medan, pembelauan sinar-x dan spektroskopi fotoelektron sinar-x. Ujikaji kelompok telah dijalankan dengan mempertimbangkan pelbagai kepekatan Pb(II) iaitu 10, 20, 50, 100, 200, dan 400 mg/L, dan mengubah pembolehubah iaitu pH, dos bahan penjerap, kepekatan awal logam, suhu dan masa sentuhan. Kecekapan penyingkiran jumlah ion logam terjerap dipertimbangkan relatif terhadap keseimbangan parameter. Kajian nyaherapan dan penjanaan semula telah dijalankan untuk menilai penggunaan semula. Bahan penjerap yang terhasil menunjukkan prestasi yang cemerlang. Pb(II) telah disingkirkan selepas 2 jam pengadukan, mencapai peratus penyingkiran optimum sebanyak 82.6% menggunakan AC-PP (dos 100 mg) dan 99.39 % menggunakan Nano-PP (dos 50 mg) selepas 3 jam, pada pH=5 dalam keadaan ambien. Keseimbangan penjerapan isoterma dan kinetik telah dipadukan dengan menggunakan model isoterma yang berbeza seperti Langmuir, Freundlich dan Temkin dan model kinetik seperti pseudo kadar pertama, pseudo kadar kedua dan resapan intrazarah. Proses penjerapan Pb(II) ke dalam Nano-PP dan AC-PP diterangkan dengan baik oleh model isoterma Langmuir menunjukkan penjerapan ekalapisan Pb(II) ke dalam permukaan bahan penjerap dan penjerapan kinetik mematuhi dengan baik oleh pseudo kadar kedua model kinetik. Selain itu, keputusan termodinamik mengesahkan proses penjerapan spontan dengan sifat luah haba dan serap haba masing-masing ke permukaan AC-PP dan Nano-PP. Keputusan yang diperoleh terutamanya bagi Nano-PP mengesahkan keupaayan kulit betik sebagai bahan penjerap baharu, murah, berkesan dan mesra alam sekitar sebagai pilihan untuk menyingkirkan Pb(II) daripada air tercemar.

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LIST OF ABBREVIATIONS

AAS	-	Atomic Adsorption Spectrophotometer
AC	-	Activated Carbon
AC-PP	-	Activated Carbon Papaya Peel
ARE	-	Average Relative Error
BET	-	Cone Penetration Test
BG	-	Brilliant Green
Char-PP	-	Charcoal Papaya peel
CPL	-	Carica Papaya Linn
EDX	-	Energy Disperse X-ray
FESEM	-	Field Emission Scanning Electron Microscopy
FT-IR	-	Fourier Transform Infrared Spectroscopy
HCL	-	Hydrochloric acid
KOH	-	Potassium Hydroxide
Nano-PP	-	Nano Papaya Peel
NaOH	-	Sodium Hydroxide
NSD	-	Normalized Standard Deviation
MB	-	Methylene Blue
PP	-	Papaya Peel
RCL	-	Recinius Communis Linn
RMSE	-	Root Mean Square Error
SEM	-	Scanning Electron Microscopy
XPS	-	X-ray Photoelectron Spectroscopy
XRD	-	Powder X-ray Diffractometery

LIST OF SYMBOLS

M	-	Molar
R	-	Universal gas constant (8.314 J/mol/K)
R_L	-	Isotherm feasibility characterization
T	-	Absolute temperature (K)
V	-	Volume of solution (L)
W	-	Mass of adsorbent (mg)
C_0	-	Initial concentration of solute (mg/L)
C_e	-	Solute concentration at equilibrium (mg/L)
C_t	-	Solute concentration at time of t (mg/L)
E_a	-	Activation Energy (KJ/mol)
R^2	-	Correlation coefficient
*S**	-	Sticking probability
at	-	Temkin sorption constant
b	-	Temkin constant
g	-	Gram of adsorbent
h	-	Hour of contact time
k_a	-	Langmuir sorption constant (L/mg)
kf	-	Freundlich sorption constant (mg/L)
k_l	-	Isotherm energy constant (J)
k_2	-	Constant rate of pseudo-second order model (g/mg/min)
min	-	Minute
q^{cal}	-	Estimated removal from experiments (mg/g)
q^{meas}	-	Observation from batch experiments (mg/g)
qe	-	Removal at equilibrium (mg/g)
qm	-	Maximum removal amount (mg/g)
qt	-	Removal amount at the time of t (mg/g)

x^2	-	Chi square test
ΔG^o	-	Free Gibbs energy (KJ/mol/K)
ΔH^o	-	Enthalpy (KJ/mol)
ΔS^o	-	Entropy (KJ/(mol K))

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CHAPTER 1

INTRODUCTION

1.1 Background of research

Anthropogenic wastewater discharge releases a high amount of toxic heavy metals into the environment, affecting the inherent quality of water and soil and causing direct/indirect risk to human health. This type of environmental pollution is becoming a worldwide concern. It is a fact that all living organisms can survive for a few days without food and a few hours without water, but only a few minutes without air. Besides air pollution problems, water contamination issues should be considered and prioritized as well, either nationally or globally. Water pollution could be categorized based on the source of pollution, such as oil and its components, pesticides and herbicides, hazardous waste, organic wastes, sediment, hazardous microorganisms, and heat and heavy metals. The presence of heavy metal affects the quality of water resources, changing its acidity and pH, which in turn negatively affects fish stock and vegetation (Wu and Zhao, 2011). As the global population keeps on growing, the quest for more metal continues. Consequently, the significance of metal for the modern society has resulted in the consumption of a large amount of resources to extract them from the Earth's crust.

Heavy metals are elements with atomic weights of 63.5-200.6 and a specific weight of > 5.0 (Singh *et al.*, 2010). These types of elements have been discharged into the environment in extreme amounts, as a result of rapid industrialization in the past decade. It has consequently become a major global concern, causing conflict in natural ecosystems. The heavy metal ions discharged from various industrial sources (Table 1.1) can contradict the reliability of ecological cycles and negatively impact human health through drinking water and the food chain. Cadmium, zinc, copper, nickel, lead, mercury, and chromium are often detected in industrial wastewater derived from different industries such as plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing, and photographic industries, etc. (Qio *et al.*, 2008; Kadirvelu *et al.*, 2001; Hajdu *et al.*, 2012; Yadav *et al.*, 2013). As a common environmental pollutant, lead can be distributed in the environmental media via natural or industrial sources. Small amounts of these elements exist in the environment and in fact they are vital for human health. In contrast to organic wastes, heavy metals are non-biodegradable and can be accumulated in living organism tissues, creating a variety of diseases and disorders in human organs i.e. the liver, brain, kidney, nerves, and the reproductive system. In particular, lead contamination in natural waters has become a major global issue, which has been reported in many countries of the world including Argentina, Bangladesh Cambodia, China, Chile, India, Japan, Mexico, Nepal, New Zealand, Taiwan, the United States, and Vietnam (Sud *et al.*, 2008; WHO, 2000). In Malaysia, like other developing nations of the world, the level of metal pollution in freshwater bodies, especially the rivers, is no longer within safe limits for human consumption. Despite existing legislation that protects water quality in Malaysia, 72 percent of 473 rivers monitored by the Department of Environment Malaysia ("the DOE") in 2013 were found polluted with 25 rivers classified as highly polluted (DOE, 2013). In 2002, the Department of Environment (DOE) reported that industries such as textile, metal finishing and electroplating, food and beverages, and animal feed did not achieve more than 65% compliance (DOE Malaysia, 2009). Some industries were operating either without an effluent treatment system (ETP) or with inefficient ETP (Ariffin and Sulaiman, 2015). These industries had difficulties complying with the standard parameters of lead, nickel, copper, zinc, and iron (DOE, 2009). Besides that, in Malaysia, lead is one of the most widely used metals in some industries i.e. in piping, conducting materials, accumulators, lead chambers, printing characters, soldering, anti-knock substances, and colored pigments (DOE, 2004). The quest towards a lead-free environment (water, soil, and air) is a challenge for scientists since the environmentally admissible levels and concentration limit of lead that are based on the health criteria of water, and especially drinking waters, is continuously decreasing.

Global concerns have prompted researchers to develop many physico-chemical metal removal methodologies from wastewater to cope with the regulations. The conventional treatment method of Pb (II) in aqueous solutions is moderately costly, requiring a centralized water supply infrastructure. Therefore, it is important to propose an effective yet environmentally friendly way to remove lead from aqueous solutions to attain admissible levels in the environment. In general, the existing methods such as liquid-liquid extraction (LLE), ion exchange, and coagulation, have weaknesses i.e. toxic residual sludge, high-energy requirements, incomplete metal removal or generation of other waste by-product, all of which take away from their advantages (Kafia and Surchi, 2011; Ahalya *et al*., 2003; Igwe *et al*., 2005). Out of all the proposed methods, the adsorption process using different kinds of synthetic/natural adsorbents has become the center of attention among industries because it is a cleaner, cheaper and more efficient technology compare to other treatment methodologies (Yalda *et al*., 2012) and number of natural or synthetic adsorbents have been tested for their lead removal capability including activated carbon, chitosan, saw dust, and metal oxide gel. Through different researchs, it is found that orange and banana peels are the most extensively studied agrowaste-derived adsorbents, whereas Pb^{2+} and methylene blue (MB) are the most efficiently removed pollutants from contaminated water samples (Pathak *et al*., 2015). Therefore, adsorption using natural, low cost adsorbents is now known to be a promising alternative for common physico-chemical wastewater-treatment techniques (Raju *et al*., 2012).

Table 1.1: Heavy metal generation in various industrial effluents (Ramachandra *et al.*, 2003).

Industries	Ag	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Hg
Mining				x	x	x	x		x	x	
Plating			x	x	x			x	x	x	
Paint products				x					x		
Fertilizers			x	x	x	x	x	x	x	x	x
Insecticides/Pesticides		x			x						x
Tanning		x		x							
Paper products				x	x			x	x	x	x
Photographic	x			x							
Fibers					x					x	
Printing/ Dyeing				x					x		
Electronics	x										
Cooling water				x							
Pipe Corrosion					x				x		

Ag:Silver; As: Arsenic; Cd: Cadmium; Cr: Cromium; Fe: Iron; Mn: Magnesium; Ni: Nickel; Pb: Lead; Zn: Zinc; Hg: Mercury.

Major attention has been focused on using the interaction of certain natural materials with metal ions in the introduction of new materials as bio-adsorbents. On the other hand, there also exists an up-to-date proficient method such as adsorption using commercial activated carbons, which is a highly efficient technique, but the production and improvement process for activated carbon substances originating from inorganic compounds is costly and complex. The papaya fruit, in particular, has received superior attention in heavy metal adsorption studies from various research teams (Rama Raju *et al*., 2013) in the countries that implement large-scale papaya cultivation since high amounts of its agricultural by-products can be employed as potential environmentally friendly low-cost adsorbents.

1.2 Overview of agro-waste adsorbent potential in treating heavy metal pollution in wastewater

Activated carbon is known as a common adsorbent for the removal of heavy metal from aqueous media and is widely used in wastewater treatments to produce drinking water, control atmospheric pollution, separate poisonous gases, and recover solvents (Karnib *et al*., 2014; Rama Raju *et al*., 2013; Yalda *et al*., 2012). Recently, use of naturally abundant or agricultural waste biomass as a base to develop novel activated carbon is known as promising technique to remove most types of heavy metals from contaminated waters through adsorption process. The key characteristics of activated carbon such as its highly developed porosity, high surface area, and high mechanical strength, lend to its great adsorption capability, yet this adsorbent remains expensive due to its costly production process. Therefore, it is essential to evaluate and provide low-cost effective carbons for water pollution control. Properties such as surface charge, type of surface functional groups, specific surface area, and pore-size distribution affect the adsorption capabilities of activated carbon in regard to metal ions and depend on the nature of the base material used and the production methodology followed (Liu *et al*., 2010).

Recently, the papaya fruit has received superior attention in heavy metal adsorption studies from the various research teams and has been reported as potential environmentally friendly low-cost adsorbents. Malaysia is now capable of producing up to 72,000 tonnes of papaya annually (Hameed *et al*., 2009). As a result, solid waste from the papaya such as its peel, skin, and seeds are produced in excess. In general, over 50% of the papayas' weight during processing will become waste materials. Instead of wasting this waste and by-products from carica papaya there is potential to produce value added products from them that could contribute toward resource conservation and environmental protection concept. Various parts of the Carica papaya tree, from its wood and leaves to fruit pulps and seeds have been examined in different experiments for their metal removal capability (Table 1.2). These studies have demonstrated the high removal efficiency of different metal ions from aqueous solutions such as cadmium, zinc, lead, chromium using the different wastes from the papaya as a bio-adsorbent (Otsuki *et al.,* 2010; Gilbert *et al.,* 2011; Egila *et al.*, 2011; Manjusha *et al.*, 2012; Ong *et al.*, 2012; Raju *et al.*, 2012; Sanusi *et al.*, 2016). Among all the Carica papaya parts, the papaya seed has been used the most for metal ion removal experiments and has proven to be a highly efficient adsorbent for various heavy metals and dye removal (Hameed *et al.*, 2009). According to the published reports (Table 1.2), the physical and chemical meditations have been made for those adsorbents derived from papaya, provides higher surface area, better porosity, more surface functional groups and consequently offers higher metal affinity and adsorption capacity for the developed adsorbents. However, the attempts conducted, were more focused on the metal adsorption capacity of papaya seeds. Despite considerable uptake potential of papaya seeds to remove metals and dye, its lead removal efficiency has shown not a strong competence towards lead ions. On the other hand, the use of waste materials generated from papaya processing industries such as food and cosmetic industries, could result in waste minimization and tremendous cost saving. Although the papaya peel produces large quantities of by-products that are considered agricultural waste, researchers are still least interested in the metal removal capability of these natural adsorbents. The papaya peel contains volatile components and similar to its pulp, includes mineral elements such as potassium, calcium, and magnesium. Despite many studies conducted (Table 1.2), yet no study has addressed the capacity of papaya peel for the removal of Pb(II) from contaminated water. This is the underlying motivation for this study i.e. to conduct research on the applicability of the papaya peel as an adsorbent in the removal of lead from aqueous solutions.

Besides all the conventional adsorbents, different types of Nanomaterials (with particle sizes of 1 μm to 100 μm) are new adsorbents that can be used in the adsorption of heavy metals from contaminated water. They have shown considerable potential for the treatment of environmental pollution, higher efficiency and faster removal rate because of their special surface characteristics and highly developed surface area that offers great adsorption potential (Lee *et al.*, 2010, Sadegh *et al.*, 2014). Different types of nanomaterial like carbon nanotubes, graphene, Nano metal or metal oxides, and polymeric sorbents have been assessed for heavy metal removal capability from aqueous solutions, and the results clearly confirm the high adsorption capacity of the nanomaterial due to its unique structure (Wu and Zhao, 2011).

Table 1.2: Bioadsorbents produced from Carica papaya waste.

Author(s)/ Year	Adsorbent/ Dye or Metal ion	Results
Karthikeyan and Ilango,2008	Papaya linn/ Cr (VI)	96%
Hameed, 2009	Papaya seeds/ MB	95%
Eglia *et al.,* 2011	Papaya seeds and African spinach/ Mn(II) and Pb(II)	95%
Manjusha *et al.*, 2012	Papaya peel/ Cr(VI)	89%
Ong *et al*., 2012	Papaya seeds/ Zn(II)	95%
Yadav *et al*., 2013	Papaya seed/ Pb(II)	68.4%
Gandhi *et al*., 2013	Papaya seed/ Cr(VI)	82%
Sanusi et al., 2015	Papaya seed and clay (Cd^{2+})	93%
Sanusi *et al*., 2016	Papaya seed & clay/ Pb(II)	94.8%

The improvement of nanoscience and nanotechnology has opened significant opportunities in remediation of environmental problems (Zare *et al*., 2013). The proposed nanoparticles as novel adsorbent for the adsorption of heavy metal should meet five criteriation: 1) presents nontoxic nature 2) demonstrates high adsorption capacity and relatively high selectivity even in low concentration of impurities 3) provides easy removal of pollutant from its surface after adsorption process 4) shows reasonable reuse and regeneration possibility 5) proposes a reversible adsorption process and reuse of loaded-adsorbent (Sadegh *et al.*, 2014). Compare to conventional adsorbents the nanomaterial has demonstrated much higher adsorption capacity and metal affinity due to their specific charecteristics as mentioned before. These Nano-based adsorbents potentially can enhance the adsorption process and therefore, may lead to higher adsorption efficiency, rapid removal of toxic heavy metal from aqueous solution (Gupta *et al*., 2015). The carbon-based Nano-adsorbent are among most effective, inexpensive adsorbent for the purification of heavy metal contaminated effluents due to their special characteristic, availability, high efficiency and regeneration potential (Zhang *et al.*, 2013). Attachment of nano-sized inorganic particle through surface modification of carbon-based material can provide highly stable Nano-adsorbent with special surface functionalities for the uptake of specific / selective metal ion from wastewater (Gupta *et al*., 2015). In fact, those types of adsorbents have drawn much attention due to their higher surface area and porosity, higher adsorption capacity, nontoxicity and faster kinetics (Singh *et al*., 2013). Various forms of efficient, environmentally friendly and cost effective nanomaterials have been proposed for the possible application in decontamination of polluted water. Although several carbon-based nano-adsorbents have been developed for water purification processes, potential papaya-originated nano-adsorbent has yet been addressed by researchers. Papaya fruit agro-wastes have been numerously studied for their heavy metal removal potential in those countries with large papaya cultivation and the results reaveled great functionality of those agro-waste originated-adsorbents from papaya. However, development of a Nano-adsorbent from papaya agro-waste to remove heavy metal from wastewater has not been explored yet which potentially can create great opportunity for local communities as well as industrial sector. This was the second main objective of this study to investigate the potential of developing Nano-adsorbent from locally available agro-waste of papaya peel for Pb(II) uptake.

1.3 Problem statement

Lead is a very poisonous metal and can be accumulated in the living organs. Thus, treatment of lead-contaminated water is becoming more urgent nowadays specifically in developing countries that are facing with drinking water shortage and high water pollution issues. Based on the report from DOE (DOE, 2013), in Malaysia heavy metal pollution in water bodies is very critical especially the level of pollution in most of the rivers is not within safe limit. In addition, the solubility of Pb(II) in water also accelerates as temperature increases. Therefore, in tropical countries like Malaysia, lead (II) removal will be that much more important and challenging than in moderate climates. Bioadsorption of heavy metals has become more advantageous by means of its efficient and flexible metal uptake process yet simple design procedure, formation of almost no harmful by-process substances, and unique chemical composition. The biomass of agro-wastes used in bioadsorption methodology are naturally abundant, generally contains natural compounds and some molecular groups that are able to bond metal cations and provide for better metal sequestering (Othman *et al*., 2013; Hashem *et al.,* 2005). Using existing activated carbon or other synthesised adsorbents is costly and ineffective for treatment of wastewater with low metal ion concentrations (Birungi and Chirwa, 2014). Therefore, researchers are continuously seeking out new yet efficient materials as adsorbents to remove toxic metal ions from contaminated water. Following are the problem statement of this work:

Given the papaya peel as a source of locally available agro-waste, it is desired to study the potential of raw, activated carbon and Nano-particle embedded papaya peel on lead removal from wastewater. Even through different studies, the metal affinity of papaya wastes have been confirmed but yet no attempt has evaluated the papaya peel and its relative Nano-adsorbent potential as an alternative solution to remove lead content from industrial wastewater discharges. This study is the first of its kind to do so. The papaya peel (PP) and its relative activated carbon (AC-PP) and Nano particles (Nano-PP) will be characterised by different methods and investigated for the removal of Pb(II) from an aqueous solution using the batch sorption mechanism. The best operating parameters involving the pH, initial ion concentration, adsorbent dosage, contact time and temperature will be determined. The thermodynamics, isotherm and kinetics experiments will be conducted and the results will be correlated with the Langmuir, Freundlich, and Temkin isotherms and the pseudo first-order, pseudo second-order and intra-particle diffusion kinetic models. The regeneration potential of the new adsorbents will also be studied.

1.4 Objectives of research

The main objective of this study is to investigate the capability of the papaya fruit peel (PP) and develop it as a natural low cost adsorbent for the removal of Pb(II) from an aqueous solution. To fulfil the aim of this research, the following sub-objectives were formulated:

1- To develop new adsorbents (activated carbon (AC-PP) and Nano particle (Nano-PP)) from papaya peel waste for the removal of Pb(II) from contaminated water.

2- To determine the adsorption potential, the optimum operating conditions and the equilibrium conditions for Pb(II) removal in aqueous solution by using activated carbon papaya peel (AC-PP) and Nano papaya peel (Nano-PP).

3- To correlate the Pb(II) uptake kinetics and isotherm results, using the developed adsorbents (AC-PP and Nano-PP), with the pseudo first-order, pseudo second-order, and inter particle kinetic models and Langmuir, Freundlich and Temkin isotherm models.

1.5 Scope of research

To achieve the objective of the study, the scope of research is formulated as follows:

- Identifying potential natural adsorbent for heavy metal removal and analyze existing adsorbent/treatment methodologies.
- Preparing raw papaya peel and two of its associated adsorbents, AC-PP and Nano-PP, for the removal of Pb(II) from an aqueous solution.
- Characterizing the raw papaya peel, and analysing the surface and porosity of the developed adsorbents (AC-PP and Nano-PP) using different surface analysis methods of BET, FT-IR, SEM, XRD, XPS, EDX, etc.
- Conducting batch mode Pb(II) adsorption processes using raw papaya peel, activated carbon papaya peel (AC-PP), and Nano papaya peel (Nano-PP) adsorbents in consideration of the influencing parameters of pH, temperature, contact time, adsorbent dosage, and initial metal concentration.

- Conducting Pb(II) adsorption equilibrium isotherm experimental studies using developed adsorbents.
- Conducting Pb(II) adsorption kinetics experimental studies using developed adsorbents.
- Investigating the Pb(II) adsorption thermodynamic parameters of ΔH^o, ΔG^o, and ΔS^o.
- Conducting Pb(II) desorption and regeneration experimental studies by using the developed adsorbents (AC-PP and Nano-PP).
- Correlating Pb(II) adsorption experimental results for raw-PP, AC-PP, and Nano-PP with the established isotherm models of Langmuir, Freundlich, and Temkin and the kinetic models of pseudo first-order, pseudo second-order, and intra-particle models.
- Analyzing experimental and modelling results.

1.6 Significant of study

As a toxic heavy metal, lead is known to be an environmental concern worldwide due to its accumulation in the human body, and its chronic toxic effects, causing malfunction of certain organs over a long period of time. The annual production of lead continues to rise and the industries/manufacturers responsible are continuously releasing toxic discharge to the environment, which poses a significant health risk to humans and the surrounding environment. Hence, the lead contamination in the natural waters becomes global problem and is always a challenge for scientists since the environmentally admissible levels and threshold limits based on health criteria, decreases continuously. Therefore, the lead pollution problem indicates the importance of water resource management in the affected countries. Besides that, using current decontamination techniques and synthetic activated carbon adsorbent is moderately costly and ineffective for low metal ion concentrations.

Taking into account the situation illustrated above, the present research proposed the use of one of the abundant agro-waste in Malaysia as an inherently benign, inexpensive with high adsorption efficiency adsorbent to remove lead from the contaminated water. The papaya fruit peel, which has high concentrations of carboxylic and hydroxyl components, was considered as the potential lead biosorbent. Hence, for this study, the papaya peel (PP), its activated carbon (AC-PP) and Nano particles (Nano-PP) were developed for the removal of Pb(II) from an aqueous solution using a batch sorption mechanism. The research considered the metal binding potential of the papaya peel and therefore, its Pb(II) adsorption practicability was evaluated. The developed adsorbents, particulary Nano-PP adsorbent, presented extraordinary surface characteristics and a great surface area that enhanced significantly its uptake capacity towards lead ions. The Nano-PP provided a tremendous interface that is an important requirement for a good adsorbent offering highly efficient adsorption process. The developed adsorbent of papaya peel (PP), which is a cheap, efficient, and environmentally benign adsorbent in removing lead (II) from an aqueous solution, can contribute towards a novel approach in the heavy metal treatment process.

1.7 Summary of thesis

This thesis is comprised of five chapters. Chapter 1 provides an overview of the research conception and background, problem statement, research objectives, and the scope and significance of this study.

Chapter 2 provides a critical review on the presence of lead in the environment, various heavy metal removal techniques, application of biosorption in lead removal from wastewater, and the use of different agro-wastes as bioadsorbents.

Chapter 3 describes the research methodology and steps followed for this research.

Chapter 4 reveals all the results and findings obtained through the research methodology (experimental and modelling studies) using developed adsorbents of AC-PP, and Nano-PP, together with the theoretical explanations of these outcomes.

Chapter 5 provides the conclusion and summary of the results presented in Chapter 4 and also some suggestions are given for future study on the adsorption potential of the papaya peel. Table B.1 which lists all the publications associated with this work, is presented in the appendix B.

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