DETERMINATION OF KINETICS AND OPTIMAL CONDITIONS FOR THE DESORPTION OF LEAD IONS OF THE PALM SHELL ACTIVATED CARBON SURFACE

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A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Hons.) Chemical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"DETERMINATION OF KINETICS AND OPTIMAL CONDITIONS FOR THE DESORPTION OF LEAD IONS OF THE PALM SHELL ACTIVATED CARBON SURFACE"** was prepared by **ADELINE LIM SZE LYNN** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Hons.) Chemical Engineering at Universiti Tunku Abdul Rahman.

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Date : _________________________

Specially dedicated to
my beloved grandmother, mother and father

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ABSTRACT

This research is conducted to evaluate desorption efficiency of lead ions from the palm shell activated carbon surface using different desorbing agents. The experiments were conducted in three consecutive cycles to determine the kinetics and optimal conditions for best performance of the palm shell activated carbon. Batch adsorption and desorption experiments were carried out with constant parameters of agitation speed of 220 rpm and temperature of 27 °C. The effect of parameters such as contact time and desorbing agent was studied. The obtained data were calculated to give desorption efficiency of lead ions from palm shell activated carbon and it was found that desorbing agent played a major role in the desorption process. The maximum desorption efficiency for lead ions from palm shell activated carbon was more than 90 % after three consecutive cycles in desorbing agent hydrochloric acid. The optimal contact time for highest desorption efficiency was found to be 240 min for both desorbing agents. Theoretical kinetic of desorption suggested the desorption process was a first-order model.

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LIST OF SYMBOLS / ABBREVIATIONS

A	pre-exponential factor
C	heavy metal concentration in the solution
C_e	equilibrium concentration of adsorbate in wastewater sample after adsorption, mg/L
C_t	concentration of metal ions in the desorption solution at time t, mg/L
C_i	initial concentration of the metal ion at equilibrium, mg/L
E_a^{des}	activation energy for desorption
$-\Delta H_{ads}$	enthalpy of adsorption
k	rate constant for the desorption process
k_1	first order rate constant
$k_{ADS,S-1}$, $k_{ADS,S-2}$	adsorption constant for site-1 and -2
$k_{DES,S-1}$, $k_{DES,S-2}$	desorption constant for site-1 and -2
K	Langmuir constant related to energy of adsorption, L/mg
K_e	equilibrium adsorption constant
M	mass of the adsorbate (palm shell activated carbon) used, g
M_1	concentration of stock solution, mg/L
M_1	concentration of lead ions solution, mg/L
n	kinetic order or desorption order
N	surface concentration of adsorbed species
q_e	amount of metal ion adsorbed per unit mass of adsorbent
q_m	maximum adsorbate uptake capacity corresponding to complete monolayer coverage, mg of adsorbate / g of adsorbent
Q_{S-1}, Q_{S-2}	heavy metal ions amounts per gram of adsorbent for site-1 and -2
R	gas constant
R_{des}	rate of desorption

T	temperature, K or °C
V	volume of the heavy metal solution, L
V	volume of the desorption solution, L
V_1	volume of stock solution, L
V_2	volume of lead ions in the solution, L
x	kinetic order of desorption
$X_{m,S\text{-}1}$, $X_{m,S\text{-}2}$	maximum numbers of adsorption sites for site-1 and -2
τ	surface residence time
τ_o	period of vibration of the bond
θ_M	instantaneous coverage of the adsorbate molecules on surface adsorption sites
CAC	commercial activated carbon
DE	desorption efficiency, %
PSAC	palm shell activated carbon

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CHAPTER 1

INTRODUCTION

1.1 Background

Lead is a naturally occurring element and is a member of Group 14 (IV) of the periodic table. Lead exists in three oxidation states: Pb(0), the bluish-gray form of metal; Pb(II); and Pb(IV). It is perhaps the earliest known industrial pollutant. In the environment, lead primarily exists as Pb(II). While Pb(IV) is only formed under extremely oxidizing conditions, it's inorganic Pb(IV) compounds are not found under ordinary environmental conditions. Although lead rarely occurs naturally, it is commonly found in copper, zinc and silver ore deposites. The principal lead mineral is lead sulphide (galena, PbS) while some other minerals from which lead is extracted are cerussite (lead carbonate, $PbCO_3$) and anglesite (lead sulphate, $PbSO_4$). A large amount of used lead worldwide is also recovered from recycling ("Lead", 2011).

Lead has both beneficial and detrimental properties. Its excellent corrosion resistance property in the environment, high density, and low melting point, made it a familiar metal in pipes, solder, weights and storage batteries. When exposed to air and water, lead sulphate, lead oxides, and lead carbonates film forms, acting as protective barriers that slows or halts corrosion of the underlying metal. The very high density of lead makes it suitable for shielding against sound, vibrations and radiation, acting as protection for computer and TV screens users. For these purposes, lead is used in metallic form or as lead compounds in lead glasses. Tetraethyl lead was widely used as an anti-knock agent in petrol, and as an additive in paints.

However, these uses have been reduced recently because of environmental concerns about cumulative lead poisoning and followed stricter environmental standards.

Because lead was historically a popular choice for plumbing and some of these pipes are still functional to this day, water delivered through these pipes paves for leaching of lead out of a plumbing system to drinking water. Besides, major pathways of lead into wastewater are also in the form of agricultural leachate from landfills and lead wastes from etching operations used in the manufacturing of printed circuit boards and semiconductor devices. These industries produce large quantities of toxic wastewater effluents. Exposures to small amounts of lead over a long time can slowly accumulate to reach harmful levels which may gradually develop harmful effects without warning. Short-term exposure to high levels of lead can adversely affect the nervous, reproductive, digestive, cardiovascular blood-forming systems, and the kidney. Symptoms of nervous system effects include fatigue and headaches, feeling anxious or irritable and difficulty sleeping or concentrating and more severe symptoms include loss of short-term memory, depression, confusion and even fatality. Children are more adversely affected as they absorb lead more readily and the developing nervous system puts them at increased risk for lead-related harm, including learning disabilities, delayed motor development and causing hearing problems to younger children. Effects on the gastrointestinal tract include nausea, constipation, and loss of appetite.

With the advancement of technology, a wide range of physical and chemical processes is available for the removal of lead from wastewater; such as electro-chemical precipitation, ultra filtration, electroplating, ion exchange and reverse osmosis (Nomanbhay and Palanisamy, 2005). Unfortunately, these methods are reported to be inefficient and costly and they may also generate undesirable secondary wastes which are difficult to treat (Deng, Su, Hua, Wang & Zhu, 2007). In contrast, adsorption processes are used as alternative to the wastewater treatment where more than one type of metal ions can be present. In this context, the regeneration of the adsorbent may be of significant importance for an economical advantage and in opening possibility of recovering the metals extracted from the liquid phase. For this reason, it is attractive to desorb the heavy metals and to regenerate the adsorbent material for more cycles of application (Ahalya, Ramachandra & Kanamadi, 2003). Adsorption using commercial activated carbon (CAC) can remove heavy metals from wastewater, such as cadmium (Cd), nickel (Ni), chromium (Cr) and copper (Cu). However CAC remains an expensive material for heavy metal removal.

On the other hand, natural biopolymers are industrially attractive due to their capability of lowering transition metal-ion concentration to parts per billion concentrations. Natural materials that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly. The oil palm *Elaeis guineensis* (native to west Africa) and *Elaeis* oleifera(native to tropical Central America and South America) can be wild, semi-wild and of cultivated type in the three land areas of the equatorial tropics: Africa, South-East Asia and America (Hartley, 1988). Due to its many uses and financial benefits, cultivation of oil palm has been rapidly expanding in different parts of the world and the most productive parts of the palm oil industry entering international trade at present are in Indonesia and Malaysia (Corley and Tinker, 2003).

Nomanbhay and Palanisamy (2005) reported that Malaysia currently records an annual production of about 30 million tonnes of oil palm biomass, including trunks, fronds, fruit waste and empty fruit brunches. Of these, fruit shell (or endocarp) comprises of about two million tonnes annually. Preliminary studies have shown that it is feasible to prepare chars with sufficient densities and high porosity from oil palm fruit waste for it to be deemed useful as an effective adsorbent. The sorption properties of palm oil shell owe it to the presence of carboxylic, hydroxyl, and lactone functional groups, which have a high affinity for metal ions. Adding to that, development of surface modified activated carbon in the recent years has generated a diverse range of activated carbons with far greater adsorption capacity. Unsurprisingly, the improved metal removal performance of the activated carbon produced from palm oil shell would add to its economic value, help reduce the cost of waste disposal, and most importantly, provide a potentially inexpensive alternative to existing CAC.

If the adsorption process is used as an alternative in wastewater treatment, desorption and regeneration of adsorbent is crucial to keep processing costs low and open possibility to recover the extracted heavy metal from the liquid phase. Desorption process which yields lead in concentrated form facilitates disposal and restore adsorbents for effective reuse. Sodium hydroxide, hydrochloric acid and nitric acid chemical compounds are most widely used in chemical extraction to regenerate exhausted adsorbent but there is little study about the mechanism of lead desorption and re-adsorption process.

1.2 Aims and Objectives

This research involves conducting experiments to determine the extent of sorption reversibility and desorption efficiency of the palm shell activated carbon (PSAC) after repeated cycles. The general objective is to evaluate desorption efficiency of lead of the PSAC using different desorbing agents in three consecutive cycles. Desorption agents that will be used to test desorption of lead ions are nitric acid and hydrochloric acid. The specific objectives are:

1. To determine better desorbing agents for best performance of desorption of lead (II) ions of PSAC.
2. To determine optimal period desorption efficiency of contact time for the efficient desorption of lead (II) ions from aqueous solutions.
3. To determine the number of cycles for optimal desorption efficiency of PSAC of lead ions in aqueous solutions.

Repeated availability usage of the PSAC will give economical interest to provide an attractive lucrative solution in wastewater treatment and heavy metals recovery from aqueous solution.

CHAPTER 2

LITERATURE REVIEW

In this chapter, an introduction to the principles of adsorption - desorption and kinetics of desorption are elaborated with theories supported by equations from different previous studies. In addition, a detailed explanation on the characteristics of the palm shell activated carbon (PSAC) and how the experimental conditions affect desorption of heavy metal ions from it are discussed. Previous studies on different raw materials to produce activated carbon are mentioned in this literature review.

2.1 Characteristics of Palm Shell Activated Carbon

Activated carbon is used extensively in the effort of removing heavy metals from wastewater because of its unique property of strong physical adsorption forces with high volume of porous surfaces for high adsorption capacity. Its surface area can reach up to more than 1000 m^2/g or put in another words, the surface area of a football field by only 5 g of activated carbon. The three main physical carbon types are granular, powder and extruded (pellet). All three types of activated carbon have properties tailored to the application. Under different parameters of the activation process, the properties of activated carbon also vary accordingly. Activated carbon is frequently used in everyday life, in; industry, food production, medicine, pharmacy, military, etc.

According to Gupta (2008), activated carbon is a carbonaceous material that has a variety of functional groups like carboxyl, aldehydes and other organic and non-organic functional groups on the surface of the material. The presence of the functional groups on the surface of activated carbon also determines the interactions of the material with certain molecules present in a gas or liquid. Hence, it is justified to say that the adsorption capacity of activated carbon can be well enhanced by increasing the concentration of appropriate surface functional groups. As reported by Wan Nik, Rahman, Yusof, Ani, and Che Adnan (2006), the surface of activated carbon can contain protonated ($C\text{-}OH_2^+$), neutral (COH) or ionized (CO^-) groups. Activated carbon with protonated surfaces are also known as H-type carbons while activated carbons with ionized surfaces are known as L–type carbons.

Despite the advantageous properties of activated carbon, the cost of commercially available activated carbon of different grades is very expensive and not economical when large-scaled treatment is employed. The efforts to find relatively efficient, cheap and easily available adsorbent for the studies of adsorption and desorption of heavy metals are growing. To name a few, these activated carbons are prepared of renewable biomass materials such as silk cotton hull carbon (Shanmugavalli et al., 2006), activated tea leaf waste (Mondal, 2009), rice husk ash (El-Said, Badawy, Abdel-Aal & Garamon, 2010), periwinkle shells (Badmus, Audu & Anyata, 2007), pecan shell (Dastgheib and Rockstraw, 2002), sawdust (Akissi, Adouby, Wandan, Yao & Kotchi, 2010), *Spartina alterniflora* – a salt-marsh plant (Li and Wang, 2009) and oil palm fruit fibre (Bello, Oladipo & Olatunde, 2010). Few researchers focused on the adsorptive- desorptive properties of palm shell activated carbon. Chun, Aroua and Wan Daud (2007) reported on the equilibrium studies of enhancing adsorption of heavy metal ions onto Polyethyleneimine-Impregnated palm shell activated carbon. Chu and Hashim (2002) investigated the application of palm oil fuel ash in removing zinc from aqueous solutions. Issabayeva, Aroua and Nik Sulaiman (2005) studied performance of PSAC for the adsorption of heavy metals from aqueous solutions. There is inadequate research on the application of PSAC for desorption of heavy metals from aqueous solutions.

Following the trend of cost-effective and environmentally-friendly initiative, abundant palm shell wastes from the palm oil industry in Malaysia are utilised as raw material for producing high surface area activated carbon. In addition to the high organic matter content of cellulose, halocellulose and lignin fibres, oil palm in Malaysia is also low in ash content with only 1.1 % in dry weight basis (Adinata, Wan Daud & Aroua, 2007a). It is a versatile adsorbent due to its good adsorption properties. There are basically two preparation methods of activated carbon from palm shell. One of them is the physical activation process which consists of carbonization of the palm shell at high temperature in the range 600 to 900 °C and then followed by the activation of the char using carbon dioxide or steam in the temperature range of 600 to 1200 °C (Adinata, Ahmad, Wan Daud & Aroua, 2007b). The second preparation method is chemical activation where the raw material (palm shell) is impregnated with an activating agent and heated in an inert atmosphere. The raw material is carbonized at lower temperatures in the range of 450 to 900 °C. These carbonization and activation steps proceed simultaneously and pores are developed with dehydration and oxidation processes. (Adinata et al., 2007b).

Chemical activation method is more preferred over physical activation to produce activated carbon using palm shell due to the lower temperature and shorter time needed for activating material. The chemical activation process is carried out first by treatment with H_2SO_4 in solution at 24 hours and then further immersed in H_2PO_4 solution for 24 hours to separate the waste floats using distilled water. Following that, the carbonization step and activation step proceed simultaneously by impregnation with activating agent at optimal carbonization temperatures of 500 °C to 800 °C for an optimal time of 2 h. Various studies employing different chemicals as activating agent have been conducted, typically acid, strong base or a salt. The acid, strong base and salt more commonly used are H_3PO_4 (Wan Nik et al., 2006), K_2CO_3 (Adinata et al., 2007a and Adinata et al., 2007b) and KOH or NaOH (Guo and Lua, 2003) respectively.

Adinata et al.(2007a and 2007b) have found that increase in activation time has widened the surface porous area as the pores of activated carbon from palm shell were converted from micropores (less than 2 nm in diameter) to mesopores (2 to 50 nm in diameter), yielding higher total surface area. They have reasoned this by stating that the increase in activation time increases the solid density progressively due to release of low molecular weight products like water, furan derivates and laevoglucose. Drying of palm shell at 110 °C for 24 h during the activation process contributes to the dehydration and elimination reactions, leading to evolution of internal porosity. Higher concentrations of the activating agent also consistently yield products with a much higher external surface area. Their studies have also found the optimum activation condition is at an impregnation ratio of 1.0 by the formula,

$$impregnation.ratio = \frac{(weight.of.K_2CO_3in.solution)}{(weight.of.palm.shell)} \tag{2.1}$$

(Adinata et. al., 2007a and 2007b)

2.2 Theoretical Principles of Adsorption

Adsorption is selective binding of a substance by another solid substance. Molecules from gas phase or in this study, solution, bind in a layer of condensed phase on a solid (or liquid) surface. The molecules are called adsorbate and the substrate is the adsorbent. Removal of the molecules is termed desorption.

In the process of adsorption, adsorbate molecules of gas, liquid or dissolved solids are adhered to the surface of the solid adsorbent (i.e. palm shell activated carbon). The adsorbed species may remain for an unknown period in that state at low temperatures. As the temperature of the substrate is increased, a molecular species may decompose to yield gas phase products or other surface species or an atomic adsorbate may react with the substrate to yield a specific surface compound or diffuse into the bulk of the underlying solid or a desorption takes place where the species desorb from the surface (“The Desorption Process”, 2011).

Almost all materials have the capacity for holding adsorbates, our interest of study is particularly in activated carbon which has a large active surface area due to the presence of mesopores. Mesoporous materials are pororus materials with regularly arranged and uniform mesopores, typically 2 to 50 nm in diameter. Adsorption reactions can be described by various models. Examples are the Langmuir adsorption isotherm model, Freundlich isotherm model and the distribution coefficient model. These empirical models provide a molecular description of adsorption using an equilibrium approach. The Langmuir adsorption isotherm and the Freundlich isotherm are the two most commonly applied models to describe the distribution of lead involving the liquid phase and the solid phase equilibria.

2.3 Langmuir Adsorption Isotherm Model

The Langmuir isotherm is based primarily on the concept that only a single adsorption layer exists on an adsorbent to represent the equilibrium distribution. It is based on four hypotheses:

- The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
- Adsorbed molecules do not interact.
- All adsorption occurs through the same mechanism.
- At maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other already adsorbed molecules of adsorbate, only on the free surface of the adsorbent (Fogler, 2006).

Langmuir model can be represented as follows,

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{2.2}$$

(Deng et. al., 2007)

where

q_e = amount of metal ion adsorbed per unit mass of adsorbent

q_m = maximum adsorbate uptake capacity corresponding to complete monolayer coverage (mg of adsorbate / g of adsorbent)

K = Langmuir constant related to energy of adsorption (L/mg)

C_e = equilibrium concentration of adsorbate in wastewater sample after adsorption (mg/L)

Equation 2.2 can be rearranged to give a linear equation for calculation of adsorption capacities,

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K} \tag{2.3}$$

(Badmus et. al., 2007)

q_m and K are obtained from the intercept and slope of plot of C_e/q_e against C_e . In this research, the evaluation of the equilibrium heavy metal concentration, q_e (mg/g) on the PSAC over time is represented by,

$$q_e = \frac{V(C_i - C_e)}{M} \tag{2.4}$$

(Badmus et. al., 2007)

where
V = volume of the heavy metal solution (L)
C_i = initial concentration of the metal ion at equilibrium (mg/L)
C_e = equilibrium concentration of adsorbate in wastewater sample after adsorption (mg/L)
M = mass of the adsorbate (palm shell activated carbon) used (g)

2.4 Freundlich Adsorption Isotherm Model

The Freundlich isotherm as mentioned by Mengistie, Siva Rao, Prasada Rao amd Singanan (2008) assumes a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site still behaving as the Langmuir isotherm. This isotherm is considered to be much realistic compared to the Langmuir isotherm which is developed on the assumption of independence and equivalence of adsorption sites ignoring the possibility that the initial layer may act as substrate for the subsequent adsorption. Badmus et al., (2007) also wrote this type of isotherm indicates the surface heterogeneity of the adsorptive sites made up of small heterogeneous adsorption patches that are homogeneous themselves.

The expression of Freundlich isotherm given by

$$q_e = KC^{1/n} \tag{2.5}$$

(Badmus et al., 2007)

where
K = measure of the capacity of adsorbent
n = measure of how affinity for the adsorbate changes with adsorption density
(n >1 indicates the affinities decrease with increasing adsorption density)

In Freundlich isotherm, the determination of coefficient K and n can be done by using the linearized form of equation (2.5):

$$\log q_e = \log K + \frac{1}{n} \log C \tag{2.6}$$

(Bello et al., 2010)

In the context of adsorption, hysteresis loops occur when the quantity adsorbed is different when adsorbate is being added than when it is being removed. The adsorption hysteresis is linked to differences in the nucleation and evaporation mechanisms inside mesopores. In relation to that, the path of desorption isotherm may differ from that of the adsorption isotherm owing to hysteresis effect. Chéry, de Marsily and Darcy (2007) wrote that desorption is a more difficult process than adsorption because the reactions are only partially irreversible. Thus, not all of the adsorbate or heavy metal ions will desorb from the surface completely. According to Chesworth (2008), heavy metals may be retained by heterogeneous type sites having a wide range of binding energies. Henceforth, binding may be irreversible at low concentrations and the irreversible amount almost always increase with time. He also suggested that hysteresis for heavy metals is probably due to extremely high energy bonding with organic matter and layer silicate surfaces.

2.5 Theoretical Principles of Desorption

Kannan and Thambidurai (2007) mentioned that protons in the acidic medium compete with lead ion and displace the maximum amount of adsorbed lead, suggesting that ion exchange mechanism is important in connection with adsorption. Hydrogen ions released from the acids replace metal cations on the adsorbent (El-Said et al., 2010). The rate of desorption, R_{des} , of and adsorbate from a surface can be expressed in the general form,

$$R_{\mathrm{des}} = kN^{x} \tag{2.7}$$

("The Desorption Process", 2011)

where
x = kinetic order of desorption
k = rate constant for the desorption process
N = surface concentration of adsorbed species

Typically, there are two types of desorption processes and the order of desorption can be predicted by the number of elementary steps involved. Atomic or simple molecular desorption as a simple molecule on the surface desorbs into gaseous form is the first-order process. The second-order process on the other hand, will be a recombinative molecular desorption of two atoms (typically hydrogen) on the surface desorb and form a gaseous molecule (H_2). The rate constant for the desorption is expressed in an Arrhenius form,

$$k_{des} = A\exp(-E_{a}^{des} / RT) \tag{2.8}$$

("The Desorption Process", 2011)

where
$E_a{}^{des}$ = activation energy for desorption
A = pre-exponential factor; also considered to be the attempt frequency, υ , at overcoming the barrier to desorption

This then gives the general expression for the rate of desorption

$$R_{des} = -dN/dt = \nu.N\ \ .\exp(-E_a^{des}/RT) \tag{2.9}$$

("The Desorption Process", 2011)

2.6 Surface Residence Time

An adsorbed species' surface residence time is very much related to the desorption kinetics. It is the average time that a species spends on the surface under a particular set of conditions, be it optimal or not optimal; before it desorbs from the surface into gas phase or liquid phase. For example, for a first order process, the average time (τ) is given by

$$\tau = 1/k_1 \tag{2.10}$$

("The Desorption Process", 2011)

where

k_1 = first order rate constant

and from equation 2.8, we have

$$k_1 = \nu \exp(-E_a^{des}/RT) \tag{2.11}$$

("The Desorption Process", 2011)

Then the surface residence time becomes:

$$\tau = \tau_o \exp(-\Delta H_{ads}/RT) \tag{2.12}$$

("The Desorption Process", 2011)

where

$-\Delta H_{ads}$ = enthalpy of adsorption (~activation energy for desorption, E_a^{des})

τ_o = period of vibration of the bond, $1/\upsilon$

2.7 Kinetics of Desorption

Chemical kinetics is the study of chemical reactions with respect to reaction rates, re-arrangement of atoms, effect of various variables etc. Kinetics of a chemical reaction, i.e desorption in this context, affect reaction rates. Typically, kinetics studies will depict how long a reaction will take to occur to be considered kinetically feasible.

The kinetics of desorption of heavy metals from the surface of PSAC can be explained by the presence of two types of binding sites with slightly different binding energies (Kolasinski, 2008). In conjunction to that, Machida, Kikuchi, Aikawa and Tatsumoto (2004) investigated the kinetics of adsorption and desorption of lead ions in aqueous solution on coconut shell activated carbon by a two-site model because they found that not all lead ions are adsorbed on the adsorption sites. A two-site model comprises of the strong binding sites and the weak binding sites characterized by its affinity towards the adsorbate molecules. Langmuir-type rate equations were introduced to represent the adsorption and desorption quantitatively and expressed as follows,

$$\frac{dQ_{S-1}}{dt} = k_{ADS,S-1}C(X_{m,s-1} - Q_{S-1)} - k_{DES,S-1}Q_{S-1} \qquad (2.13)$$

(Machida et al., 2004)

$$\frac{dQ_{S-2}}{dt} = k_{ADS,S-2}C(X_{m,s-2} - Q_{S-2)} - k_{DES,S-2}Q_{S-2} \qquad (2.14)$$

(Machida et al., 2004)

where

C = heavy metal concentration in the solution

Q_{S-1}, Q_{S-2} = heavy metal ions amounts per gram of adsorbent for site-1 and -2

$k_{ADS,S-1}$, $k_{ADS,S-2}$ = adsorption constant for site-1 and -2

$k_{DES,S-1}$, $k_{DES,S-2}$ = desorption constant for site-1 and -2

$X_{m,S-1}$, $X_{m,S-2}$ = maximum numbers of adsorption sites for site-1 and -2

Equilibrium adsorption constant, K_e can be expressed as,

$$K_e = \frac{k_{ADS}}{k_{DES}} \tag{2.15}$$

(Machida et al., 2004)

and concentration of heavy metal, C, be represented by,

$$C = C_o - (Q_{S-1} + Q_{S-2})\frac{M}{V} \tag{2.16}$$

(Machida et al., 2004)

where

C_o = initial heavy metal concentration

V = volume of solution

M = amount of adsorbent

Another theoretical model of desorption kinetics is the Polanyi-Wigner equation which follows Arrhenius type behaviour,

$$-\frac{d\theta_M}{dt} = \frac{\nu.\theta_M^n}{\beta}.\exp\left(\frac{-E_{DES}}{R.T}\right) \tag{2.17}$$

(Venables, 1997)

where

$\nu.\theta_M$ = frequency factor

θ_M = instantaneous coverage of the adsorbate molecules on surface adsorption sites

n = kinetic order or desorption order

$E_{DES}(\theta_M)$ = activation energy to desorption

R = gas constant

The rate contains a coverage term (θ_M^n) and energy term ($\frac{-E_{DES}}{R.T}$).Several kinetic information can be interpreted from the Polanyi-Wigner equation:

- Zero-order desorption kinetics implies that desorption rate does not depend on coverage and increases exponentially with temperature. There is a rapid drop when all molecules have desorbed from the adsorbent and is observed in thick (multi) layers when supply of adsorbate molecules is infinite.
- First-order desorption kinetics illustrates a proportional desorption rate to instantaneous coverage. It means as there are more adsorbate molecules adsorbed on the surface sites, the rate of desorption will also increase (in a normal distribution pattern). This indicates non-dissociative molecular and atomic adsorption.
- Second-order desorption kinetics takes into context of desorption rate proportional to instantaneous coverage^2 and is strictly observed for recombinative desorption, $A_{ad} + B_{ad} \rightarrow AB_{ad} \rightarrow AB_g$. It is usually observed for lighter elements like hydrogen.

2.8 Desorption Optimal Conditions

Desorption takes place under optimal conditions of temperature, pH, initial concentration, contact time and appropriate desorbing agent. Regulation of the optimal parameters gives better efficiency for desorption of lead from PSAC and significant advantage in repetitive usage of the PSAC.

2.8.1 Effect of pH

pH value of aqueous solution is an important controlling parameter in desorption process because it affects the solubility of the metal ions, degree of ionisation of the adsorbate and the concentration of the counter ions on the functional groups of the adsorbent (Badmus et al., 2007). As reported by Mengistie et al. (2008), the initial pH value of the solution has more influence than the final pH as it influences both the adsorbent surface metal binding sites and the metal chemistry in water. They also stated that adsorption of Pb^{2+} ions on the surface of activated carbon produced from biomass *Militia Ferruginea* plant leaves could facilitate release of more H^+ ions from the surface due to ion exchange mechanism, supporting the decrease of the pH from the initial pH value of their experiments where adsorption efficiency reached 97.3 %.

For desorption, Li et al. (2005) have found that the Pb^{2+} desorption increases as the pH value of the solution is reduced. From Figure 2.1, it is apparent that at low pH of the aqueous solutions, the desorption percentage is higher and eventually reaches 100 % at pH 2.0.

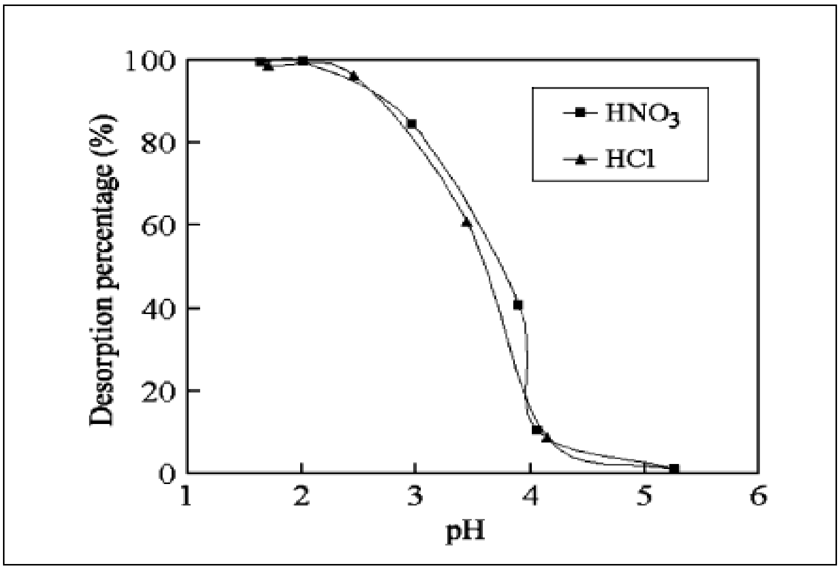

Figure 2.1: Desorption of Pb2+ from Carbon Nanotubes at Different pH (Li et al., 2005)

Deng et al. (2007) also investigated the effect of pH on desorption efficiency of Pb^{2+} from aqueous solution using different desorbent agents with different pH values. They have discovered that at higher concentrations of stronger acids of HNO_3 and ethylenediaminetetraacetic acid (EDTA), Pb^{2+} recovery of 85 % and 82 % was achieved, respectively, as shown in Figure 2.2. The high value of the conditional formation constant of the complex Pb(II)-EDTA is a contributing factor which favours desorption of the Pb^{2+} ions from the biomass green algae studied.

Conditional constants, also known as apparent constants, are concentration quotients which are not true equilibrium constants but can be derived from them. It has a maximum at a certain pH where the ligand sequesters the metal most effectively.

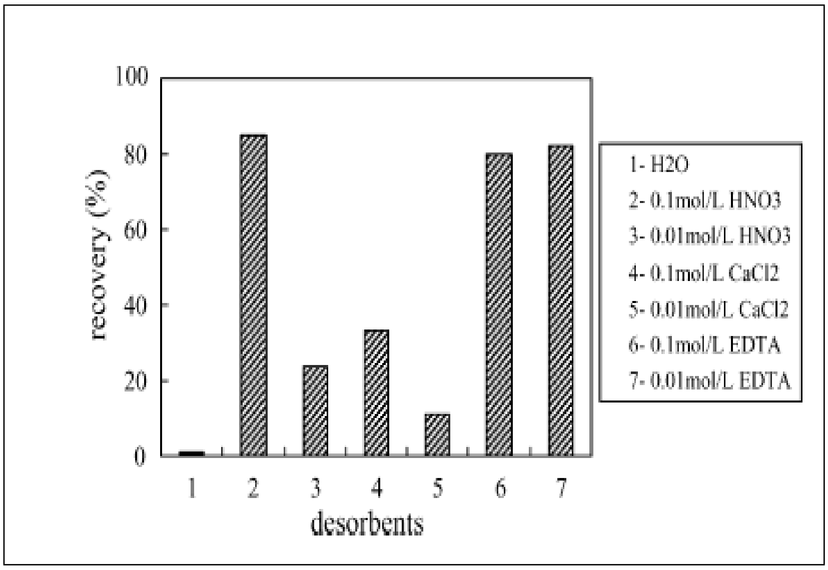

Figure 2.2: Pb^{2+} Recoveries by Different Desorbents (Deng et al., 2007)

While many researchers have found that at higher pH values, the adsorption efficiency increases for removal of Pb^{2+} from wastewater (Li and Wang, 2009; Issabayeva et al., 2005; Mondal, 2010; El-Said et al., 2010; Ashtoukhy et al., 2008), the pattern for desorption is the reverse. Noteworthy researches have indicated that at low pH values of the aqueous desorbent solutions, desorption efficiency will be greatly enhanced and recovery of metal ions will be more significant to serve its purpose.

2.8.2 Effect of Desorption (Elution) Agents

Chai, Li, Zhao, Yang and Wang (2009) and Deng et al., (2007) have conducted studies using both acidic and basic agents to desorb Pb^{2+} from the lead-adsorbed PSAC and found that each agent have a significant influence on the desorption efficiency. Chai et al. (2009) used seven different chemical agents of the same concentration of 0.1 M to study desorption of lead from modified spent grain and found that HCl is the most efficient desorbent followed by H_3PO_4, HNO_3, H_2SO_4, NaOH, deionised water and NaCl. Figure 2.3 below depicts the obvious desorption efficiency of activated carbon produced from modified spent grain in strong acids HCl, H_3PO_4, HNO_3 and H_2SO_4.

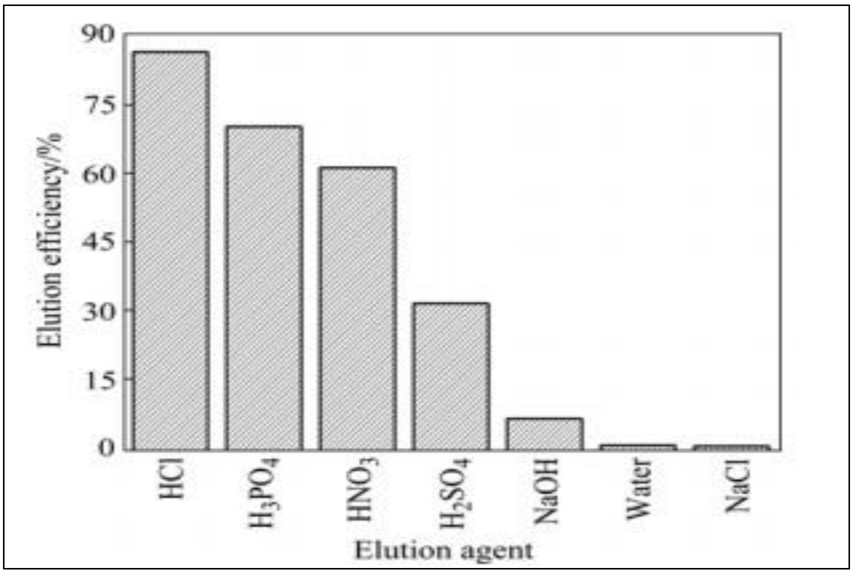

Figure 2.3: Desorption of Lead from Modified Spent Grain by Various Chemical Agents (Chai et al., 2009)

In acidic medium, the protons replace the metal ions sorbed on the adsorbent. On the other hand, in basic medium, there is a poorer desorption efficiency due to the deprotonated ions of coordinating ligands (Chai et al., 2009). Consequently, metal ions are less prone to be desorbed from the adsorbent surface. Previous work from Deng et al. (2007) reported the superiority of EDTA as the desorbing agent but it is not economical to be applied in commercial process due to its high cost and harmful disposal problems.

2.8.3 Effect of Contact Time

Optimum time is an important consideration for an economical waste water treatment system. Issabayeva et al., (2005) reported significant amount of acidic functional groups on the PSAC having strong adsorption capacity for lead, coinciding with its suitability to treat wastewater polluted with lead. It is reasonable to predict that the desorptive property of PSAC is the opposite of that of its adsorptive properties. In another words, the rate of lead desorption from adsorbent should increase with contact time.

Separately, Wilczak and Keinath (1993) studies have also found that rate of desorption of Pb^{2+} from the surface of commercial activated carbon (Nuchar SA and Filtrasorb 400) was rapid within the first few minutes of mixing. It was apparent at the start of the experiment even by visual observation but when the Pb^{2+}concentration were brought to analytical tests, the results showed the increase of Pb^{2+}concentration after 1 h of mixing were not nearly as rapid as at the beginning. This observation shown in Figure 2.4 is a concrete reasoning to show desorption of Pb^{2+} into the aqueous solutions will be of an almost constant value after reaching an optimum contact time.

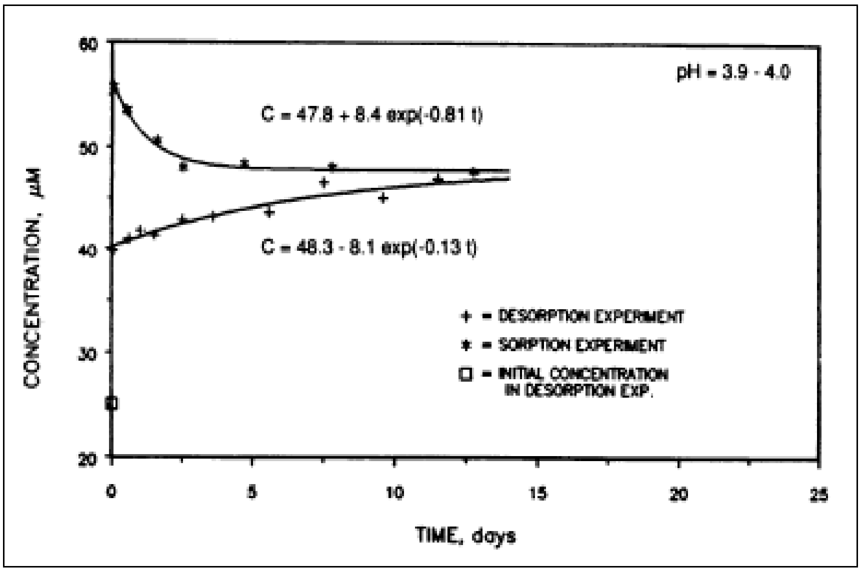

Figure 2.4: Kinetics of Lead Sorption and Desorption on Activated Carbon Nuchar SA (Wilczak and Keinath, 1993)

Wambu, Muthakia, shiundu and wa Thiongo (2009) reasoned that in the presence of ligands, metal ions form ligand complexes with larger spatial radius and viscous drag in solution than the corresponding hexaaqua species, slowing down heavy metal ions diffusion through the aqueous matrix and into adsorbent mesopores. Hexaaqua ion is an aqueos metal ion that accepts six lone pair of electrons from six water molecules to form coordinate bonds to it. However, the nature of gradual slow reactions that lead to decrease of desorption rate is not well researched and understood, so far.

Jeon, Yoo and Hoell (2005) studied the effect of contact time on desorption efficiency of lead- adsorbed carboxylated alginic acid biomass using 0.01 M of organic acid, nitrilotriaceticacid (NTA) as desorption agent. They reported that desorption efficiency increased with contact time. Their studies showed that desorption processes were completed within 180 min and almost a constant range over 250 min as shown below.

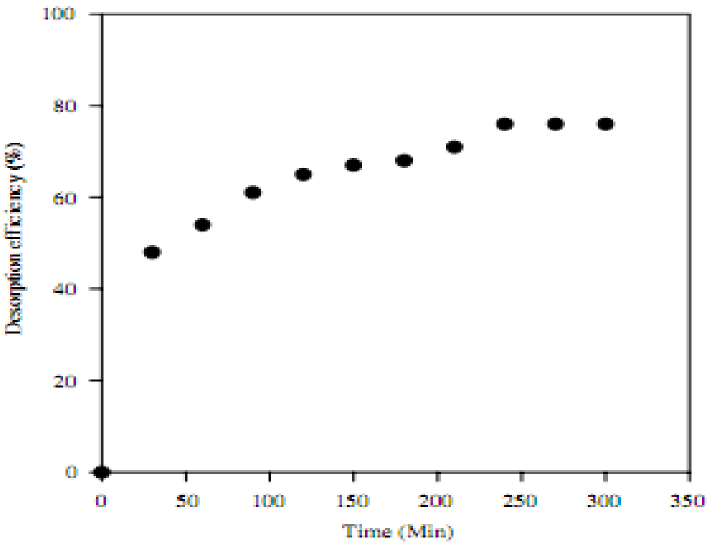

Figure 2.5: Desorption Efficiency Profile Using 0.01 M NTA (Jeon et al., 2005)

2.8.4 Effect of Temperature

As temperature increases, mobility and diffusion of ionic species also increases. Li et al., (2005) reported that adsorption on activated carbon produced from modified spent grain is an endothermic process due to the positive entropy change. Thus, a higher temperature would result in enlargement of pore size due to "activated diffusion" causing the micropores to widen and deepen, creating more surface area (Mengistie et al., 2008). Then again, the pattern is the reverse for desorption. Chai et al. (2009) presented results of decreasing desorption efficiency over temperature increase.

2.8.5 Adsorption – Desorption Cycles

The repeated availability of an adsorbent is an important criterion for an economical and advanced adsorbent. PSAC has a considerably low value of pH_{pzc} (point of zero charge) of 1.43 (Issabayeva et al., 2005), it could adsorb much heavy metal ions even in low pH solution. As a result, desorption process may not be completely performed.

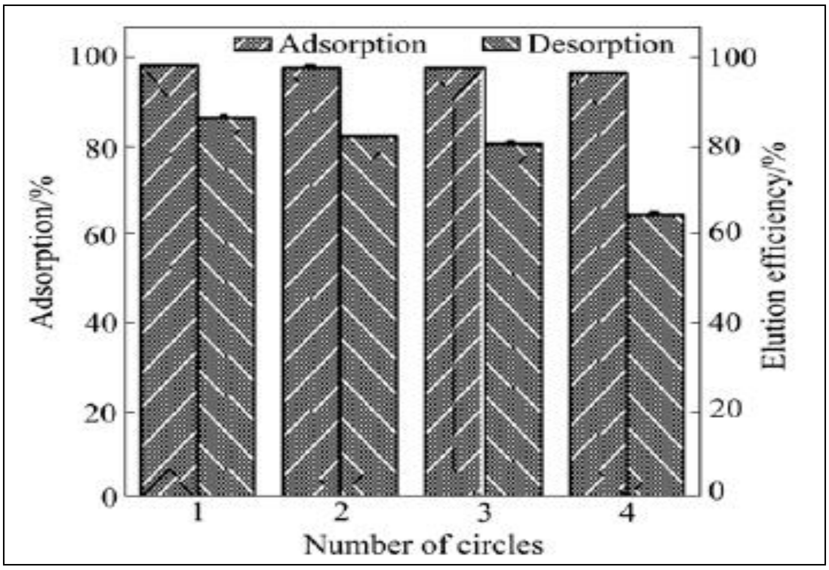

Figure 2.6: Adsorption-desorption Cycles for Activated Carbon from Modified Spent Grain (Chai et al., 2009)

Jeon et al., (2005) developed a batch process treatment process to study the efficiency of adsorption-desorption cycles and the results shown in Figure 2.6 indicated a slight decreasing order after each cycle. Chai et al., (2009) reported the same pattern with four successive cycles of adsorption and desorption of Pb^{2+} in the batch system. The decreasing efficiency for desorption was reported to be much higher than that of adsorption in their work.

Researchers Huang, Lu and Li (2007) conducted similar adsorption-desorption repetition on artificially modified activated carbon of fine poly (*m*-phenylenediamine) microparticles and found the same pattern for decrease in the desorptive efficiency. They reasoned that the lead ions are bound irreversibly to the adsorption sites could be responsible for the rapid decrease in Pb^{2+} ion uptakes during the successive cycles. When the activated carbon at sorption equilibrium was used for the next cycles, it would disturb the previous equilibrium and result in much lower adsorptivity. Following that, values of desorption efficiency were lower as there were less lead ions to be eluted from the solid surface.

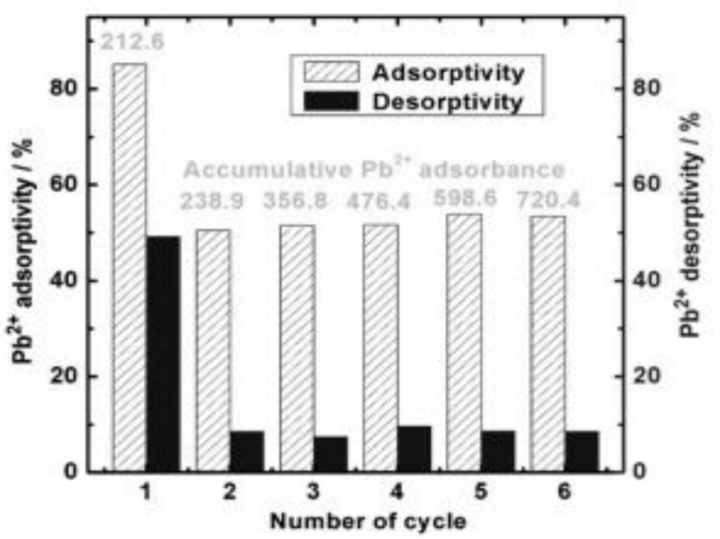

Figure 2.7: Adsorption-desorption Cycles for Activated Carbon (poly(*m*-phenylenediamine) Microparticles (Huang et al., 2007)

CHAPTER 3

METHODOLOGY

In this chapter, the various experimental procedures and materials used are described. Prior to adsorption-desorption cycles, equations to determine the amount of chemical powder and solutions required are demonstrated to calculate for the solutions used. In batch adsorption and desorption experiments, 24 conical flasks were prepared to provide two sets of data, one set being the replicate control. The PSAC used was from a local manufacturer of the material, Bravo Green Sdn. Bhd. Lead ions adsorption experiments onto PSAC were carried out, followed by desorption of lead ions from PSAC in two desorbing agents, namely HCl and HNO_3. The PSAC samples were placed overnight in an oven for drying after each separate cycle of adsorption and desorption.

3.1 Preparation of Solutions

3.1.1 Blank Solution Preparation

A blank solution of 0.15 M of sodium nitrate ($NaNO_3$) (Merck kGaA Darmstadt Germany, MW = 84.99 g/mol) was prepared by diluting sodium nitrate solids in deionised water. For every 1 L of blank solution to be prepared, 12.75 g of sodium nitrate salts is dissolved with deionised water. $NaNO_3$ was used as a swamping electrolyte throughout to maintain a constant ionic strength of the solution (Wilczak and Keinath, 1993). The procedure was repeated as many times as required to prepare the desired volume of the blank solution. A sample of 10 ml of the solution was collected in a 15 ml plastic container for pH testing.

3.1.2 Lead Nitrate Solution Preparation

The molecular weight for lead is 207.2 g/mol and the molecular weight of lead nitrate, $Pb(NO_3)_2$ is 331.2 g/mol. The stock solution of 0.1 M of $Pb(NO_3)_2$ (R & M marketing Essex U. K. , M = 331.2 g/mol) was prepared for use throughout the experimental work. The amount of lead nitrate needed to prepare stock solution was determined as follows,

$$Mass \cdot of \cdot Pb(NO_3)_2 = MW_{Pb(NO_3)_2} \times Molarity \times Volume \qquad (3.1)$$

(Pilgrim, 2010)

From Equation 3.1, it was determined that for every 100 ml of stock solution, a mass of 3.312 g of lead nitrate is needed to be dissolved in 100 ml of deionised water.

Subsequent preparation of 100 ppm of $Pb(NO_3)_2$ for adsorption experiments were carried out by diluting this stock solution with the blank solution of $NaNO_3$. To prepare 100 ppm of $Pb(NO_3)_2$, the following formula was used to calculate the amount of stock solution required to mix with blank solution.

$$M_1V_1 = M_2V_2 \qquad (3.2)$$

(Pilgrim, 2010)

where

M_1 = concentration of stock solution (mg/L)

V_1 = volume of stock solution (L)

M_2 = concentration of lead ions solution (mg/L)

V_2 = volume of lead ions in the solution (L)

From Equation 3.2, for every 100 ml of 100 ppm of $Pb(NO_3)_2$, 0.485 ml of stock solution is needed to be topped up to 100 ml of blank solution. The measurement of the small amount of stock solution was achieved accurately using a micropipette and the larger amount of blank solution using a 100 ml measuring cylinders and a micropipette.

3.1.3 Desorption Agent Solution Preparation

Nitric acid was used as a desorbing agent in our experiments. Concentrated nitric acid is extremely corrosive and constantly gives off acid corrosive fumes. Owing to the fact that it is a strong oxidizer, its contact with other material may cause fire and burn all body tissue. A secondary containment tray in the fume hood was used when handling and pouring concentrated acids to avoid contact in case of overfill or spillage. All dilutions of concentrated acids were carried out in the fume hood with appropriate goggles, laboratory coat and gloves. The protective shield on the fume hood was drawn down as much as possible but allowing to work comfortably.

Similarly, using Equation 3.2, the volume of concentrated HNO_3 (65 % Fischer Scientific) was determined to prepare 0.1 M of nitric acid, HNO_3 using dilution method with deionised water. Using a 100 – 1000 μL adjustable single channel micropipette (Transferpette ®), 6.925 ml of the concentrated acid was slowly added to a 1 L volumetric flask containing deionised water. The solution was then added with deionised water until the meniscus level of the calibrated mark of the volumetric flask. Thereafter, a stopper was placed on the volumetric flask and then swirled carefully to ensure an even and thorough dilution. The solution was stored in the volumetric flask in room temperature of 25 °C and was only prepared freshly before each experiment.

Following the same procedures and safety precautions, the second desorbing agent, hydrochloric acid (HCl), was prepared. Using Equation 3.2, 0.1 M of HCl was prepared by diluting 8.333 ml of concentrated HCl (37 % Fischer Scientific, Analytical R. Grade, S. G = 1.18) in deionised water to make 1 L of 0.1 M HCl.

3.2 Adsorption Lead Experiments

In the adsorption experiments, 24 conical flasks containing 100 ml of 100 mg/ L $Pb(NO_3)_2$ solution were prepared by using a 100 ml measuring cylinder. 24 samples of 100 mg of dry PSAC (1-2 mm) were carefully weighed using the electronic balance (ADAMS Model PW254 250g × 0.1 mg) on 24 separate sheets of filter paper (Filtres Fioroni, pore size = 150 mm). The individual samples were transferred carefully into each of the conical flasks, respectively, and covered with a piece of aluminium foil. Subsequently, the flasks were placed on an automatic shaker (DaiHan Labtech Co. Ltd Korea) under the pre-set constant condition of 27 °C and rotational speed of 220 rpm for 24 h.

After 24 h, the flasks were removed from the shaker and the solutions containing the PSAC were carefully poured into a bigger conical flask (3 L) using a glass funnel and filter paper. The solution was collected into a 15 ml plastic centrifuge tube to be tested for its pH with pH meter (Cyberson pH510, Wagtech WTD, UK) and analytical test with the inductively coupled plasma – optical emission spectrometer (ICP-OES) (Optima 7000 DV; Perkin Elmer, Uberlingen, Germany) to determine the concentration of lead ions in the samples. Prior to solution analysis on ICP-OES, calibration was made with different concentrations of $Pb(NO_3)_2$ (range 10 – 150 mg/ L) solution to ensure sensitivity and optimization of the machine when test solutions are to be analysed. The PSAC was then dried in the oven (Memmert – USA; UNB 400 190-G) overnight at 80 °C before being used in desorption cycles.

3.3 Desorption Lead Experiments

100 mg of dry PSAC was weighed to make 24 samples using analytical electronic balance. In the desorption run, 24 conical flasks each contained 100 ml of aqueous solution of 0.1 M HNO_3 were prepared using a 100 ml measuring cylinder. After that, 100 mg of PSAC were transferred carefully into each of the conical flasks and covered with aluminium foil. The flasks were placed in an automatic shaker under

the same pre-set condition as adsorption runs of 27 °C and rotational speed of 220 rpm. Two samples (one being the control set) were taken at pre-determined time intervals of 10 min, 20 min, 40 min, 60 min, 80 min, 100 min, 120 min, 150 min, 180 min, 240 min, 300 min and 360 min.

The collected samples of the solutions were filtered carefully using a glass funnel for subsequent adsorption-desorption cycles to ensure that there are no solids in the solution. The reason for that is because the ICP-OES machine is not able to tolerate contamination by solid particles. The filter paper used was the same one from Filtres Fioroni with pore size of 0.4 mm diameter circles. The solution filtered has to be disposed responsibly as toxic waste and not down the piping drainage. The filtered PSAC was then subjected to drying in the oven at 80 °C overnight. The temperature was fixed at 80 °C to ensure a constant parameter because it is 80 °C for drying of PSAC in the adsorption experiments. Both the adsorption and desorption cycles were carried out for another two cycles using the same batch of PSAC sample to evaluate the desorption efficiency of the activated carbon.

The solutions subjected to test gave readings of lead concentration with the ICP-OES instrument. The desorption efficiency, DE, can be further calculated as follows,

$$DE = \frac{C_t V}{q_e M} \times 100\% \tag{3.3}$$

(Mondal, 2009)

where

C_t = concentration of metal ions in the desorption solution at time t (mg/L)

q_e = amount of metal ions adsorbed on the adsorbent before desorption (mg of adsorbate per g of adsorbent)

V = volume of desorption solution (mL)

M = amount of adsorbent used in desorption experiment (g)

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter discussed the results obtained from instrumental analysis and calculations to study the various parameters on the desorption efficiency of lead ions from PSAC. The potential of the biomass adsorbent PSAC to be used repeatedly to desorb lead ions (in two different desorbing agents) are evaluated. Further theoretical discussion on the determination of kinetics for desorption of lead ions from PSAC are also reasoned in this chapter.

4.1 Effect of Desorbing Agent on Desorption Efficiency

The two desorbing agents used in the experiments are HNO_3 and HCl and comparisons have been made in accordance to each cycle respectively. The purpose is to compare the strength of desorbing agent to desorb lead ions from PSAC. Table 4.1 shows the calculated values of DE from concentration of lead ions obtained via the ICP-OES instrument using Equation 3.3. The values of DE are plotted against time in Figure 4.1 for both desorbing agents.

Table 4.1: Desorption Efficiency of PSAC in Cycle 1

Time (min)	Desorption Efficiency, DE (%)	
	HNO_3	HCl
10	71.32	54.33
20	69.23	76.53
40	79.65	75.65
60	83.56	83.27
80	83.74	86.38
100	84.30	82.23
120	84.16	90.28
150	85.37	78.61
180	84.48	91.00
240	87.01	97.58
300	84.34	91.00
360	82.81	90.31

At the beginning of desorption experiment, the concentration of lead ions recorded gave a DE of 71.32 % for PSAC in HNO_3 and 54.33 % for PSAC in HCl for the first cycle. Desorption efficiency of PSAC recorded a rapid increase to 76.53 % in HCl at 20 min and subsequent gradual increasing pattern until the optimum DE of 97.58 % at 240 min.

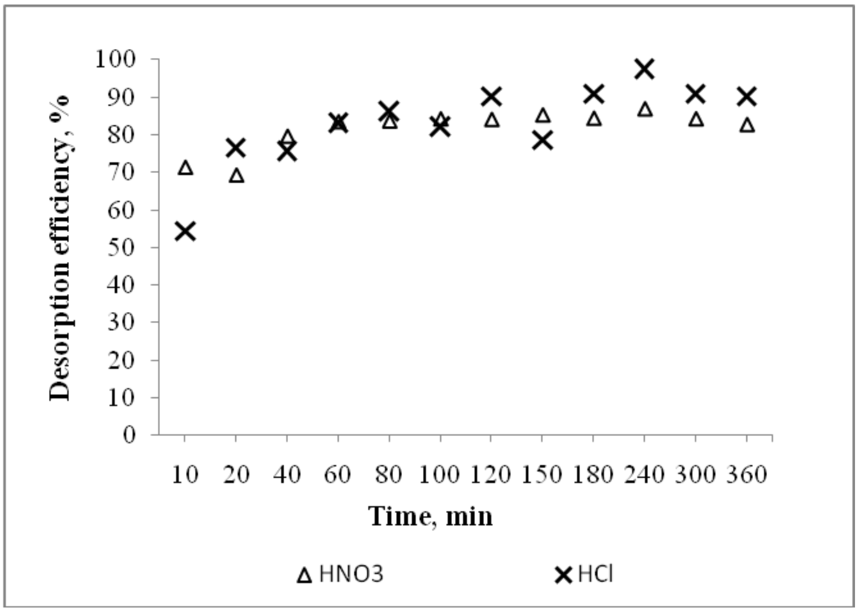

Figure 4.1: Desorption Efficiency of PSAC in Cycle 1

Similarly, DE of PSAC in HNO_3 was also the highest at 87.01 % at 240 min. The data for DE of PSAC in HNO_3 displayed a steadier increasing pattern as shown in Figure 4.1. The DE of PSAC in both HNO_3 and HCl is the highest at 240 min indicates a hypothetical optimum contact time (elaborated in subsection 4.2 in page 34).

Table 4.2: Desorption Efficiency of PSAC in Cycle 2

Time (min)	Desorption Efficiency, DE (%)	
	HNO_3	HCl
10	37.61	45.76
20	41.12	50.56
40	45.62	54.13
60	46.52	64.46
80	48.39	72.71
100	52.48	74.69
120	62.53	63.01
150	62.80	75.02
180	63.43	85.24
240	74.93	94.85
300	71.78	92.55
360	70.37	79.42

Table 4.2 and Figure 4.2 show tabulated and graphical representation of DE of lead ions of PSAC in the second cycle for both desorbing agents. Similarly, DE of PSAC was highest at 240 min in both desorbing agents. However, the percentage of decrease of DE of PSAC in HNO_3 is higher than in HCl. The optimum DE of PSAC in desorbing agent HCl in cycle 2 still remains high at 94.85 % while the optimum DE of PSAC in HNO_3 decreases to 74.93 %.

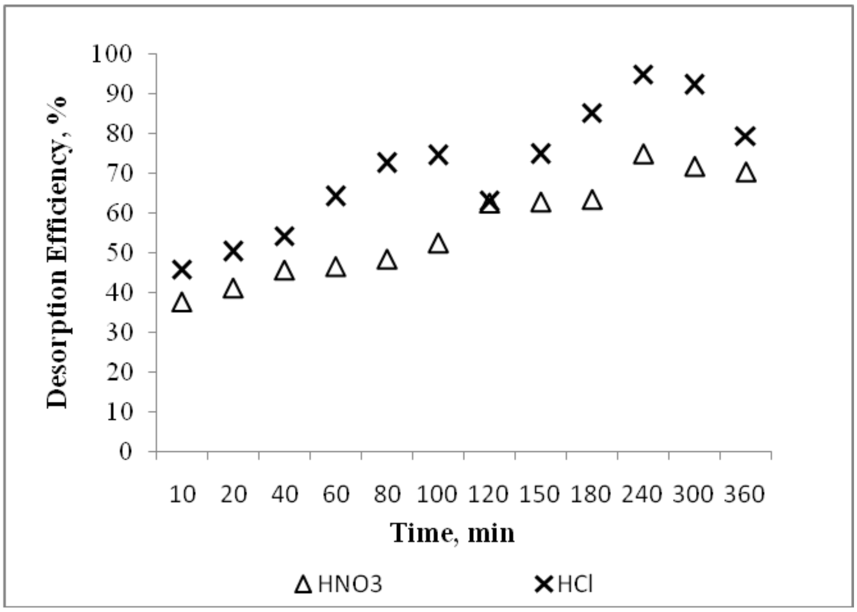

Figure 4.2: Desorption Efficiency of PSAC in Cycle 2

In the second successive cycle usage of PSAC, desorption efficiency of PSAC in both HNO_3 and HCl were less than that in the first cycle. This could be explained by the lower adsorption capacity of the PSAC after first cycle. Based on Langmuir isotherm, the surface of adsorbent has a specific number of surface binding sites where the solute molecules can be adsorbed (Fogler, 2006). As Pb^{2+} ions were not 100% desorbed from PSAC, the surface binding sites available for adsorption on the surface of PSAC have been reduced. This means that there are fewer uptakes of lead ions from aqueous solution to the surface binding sites of PSAC. Consequently, less Pb^{2+} ions are available to be desorbed from PSAC in the second and third cycle than as compared to in the first cycle.

Unsurprisingly, in cycle 3, DE of PSAC in both HNO_3 and HCl were also the highest after 240 min. DE of PSAC in HCl is still considered high with an excellent performance of 91.67 %, compared to 65.44 % of HNO_3. Table 4.3 and Figure 4.3 show tabulated and graphical representation of DE of lead ions of PSAC in the second cycle for both desorbing agents.

Table 4.3: Desorption Efficiency of PSAC in Cycle 3

Time (min)	Desorption Efficiency, DE (%)	
	HNO_3	HCl
10	25.63	40.25
20	34.51	50.78
40	35.77	59.50
60	43.37	64.50
80	44.55	68.48
100	46.68	72.84
120	46.12	83.19
150	54.36	75.38
180	56.47	81.25
240	65.44	91.67
300	59.63	80.53
360	56.54	86.57

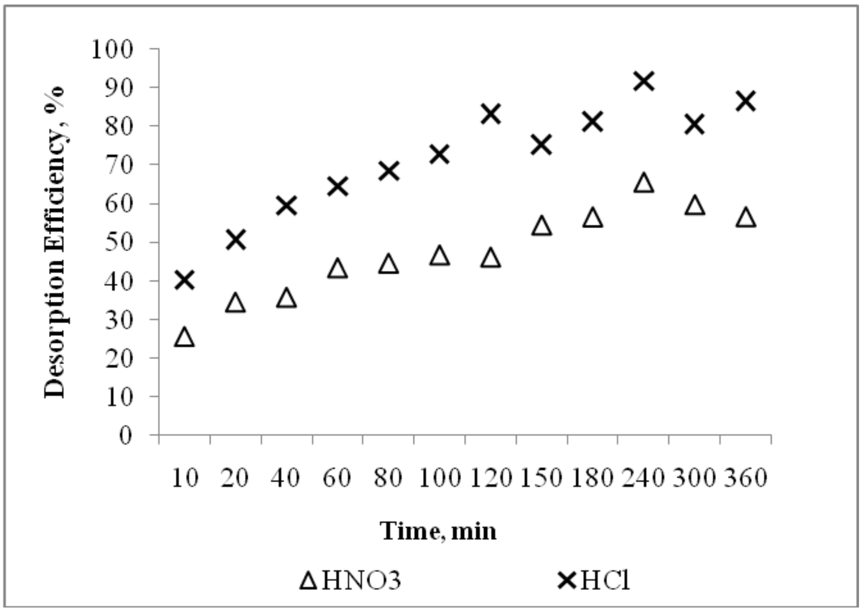

Figure 4.3: Desorption Efficiency of PSAC in Cycle 3

The behaviour of desorption is quite similar for each cycle with an increasing efficiency until an optimum time when the efficiency is the highest; then subsequent decreasing efficiency thereafter. However, the percentage of lead desorption efficiency (DE) of PSAC differs for both desorbing agents.

The higher DE exhibited by PSAC in HCl is because HCl is a stronger acid than HNO_3. pK_a, the logarithmic constant or sometimes referred to as acid dissociation constant, is a quantitative measure of the strength of an acid in solution. A stronger acid has a smaller value of pK_a indicating the higher extent of dissociation. HCl has a pK_a value of -8.0 ("Hydrochloric Acid", 2011) while pK_a of HNO_3 is -1.4 ("Nitric Acid", 2011). Stronger acid (HCl) will dissociate more in aqueous solution, contributing more H^+ ions to compete with Pb^{2+} for adsorption on surface binding sites on PSAC surface (Chai et al., 2009).

When stronger acids like HNO_3 and HCl are used as desorption agents, the adsorbent surface is completely covered by H^+ ions, at the same time disrupting the coordination sphere of chelated Pb^{2+} ions. Chelated iron is a soluble complex of iron, sodium and a chelating agent such as EDTA to make the iron soluble in water. Pb^{2+} are not be able to compete with the H^+ ions for adsorption sites, consequently liberated into the aqueous solution giving higher desorbing efficiency performance of Pb^{2+} ions from PSAC. As a result, the biomass (of adsorbent) becomes totally protonated to be ready for the next adsorption cycle. Therefore, we conclude that HCl is a more effective desorbing agent of lead ions from lead adsorbed PSAC.

4.2 Effect of Contact Time on Desorption Efficiency

Desorption of Pb^{2+} ions from PSAC in aqueous desorbing agent involves two phases, solid adsorbent and aqueous solute. For this reason, desorption can be classified as a biphasic system; one which has two phases.

Typically, desorption studies have biphasic reaction processes, a fast reaction followed by a slow reaction (Violante and Pigna, 2008). Figure 4.4 shows the obvious pattern of desorption kinetics where efficiency of desorption reaches the optimal performance at optimal contact time in Violante and Pigna's works. Another aspect studied was the residence times of heavy metals on the surfaces of andisol. Violante and Pigna (2008) reasoned longer residence time decreases trace element desorption because of a rearrangement of surface complexes. Thus, the determination of optimal contact time for best usage of adsorbent is crucial to obtain optimal performance from the adsorbent.

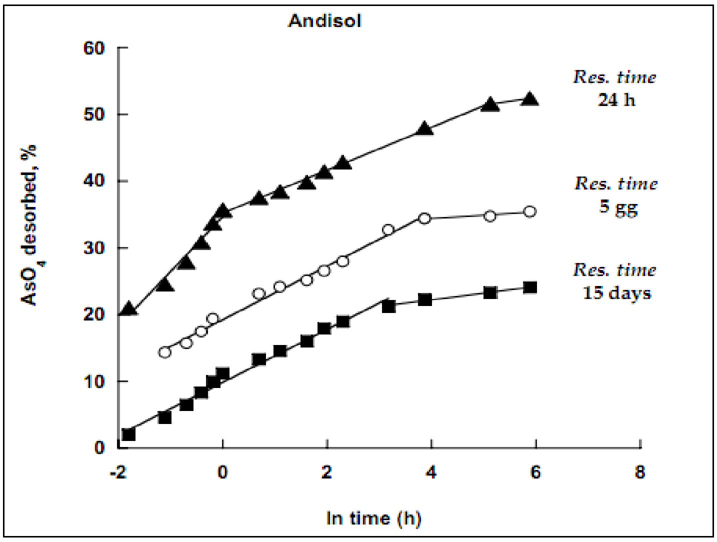

Figure 4.4: Kinetics of Desorption of Arsenate, AsO_4 from Adsorbent Andisol (Violante and Pigna, 2008)

Desorption efficiency of PSAC to desorb lead ions records an optimum performance at an optimum contact time of 240 min for both desorbing agents. When experiments took place continuously until 360 min, desorption efficiency was found to be lower after the optimum contact time. Similar patterns were reported by Wilczak and Keinath (1993) and Jeon et al. (2005) on different activated carbons as discussed in subsection 2.8.3 (page 20). Experimental data for desorption efficiency of PSAC in HNO_3 are shown in Table 4.4 with corresponding graphical representation in Figure 4.5.

Table 4.4: Desorption Efficiency of PSAC in HNO_3

Time (min)	Desorption Efficiency, DE (%)		
	Cycle 1	Cycle 2	Cycle 3
10	71.32	37.61	25.63
20	69.23	41.12	34.51
40	79.65	45.62	35.77
60	83.56	46.52	43.37
80	83.74	48.39	44.55
100	84.30	52.48	46.68
120	84.16	62.53	46.12
150	85.37	62.80	54.36
180	84.48	63.43	56.47
240	87.01	74.93	65.44
300	84.34	71.78	59.63
360	82.81	70.37	56.54

Desorption efficiency of PSAC in HNO_3 reaches the highest level after 240 min. Subsequent data after 240 min; at 300 min and 360 min recorded a decrease in DE of PSAC. In the first cycle, DE of lead ions from PSAC was 87.01 % and decreased almost to the similar extent in cycles 2 and 3, reaching 74.93 % and 65.44 % respectively.

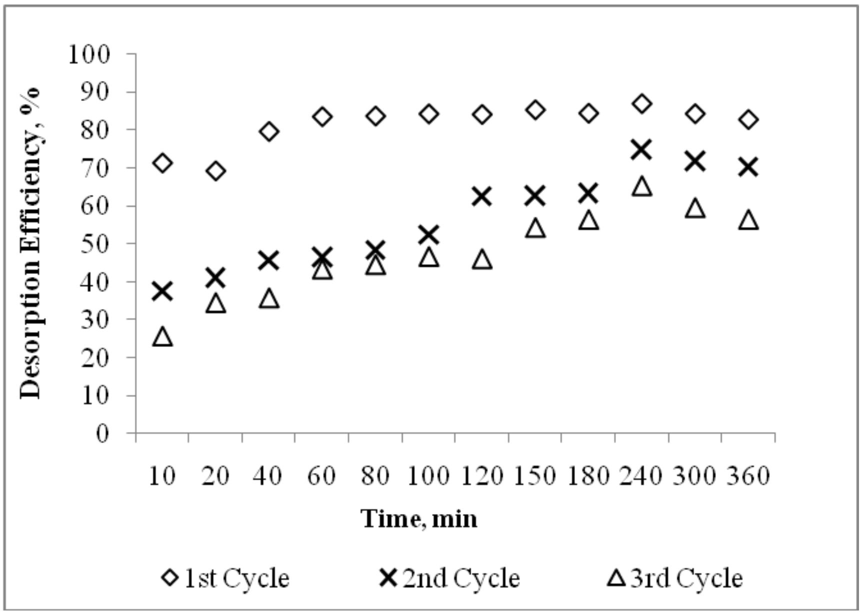

Figure 4.5: Desorption Efficiency of PSAC over time in HNO_3

The increase in DE from the start of the experiment until the optimal contact time recorded a rapid and significant difference for cycles 2 and 3 but was lower for cycle 1. This is probably because the lead-adsorbed PSAC used for this set of experiment (desorbing agent HNO_3) was obtained the research lab in the university. The parameter used in the samples' adsorption experiments was rotational 20 rpm in centrifugal columns. Studies on the effect of agitation speed during adsorption have been conducted by Nomanbhay and Palanisamy (2005) provided an explanation for the significant difference in the increasing pattern of DE from 10 min to 240 min for cycle 1. Their works were of removing heavy metals using chitosan coated acid treated beads (CCAB), CAC and acid treated PSAC (AOPSC). They reported that agitation speed must be sufficient to assure that all the surface binding sites are made readily available for solute ions uptake. They have found that the removal efficiency of adsorbent increased from 70 % to 90 % when agitation speed increased from 50 rpm to 100 rpm. Therefore, since amount of lead adsorbed is less, the available amount to be desorbed should be less (less rapid increase in desorption efficiency).

Table 4.5: Desorption Efficiency of PSAC in HCl

Time (min)	Desorption Efficiency, DE (%)		
	Cycle 1	Cycle 2	Cycle 3
10	54.33	45.76	40.25
20	76.53	50.56	50.78
40	75.65	54.13	59.50
60	83.27	64.46	64.50
80	86.38	72.71	68.48
100	82.23	74.69	72.84
120	90.28	63.01	83.19
150	78.61	75.02	75.38
180	91.00	85.24	81.25
240	97.58	94.85	91.67
300	91.00	92.55	80.53
360	90.31	79.42	86.57

Although DE of PSAC in HCl recorded higher percentage, the optimum contact time for optimum desorption performance was found to be similar to that in HNO_3. Same observation was recorded with the optimum contact time of 240 min as shown in Table 4.5 and Figure. 4.6. This set of data shows a more consistent pattern of rapid increase of DE of lead ions from PSAC from 10 min to 240 min for the three cycles followed by slight decrease after 300 min and 360 min.

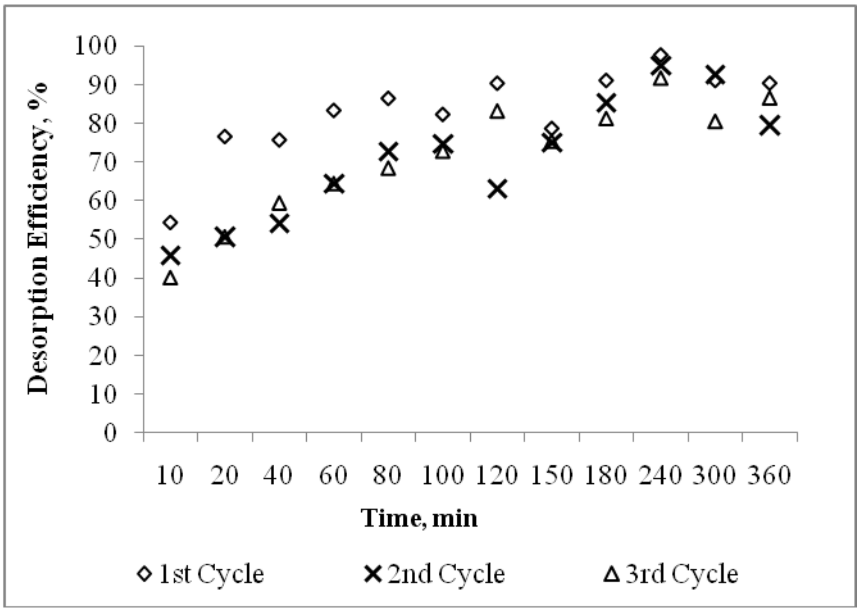

Figure 4.6: Desorption Efficiency of PSAC over Time in HCl

The lead-adsorbed PSAC samples used for HCl experiments were prepared by us from the virgin PSAC before adsorption. The increasing pattern is similar for cycles 1, 2 and 3 with only a deviation for DE at 120 min in cycle 2 which recorded a decrease in efficiency. The optimal contact time for best performance of desorption of lead from PSAC in both desorbing agents is 240 min. This result is important, as optimal contact time is one of the important parameters for an economical wastewater treatment system. There is a slow phase for DE from 60 min to 150 min where increase in DE of lead ions from PSAC is minimal. This slow phase in our observations is due to the diffusion control regime contributed by external mass transfer resistance and intraparticle diffusion on the surface of PSAC (Fogler, 2006).

Since extending contact time over 300 min and 360 min does not bring much increase in DE of PSAC, we can relate to our specified objective by concluding that optimal contact time for PSAC is 240 min or 4 h.

4.3 Desorption Efficiency of PSAC after Successive Cycles

Figure 4.7 shows the comparison of highest desorption efficiency of PSAC of lead ions in both desorbing agents at optimal contact time 240 min.

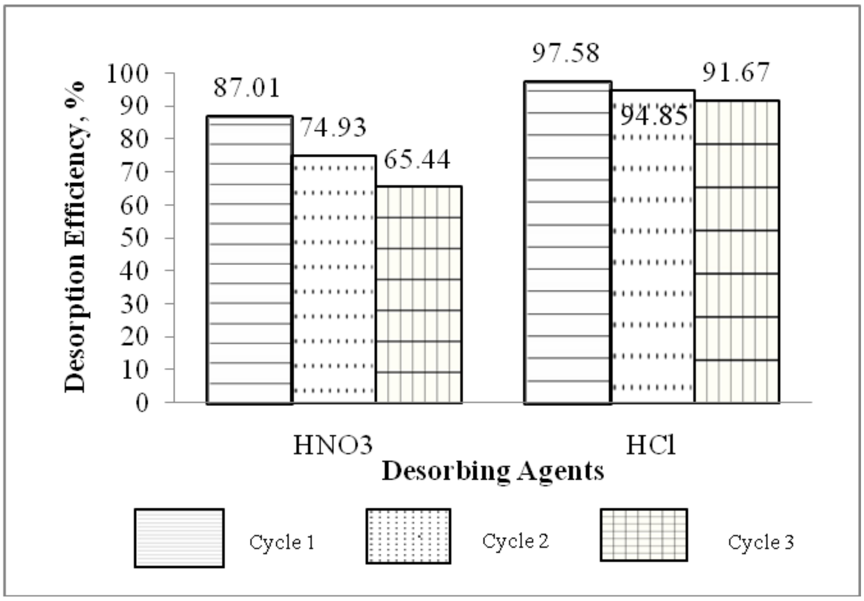

Figure 4.7: Comparison of Optimum DE of PSAC in HNO_3 and HCl

From Figure 4.7, optimum DE of PSAC in HNO_3 was 87.01 % in cycle 1 and decreased 13.88 % to 74.93 % in cycle 2 and sequentially 12.67 % decrease from cycle 2 to 65.44 % in cycle 3. The overall decrease in optimum DE of PSAC from cycle 1 to cycle 3 in desorbing agent HNO_3 is 24.97 %. On the other hand, the desorption efficiency performance of PSAC is more promising in desorbing agent HCl. There is a smaller margin of decrease in optimum DE of PSAC with 2.79 % from 97.58 % in cycle 1 to 94.85 % in cycle 2. Sequentially, there is a 3.35 % decrease in optimum DE of PSAC in cycle 2 to cycle 3. Desorption efficiency of PSAC at its highest performance in desorbing agent recorded an overall 6.06 % decrease from cycle 1 to cycle 3.

The desorbing performance of PSAC in HCl as desorbing agent is more than 4 times-fold of that in HNO_3. The significant decrease of nearly one-forth performance of desorption efficiency of PSAC in HNO_3 illustrates the comparatively unfavourable choice of HNO_3 as a desorbing agent. From Figure 4.7, we can also conclude that repeated usability of PSAC is promising with HCl as desorbing agent. The much lower DE of PSAC in the third cycle in HNO_3 clearly indicates that PSAC is not valuable to be used after the second cycle, if the choice of desorbing agent is a constraint. This is otherwise for HCl as the performance of PSAC is high at over 90 % after the third cycle, indicating recommended reuse of PSAC to an economical advantage.

4.3 Changes of pH over Time during Desorption

Figure 4.8 presents data on pH changes at time intervals during lead ions desorption from PSAC in desorbing agent, HNO_3. As observed from the data, pH values remain almost constant from 10 min to 360 min for cycle 1, cycle 2 and cycle 3. pH of the solutions exhibited a slight increase after successive cycles from 1.69 for cycle 1 to 1.75 for cycle 3 at 360 min. The increase in pH is due to lower concentration of lead ions present in the solutions as desorption efficiency is decreased after each cycle (as explained in subsection 4.3 in page 40). This is attributed to the nature of lead ions that form a slightly acidic solution in aqueous solution with a pH of 3.0 to 4.0 for a 20% aqueous solution (Ferris, 1960). Stock solution, $Pb(NO_3)_2$, is an ionic substance whereby its dissolution involves dissociation into its constituent ions, Pb^{2+} (aq) and NO_3^- (aq).

$$Pb(NO_3)_2(s) \rightarrow Pb^{2+}(aq) + 2NO_3^-(aq) \tag{4.1}$$

("Lead Nitrate", 2011)

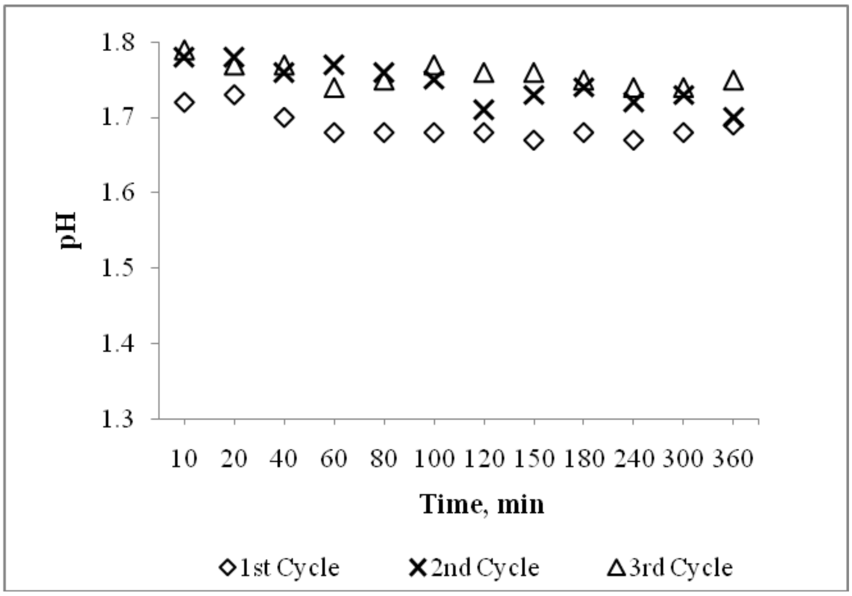

Figure 4.8: Changes of pH over time during Desorption for HNO_3

For HCl, similar insignificant pH changes during desorption were recorded and are shown in a graphical representation in Figure 4.9. Since both desorbing agents are strong acids, the small pH changes are not surprising as pH was not a focal parameter in this experiment but was recorded for overall observation.

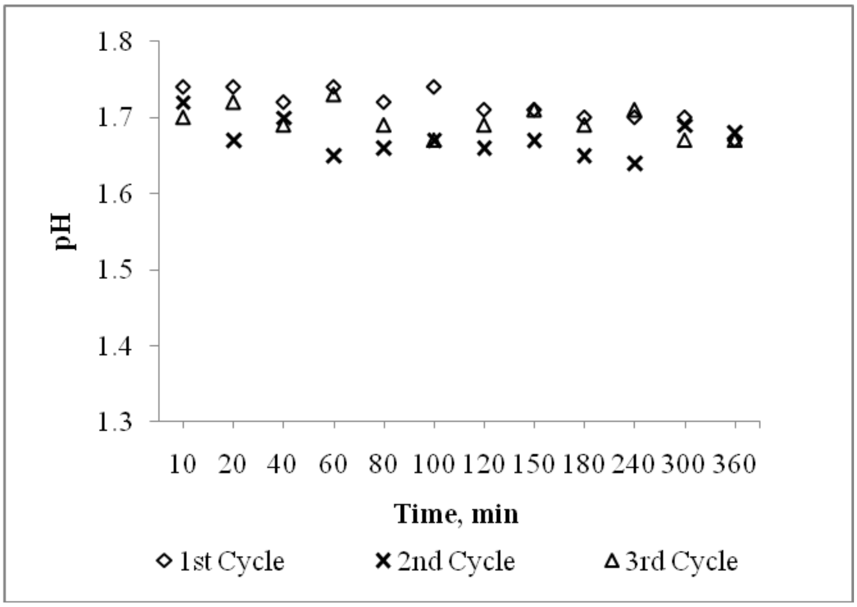

Figure 4.9: Changes of pH over time during Desorption for HCl

4.4 Determination of Kinetics for Desorption of Lead Ions from PSAC

The Arrhenius equation has found numerous applications throughout chemical kinetics for diverse rate processes that include both homogeneous and heterogeneous reactions. As temperature was not parameter to be studied for in this works, the variations in rate coefficient with temperature cannot be clearly analysed. Therefore, the determination of order of kinetics for desorption of lead ions from PSAC in aqueous solution are strongly reasoned out in this section.

From the Equation 2.17 (Polanyi-Wigner equation), desorption of lead ions from PSAC portrayed a first-order desorption kinetics. As discussed in subsection 4.1 (page 29), when higher concentration of lead ions are adsorbed from the aqueous solution, PSAC tend to exhibit a higher desorption efficiency of lead ions. The adsorption capacity of the PSAC is proportional to desorption efficiency of PSAC, where it is also consistent with Langmuir adsorption isotherm model of single adsorption layer exists on PSAC to represent equilibrium distribution. In addition, desorption of lead ions from PSAC is not zero-order because the supply of adsorbate molecules in this work (surface binding sites on PSAC) is not infinite. Desorption of lead ions from PSAC is also not of second-order because a second-order desorption kinetics usually is observed for elements like hydrogen where recombinative desorption is involved.

A summary of findings from the results are the optimal contact time for highest DE recorded at 240 min for both desorbing agents, HNO_3 and HCl but a higher DE is recorded when PSAC samples were in HCl. Overall decrease of DE in both desorbing agents decreased from 87.01 % in cycle 1 to 65.44 % in cycle 3 for HNO_3 and 97.58 % to 91.67 % for HCl shows that the PSAC can be reused up to 3 times and still exhibit high performance. The pH changes were almost insignificant with a slight increase from the beginning at 10 min to 360 min due to lower concentration of lead ions present in the solutions as desorption efficiency is decreased after each cycle.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

This chapter summarizes the key findings and conclusions of the optimal experimental conditions for desorption efficiency of lead of PSAC using different desorbing agents in three consecutive cycles. Additionally, this chapter concludes with recommendations for future research.

5.1 Conclusions

A series of batch tests were performed to desorb lead from PSAC. The parameters of temperature, initial concentration of desorbing agents and agitation speed were fixed at constant values of 27 °C, 0.1 M and 220 rpm respectively. The results reported in this work show that desorption efficiency of lead of the PSAC using nitric acid as desorbing agent is slightly poorer as compared to hydrochloric acid.

In all cases, the optimal contact time of 240 min is of paramount importance for desorption of lead from PSAC to achieve the maximum performance. Since desorption efficiency performance of the PSAC decreases after optimal contact time, it would be ineffective to prolong the contact time for primary and consecutive usage of PSAC in desorbing lead in aqueous solutions.

Comparison of desorption efficiency of PSAC showed significant decrease after two successive cycles when desorbing agent nitric acid was used. On the contrarily, PSAC could be used up to three consecutive cycles as when desorbing agent hydrochloric acid was used. It was found that the highest DE of lead ions from PSAC in HCl is 91.67 % and 65.44 % in HNO_3 in the third cycle. This is due to more H^+ ions in stronger acid (HCl) to compete with Pb^{2+} for adsorption on surface binding sites on PSAC surface, giving higher desorbing efficiency performance of Pb^{2+} ions from PSAC.

It can be concluded that lead ions can be effectively desorbed from PSAC in aqueous solutions and it can be reused for three consecutive cycles. The research shows potential of further process modification and optimization to develop higher desorption efficiency of PSAC for lead in aqueous solutions.

5.2 Recommendations for Future Works

There are several recommendations for future projects regarding the study of desorption efficiency of lead ions of PSAC.

1. The concentration of desorbing agents used was 0.1 M HNO_3 and 0.1 M HCl. Future works can involve higher concentration of desorbing agents. At low pH, the acids dissociate to a greater extent, creating competition Pb^{2+} with H^+ ions for adsorption on surface binding sites on PSAC surface. In this context, it is anticipated that H^+ ions reign over $Pb^{2+,}$ giving higher desorbing efficiency performance of Pb^{2+} ions from PSAC.

2. Activated carbons' porous structure and product yield are functions of operating conditions. Production of PSAC with relatively large surface area and high reaction yield would greatly enhance adsorption and consequently desorption efficiency of lead in aqueous solutions. Analysis of porous characteristics by Azargohar (2009) showed that acid-treatment/ thermal desorption method increases micropore, mesopore and total pore volume, providing larger surface area for better access of adsorbate molecules to active sites on CAC. Since PSAC used in this research did not undergo any

chemical or physical pre-treatment, an improvement in preparation of PSAC should be taken into big account for future studies.

3. Results obtained from desorption experiments have shown that desorption efficiency decreases slightly after optimal contact time of 240 min. The pattern in the results suggests that desorption still takes place after 360 min or 6 h. Thus, experiments in the future can be prolonged until desorption reaches an equilibrium to determine the duration of usability of PSAC in heavy metals recovery in water treatment systems.

4. Adsorption is an endothermic process which means than lower temperature is unfavourable for adsorption. Decreasing the temperature will also decrease the rate of diffusion of the lead ions across external boundary layer from the aqueous solution and in the internal pores of the adsorbent particle. This will prevent a reverse adsorption of the lead ions onto the surface of PSAC. In addition, lower temperatures during desorption of lead from PSAC can improve the solvent desorption capability. Therefore, this parameter deserves further study to optimize desorption efficiency of PSAC.

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