

Utilization of *Artocarpus* hybrid (Nanchem) skin for the removal of Pb(II): equilibrium, thermodynamics, kinetics and regeneration studies

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Article history

Received: 20 September 2014

Received in revised form:

19 November 2014

Accepted: 27 November 2014

Abstract

Batch experiments were conducted for the adsorption of Pb(II) using Nanchem skin (NS) under optimized conditions of shaking and settling times set at 3.5 h and 1.0 h, respectively, at the ambient pH. Functional group characterisation using Fourier Transform Infrared (FTIR) revealed that O-H, N-H and C=O groups were involved in the binding of Pb(II) with NS. Elemental characterization of NS was carried out using X-ray Fluorescence (XRF) spectroscopy and changes in the surface morphology were observed by Scanning Electron Microscopy (SEM). The point of zero charge (pH_{pzc}) of NS was found to be at pH 4.56. The adsorption isotherm was fitted to four different models: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich and together with error analyses, the Langmuir model gave the best fit for the experimental data with the maximum adsorption capacity of 57.0 mg g⁻¹. Kinetics studies obeyed the pseudo-second order and intraparticle diffusion was not the rate-determining step. The thermodynamic characteristics of the adsorption of Pb(II) by NS were exothermic, spontaneous in nature with increase in degree of freedom in the liquid/solid interface during sorption. The NS was able to retain its adsorption ability even after five consecutive cycles in regeneration studies. Hence, this study shows that NS has great potential to be utilized as a low-cost biosorbent in wastewater treatment for the removal of Pb(II).

Keywords

Nanchem skin

Artocarpus

Lead adsorption

Kinetics

Thermodynamics

Regeneration studies

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Introduction

Lead (Pb) is one of the most toxic heavy metals in the environment and has caused concern worldwide. Lead was mainly used when leaded petrol was introduced due to more long-lasting energy and provides more driving power to the car users. When the leaded petrol combusted, particles of lead will be released from the car exhaust and spread into the atmosphere. From there, the lead particles may deposit on the soil or water which can cause contamination and the continuation of the food chain toxicity (Emran *et al.*, 2001). Other main sources of lead are from leaded-paint based, drinking water from leaded pipes, from industrial effluents, and the manufacture of leaded-car batteries. Children are at higher risk as lead exposure can lead to the damage in their central nervous system, cause problems in their growth, learning abilities, hearing, and some health problems such as vomiting poor appetite, and stomachache. Due to all the problems caused by lead, the Environmental Protection Agency has set a guideline and regulation for the amount of lead that should be allowed in water at the Action Level

(for treatment technique) of at most 0.015 mg L⁻¹ although their main goal of Maximum Contaminant Level Goal (MCLG) is actually 0 mg L⁻¹ because they believed that there should not be traces of lead allowed in the water system.

There are several methods of removing toxic heavy metals from industrial effluents. Some examples include ultrafiltration (Baharuddin *et al.*, 2014), ion exchange (Rafati *et al.*, 2010), photocatalytic oxidation (Fathizadeh *et al.*, 2011), and many others. There are pros and cons of these methods and because of the high cost of maintenance and disposal of sludge, researchers are on the lookout for other alternative methods which are conventional and cost-effective. Adsorption, being a cost-effective and economical method, has provided a better alternative route for cleaning wastewater. Adsorption is a preferable method because the adsorbents can be regenerated. Recent studies showed that adsorption of heavy metals and toxic dyes by a wide-range of low-cost adsorbents have been successful (Sakthi *et al.*, 2010; Zewail and El-Garf, 2010; Chen *et al.*, 2012; Dahri *et al.*, 2013; Dahri *et al.*, 2014; Lim *et al.*, 2013a; Lim *et al.*, 2014; Zehra *et al.*, 2014).

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In this study, an *Artocarpus* species, locally known as “Nanchem”, was investigated for its potential as a low-cost biosorbent for the removal of Pb(II) from aqueous solution. Nanchem is a hybrid of *Artocarpus heterophyllus* (Jackfruit, locally known as Nangka) and *Artocarpus cempedan* (Chempedak). Hence the name ‘Nanchem’ is derived from the first syllable of these two fruits of ‘Nangka’ and ‘Chempedak’. Generally, the inedible parts of *Artocarpus* fruits are comprised of its skin and core of which the skin makes up to almost 60% of the whole fruit and is discarded as waste (Chieng *et al.*, 2011; Tang *et al.*, 2013). Various studies have shown that *Artocarpus* wastes such as *A. heterophyllus*, *A. altilis*, *A. odoratissimums* and *A. camansi* have been successfully used for the removal of toxic heavy metals (Priyantha *et al.*, 2013a; Lim *et al.*, 2012) and dyes (Hameed, 2009; Uddin *et al.*, 2009; Jayarajan *et al.*, 2011; Saha *et al.*, 2012; Lim *et al.*, 2015a; Lim *et al.*, 2013b; Lim *et al.*, 2015b; Chieng *et al.*, 2015). To date there has been no report on the use of Nanchem skin for the removal of heavy metals. This study will therefore provide an insight into the feasibility and effectiveness of using Nanchem skin as a biosorbent for the removal of Pb(II).

Materials and Methods

Preparation of samples

The fruits were purchased from the local open market in the Brunei-Muara District and the inedible parts were separated from the edible parts of the fruit. The fruit peels were dried in an oven at 70°C to remove the moisture in the samples until a constant mass was obtained. The dried samples were then grinded using a blender and sieved to obtain particle size in the range of 330 - 850 µm.

Instrumentation

Shimadzu Atomic Absorption Flame Emission Spectrophotometer AA-6701F was used for the analyses of all metals. The analyses of metals Pb(II), Cd(II), Cu(II) and Mn(II) were set at the wavelengths of 217.0 nm, 228.8 nm, 324.8 nm, and 279.5 nm respectively. Elemental characterization of NS, before and after adsorption of Pb(II), was carried out using X-Ray Fluorescence (XRF) PANalytical Axiosmax instrument. Functional group characterization was carried out using Fourier Transform Infrared (FTIR) spectrophotometer (Shimadzu Model IRPristige-21). SEM imaging for the biosorbents was carried out using JEOL JSM-5800LV and SPI-Module 1143 Sputtering Coater was used for surface coating of the samples.

Effect of shaking time and settling time

A set of flasks each containing a mixture of 0.050 g of the biomass in 25.0 mL of 10 mg L⁻¹ of Pb(II) solution were prepared and agitated at ambient temperature at 250 rpm. For every 30 min interval, the contents of each flask were gravity filtered, and the filtrate was analysed for its Pb(II) content. Once the optimized shaking time to reach equilibrium has been determined, the above experiment was repeated by agitating the mixture according to the pre-determined optimized shaking time, after which one flask was filtered at every 30 min interval and the Pb(II) content was analysed to determine the settling time.

Effect of pH

Solution pH of Pb(II) solutions of concentration 10 mg L⁻¹ of was adjusted to 2, 3, 4, 5, 6, and 7 by using 0.1 M HCl and/or 0.1 M NaOH solutions. For each pH, 25.0 mL of the adjusted Pb(II) solution was mixed separately with 0.050 g of biosorbent. The mixture was then agitated on an orbital shaker to its optimized shaking time and settling time. Filtrates were then collected and analysed.

Determination of Point of zero charge (pHpzc)

Point of zero charge was used to determine the pH at which the surface charge is at zero. The initial pH of the 0.1 M KNO₃ was adjusted by using 0.1 M HCl and 0.1 M NaOH to obtain the pH of 2, 4, 6, 8, 10 and 12 of 0.1 M KNO₃. 25.0 mL of 0.1 M of the adjusted pH of KNO₃ solution was then mixed separately with 0.050 g of the biosorbent. The mixture was shaken at 250 rpm for 24 h, and the pH of the filtrate was recorded.

Effect of ionic strength

10 mg L⁻¹ of Pb(II) was prepared with KNO₃ solutions of different concentrations ranging from 0.02 to 1.0 M. Aliquots of 25.0 mL of each of the above solution was separately mixed with 0.050 g of the biosorbent. Each mixture was agitated at 250 rpm according to the pre-determined shaking time and settling time. Filtrates were collected and analysed using AAS spectrophotometer.

Adsorption isotherm and thermodynamic studies

Batch isotherm study was conducted with 0.050 g adsorbent in 25.0 mL of Pb(II) solution of concentrations ranging from 0 to 500 mg L⁻¹. The flasks with their contents were then stirred according to the optimized shaking time and settling time at room temperature with the stirring speed of 250 rpm. The solutions were filtered and the filtrates

were analysed using an AAS spectrophotometer to determine the concentrations of the metal ions present. For thermodynamic studies, the batch isotherm study was repeated at temperatures of 40, 50, 60 and 70°C in a thermal shaker with the stirring speed of 250 rpm.

Kinetics study

Aliquots of 25.0 mL Pb(II) solutions of concentrations of 50 mg L⁻¹, 100 mg L⁻¹ and 400 mg L⁻¹ were separately mixed with 0.050 g adsorbent, and agitated at 250 rpm as soon as the mixing commenced. Samples were withdrawn at every 5 min within the first 30 min, and analyzed for the Pb(II) content. Thereafter, filtrates were analysed for Pb(II) at every 30 min interval using AAS spectrophotometer.

Regeneration of NS

Regeneration study of NS was performed by agitating adsorbent with 100 mg L⁻¹ Pb(II) solutions using the optimized contact time to ensure that the active sites were fully saturated. Ratio of NS:Pb(II) solution was fixed at 1:100. The mixture was then gravity filtered and the Pb-loaded NS was washed gently with doubly distilled water to eliminate the excess Pb(II) on the surface and dried overnight at 60°C. Pb-loaded NS was regenerated by desorption with 1 M HNO₃, 1 M NaOH, heat at 200°C for 1.0 h, microwave at medium heat for 10 min or stirring in water for 2.0 h. A control (without washing) was kept to compare the adsorption capacity with the desorbed adsorbent. In order to check the reusability of the regenerated adsorbents, five cycles of consecutive adsorption-desorption studies were performed. The amount of Pb(II) adsorbed for five successive adsorption-regeneration cycles was analysed using AAS.

Results and Discussion

Removal of Pb(II) in binary systems

To investigate the effect of the presence of other divalent metal ions in the Pb(II) system on the adsorption by NS, three different metals, namely Cd(II), Cu(II), and Mn(II), were added separately to the Pb(II) solution with the same concentration ratio of 1:1. Fig. 1 shows that NS is able to retain high percentage removal of Pb(II) of > 80% even in the presence of other heavy metals. This is favourable in real life application since wastewater usually contains more than one heavy metal.

Effects of contact time and pH

The shaking time of the adsorption of Pb(II)

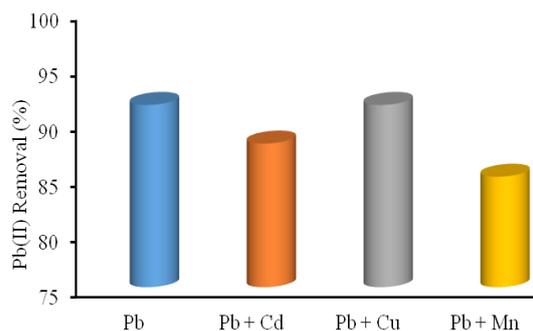


Figure 1. The percentage removal of Pb(II) on the single-metal system and the binary-metal systems with Cd(II), Cu(II), and Mn(II)

onto NS was investigated in order to determine the time required to reach its equilibrium. During the first 30 min, fast removal (67.0%) of Pb(II) by NS was observed owing to the initially available empty sites on the surface of NS. As more Pb(II) ions are being adsorbed onto the surface of NS, there was a gradual decrease in the removal of Pb(II) until finally an equilibrium was reached. The maximum shaking time was taken as 3.5 h with settling time of 1.0 h.

The study of pH effect is very important because in real life situation, the actual pH of the wastewater may be more or less acidic or basic than the ambient pH. In this study, seven different pHs of Pb(II) solutions ranging from pH 2 to 7, including the ambient pH (pH = 5.1), were investigated. Due to the formation of precipitate of Pb(OH)₂, pH could not be carried out beyond pH 7.4. It was observed that below pH 4, the percentage removal of Pb(II) was very much reduced by approximately 54.3% compared to those pH at above 4. This can be explained by the presence of H⁺ ions under strong acidic condition causing protonation of the surface of the adsorbent. Thus there will be electrostatic repulsion between Pb(II) ions and positively charged adsorbent surface thereby resulting in the lowering of percentage removal of Pb(II). At ambient pH, the percentage removal was good (87.2%) with a small difference of approximately 2% compared to optimum pH 5.6. Hence there is no necessity to adjust the pH of the solution and all subsequent experiments were carried out at ambient pH.

Characterization of NS

Functional group characterization of NS, before and after adsorption with Pb(II), was carried out using Fourier Transform Infrared Spectroscopy (FTIR) to provide information on the possible functional groups involved in the binding of the metal ions onto the adsorbent surface. FTIR spectra, taken in the range of 4000-500 cm⁻¹, for the untreated NS and

the Pb-treated NS showed a broad peak at 3405 cm^{-1} which can be attributed to the O-H group in alcohols and N-H group in amides and amines while the peak at 2929 cm^{-1} is due to C-H group in hydrocarbon chains. The sharp peak at 1742 cm^{-1} is due to C=O group from aldehydes, ketones or carboxylic acids. Meanwhile the peak at 1630 cm^{-1} is attributed to the asymmetric -COO and amide groups, and 1443 cm^{-1} to symmetric -COO. Lastly a sharp peak at 1061 cm^{-1} is a result of -C-O stretching vibrations. Upon adsorption with Pb(II), major shifts can be observed for the broad band at 3421 cm^{-1} and peak at 1640 cm^{-1} . This shows that functional groups such as O-H, N-H and carbonyl groups could be involved in the binding with Pb(II) ions.

Elemental characterization of NS using XRF clearly shows that the untreated NS has no traces of Pb(II) present. However when the NS was loaded with 100 mg L^{-1} Pb(II), there is an increase in Pb from 0 to 73.1%, clearly indicating that Pb(II) was adsorbed onto NS. It was also observed that some of elements such as Zn and K have decreased upon adsorption of Pb(II). Similar observations have previously been reported for adsorption of cationic dyes and heavy metals by other adsorbents (Lim *et al.*, 2013b; Priyantha *et al.*, 2013b; Chieng *et al.*, 2014), suggesting that K^+ ions were replaced by the cationic dyes or heavy metal ions. SEM (Scanning Electron Microscope) imaging was done by scanning the untreated NS and the Pb-treated NS with 2000x magnification as shown in Fig. 2. The surface morphology of untreated NS showed the rocky and uneven surface of the biosorbent and compared to the Pb-treated NS, the surface of the biosorbent became smoother.

The point of zero charge (pHpzc) of NS is the pH when the surface electric density charge on the NS is zero. A graph of ΔpH versus pH was plotted (not shown) and the point of zero charge of NS, being the point where the line cuts the X-axis, was found to be at pH 4.56. Below pH 4.56, the surface charge will be predominantly positively charged and when above this pH, the surface charge will be predominantly negatively charged. The pHpzc of the NS is relatively similar to the other Artocarpus fruits such as the *A. odoratissimus*, *A. altilis* and *A. camansi* which was found to have pHpzc of 4.4, 4.7 and 4.8 respectively (Lim *et al.*, 2013b; Lim *et al.*, 2014b; Lim *et al.*, 2013c).

Adsorption isotherm and thermodynamic studies

The purpose of carrying out the batch adsorption isotherm is to determine the best isotherm model for Pb(II) adsorption by NS and to determine the

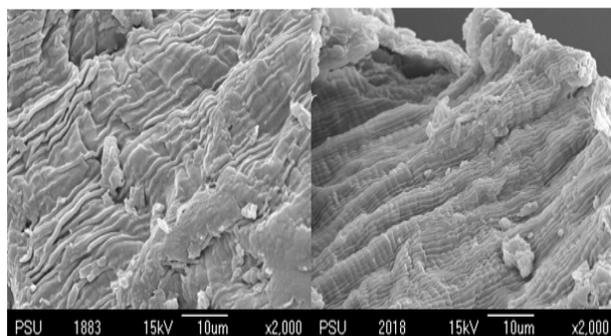


Figure 2. SEM images of the surface morphology of the untreated NS (left) and Pb-treated NS (right) at 2000x magnification

maximum adsorption capacity (q_{max}) the NS can adsorb Pb(II). Batch adsorption study was carried out using concentrations of Pb(II) ranging from 0 to 500 mg L^{-1} with the adsorbate:adsorbent ratio fixed at 1:500. Four isotherm models, namely Langmuir (Langmuir, 1916), Freundlich (Freundlich, 1906), Dubinin-Radushkevich (D-R) (Dubinin and Radushkevich, 1947) and Temkin, (Temkin, 1940) were then used to model the adsorption of Pb(II) onto NS. Six error function analyses were employed to further confirm the best fit adsorption isotherm model.

The Langmuir model describes the monolayer adsorption of the adsorbate onto the sorbent. The linear equation for this model is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} C_e + \frac{1}{q_{\text{max}} k_L} \quad (1)$$

where C_e is the equilibrium concentration of metal ion in the solution, q_e is the equilibrium metal ion concentration on the biosorbent, q_{max} is the maximum adsorption capacity of the metal ion onto the biosorbent and k_L is the Langmuir rate of adsorption.

The Freundlich adsorption model describes the heterogenous adsorption and the linear equation for this model is:

$$\log q_e = \frac{1}{n} \log C_e + \log k_F \quad (2)$$

where C_e is the equilibrium concentration of metal ion in the solution, q_e is the equilibrium metal ion concentration on the biosorbent, k_F (L mg^{-1}) is the Freundlich adsorption constant. n describes the empirical parameter relating to the adsorption capacity which varies the adsorption when $0 < n < 1$ indicates a favourable parameter.

The Temkin isotherm describes the non-direct effects of the interaction of the adsorbate/sorbent which assumes that the heat of adsorption of the adsorbent in the layer would reduce linearly than logarithmic coverage. The linear equation for this

Table 1. Parameters and error functions for different isotherm models

Isotherm	Parameters	Value	APE	EERSQ	HYBRID	EABS	MPSD	χ^2
Langmuir	q_{max} (mg g ⁻¹)	57.0	10.2	0.005	0.23	0.25	16.7	0.04
	K_L (L mg ⁻¹)	0.125						
	R^2	0.993						
Freundlich	K_F (mg g ⁻¹)	17.8	33.3	0.115	3.17	1.18	40.7	0.54
	n	4.72						
	R^2	0.763						
D-R	q_{max} (mg g ⁻¹)	54.4	40.2	0.104	1.35	1.04	25.7	0.94
	B (J mol ⁻¹)	4.61×10 ⁻⁷						
	E (J mol ⁻¹)	1015						
	R^2	0.948						
Temkin	B (kJ mol ⁻¹)	68.8	11.9	0.010	0.37	0.35	17.2	0.06
	k_t (L mg ⁻¹)	5.60						
	R^2	0.892						

model is given by:

$$q_e = \frac{RT}{b_t} \ln k_t + \frac{RT}{b_t} \ln C_e \quad (3)$$

where C_e is the equilibrium concentration of metal ion in the solution, q_e is the equilibrium metal ion concentration on the biosorbent, R is the gas constant, T is the temperature of the adsorption taken place in Kelvin, k_t is the Temkin equilibrium binding constant and b_t is the Temkin constant related to the heat of adsorption.

Dubinin-Radushkevish model helps to determine the free energy of the adsorption, the porosity and to understand the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface and it is generally expressed using the non-linear equation as shown below :

$$q_e = q_{max} e^{(-B[\ln(1+1/C_e)]^2)} \quad (4)$$

where C_e is the equilibrium concentration of metal ion in the solution, q_e is the equilibrium metal ion concentration on the biosorbent, q_{max} is the maximum adsorption capacity of the metal ion onto the biosorbent, R is the gas constant of 8.314 J mol⁻¹ K⁻¹, T is the temperature of the adsorption taken place in Kelvin, B is the D-R constant in J mol⁻¹. The free energy of adsorption, E (J mol⁻¹), was calculated using the equation below:

$$E = \frac{1}{\sqrt{2B}} \quad (5)$$

The error analyses and the parameters of the four isotherm models used are tabulated in Table 1. The Freundlich isotherm model, on the other hand, has the lowest R^2 (0.763) and the n value of 4.73 indicates that it is not a favourable model for this isotherm. This can be further confirmed by its high errors. Similarly, even though the D-R model gave a good R^2 of 0.948, nevertheless its errors proved that it is not a suitable model for the adsorption of Pb(II) by NS.

Studies have shown that the Temkin model is more suitable for gas phase equilibria. In this present study, the adsorption system of Pb(II) by NS also does not fit well into the linear Temkin plot and R^2 of 0.890 was obtained, confirming that the Temkin model is not useful to describe the adsorption system since adsorption of heavy metals onto adsorbents is considered as a liquid-solid sorption system. Comparing the correlation coefficient (R^2) of each isotherm, as shown in Table 1, the Langmuir achieved the highest R^2 (0.997) close to unity with maximum adsorption capacity, q_{max} , of 57.0 mg g⁻¹. Based on the six different types of error analyses used in this study, the Langmuir model also has the least errors, further confirming that it is the most suitable model to describe the adsorption of Pb(II) by NS.

By comparing the adsorption capacity of NS with other adsorbents, NS is found to have good q_{max} . This clearly shows that the NS has a great potential to be used as a low-cost biosorbent for the removal of Pb(II). Investigation of the effect of different temperatures (25°C–70°C) on the adsorption isotherm system was carried out. The thermodynamic parameters i.e.

Table 2. Comparison of the maximum adsorption capacity (q_{max}) of NS with other adsorbents

Adsorbent	q_{max} (mg g ⁻¹)	Reference
NaOH-modified Peach palm waste	65.3	(Salvadoet al., 2012)
Waste tire rubber ash	22.4	(Mousavil et al., 2010)
Sago waste	46.6	(Quek et al., 1998)
Carica Papaya leaf powder	11.1	(Raju et al., 2012)
Apple pomace	16.4	(Pakade et al., 2013)
Groundnut hull	31.5	(Qaiser et al., 2009a)
<i>Ficus religiosa</i> leaves	37.5	(Qaiser et al., 2009b)
Fluted pumpkin seed shell	14.3	(Okoye et al., 2010)
Activated coconut	4.4	(Gueu et al., 2007)
Olive stone activated carbon	22.4	(Alslaibi et al., 2013)
Date tree leaves	58.8	(Boudrahem et al., 2011)
Calcium chloride treated <i>Ulva fasciata</i> sp.	22.9	(Jeyakumar et al., 2014)
<i>Parkia speciosa</i> pod	68.8	(Lim et al., 2015c)
Nanchem Skin	57.0	This work

enthalpy (ΔH°), entropy (ΔS°), and Gibbs free energy (ΔG°) were determined as follows:

The Gibbs free energy was calculated by the following equation below:

$$\Delta G^\circ = -RT \ln K_c \quad (6)$$

where ΔG° (kJ mol⁻¹) is the Gibbs free energy, R is the gas constant of 8.314 (J mol⁻¹ K⁻¹), T is the temperature applied in the adsorption system in K and K_c is the distribution coefficient.

K_c can be determined by the following equation below:

$$K_c = \frac{C_s}{C_e} \quad (7)$$

where C_s is the amount of the metal ions adsorbed onto the biosorbent (mg g⁻¹) and C_e is the amount of the metal ions in the equilibrium system (mg L⁻¹).

The values for enthalpy and entropy are calculated from the equation below:

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

By plotting a graph of $\ln K_c$ against T^{-1} (not shown), the entropy (ΔS°) and the enthalpy (ΔH°) values can be determined from the gradient and the slope of the linear equation. The negative values of ΔG° , ranging from -4.33 to -4.76 kJ mol⁻¹, show that the adsorption process of Pb(II) by NS is spontaneous and thermodynamically feasible. The positive value

of ΔS° (9.46 J mol⁻¹ K⁻¹) indicates the increase in degree of freedom of the solid/liquid interface for the adsorption of Pb(II) by NS while the negative ΔH° (-1.50 kJ mol⁻¹) shows the adsorption process of Pb(II) by NS is exothermic in nature, which means it is temperature independent and does not need to spend cost and energy to make the adsorption more efficient.

Kinetics studies

Kinetics studies of adsorption can provide a better understanding of the binding mechanism of the adsorbate (liquid phase) and the biosorbent (solid phase). In this study, kinetics studies were carried out using three different concentrations of Pb(II) solution (50 mg L⁻¹, 100 mg L⁻¹, and 400 mg L⁻¹). The kinetics data obtained were analysed using three different kinetics models, namely the pseudo-first order (Lagergren, 1898), pseudo-second order (Ho and McKay, 1998), and Weber-Morris intraparticle diffusion (Weber, 1963) models. Based on their linear correlation coefficients, the kinetics model that best fit the adsorption process can thus be determined.

The pseudo-first order, also known as the Lagergren's kinetics model, is most commonly used to describe the kinetics models of adsorption process and is expressed by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (9)$$

where, q_t (mg g⁻¹) is the adsorption capacity at the

particular time t , k_1 is the rate constant for pseudo-first order, q_e (mg g^{-1}) is the adsorption capacity achieved at equilibrium. Intergration of Equation (9) will give a linearized equation as shown below:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (10)$$

The pseudo-second order is described as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (11)$$

where, q_t (mg g^{-1}) is the adsorption capacity at the particular time t , k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant for pseudo-second order, q_e (mg g^{-1}) is the adsorption capacity achieved at equilibrium. Integration of Equation (11) will give a linearized equation as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

From the two linear plots of pseudo-first order and pseudo-second order, the correlation coefficients of the pseudo-second order gave better linearity with R^2 values very close to 1 ($R^2 = 0.996 - 0.999$) for all the three different concentrations of Pb(II) used in this study. On the other hand, compared to the pseudo-second order kinetics, only the 50 mg L^{-1} Pb(II) for pseudo first order kinetics gave $R^2 > 0.9$, while for both 100 mg L^{-1} and 400 mg L^{-1} Pb(II), the R^2 values were below 0.8. Therefore all the R^2 values for pseudo first order were lower than the corresponding R^2 for pseudo-second order, which further confirms that the adsorption does not obey the pseudo-first order and that the kinetics of adsorption Pb(II) onto NS follows the pseudo-second order.

Another way to confirm the kinetics mechanism of adsorption is by comparing the $q_{e,exp}$ (biosorption capacity obtained from isotherm experiment) and $q_{e,cal}$ (calculated biosorption capacity from kinetics study). In this case, the $q_{e,cal}$ values obtained for pseudo-first order are not compatible to the $q_{e,exp}$ values. For example, the $q_{e,exp}$ values for 50 mg L^{-1} , 100 mg L^{-1} and 400 mg L^{-1} Pb(II) are 19.31 mg g^{-1} , 39.29 mg g^{-1} and 52.14 mg g^{-1} respectively but the $q_{e,cal}$ values based on the pseudo-first order were found to be only 6.89 mg g^{-1} , 9.82 mg g^{-1} and 16.75 mg g^{-1} at these respective concentrations. This clearly shows that pseudo first order is not the mechanism involved. On the other hand, the $q_{e,cal}$ values obtained for pseudo-second order were much closer to the $q_{e,exp}$ values with 18.87 mg g^{-1} and 35.71 mg g^{-1} for 50 mg L^{-1} , 100 mg L^{-1} Pb(II) respectively. For the 400 mg L^{-1} Pb(II), despite the $q_{e,cal}$ and $q_{e,exp}$ values of 83.33 mg g^{-1} and 52.14 mg g^{-1} respectively are quite far apart

but however the R^2 value shows a good correlation coefficient of 0.996 so it still shows it follows the pseudo-second order. By observing the correlation coefficient values and comparison of the $q_{e,cal}$ and $q_{e,exp}$ values, it can be concluded that the adsorption of Pb(II) by NS follows the pseudo-second order kinetics, suggesting that the adsorption could involve a chemisorption process.

Weber-Morris's intraparticle diffusion helps to provide a better understanding of the process of transferring the liquid phase to solid phase and determining the rate-limiting step. It is believed that the rate could occur through several processes as stated below:

1. Transfer of adsorbate from the bulk solution onto boundary film then onto the surface of the sorbent
2. Adsorbate transferred from surface of sorbent into the sorbent by intraparticle diffusion
3. Adsorbate retained inside the active sites of the sorbent

The intraparticle plot can be divided into two zones. The first slope described the first process where Pb(II) is transferred from the solution onto boundary film then onto the surface of NS and the second slope describes as the Pb(II) transferred from the surface into the NS by intraparticle diffusion as the rate limiting step and also shows the concentration of Pb(II) in the solution has finally reached its equilibrium stage. All the three linear plots at different concentrations did not pass through the origin. Hence the intraparticle diffusion is not the rate determining step for this adsorption process.

Effect of ionic strength on adsorption

In a real-life situation, the industrial wastewater may be polluted with different kinds of cations and anions with different concentrations. Here, the effect of ionic strength was investigated to see if increasing concentration of KNO_3 will influence the adsorption of Pb(II) on NS. It was found that as the increase in concentration from 0.02 M to 1 M KNO_3 , the removal efficiency of Pb(II) on NS shows a gradual decrease from 95.3% to 80.4% . This decrease may be due to competitive effects of the electrolyte ions and adsorption of anions onto the surface. Introducing K^+ and NO_3^- ions to the system may have caused competition to the surface sites of the adsorbent. Most possibility is that the anion NO_3^- may occupy the surface sites of the adsorbent since the surface charge of the adsorbent is positively charged; hence

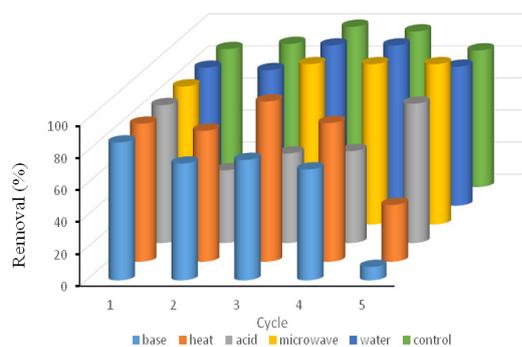


Figure 3. Regeneration of NS using various methods

more anions will be adsorbed to the surface than the cations.

Regeneration of NS

NS was investigated for its reusability as an adsorbent for the removal of Pb(II) through regeneration studies. Of the six methods investigated (Fig. 3), regeneration using 1 M NaOH generally resulted in decrease in adsorption ability with a drastic decrease of about 60% in the fifth cycle. Heating NS after each cycle was able to maintain Pb(II) adsorption at > 80% up to the fourth cycle. Thereafter in the fifth cycle, a reduction in adsorption of approximately 50% was observed. Except for cycle 2, generally microwave regeneration is a good method with high Pb(II) removal. Of the six methods studied, washing with water and control gave good adsorption of Pb(II) throughout the five cycles and maintaining removal at > 85% even at the fifth cycle. Hence, it can be observed that NS has the potential to be regenerated and reused as an adsorbent using simple regeneration methods.

Conclusion

This study clearly shows that Nanchem skin has great potential as a low-cost adsorbent for the removal of Pb(II). Not only does NS have the ability to remove Pb(II) with a good maximum adsorption capacity better than many reported adsorbents, it was able to retain its adsorption capability in the presence of other metals. Adsorption of Pb(II) is best described by the Langmuir isotherm model while its kinetics follows the pseudo second order. The ability to regenerate and reuse further enhances NS as a potentially attractive adsorbent for the removal of Pb(II).

Acknowledgements

The authors wish to thank the Government of Negara Brunei Darussalam and the Universiti Brunei

Darussalam for their financial support. The authors also wish to thank the CAMES for the use of XRF.

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