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Leaves of *Averrhoa bilimbi* as a Superior Low-cost Adsorbent for Lead (II) Removal

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Abstract

Bilimbi leaves (BL) as a low-cost adsorbent were effectively used to remove lead Pb(II) from aqueous solution in a batch adsorption experiment. The effects of multiple parameters such as pH, ionic strength and contact time were also thoroughly investigated and optimal experimental conditions were ascertained. Based on the isotherm studies on the adsorption of Pb(II) on to BL, the maximum adsorption capacity was found to be1597.63 mg/g. Kinetic studies implicated that the adsorption data were best designated by the pseudo second order and the adsorption process of Pb(II) was concluded to be exothermic and it occurred spontaneously from thermodynamic study. While, regeneration study showed that base treatment was able to regenerate and improve the adsorption capability of BL. Based on the overall data obtained in this study, BL proves to be a potential low-cost material and could be employed as low-cost alternatives in wastewater treatment for the removal of Pb(II).

Keywords: Adsorption; *Bilimbi* leaves; Heavy metals; Lead; Regeneration

Introduction

There are no specific definitions of heavy metals however they are commonly known as those that have a specific density greater than 5g/cm^3 [1]. They are elements found naturally on the crust of the Earth and are non-degradable [2]. At higher concentrations they may pose a threat to human health. Heavy metal poisoning could be possible due to instances such as from drinking water that was polluted with lead or inhaling mercury. In the past heavy metals were used on a regular basis as a means of construction and even in food and beverages [1].

Even in recent times heavy metals are still incorporated into our daily lives for instance, in gold mining, mercury is still being used. Heavy metal pollution is more dominant around industrial areas such as mining. When mining takes place, the soils get exposed and thus lead to the release of these heavy metals. These metals will then be transported via rainwater through rivers and streams whereby the metals may be deposited on the beds or may even dissolve in the water disrupting the ecosystem surrounding it [2]. Accumulation of these toxic heavy metals in the rivers or ocean poses a threat to multiple aspects of the environment. Hence, handling of heavy metals should be notably taken as a serious matter in which proper management of disposal and usage should be implied to reduce adverse effects towards the environment. Therefore, the need to counter this issue becomes increasingly popular in order to sustain the quality of living of not just individuals but the environment as well.

Various techniques of heavy metals removal from wastewater have been developed and tested to assist in saving the environment. These methods such as reverse osmosis [3], coagulation and flocculation [4], activated carbon adsorption [5], nano filtration [6] and many more [7-11]. However, some of these are costly for the developing countries and incapable to perform effectively in treating a wastewater. Amongst all the methods, adsorption seems to provide a more promising approach in removing heavy metals from wastewater treatment processes. As time progresses, there are numerous scientific discoveries and researches towards various techniques in treating wastewater and adsorption seems to form a plausible impact towards becoming a sufficiently effective technique amongst others. It has several enhanced attractions as a technique for wastewater treatment. For instance the cost of said experiment being relatively cheaper has proven to be efficient in helping not only developed countries but also may contribute in helping developing countries [12]. The actual technique is

very simple and does not require very skilled or highly trained workers.

For an adsorption Process to be of high quality, expenditure as well as removal Capability of the said adsorbent plays a vital role. The adsorbents should be cheap and are readily available in abundance. Hence, over the past decades, multiple potential adsorbents were tested ranging from fruit wastes [13-16], remainders from industries [17-19] as well as cultivates wastes [20-23] in removing of dyes and heavy metals from aqueous solutions. In this study, *Averrhoa bilimbi*, commonly known asbilimbi or 'Belimbing', was being used and investigated. *Bilimbi* is a remedial plant belonging to the Oxalidaceae family [24]. A. *bilimbi* is closely related to A. Carrabolla generally known as 'star fruit'. It originated in the Southeast Asia and is easily available here in Brunei Darussalam. Mostly used in cooking, the fruits are sour and are extremely acidic. It is believed that A. bilimbi and its leaves possess a very high value in medicine through various studies and research [24]. It is alleged that the fruits have been used in traditional medicine for the treatment of a variety of ailments. Brewed *Bilimbi* Leaves (BL) is used as an alternative method to modern medication and as an antibacterial, postpartum protective medicine and in the treatment of fever. The paste of leaves is used in the treatment of multiple skin disorders such as acne, rashes, itch and many more [25, 26]. These techniques are commonly used amongst the natives, however are not regularly used on a daily basis. To date, literature search indicated a *Bilimbi* has never been utilised for the removal of dyes or heavy metals. In this study *Averrhoa bilimbi* leaves were chosen as the adsorbent instead of *Averrhoa bilimbi* itself.

The study focused on whether *Bilimbi* Leaves (BL) could be a possible candidate as a low-cost adsorbent for removal of PB (II) from aqueous solutions. This is due to the usage of lead throughout the years has transitioned immensely, from being a coating material to be a constituent in paint for the vast infrastructures that exist nowadays. Although it may serve as a multifunctional material in various areas of needs, however this metal with the molecular weight of 207.2 g/mol causes a greater amount of damage to the environment. Upon entering the human body, it attacks the normal metabolic processes as well as vital organs especially the brain [27, 28]. Therefore, the need to suitably dispose of this particular heavy metal is highly required.

Materials and Methods

Preparation of *Bilimbi* Leaves and Chemical Reagents: The *Bilimbi* Leaves (BL), used as the adsorbent in this study, were freshly obtained from the *bilimbi* tree homegrown at the back of a house in Kampong Telanai. The BL were plucked from the tree and cleansed with distilled water followed by oven dried at 80°C for about a week a constant mass is obtained. The dried sample was subsequently blended and sieved using laboratory metal sieves. Samples of particle size < 355µm were used throughout this study. To avoid contamination and reduce moisture build up, the samples were stored in zip-lock bags that were tightly sealed.

Acquired from Sigma Aldrich Corporation, Lead (II) Chloride ($PbCl_2$) was used directly without supplementary refining steps. Pb(II) stock solution (1000 mg/l) was prepared via calculation, i.e.0.14g of Pb(II) were dissolved in distilled water a 1 L volumetric flask. Solutions of different Pb(II) concentrations (500mg/L and 100mg/L) were prepared by diluting this stock solution.

Instrumentation: The Analytic Jena novAA300 Atomic absorption spectrophotometer was used to measure the absorbance of PB(II) solutions. For the calibration curves for Pb(II), standard solutions in the range of 2 to 10 mg/L concentrations were Prepared. Both the Thermo scientific MaxQ 3000 shaker and the Stuart Scientific Flask Shaker SF_1 were used to shake the mixture of adsorbent with adsorb ate solution at 250 rpm. The Shimadzu IRPrestige-21 spectrophotometer (FTIR) was used to identify the functional groups present in BL. Furthermore, to determine the surface morphology of the adsorbent, the Tuscan Vega XMU Scanning Electron Microscope (SEM) was used.

Characterization of BL: To determine the point of zero charge (PH_{PZC}) of BL, BL (0.05 g) was weighed into six labeled 250 ml conical flasks then 25.0 ml of different pH values of 0.1M of KNO_3 were added. Adjustment of the pH values of the 0.1 mol/L KNO_3 (values of 2 to 10) solutions by done by adding either 0.01mol/L HCl or 0.01mol/L NAOH solution. After 24 h of shaking at 250 rpm, the mixtures were filtered, and the final pH of the solutions was measured. The graphs of pH_{final} versus $pH_{initial}$ were plotted. The pH_{PZC} of BL is the point of intersection on the x-axis.

For the morphological analysis using Scanning electron microscope (SEM), the solid residues of lead–loaded adsorbent were left to dry in an oven at around 50°C. The original adsorbent was used as well in the analysis, as it provides the comparison of surface structure before and after being treated with Pb(II).

The original adsorbent and lead-treated adsorbent were also characterized using Fourier Transform Infrared Spectroscopy (FTIR). These samples were then analyzed by FTIR to determine the presence of functional groups. Potassium bromide (KBr) crystals (0.15 g) were weighed and dried in an oven. After 2 h of drying, KBr crystals were grinded into powder in order to make into pellet by using a presser. This KBr pellet was then run in FTIR as background. Each sample (0.0015 g) was then mixed and grinded with the dried powder of KBr to make into pellet using presser. The pellet was run in FTIR under the wavelength ranges from 600 cm^{-1} to ~3800 cm^{-1}.

Batch adsorption Experiment: The effect of contact time was investigated where BL (0.05 g) was weighed into eight labeled 250

ml conical flasks. Lead solutions (25.0 ml) of known concentrations were then pipette respectively into each flask containing the sample. The conical flasks containing mixtures of adsorbent and adsorb ate solutions were then shaken at room temperature at the speed of 250 rpm for 4 h. The samples were withdrawn from the shaker at a 30 min interval. They were filtered using filter paper into plastic bottles. The filtrates were then diluted to 10 mg/L for the analysis of absorbance using Atomic Absorption Spectrophotometer (AAS). This experiment was carried out in duplicates.

For isotherm studies, the adsorbent, BL (0.05 g) was weighed into twenty labeled 250 ml conical flasks and treated with a series of concentrations of lead solutions (0-1000 mg/L). These series of concentrations were then shaken at 250 rpm according to its optimum shaking time.

In investigation of kinetics studies, roughly 0.05 g of sample was used and mixed with 100 and 500 mg/Lof lead solution in 250 ml conical flask. The solutions were stirred using a shaker at 250 rpm up to the optimum contact time. For every 3 min interval up to 30 min, each of the samples was withdrawn and filtered. For the following 30 min, the solutions were shaken at 10 min interval and the remainder of the solutions was shaken at 30 min interval. Gravity filtration was carried out for each solution and the filtrate was analyzed using AAS instrument. This experiment was carried out in duplicate.

While for the removal of Pb(II) in different medium pH, the effect of pH was studied by adding the sample (0.05 g) into six labeled 250 mL conical flasks containing adjusted pH values of 100 mg/Lof lead solution. The untreated pH of lead solution, known as ambient pH, was measured and recorded. A total of seven different pH ranges from 2 to 10 including the ambient pH was used. The pH values of these solutions were adjusted by adding 0.1 mol/LNaOH or 0.1 mol/LHCl solution. Once the desired pHs were obtained, 25.0 ml of this solution were then pipette into 250 ml conical flasks containing the adsorbent. The solutions were then shaken at 250 rpm under its optimum shaking time. After filtration of the solutions, the filtrates were diluted to 10 mg/L for the analysis of absorbance.

Thermodynamic studies involved two different concentrations of lead solutions (100 and 500 mg/L) were used. The adsorbent (0.05 g) was mixed with individual concentration of lead solution into separate 250 ml conical flasks and shaken using a water-bath shaker at 250 rpm with temperature altered to 298 K, 313 K, 323 K, 333 K and 343 K under optimum shaking time. After gravity filtration, the diluted filtrate (10 mg/L) was analyzed. The Gibbs free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) were used to investigate the nature of adsorption process.

Ionic strength effect on the removal of Pb(II) by BLwas investigated using potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$), potassium chloride (KCl) and sodium chloride (NaCl) salts. These salts were prepared in 2mol/L and diluted into a range of 0.01mol/L to 0.1mol/L using a serial dilution. The solutions were mixed with 10 ml of 1000 mg/Lof the lead solution into 100 ml volumetric flask. The adsorbent (0.05 g) was then weighed into 250 ml conical flask containing 25.0 ml of the mixture of different concentrations of salt and lead solution. The solutions were shaken at room temperature to the optimum shaking time on a shaker set at 250 rpm. After respective allocated shaking times, the solutions were filtered and the filtrates were diluted to 10 mg/L for the analysis.

Regeneration Studies: The adsorbent (1.0g) was weighed into a 1000 ml conical flask with 100 mg/Lof respective adsorb ate solution (500 ml) added onto it. The volume of adsorb ate to mass of adsorbent was in 1:500 ratios in which 1.0g of sample was combined with 500 ml of Pb(II). The flask was then shaken using a shaker at 250 rpm at room temperature under optimum shaking time. During the filtration, the solid residues were collected and dried in an oven at ~70 °C overnight while the filtrate was diluted to 10 mg/L for the analysis of absorbance using mentioned instrument.

The dried solid residues were weighed and divided into four portions into 250 ml of labeled conical flasks for allocated treatment purposes. The solids were then further treated with either 0.1mol/L NAOH, 0.1mol/L HCL or distilled water and a control experiment was also carried out. In the treatment with acid, base and distilled water, the volume used was based on the 1:50 ratio. The washed adsorbents were then dried in an oven. Then, another cycle of adsorption was continued and the regeneration studies were carried for five consecutive cycles.

Results and Discussions

Bilimbi Leaves (BL), the adsorbent used in this study to remove Pb(II) from aqueous solutions, was characterized by Fourier Transform Infrared (FTIR) spectroscopy and scanning electron microscope (SEM). Batch adsorption experiments were performed to investigate how parameters such as contact time, pH_{PZC}, pH and ionic strength could affect the adsorption process. The Lagergren pseudo-first order and pseudo-second order models were applied to study the adsorption kinetics mechanism. Followed by, the adsorption isotherm data were investigated using six different isotherm models. The changes in enthalpy ($\Delta H°$), entropy ($\Delta S°$) and Gibb's free energy ($\Delta G°$) of the BL-Pb(II) system were also investigated and the results obtained are shown and discussed below.

Characterization of Adsorbent: The point of zero charge (pH_{PZC}) (Figure 1) of an adsorbent determines the pH at which the adsorbent's surface has zero charge. As shown in Figure1, the pH_{PZC} of BL was determined to be at pH 4.5. This value also helps to determine whether the surface of the adsorbent is positively or

negatively charged. A negatively charged surface occurs when the pH is greater than the pH_{PZC} due to deprotonation of the surface functional groups and thereby attracts cat ions, whereas when the pH of the solution < pH_{PZC}, the opposite reaction occurs where the surface of the adsorbent is positively charged due to prolongation of the surface functional groups with excess H^+, hence, can attract anions. The adsorbent's surface in this study, has positive charge at pH < 4.5, negative charge at pH > 4.5 and net zero charge at pH=4.5.

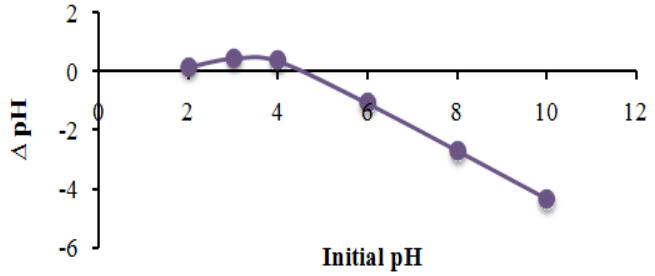
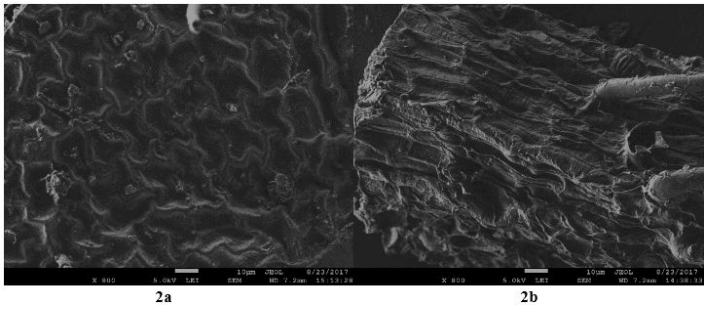


Figure 1: Plot to determine the point of zero charge of BL.

SEM micrographs of BL and its treated with Pb(II) at ~600-800× magnification depicted in (Figures 2(a)) and 2(b)). This was done in determining the surface morphology of BL, prior to and after adsorption of adsorbents. Smooth and coarse textures with numerous asymmetrical folding on the surfaces of BL can be denoted. This feature increases the surface area for adsorption process and are possible adsorption sites for the adsorption of Pb(II). After treatment, the molecules of Pb(II) were adsorbed onto the surface of BL as the surface of BL clearly showed significant differences as shown in the figures.



Figures 2(a-b): Surface morphology of BL before (left) and after (right) after treatment of Pb(II).

In (Figure 3), the comparison of FTIR spectra for Pb(II) treated BL with untreated BL and Pb(II) is shown. Obvious shifts in wavelengths gave the impression that there was positive adsorption of Pb(II) onto BL. Noticeable shifts can be noted, for instance the broad peak at 3349 cm^{-1} that represents OH and NH stretching vibration shifts to 3336cm^{-1}. Whereas the peak at 1649 cm^{-1} representing the C=C group is shifted to 1629cm^{-1}. Lastly, the carbonyl group (C=O) initially seen at 1750 cm^{-1} has then shifted to 1736cm^{-1} upon treatment with Pb(II), again provided more evidence in the adsorption of Pb(II) onto BL.

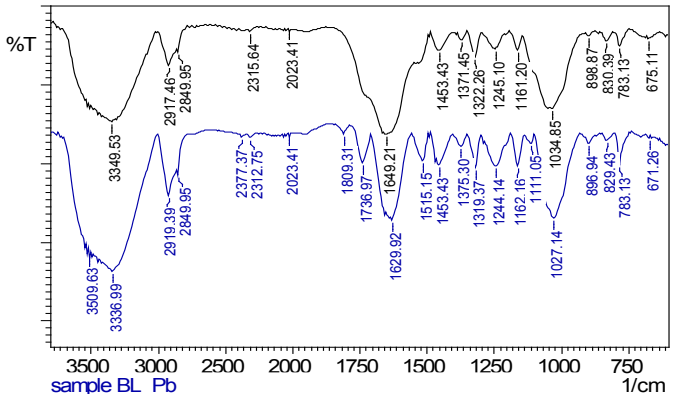


Figure 3: FTIR spectra for functional group characterization of BL (top-black) and Pb-BL (bottom-blue).

Effect of Contact Time and Adsorption Kinetics: The adsorption of Pb(II) was calculated as a function of contact time in order to determine the time for adsorb ate-lead system to reach equilibrium. In this study, the effect of contact time was performed using 100 mg/Lof Pb(II). The results (Figure 4) showed that rapid adsorption of Pb(II)was observed at the initial 30 min of the contact period. More than 70% of Pb(II) was absorbed by the adsorbent and equilibrium was reached within the time. An increase in contact time increased the percentage removal, but as time progressed, it gradually approached almost constant value, indicating reaching of equilibrium. This is most likely due to the fact that initially all the sites on the adsorbent's surface were vacant and high solute concentration gradient. As time progressed, the rate of Pb(II) uptake by BL decreased due to the adsorption sites being gradually filled up. Eventually the rate of adsorption gradually slowed down until it reached equilibrium. Hence, the optimum contact time of Pb(II) was denoted at 1.5 hand was used throughout the study in order to ensure that optimum adsorption was reached.

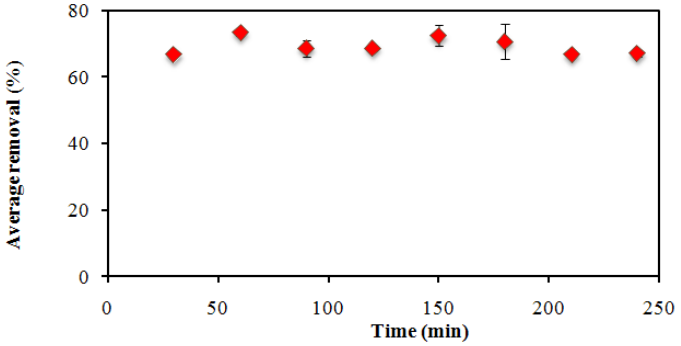


Figure 4: Contact time required for BL-Pb system to reach equilibrium.

The experimental data in this study were fitted onto two kinetics models namely the pseudo first order and pseudo second order with their linear equations shown in (Table 1). This was done to investigate the potential rate-determining steps involved in the process of adsorption. As for the removal of Pb(II), it can be observed that the pseudo second order model has the highest R^2 values with lowest values of errors than the pseudo first order as can be seen in (Table 2) and from (Figure 5). Thus, it can be concluded that the kinetics adsorption system of Pb(II) onto BL follows the pseudo second order process.

Kinetics model	Linear equation	Plot
Pseudo first order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$	log (q_e-q_t) vs. t
Pseudo second order	$\frac{t}{q_t} = \frac{q}{k_2 q_e^2} + \frac{1}{q_e}t$	t/q_t vs. t

Table 1: Linear equations of kinetics models.

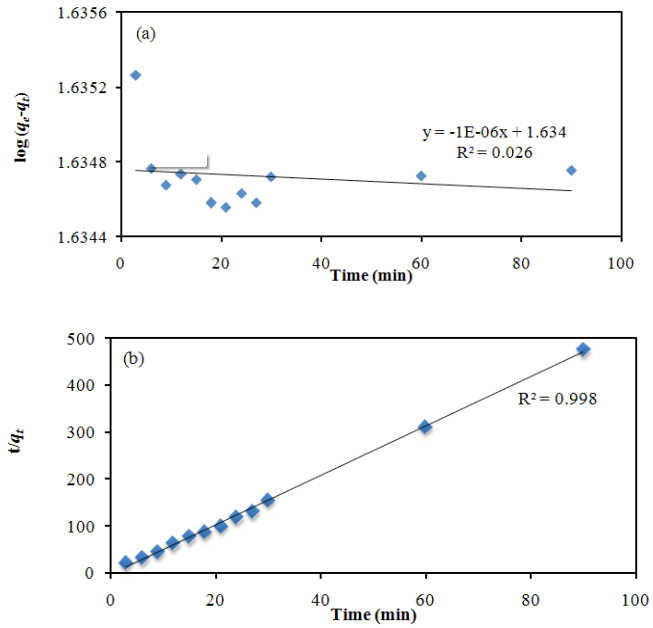


Figure 5: Linear plot of (a) pseudo first order and (b) pseudo second order model of the adsorption of Pb(II) onto BL at 100 mg/L.

Model	R^2	ARE	SSE	HYBRID	EABS	MPSD	χ^2
Pseudo first order	0.03	98.40	0.434	22.35	2.27	66.86	2.24
Pseudo second order	0.99	19.44	0.053	3.77	0.37	38.58	0.38

Table 2: Kinetics parameters and error values for adsorption of Pb(II) onto BL at 100 mg/LPb(II) concentrations.

Adsorption Isotherm: The importance of adsorption isotherm in adsorption studies cannot be overly stressed as it describes the interaction between adsorbate and adsorbent. In this study, batch adsorption studies were carried out to investigate the adsorption ability of BL using Pb(II). The results obtained were then further evaluated by fitting the experimental data obtained onto six adsorption isotherm models namely Langmuir, Freundlich, Temkin, Dubinin-Radushkevic (D-R), Redlich-Peterson (R-P) and Sips models in order to determine the best fit isotherm model.

In brief the Langmuir isotherm model is effective for monolayer adsorption onto a homogenous surface of adsorption[29]. The Freundlich model is suitable for the adsorption on heterogeneous surface and multilayer adsorption to the binding sites on the surface of the adsorbent[30]. The Temkin model, states that there is a linear decrease of heat of adsorption with increasing surface coverage due to the adsorbate or adsorbent interactions[31]. Whilst for D-R model expresses the adsorption mechanism onto heterogeneous surface and to estimate the porosity characteristics of the adsorbent [32]. R-P however, incorporates three parameters into a pragmatic model, which combines the qualities from both the Freundlichand Langmuir isotherm models [33]. Like R-P, the Sips model is also a three-parameter model combining both the Freundlich and Langmuir models [34].

Amongst the six isotherm models, the Langmuir model was fitted well for the adsorption of Pb(II) due to the higher R^2 value, as shown in (Table 3). This therefore indicates the monolayer coverage of Pb(II) onto the absorbent. The simulation plots of data from the six isotherm models together with the experimental isotherm data for Pb(II)removal for comparison are shown in (Figure 6). To further verify this study's best-fit isotherm model in describing the adsorption process, error analyses were performed using six error functions. Higher error values indicate of greater

errors. The error analyses of adsorption of Pb(II) onto BL. showed that the Langmuir model have the lowest error value, Thus, it can be concluded that the Langmuir model provided the best fit for Pb(II) adsorption on BL giving maximum adsorption capacity (q_{max})(Table 4) of 1597.63mg/g, a value far higher than most reported adsorbents.

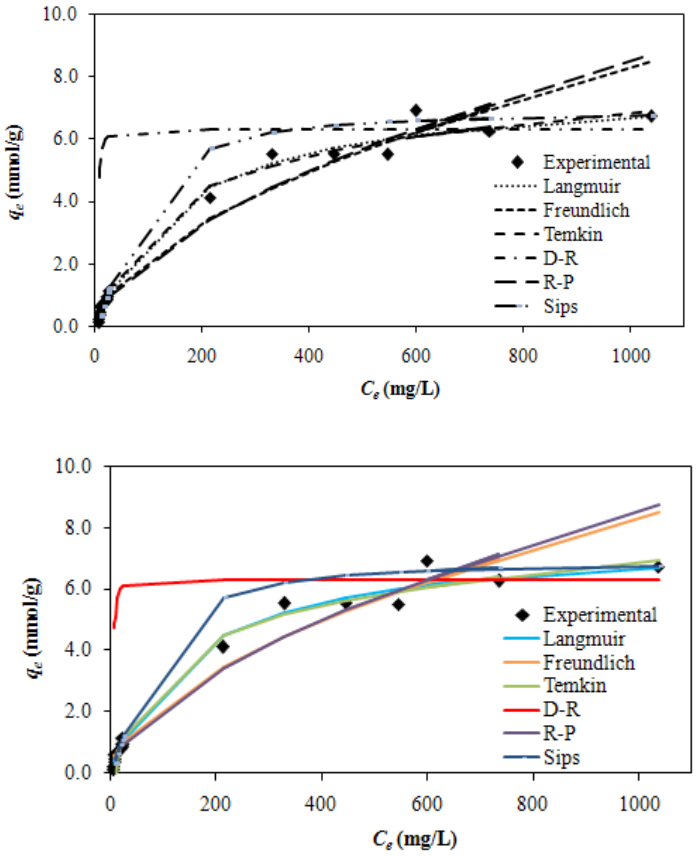


Figure 6: Comparison between the simulation plots of different isotherm models with the experimental data of the adsorption of Pb onto BL.

Model	Values	ARE	SSE
Langmuir			
q_{max} (mmol/g)	7.71	6.83	1.18
q_{max} (mg/g)	1597.63		
K_L(L/mmol)	0.01		
R^2	0.9890		
Freundlich			
K_F (mmol/g)	0.16	11.98	6.10
K_F (mg/g)	33.62		
N	1.75		
R^2	0.9831		
Temkin			
K_T (L/mmol)	0.09	39.55	3.72
b_T (J/mol)	1614.63		
R^2	0.9815		
Dubinin-Radushkevich			
q_{max} (mmol/g)	6.32	331.82	196.32
q_{max} (mg/g)	1309.62		
B (J/mol)	3.58E-06		
E (kJ/mol)	373.84		
R^2	0.9858		
Redlich Peterson			
K_R(L/g)	1.00	10.63	7.11
a_R(L/mmol)	6.69		
R^2	0.9598		
Sips			
q_{max} (mmol/g)	6.91	14.99	5.32
q_{max} (mg/g)	1431.75		
K_S (L/mmol)	0.00		
1/n	1.43		
n	0.70		
R^2	0.7625		

Table 3: Adsorption isotherm parameters of adsorption of Pb(II) onto BL for different models.

Adsorbent	q_{max}(mg/g)	Reference
Banana pseudostem	34.2	[13]
Artocarpus hybrid (Nanchem) skin	57.0	[35]
Peat	15.0	[36]
Modified *Punica granatum* L. peels	371.4	[37]
Polyethylenimine-functionalised oil palm leaves	143.0	[38]
P. eldarica leaves	40.0	[39]
Citric acid treated rubber leaf	97.2	[40]
Monosodium glutamate treated rubber leaf	110.0	[40]
Alkali treated persimmon leaves	256.0	[41]
Sulphuric acid treated palm tree leaves	72.3	[42]
Cattails leaves	51.0	[43]
Activated palm kernel husk carbon	98.0	[44]
Aluminate treated *Casuarina equisetifolia* leaves	28.0	[45]
Curcuma longa leaf	35.9	[46]
Infused tea leaves	26.3	[47]

Chitosan nanoparticles	734.3	[48]
Activated carbon from molasses	303.0	[49]
Mesoporous activated carbon	20.3	[50]
Cherry kernels	171.4	[51]
BL	1597.6	This study

Table 4: Comparison of maximum adsorption capacities between BL and other selected adsorbents.

As a comparison with other selected adsorbents in adsorbing Pb (II), shown in Table 4, BL has shown a superior q_{max} than many of the reported agricultural waste adsorbents, even when compared to those that have been undergone modification. Besides, the use of chitosan nano particles had shown high q_{max} of 734.3 mg/g but still not as high as BL. The fact that the particle sizes of BL used in this study were only in microns size and to compare with the chitosan that is in nano size, this provides an idea that smaller particles of BL can be used to gain higher q_{max}.

Thermodynamic Studies: The removal of Pb(II) was performed under five different temperatures at 298 K, 313 K, 323 K, 333 K and 343 K for the determination of thermodynamic parameters. This was to conclude whether the adsorption processes occurred spontaneously and are thermodynamically promising. The said parameters were obtained with the following equations:

$$\Delta G° = \Delta H° - T\Delta S° \quad (1)$$

$$\Delta G° = -RT\ln k,\ k = \frac{C_s}{C_e} \quad (2)$$

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (3)$$

where $\Delta H°$, $\Delta G°$ and $\Delta S°$ are the enthalpy change, Gibbs free energy, and the entropy change, respectively is the temperature in Kelvin (K), k being the adsorption distribution coefficient, C_S is the adsorbed Pb(II) concentration at equilibrium (mg/L), C_e is the remaining Pb (II) concentration in solution at equilibrium (mg/L), and R is the gas constant (J/mol K).

A plot of ln K versus 1/T (Figure 7) enables the values of $\Delta H°$ and $\Delta S°$ to be obtained from the slope and the y-intercept. Calculation of the thermodynamics parameters based on (Equations (1) to (3)) above showed that the adsorption processes of Pb(II) was exothermic in nature with $\Delta H°$ being negative for removal of Pb(II) (Table 5). Negative values of $\Delta G°$ were observed, suggesting that the adsorption process was favorable and spontaneous. The $\Delta S°$ values were found to be negative thereby suggesting that there may be an increased orderliness with the increase of temperature in the Pb-BL system.

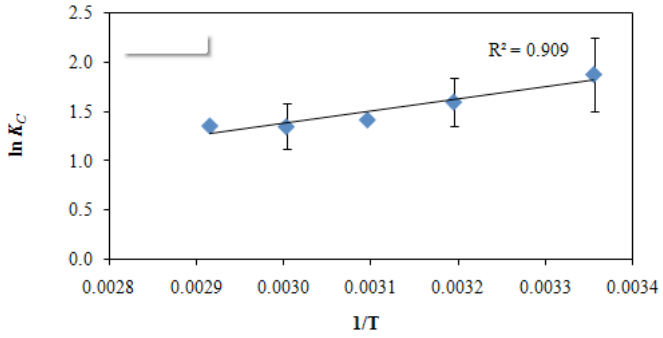


Figure 7: The Van't Hoff plot for the adsorption of Pb(II) onto BL at 100 mg/L.

$\Delta H°$ (kJ/ mol)	$\Delta S°$ (J/mol K)	ΔG^0 (kJ/mol)					R^2
-	-	298K	313K	323K	333K	343K	-
-10.29	-19.37	-4.66	-4.17	-3.87	-3.75	-3.89	0.910

Table 5: Thermodynamic parameter values for the adsorption of Pb(II) onto BL at 100 mg/L.

Effect of Medium pH: Figure8 illustrates the adsorption ability of BL towards Pb(II) increases as the pH of solution increase from pH 2 to pH 4. At its untreated pH (5.43), a removal of 96.8% of Pb(II) was observed. Above this pH, the BL was able to maintain good adsorption capacity up till pH 6. At pH values higher than pH 6, precipitate formation were observed indicating that Pb(II) were no longer absorbed by BL hence the readings obtained at these pH values are invalid.

All in all, this suggests that the major influence in the adsorption of Pb(II) onto the BL might be electrostatic interactions (Figure 8). As pH increases, more surfaces of the adsorbent become negatively charged resulting in the lowering of the repulsion of Pb(II) ions that are positive. Though, under strong acid (pH 2), a slightly lowered adsorption of 88% was observed. This is perhaps due to functional groups being protonated on the adsorbent's surface making it more positively charged which results in electrostatic repulsion with the positively charged Pb(II) ions.

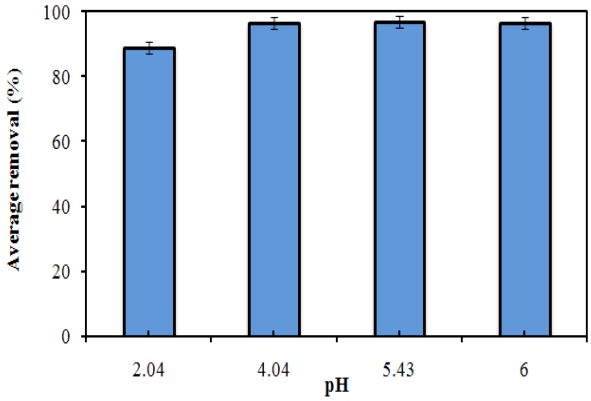


Figure 8: Adsorption of Pb(II) onto BL under various pH medium.

Effect of Salt Concentration: It is essential to study the effects of ionic strength on the adsorption process as wastewater effluents commonly have higher salt concentrations. The effects of NaCl, KCl, KNO_3 and $NaNO_3$ salts on adsorption varied and the interactions of salts with the adsorbent and lead solutions were depended upon.

From the results, NaCl showed a greater influence on BL's adsorption towards Pb(II) (Figure 9), amongst the four salts examined. A drastic decrease in adsorption of Pb(II) was observed as the concentration of NaCl increased. This could be due to the relatively smaller size of Na^+ ions when compared to the Pb^{2+} ions therefore enabling them to occupy the surface-active sites better. This matter also may be caused by the opposition between the positively charged Pb^{2+} ions and the Na^+ ions for the same active adsorption sites of the adsorbent. Both $NaNO_3$ and KNO_3 showed similar trends where there was an initial decrease in the adsorption of Pb(II) as the concentrations of respective salts increased, above this point, the removal capacity further deteriorated as the salt concentration increased.

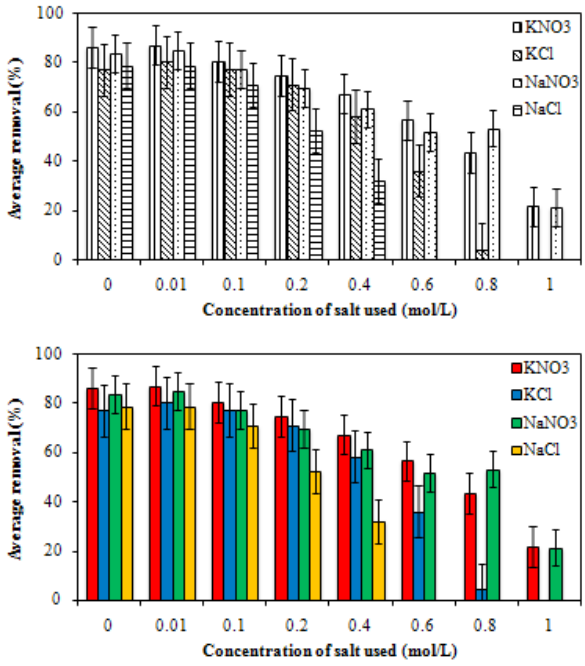


Figure 9: Effect of ionic strength using different salts of KNO_3, KCl, $NaNO_3$ and NaCl on the adsorption of Pb(II) onto BL.

Regeneration Studies: In order to assess the practicality in terms of cost of the BL in this study, desorption experiments were conducted. This is to see whether the original set of BL can be used multiple times instead of using new sets every time. Pb(II) loaded adsorbents were treated in different techniques. Additional of HCl and NaOH solutions, respectively were carried out as well as washing with distilled water and a control for comparison before and after the treatment with three different methods was used. (Figure 10) show the performance of BL on the removal of Pb(II), respectively within five cycles of regeneration study.

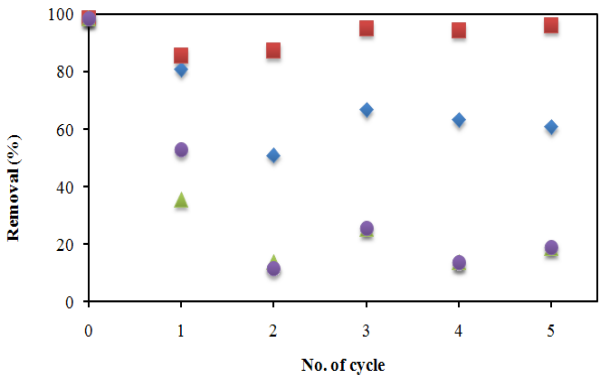


Figure 10: Regeneration of BL with Pb(II) showing five consecutive cycles using different treatment methods of HCl (blue rhombus), NaOH (red square), water (purple circle) and control (green triangle).

A reduction of 58.4% of Pb(II) at the 5th cycle was seen. When washed with distilled water, a reduction of 44.6% of Pb(II) was seen by BL. In contrast, when treated with HCl, a higher value of 58.4% reduction was observed for Pb(II) at the 5th cycle. Treatment with NAOH was found to be the best method in regenerating BL in adsorbing Pb(II) within the three methods carried out. It is believed that treatment with a base results in removal of surface fats and waxes, which enhances adsorption. As observed from the figure, the adsorption ability of BL in the removal of Pb(II)was enhanced from the 1st cycle (72.1%) and further able to increase the removal of Pb(II) to > 90% adsorption at the 5th cycle.

1. Conclusion

In conclusion, bilimbi leaves (BL) is a potentially great low-cost adsorbent for Pb(II) removal as it exhibits exceptionally high adsorption capacities (1597.93 mg/g), based on the Langmuir model. Particularly NaCl, showed a greater influence on the adsorption potential of BL towards Pb(II). Upon characterization of Pb(II) via SEM and FTIR, from the SEM images that were obtained, the difference in surface morphology of the adsorbent before and after adsorption of both adsorbates indicated the success of adsorption of Pb(II) onto BL. Whilst the presence of shifting of peaks in FTIR spectra further confirmed the adsorption of heavy metal onto BL.

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