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Adsorption isotherm for the removal of lead(II) using mixed sugarcane bagasse and banana peel matrices

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ABSTRACT

Lead has unique physical and chemical properties that make it suitable for a large number of industrial applications. Due to the increasing and continuous usage of lead, it poses a serious threat to the environment and the biota. Conventional method of removing lead using physical and chemical approach has many limitations, including generation of secondary waste. Thus, the potential of using a bio-adsorbent consisting of mixed sugarcane bagasse and banana peel was assessed. Bio-absorption data were used to plot isotherm model to gauge how Pb(II) ions attach to the bio-adsorbent surface. It was found that the data fitted the Freundlich isotherm, indicating that Pb(II) ions attached to the bio-adsorbent surface in multiple layers. The bio-adsorbent was found to have several negatively charged binding sites including hydroxyl group (-OH) and carbonyl group (C=O) that allow Pb(II) ions to bind.

KEYWORDS: Freundlich isotherm, FTIR, heterogenous surface, Langmuir isotherm.

INTRODUCTION

Lead possesses several important properties like malleability, ductility, and resistance to corrosion which ensure the continuous and increasing use of this heavy metal. Industries like paint and pigment production, battery manufacturing, fuel refining, and smelting are the main sources of lead that pollute the environment. The non-biodegradable nature of lead is the main reason for its accumulation in the environment, with increasing hazards and devastating effects to human body [1, 2].

Lead can easily enter the blood stream and have adverse effects on the central nervous system, the cardiovascular system, kidneys, and the immune system [3]. Long-term exposure to Pb leads to decrease in the cognitive performance, behavioural problems and learning deficits [4]. Lead is also reported to disrupt cell membrane, red blood cells [5] and alter the permeability of blood vessels [6]. Furthermore, lead has been known to inhibit the activity of polymorphonuclear leukocytes resulting in the decrease of immune activity [7].

In light of this, various bio-adsorbents have been proposed as materials to remove lead from the environment, particularly from wastewater [8]. Both sugarcane bagasse and banana peels can serve as alternative source of bio-adsorbent since both are listed as the main agricultural waste in Malaysia [9]. It was reported that a bio-adsorbent matrix that comprised of sugarcane bagasse and banana peel treated with sodium hydroxide was able to remove approximately 60% of lead from water [10]. Thus, to understand better how this bio-adsorbent works, the binding sites of lead on

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the matrix needs to be understood. Therefore, the first objective of this study was to determine the various binding sites for Pb(II) in the bio-adsorbent. The second objective was to determine how the Pb(II) ions interact with the bio-adsorbent by using the isotherm model.

MATERIALS AND METHODOLOGY

Bioadsorbent experiment

A mixed bio-adsorbent matrix was prepared by adding equal ratio of oven-dried banana peels and sugarcane bagasse. The dried materials were ground into powder and then mixed with equal volume of 0.5 N of sodium hydroxide (NaOH) for 20 minutes. The bio-adsorbent powder was then dried in the oven prior to use [10]. 0.1 g of the bio-adsorbent was taken in conical flasks containing 1.0 mg/L of Pb(II) and the flask was placed on a rotary shaker for 60 min at room temperature. The content of the flask was filtered and the filtrate was analysed by atomic absorption spectroscopy (AAS) to determine the concentration of Pb(II) ions left after the bio-adsorption process. The process was repeated using different mass (g) of bio-adsorbent (0.5, 0.7, 1.0 and 2.0) in order to obtain data to plot the isotherm model.

Isotherm modelling

The data on the residual concentration of Pb(II) left in the solution was used to plot the Langmuir and Freundlich model. When an adsorbate monolayer saturates the adsorbent, the Langmuir model assumed that equilibrium has been attained [11].

Langmuir isotherm expression is given by the equation as below:

$$\frac{C_e}{q_e} = \frac{1}{qb} + \frac{1}{q}\,C_e$$

where C_e = Concentration of the adsorbed Pb(II) ions at equilibrium (mg/L); q_e = Amount of the adsorbed Pb(II) ions at equilibrium (mg/g); q = Maximum sorption capacity of the Pb(II) ion-adsorbent system; b = Constant related to the binding energy of the sorption system.

C_e/q_e versus C_e is plotted to represent Langmuir isotherm equation. From this graph, values of q and b can be obtained.

The Freundlich model is a simple experimental equation used to illustrate multi-layer adsorption on heterogeneous surfaces under non ideal adsorption equilibrium [12].

Equation below shows Freundlich isotherm expression:

$$\log q_e = \log k_f + \left(\frac{1}{n}\right)\log C_e$$

where k_f = Freundlich constant;
$1/n$ = Heterogeneity factor.

Graph of $\log q_e$ versus $\log C_e$ was plotted to represent Freundlich isotherm equation. Freundlich constant, k_f and heterogeneity factor, $1/n$ can be calculated from the intercept and slope of the plot respectively.

Fourier transform infrared spectroscopy (FTIR) analysis

2.0 mg of dried bio-adsorbent was analysed using Fourier transform infrared spectroscopy (FTIR). Briefly, the FTIR studies were conducted using Thermoscientific Nicolet iS10 FTIR spectrometer, which was equipped with an internal reflection accessory. The resolution spectrum was set at 4 cm^{-1} in the wavenumber region between 4000 cm^{-1} and 400 cm^{-1} recorded in the transmittance mode [13].

Analysis of elemental composition of the bio-adsorbent

The bio-adsorbent was placed inside an oven to remove water content, until a constant weight was achieved. The dried bio-adsorbent was analysed using energy dispersive X-ray (EDX). EDX elemental composition was expressed quantitatively as weight percentage [14].

RESULTS AND DISCUSSION

Data of the concentrations of the Pb(II) residues obtained from the bio-adsorption experiment were used to plot the Langmuir and Freundlich isotherm model as shown in Figures 1 and 2, respectively. Based on the plot of C_e/q_e versus C_e (Figure 1), the maximum sorption capacity of the Pb(II) ion-adsorbent system, q is 0.06 mg/g whereas the value of the constant related to the binding energy of the sorption system, b is 0.37 L/mg. On the other hand, from the plot of

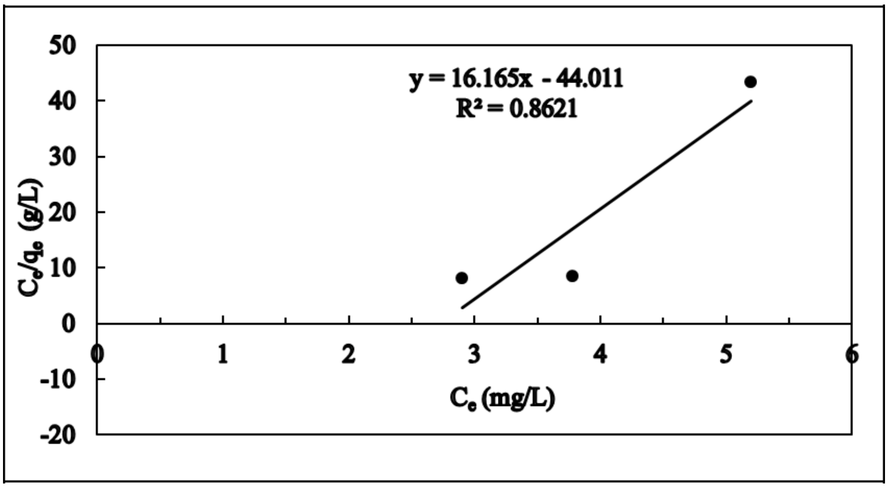

Figure 1. Langmuir isotherm plot for the adsorption of Pb(II) ions onto the mixture of sugarcane bagasse and banana peels.

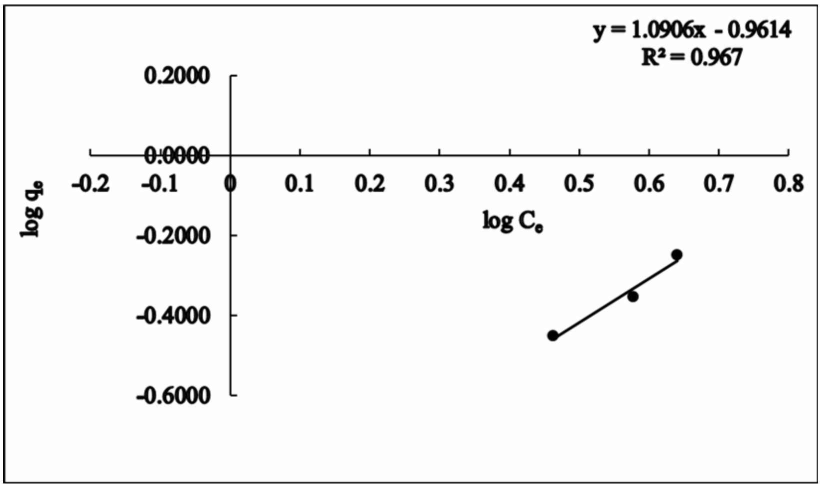

Figure 2. Freundlich isotherm plot for the adsorption of Pb(II) ions onto the mixture of sugarcane bagasse and banana peels.

$log\ q_e$ versus $log\ C_e$ (Figure 2), the values of Freundlich constant, k_f is 0.11 mg/g and the heterogeneity factor, $1/n$ is 1.09, as summarised in Table 1.

The Freundlich isotherm model parameters (Table 1) are derived from the best line of fit's slope, intercept, and correlation coefficient (Figure 2). The data reveal that the simultaneous adsorption of Pb(II) fits well the Freundlich isotherm model, with the value of R^2 nearing 1.0, which shows that Freundlich isotherm model is more accurate compared to Langmuir in describing how Pb(II) ions adsorb onto the surface of the bio-adsorbent. This suggests that the mixed sugarcane bagasse and banana peel bio-adsorbent has a heterogeneous adsorbing surface area. This allows the Pb(II) ions to interact with the bio-adsorbent surface in more than a single layer, and with each other [15]. This empirical relation also assumes that the heat of adsorption is not equally distributed on the adsorbent heterogenous surface [16]. Collectively, these two observations suggest the existence of

Table 1. Constants for Langmuir and Freundlich isotherm for the adsorption of Pb(II) ions onto the mixture of sugarcane bagasse and banana peels.

Langmuir isotherm			**Freundlich isotherm**		
***q* (mg/g)**	***b* (L/mg)**	**R^2**	**k_f (mg/g)**	**1/*n***	**R^2**
0.06	0.37	0.8621	0.11	1.09	0.9670

Table 2. Identification of functional groups present in the bio-adsorbent using FTIR.

Wavenumber (cm^{-1})	**Identity of the peak**	**Reference**
3420	O-H	[18]
1600	C=O	[19]
1559	Deformation stretching mode of the N–H and C–N	[20]
1345	Deformed vibration of a $–CH_2$ group	[21]

Table 3. Elemental composition of the bio-adsorbent.

Parameter	**Parameter content in percentage (%)**
Carbon	76.0
Hydrogen	19.8
Nitrogen	3.5
Sulphur	0.7

a variety of active functional groups on the surface of the bio-adsorbent interacting with the Pb(II) ions.

The various active functional groups on the surface of the bio-adsorbent were analysed using FTIR spectroscopy using a spectrum range between 400 to 4000 cm^{-1}. The results of the FTIR analysis confirmed the presence of five different functional groups that appear to be responsible for the adsorption of Pb(II) onto the surface of the bio-adsorbent (Table 2). It is interesting to note that Pb(II) ions which are positively charged can form a bond with negatively charged hydroxyl group (-OH), carbonyl group (C=O) and NH_2 groups [17].

When the bio-adsorbent was subjected to the energy dispersive X-ray (EDX) analysis, result shows that the bio-adsorbent comprised of carbon, hydrogen and nitrogen (Table 3), elements that were necessary to form the various active groups to interact with the Pb(II) ions as shown in FTIR results (Table 1). However, the presence of sulphur is unaccounted for since no sulfhydryl group (-SH) was detected in the FTIR analysis.

When it comes to Pb(II) removal, most of the plant biomass reported in literature such as sugarcane bagasse [22], *Albizia lebbeck* pods [23], soya bean [24] and ground coconut husk fitted the Langmuir isotherm [25]. However, other bio-adsorbents such as date seed [26] and cashew nutshell (*Anacardium occidentale*) [27] fitted both Langmuir and Freundlich isotherms. Hence at present, it is difficult to establish whether the presence of certain types of binding sites can influence how Pb(II) binds to these bio-adsorbents. More characterization including scanning electron microscopy or X-ray diffraction analysis might shed some further information in this aspect.

CONCLUSION

The bio-adsorbent comprised of a mixture of sugarcane bagasse and banana peels showed the capacity to bind to Pb(II). The binding of Pb(II) ions on the surface of the bio-adsorbent fitted the Freundlich isotherm model. The bio-adsorbent has various binding sites due to the presence of hydroxyl group, carbonyl group and -NH group. No sulfhydryl functional group was detected despite the presence of sulphur element in the bioadsorbent.

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CONFLICT OF INTEREST STATEMENT

There is no conflict of interest.

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