Ali Hashem* and Sayed M. Badawy

Sesbania sesban L. biomass as a novel adsorbent for removal of Pb(II) ions from aqueous solution: non-linear and error analysis

Abstract: In the present study, we reported the feasibility of the *Sesbania sesban* L. as a biosorbent to remove Pb(II) from aqueous solutions. The ability of *S. sesban* L. to adsorb Pb(II) was investigated by using batch adsorption procedure. Such effects as pH, contact time, adsorbate concentration, and biosorbent dosage on the adsorption capacity were studied. The experimental data were analyzed using various adsorption kinetic models, namely, pseudo-first-order model, the pseudo-second-order model, Batacharia-Venkobachar, the Elovich equation, the intraparticle diffusion model, and Bangham equation. Results show that the pseudo-second-order equation provides the best correlation for the biosorption process. To determine the best fit isotherm, the experimental equilibrium data were analyzed using two-parameter (Langmuir, Freundlich, Dubinin-Radushkevich, and Tempkin) and three-parameter isotherms (Redlich-Peterson, Sips, Khan, and Toth). The examination of error analysis methods showed that the Langmuir isotherm model and Redlich-Peterson models provide the best fit for experimental data than other isotherms. *Sebania sesban* L. is found to be inexpensive and effective adsorbent for removal of Pb(II) from aqueous solutions.

Keywords: contaminated water; error analysis; isotherm models; Pb(II) adsorption; *Sesbania sesban* L.

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1 Introduction

Heavy metals are found in the wastewater streams of industrial processes, including paint manufacture, leather tanning, battery manufacture, electroplating, plastics manufacturing, fertilizers, pigments, mining, and metallurgical processes and others. Their removal has attracted much practical and academic interest owing to increased concerns with their environmental impact [1]. The chemical methods used for the removal of metal ions from industrial effluents, such as precipitation, ion exchange and solvent extraction, have high chemical and energy requirements, hazardous sludge formation, and high cost requirements for large scale processing [2–4]. This has led to a search for cheaper adsorbents. With this aim in mind, numerous low-cost alternative adsorbents have been proposed, including ligno-cellulosic wastes and polysaccharide biopolymers, such as chitin and starch [5].

Agricultural by-products are mainly composed of cellulose and lignin, which are available in large quantities and constitute one of the most abundant renewable resources in the world. Lignin has polar functional groups, which include alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. To some extent, these groups have the ability to bind heavy metals by donating an electron pair from these groups to form complexes with the metal ions in solution.

Agricultural by-products have been examined for potential use as inexpensive adsorbents for heavy metal removal [6–10]. The abundance and availability of *Sesbania sesban* L. residues as desert plants make them good candidates for incorporation as adsorbent of heavy metals from wastewater.

Pb(II) is a metal that can be considered an environmental concern. The problem of Pb(II) pollution due to use in lead service pipes, particularly with soft water was the first recognized form of metal pollution. Other sources of Pb(II) pollution are battery industry, auto-exhaust, paints, etc. Major health effects due to Pb(II) poisoning are nervous and renal breakdown, weakness,

headache, brain damage, convulsions, behavioral disorders and constipation [11]. Biosorption is defined as a process in which solids of natural origin are employed for the sequestration of heavy metals from an aqueous environment.

The aim of the present work is to explore the possibility of utilizing *S. sesban* L. for the adsorption of Pb(II) from contaminated water. The effects of such factors as pH, adsorbent dose, adsorbate concentration, contact time, and initial concentration were investigated. The kinetics of Pb(II) adsorption on the adsorbent was analyzed by fitting various kinetic biosorption isotherm models. Using biosorption isotherm models can help determine the best-fit isotherm equation that, in turn, can be used to optimize the design of biosorption system for the removal of lead utilizing *S. sesban* L. Experimental equilibrium data were fitted to two-parameter (Freundlich, Langmuir, Dubinin-Radushkevich, and Temkin), three-parameter (Redlich-Peterson, Sips, Khan, and Toth), four-parameter (Weber-van Vliet, Fritz-Schlunder, and Baudus) and five-parameter models (Fritz-Schlunder). Error analysis was carried out to test the adequacy and accuracy of the isotherm models.

2 Materials and methods

2.1 Materials

2.1.1 Adsorbent: *Sesbanias sesban L.* is a desert plant obtained from Sabha in Libya. The residues of its fruity part were ground and passed through 50–150 μm sieves, washed with distilled water until the filtrate was colorless, washed with acetone, and then finally dried in an electric oven at 60°C for 3 h.

2.1.2 Reagents: Lead(II) acetate, cadmium(II) acetate, nickel(II) acetate, mercury(II) acetate, zinc(II) acetate, EDTA, sodium carbonate, acetic acid, and acetone were all used as laboratory grade chemicals (Merck, Germany).

2.2 Methods

2.2.1 Adsorption studies: A known volume (100 ml) of a Pb(II) ion solution with a concentration in the range 100–1000 mg/l was placed in a 125 ml Erlenmeyer flask. An accurately weighed sample of *S. sesban* L. adsorbent (0.05 g) with a particle size in the range 50–150 μm was then added to the solution. A series of such flasks was prepared; the pH values of the contents adjusted by the addition of 0.1 M HNO_3 or 0.1 M Na_2CO_3 and then shaken at a constant speed of 150 rpm in a shaking water bath at 30°C for a known time length. At the end of the agitation time, the metal ion solutions were separated by filtration. Blank experiments were carried out simultaneously without the addition of the *S. sesban* L. adsorbent. The extent of metal ion adsorption onto the adsorbent was calculated mathematically by measuring the metal ion concentration before and after the adsorption through direct titration against the standard EDTA solution. The amount of Pb(II) adsorbed on *S. sesban* L. at equilibrium, q (mg/g), and percent removal of lead were calculated according to the following relationships:

$$q_e = \frac{(C_o - C_e).V(l)}{W}, \tag{1}$$

$$\text{Percent removal} = \frac{C_o - C_e}{C_o} \times 100\%, \tag{2}$$

where C_o and C_e are the initial and final concentrations of Pb(II), respectively, V is the volume of Pb(II) (l), and W is the weight of *S. sesban* L. adsorbent (g). The extent of Hg(II), Cd(II), Ni(II), and Zn(II) ion adsorption onto adsorbent was also measured by calculating the metal ion concentration before and after the adsorption through direct titration against the standard EDTA solution. All experiments were carried out in duplicate and the mean values of q_e were reported. Microsoft Office Excel and Excel solver softwares were used for kinetic and modeling calculations.

2.3 Error analysis

In the single-component isotherm studies, the optimization procedure requires that an error function be defined to evaluate the fit of the isotherm to the experimental equilibrium data. The common error functions for determining the optimum isotherm parameters included the following: average relative error (ARE), sum of the squares of the errors (ERRSQ), hybrid fractional error function (HYBRID), Marquardt's percent standard deviation (MPSD), and sum of absolute errors (EABS) [11]. In the present study, all error functions were used to determine the best fit in isotherm model. The expressions are provided below.

2.3.1 ARE:
$$\text{ARE} = \sum_{i=1}^{n} \left| \frac{(q_e)_{\text{exp.}} - (q_e)_{\text{calc.}}}{(q_e)_{\text{exp.}}} \right|_i \tag{3}$$

2.3.2 APE:
$$\text{APE}\% = \frac{\sum_{i=1}^{N} \left| [((q_e)_{\text{exp.}} - (q_e)_{\text{calc.}}) / q_{\text{exp.}}] \right|}{N} \times 100 \tag{4}$$

2.3.3 ERRSQ:
$$\text{ERRSQ} = \sum_{i=1}^{n} [(q_e)_{\text{calc.}} - (q_e)_{\text{exp.}}]^2 \tag{5}$$

2.3.4 HYBRID:
$$\text{Hybrid} = \frac{100}{n-p} \sum_{i=1}^{n} \left[\frac{((q_e)_{\text{exp.}} - (q_e)\text{calc.})^2}{(q_e)_{\text{exp.}}} \right]_i \tag{6}$$

2.3.5 MPSD:
$$\text{MPSD} = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \left[\frac{((q_e)_{\text{exp.}} - (q_e)_{\text{calc.}})}{(q_e)_{\text{exp.}}} \right]^2} \tag{7}$$

2.3.6 EABS
$$\text{EABS} = \sum_{i=1}^{n} \left| (q_e)_{\text{exp.}} - (q_e)_{\text{calc.}} \right|_i \tag{8}$$

Table 1: Adsorption of different metal ions onto the *S. sesban* L. adsorbent at 30°C.

Metal cations	Percent removal (%)
Pb(II)	98.3
Hg(II)	37.6
Cd(II)	88.5
Ni(II)	72.4
Zn(II)	19.1

Adsorption conditions: Metal ion concentration, 400 mg/l; pH, 4; adsorbent concentration, 0.5 g/l; contact time, 2 h; adsorption temperature, 30°C.

3 Results and discussion

3.1 Characterization of adsorbent (adsorption of metal cations)

The adsorption of Pb(II), Cd(II), Hg(II), Ni(II), and Zn(II) ions in the concentration of 400 mg/l by *S. sesban* L. biomass was carried out at pH 4, as shown in Table 1. The results indicate that the adsorption capability for these heavy metal ions is in the following order: Pb(II)>Cd(II)> Ni(II)>Hg(II)>Zn(II). Hence, the adsorption properties of Pb(II) were investigated in detail.

3.2 Factors affecting the adsorption of Pb(II) onto *S. sesban* L.

The biosorption process of heavy metals is influenced by several factors, such as pH, adsorbent dose, contact time, and adsorbate concentration. The effects of these parameters were investigated in this section.

3.2.1 Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process [12]. In the present work, the adsorption of Pb(II) onto the *S. sesban* L. adsorbent was studied over the pH range of 2–4.5 for a constant adsorbent dose and constant concentration of adsorbate at 30°C. As the pH of the adsorption medium decreases, the extent of adsorption capacity, q_e, decreases (Figure 1). At high acidity, the *S. sesban* L. particle surface will be completely covered with H_3O^+ ions, and Pb(II) ions would be able to compete with them for adsorption sites. With the increase in pH, the competing effect of hydronium ion decreases and the positively charged Pb(II) ions would adsorb on the free binding sites of the adsorbents. This is a common observation for all cases of adsorption of metal cations on the solid surface in media of different acidity and basicity [13]. It is also significant that the active sites on the *S. sesban* L. are weakly acidic in nature and with increasing pH, they are gradually deprotonated making available more and more sites for metal ion uptake [14]. At a pH value that is more than 4.5, the adsorption studied could not be carried out because metal ion will precipitate as lead hydroxide in this range.

3.2.2 Effect of adsorbent concentration (adsorbent dose)

The effect of adsorbent dose on both the adsorption capacity and the percentage removal of Pb(II)ions onto *S. sesban* L. were studied at pH 4.5 employing adsorbent doses within the range of 0.3–10 g/l and at a fixed initial metal ion concentration of 200 mg/l (Figure 2). It is clear from this figure that the percent removal of Pb(II)

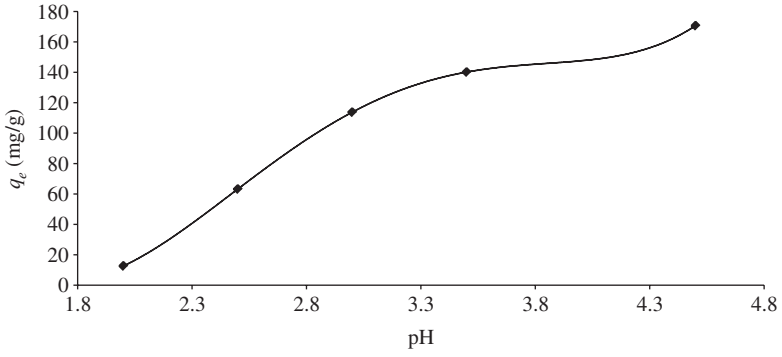

Figure 1: Effect of pH on the adsorption capacity of Pb(II) onto *S. sesban* L. at 30°C.
[Adsorption conditions employed: Pb(II) ion concentration, 300 mg/l; adsorbent concentration, 0.3 g/l; agitation time, 2 h; adsorption temperature, 30°C; particle size, 50–150 μm.]

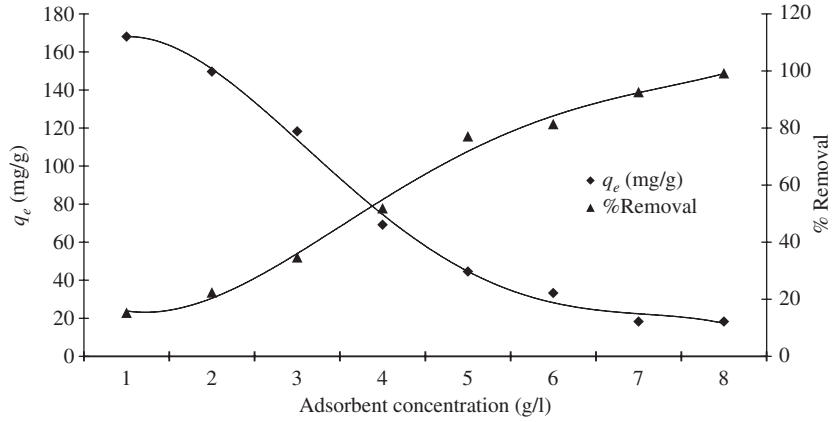

Figure 2: Effect of sample dose on both adsorption capacity and % removal of Pb(II) onto *S. sesban* L. at 30°C.
[Adsorption conditions employed: Pb(II) ion concentration, 300 mg/l; pH, 4.5; agitation time, 2 h; adsorption temperature, 30°C; particle size, 50–150 μm.]

increases from 15.3% to 99.2% by increasing the concentration of adsorbent from 0.3 to 10 g/l. On the one hand, the increase in percent removal of Pb(II) with increasing adsorbent concentration could be attributed to the greater availability of the exchangeable sites of the adsorbent. On the other hand, the adsorption capacity (q_e), or the amount of Pb(II) adsorbed per unit mass of adsorbent (mg/g), decreases by increasing the concentration of adsorbent (Figure 2). The decrease in adsorption capacity with increasing adsorbent concentration is mainly due to the fact that the sorbent has high maximal adsorption capacity; furthermore, at tested Pb(II) concentration, when almost total and constant amount of Pb(II) is adsorbed, the adsorption capacity (q_e) decreases.

3.2.3 Effect of contact time

Figure 3 shows the effect of agitation time at various initial adsorbate concentrations on the adsorption capacity of *S. sesban* L. towards Pb(II) ions. As can be seen, the adsorption capacity increased with increasing agitation time and initial concentration of the adsorbate, remaining virtually constant after equilibrium had been attained. The time necessary to achieve equilibrium increased with increasing adsorbate concentration, being 30 and 60 min for adsorbate concentrations of 246.6 and 474.2 mg/l, respectively. This contact time, which is one of the parameters for economical wastewater treatment plant operations, is very small.

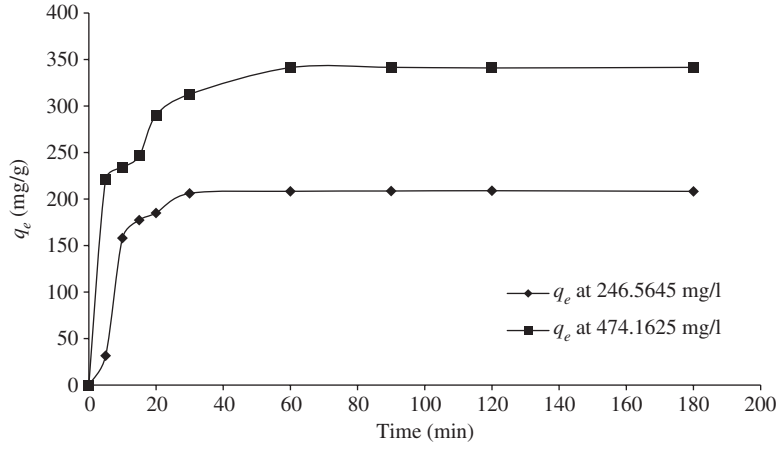

Figure 3: Effect of contact time on adsorption capacity of Pb(II) onto *S. sesban* L. at 30°C.
[Adsorption conditions employed: Pb(II) ion concentrations, 247, 474 mg/l; pH, 4.5; adsorbent concentration, 0.3 g/l; adsorption temperature, 30°C; particle size, 50–150 μm.]

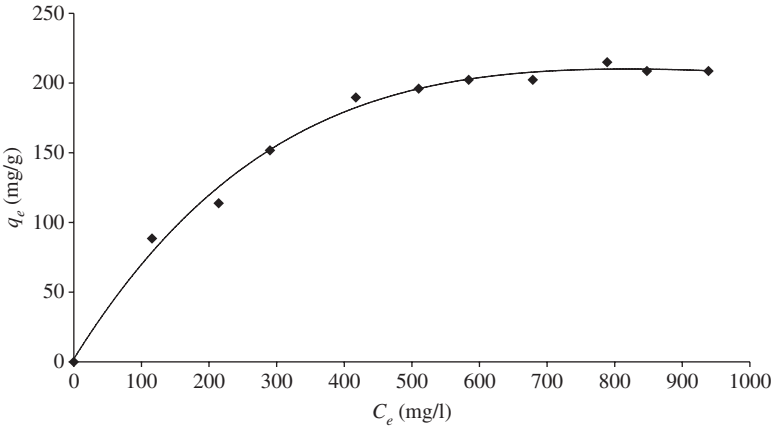

Figure 4: Equilibrium adsorption isotherm of Pb(II) onto *S. sesban* L. at 30°C.
[Adsorption conditions employed: pH, 4.5; adsorbent concentration, 0.3 g/l; adsorption temperature, 30°C; agitation time, 2h; particle size, 50–150 μm.]

3.2.4 Effect of adsorbate concentration

3.2.4.1 Adsorption isotherm

Adsorption isotherm describes how adsorbates interact with adsorbents are critical in optimizing the use of adsorbents. The amount of adsorbate per unit mass of adsorbent at equilibrium, q_e (mg/g), and the adsorbate equilibrium concentration, C_e (mg/l), allows plotting the adsorption isotherm, q_e vs. C_e (Figure 4) at 30°C; here, mathematical models can be used to describe and characterize the adsorption process. The most common isotherms for describing solid-liquid sorption systems are two-parameter isotherms (Langmuir, Freundlich, Temkin, and Dubinin) and three-parameter isotherms (Redlich-Peterson isotherms, Toth, Sips, Khan, and Hill). Therefore, in order to investigate the adsorption capacity of Pb(II) onto *S. sesban* L., the experimental data were fitted to these equilibrium models.

3.2.4.1.1 Two parameter isotherms

The Langmuir model: Langmuir equation [15] was applied for adsorption equilibrium of Pb(II) by *S. sesban* L. This model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, and that the energy of adsorption is constant because there is no transmigration of adsorbate in the plane surface. The non-linear form of Langmuir isotherm is given by the following equation:

$$q_e = \frac{K_L.C_e}{1+a_L.C_e}, \tag{9}$$

where a_L is Langmuir isotherm constant (l/mg), K_L is the Langmuir constant (l/g), and k_l/a_L represents the adsorption capacity, q_{max} (mg/g).

The Freundlich model: The Freundlich model [16] is a special case applied to non-ideal adsorption on heterogeneous surfaces and to multilayer adsorption, suggesting that binding sites are not equivalent and/or independent. This model is described by Eq. 10 as follows:

$$q_e = K_F.C_e^{1/n}, \tag{10}$$

where q_e is the equilibrium concentration of Pb(II) on *S. sesban* L. adsorbent (mg/g), C_e is the equilibrium concentration of Pb(II)ions (mg/l), and K_F (mg/g) and n are the Freundlich constant characteristic of the system, which are the indicators of adsorption capacity and adsorption intensity, respectively.

The Temkin model: The Temkin isotherm [17] has been used in the following form:

$$q_e = \frac{RT}{b_T}\ln(A_T C_e), \tag{11}$$

where R is the universal gas constant (8.31441 $J^{-1}.mol^{-1}.K^{-1}$), T is the absolute temperature (K), A_T is the Temkin isotherm constant (g/mg), and b_T is the Temkin constant.

Dubinin-Radushkevich model: This isotherm [18] is generally expressed as follows:

$$q_e = q_D.\exp\left(-B_D[RT\ln(1+\frac{1}{C_e})]^2\right) \tag{12}$$

Dubinin-Radushkevich have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The constant, B_D is, related to the mean free energy of sorption per mole of the sorbate as it is

transferred to the surface of the solid from infinite distance in the solution. This energy can be computed using the following relationship by Hasany and Chaudhary [19]:

$$E=\frac{1}{\sqrt{2B_D}}. \tag{13}$$

3.2.4.1.2 Three-parameter isotherms

Redlich-Peterson model: The Redlich-Peterson model is used as a compromise between the Langmuir and Freundlich models, and is written as follows [20]:

$$q_e=\frac{A\cdot C_e}{1+B\cdot C_e^g}, \tag{14}$$

where q_e is the amount of lead adsorbed (mg/g) at equilibrium, C_e(mg/l) is the concentration of adsorbate at equilibrium, and A (L/g) and B are the Redlich constants and gis exponent, respectively, which lie between 1 and 0.

Toth model: The Toth isotherm model [21] is useful in describing heterogeneous adsorption systems, which satisfy both the low and high-end boundaries of the concentration [22]. It can be represented by the following equation:

$$q_e=\frac{K_tC_e}{(a_t+C_e)^{1/t}}, \tag{15}$$

where K_t, a_t, and t are the Toth isotherm constants.

Sips model: Sips isotherm [23] is a combined form of Langmuir and Freundlich expressions deduced for predicting the heterogeneous adsorption systems [24], and circumventing the limitation of the rising adsorbate concentration associated with the Freundlich isotherm model. The Sips model can be represented by the following equation:

$$q_e=\frac{K_sC_e^{B_s}}{1+a_s\cdot C_e^{B_s}}, \tag{16}$$

where K_s is the Sips model isotherm constant (L/g), a_s is the Sips model constant (L/mg), and B_s is the Sips model exponent. At low sorbate concentrations, it effectively reduces to the Freundlich isotherm and does not obey Henry's law.

Khan model: Khan isotherm [25] is a generalized model suggested for the pure solutions, in which b_K and a_K are devoted to the model constant and model exponent, respectively. The Khan isotherm model can be represented as follows:

$$q_e=\frac{q_k.b_K.C_e}{(1+b_K.C_e)^{a_K}}, \tag{17}$$

where b_k is the Khan model constant, a_k is the Khan model exponent, and q_k is the maximum uptake (mg/g). The maximum adsorption capacity, q_{max}, is considered to be the most important parameter for the comparison of adsorbents. The adsorption capacity values for Pb(II) obtained from the Langmuir isotherm model was found to be 303.03 mg/g. In comparison with other adsorbents reported in the literature for adsorption of Pb(II), the *S. sesban* L. biomass had a better affinity for removal of Pb(II) ions [2].

3.3 Error analysis and the non-linear regression method

In the nonlinear regression method, the validity of the widely used isotherm models to the experimental data was examined by trial-and-error using the solver add-in with Microsoft Excel. The R^2 value is used to minimize the error distribution between the experimental equilibrium data and the predicted isotherms.

The fitting presentation of two and three parameter models are shown in Figures 5 and 6. The constants and error analysis of the two- and three-parameter models are given in Tables 2 and 3.

Among the two- and three-parameter models, the highest R^2 value and lowest ARE, APE%, EABS, ERRSQ, MPSD, and Hybrid values are observed with the Langmuir (two-parameter) followed by Redlich-Peterson (three-parameter) models, indicating that they have better fit than the rest of the isotherm models.

3.4 Kinetics of adsorption

Six kinetic models, namely, the pseudo-first-order, Bhattacharya-Venkobachar, pseudo-second-order, Bangham, intraparticle diffusion and Elovich models, were used to investigate the adsorption process of Pb(II) on *S. sesban* L.

3.4.1 Pseudo-first-order model

The pseudo-first-order equation [26] is given by the following:

$$\frac{dq_t}{dt}=k_1(q_e\text{-}q_t), \tag{18}$$

where q_t is the amount of adsorbate adsorbed at time t (mg/g), q_e is the adsorption capacity at equilibrium

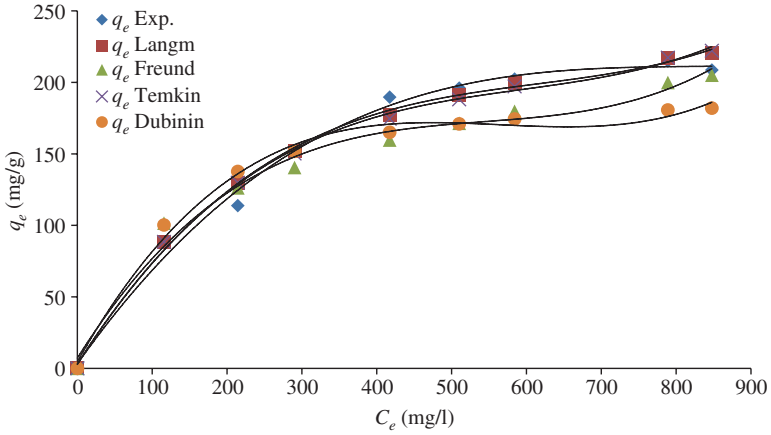

Figure 5: Comparison of two-parameter isotherm models with experimental data of Pb(II) onto *S. sesban* L. at 30°C.

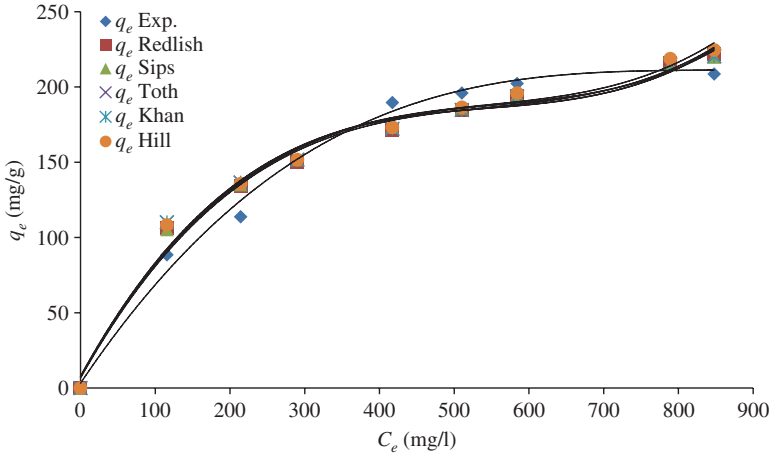

Figure 6: Comparison of three-parameter isotherm models with experimental data of Pb(II) onto *S. sesban* L. at 30°C.

(mg/g), k is the pseudo-first-order rate constant (min^{-1}), and t is the contact time (min). By integrating Eq. (18) with the initial condition, q_t=0 at t=0, the following equation is obtained:

$$\log(q_e\text{-}q_t)=\log q_e\text{-}\frac{k.t}{2.303}. \quad (19)$$

In order to obtain the rate constants, the straight line plot of $\log(q_e\text{-}q_t)$ against t for Pb(II) onto *Sesbania sesban* L. was tested. The intercept of this plot should give $\log q_e$. However, if the intercept is not equal to q_e, the reaction is not likely to be first order even if this plot has high correlation coefficient (R^2) with the experimental data [27]. For the data obtained in the present study, the plots of $\log(q_e\text{-}q_t)$ vs. t as required by Eq. 19 for the adsorption of Pb(II) at initial concentrations of 246.6 and 474.2 mg/l by *S. sesban* L. (figure not shown) give correlation coefficients, R^2, with low values. This indicates that the adsorption of Pb(II) onto *S. sesban* L. is not acceptable for this model.

3.4.2 Bhattacharya-Venkobachar model

The Bhattacharya-Venkobachar [28] equation is expressed as

$$\log[1\text{-}U_t]=\text{-}\left(\frac{k}{2.303}\right)t \text{ where } U_t=[(C_o\text{-}C_t)/(C_o\text{-}C_e)] \quad (20)$$

where C_o, C_t, and C_e are the concentrations of Pb(II) (mg/l) at time zero, time t and at equilibrium time, and k is the first order rate constant (min^{-1}) for adsorption of Pb(II) onto *S. sesban* L. The R^2 values for the concentrations of 246.6 and 474.2 mg/l (figure not shown) are very low, indicating that the adsorption of Pb(II) onto *S. sesban* L. is not acceptable for this model.

Table 2: Constants and error analysis of two-parameter models for adsorption of Pb(II) onto *S. sesban* L. at 30°C.

Isotherm model	Parameter	Value	Error analysis	Value
Langmuir	a_L	0.003643	ARE	0.081949
			APE%	3.582562
	k_L	1.083313	EABS	9.827173
			ERRSQ	54.5608683
	R^2	0.9993	Hybrid	7.289455
			MPSD	0.928260979
Freundlich	$1/n$	0.457034	ARE	0.44113
			APE%	6.301855
	k_F	11.00562	EABS	66.09527
			ERRSQ	877.0452465
	R^2	0.9932	Hybrid	111.1068
			MPSD	0.952659911
Tempkin	A_T	0.030577	ARE	0.284302
			APE%	4.061461
	b_T	0.354287	EABS	42.37424
			ERRSQ	533.0907543
	R^2	0.9985	Hybrid	78.48461556
			MPSD	0.950333168
Dubinin-Radushkevich	q_D	254.5765	ARE	0.376264
			APE%	5.375206
	B_D	2.6860806	EABS	44.856802
			ERRSQ	691.1824974
	R^2	0.9986	Hybrid	99.48582
			MPSD	0.953737

Table 3: Constants and error analysis of three-parameter models for adsorption of Pb(II) onto *S. sesban* L. at 30°C.

Isotherm model	Parameter	Value	Error analysis	Value
Redlich-Peterson	A	1.300678	ARE	0.276685114
			APE%	3.952644
	B	0.012595	EABS	43.8983
			ERRSQ	499.5646306
	G	0.84573534	Hybrid	54.47489934
			MPSD	0.945917
	R^2	0.9978		
Toth	k_t	11.48352	ARE	0.35602695
			APE%	5.086099
	a_t	32.83996	EABS	62.11466714
			ERRSQ	962.905
	$1/t$	0.541661964	Hybrid	85.95346521
			MPSD	0.94817191
	R^2	0.9967		
Sips	K_s	3.819127	ARE	3.08E-01
			APE%	4.394151
	a_s	0.007387	EABS	51.36080064
			ERRSQ	6.14E+02
	B_s	0.701091	Hybrid	5.98E+01
			MPSD	9.46E-01
	R^2	0.9968		
Khan	q_k	8.11541	ARE	0.415353
			APE%	5.93361
	a_k	0.526693	EABS	65.51011
			ERRSQ	883.0889
	b_k	1.530914	Hybrid	86.105277
			MPSD	0.949273
	R^2	0.9941		

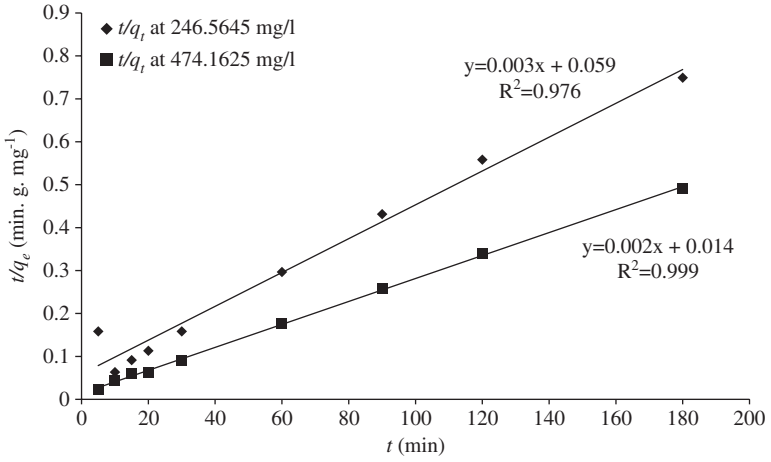

Figure 7: Pseudo-second order reaction of Pb(II) onto *S. sesban* L. at 30°C.

3.4.3 Pseudo-second-order model

The pseudo-second-order model [27] is represented as follows:

$$\frac{dq_t}{dt}=k_2(q_e-q_t)^2, \tag{21}$$

where k_2 is the pseudo-second-order rate constant (g/mg.min). By integrating Eq. (21) with the initial condition, q_t=0 at t=0, the following equation is obtained:

$$\frac{t}{q_t}=\frac{1}{(k_2.q_e^{\,2})}+\frac{t}{q_{e_t}}, \tag{22}$$

where k_2 is the pseudo-second-order adsorption rate constant. This equation predicts that if the system follows pseudo-second-order kinetics, the plot of t/q_e vs. t should be linear. Plotting the experimental data obtained for the adsorption of Pb(II)at initial concentrations of 246.6 and 474.2 mg/l onto *S. sesban* L. according to the relationship given in Eq. (22) gives linear plots. The correlation coefficient values, R^2, are 0.977 and 0.999 for the initial concentrations of 246.6 and 474.2 mg/l, respectively (Figure 7 and Table 4), indicating the applicability of the pseudo-second-order kinetic equation to the experimental data. Given that the first-order and pseudo-second-order models cannot identify the diffusion mechanism, the kinetic results were then subjected to analysis using the intra-particle diffusion model.

3.4.4 Bangham model

Bangham's equation [29] was employed for applicability of adsorption of Pb(II) onto *S. sesban* L., whether the adsorption process is diffusion controlled. This is expressed as follows:

$$\log\log\left(\frac{C_o}{C_o\text{-}q.m}\right)=\log\left(\frac{k_o m}{2.303V}\right)+\alpha\log t, \tag{23}$$

where C_o is initial concentration of adsorbate (mg/l), V is the volume of metal ion (ml), m is the weight of adsorbent used per liter of solution (g/l), q is the amount of adsorbate retained at time t (mg/g), and $\alpha(\prec 1)$ and k_0 are constants. The double logarithmic plot, according to Eq. 23, yields satisfactory linear curves for the adsorption of Pb(II) by

Table 4: Kinetic parameters for the adsorption of Pb(II) onto *S. sesban* L. at 30°C.

Parameters	Models	Values	
		(247 mg/l)	(474 mg/l)
k_1	Pseudo-first order	---	---
R^2		---	---
k_1	Bhattacharya-Venkobacher	---	---
R^2		---	---
k_1	Pseudo-second order	2.58×10^{-4}	5.17×10^{-4}
q_e(Exp.)		214.954	354.041
q_e (Calc.)		256.41	370.37
R^2		0.9769	0.9992
K_o	Bangham's equation	---	---
α		---	---
R^2		---	---
K_P	Intra-particle diffusion	6.0487	5.0876
C		153.3	300.5
R^2		0.9484	0.9897
α	Elovich equation	---	---
β		---	---
R^2		---	---
R^2		---	---

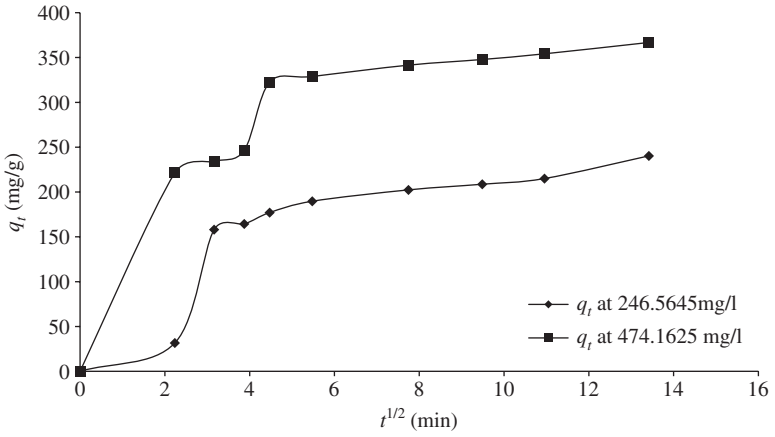

Figure 8: Intra-particle diffusion of Pb(II) onto *S. sesban* L. at concentrations of 246.5645 and 474.1625 mg/L.

S. sesban L. The R^2 values of 246.6 and 474.2 mg/l (figure not shown) are very low, indicating that the adsorption of Pb(II) onto *S. sesban* L. is not acceptable for this model.

3.4.5 Intra-particle diffusion

The intra-particle diffusion model [30] can be expressed by the following equation:

$$q_t = k_p . t^{\frac{1}{2}} + C, \tag{24}$$

where k_p is the intra-particle diffusion rate constant (mg. $g^{-1}.min^{-1/2}$), and q_t is the amount of solute adsorbed per unit mass of adsorbent. The data of solid phase metal concentration against time t at the initial concentrations of 246.6 and 474.2 mg/l of Pb(II) were further processed in order to test the rate of diffusion in the adsorption process. Adsorption process incorporates the transport of adsorbate from the bulk solution to the interior surface of the pores in *S. sesban* L. The rate parameter for intra-particle diffusion, k_p, for the Pb(II)on *S. sesban* L. is measured according to Eq. 24. The plots of q_t vs. $t^{1/2}$for the Pb(II) concentrations of 246.6 and 474.2 mg/l is shown in Figure 8. As can be seen, the plot is curved at the initial portion followed by linear portion and plateau. The initial curved portion is attributed to the bulk diffusion and the linear portion to the intra-particle diffusion, while the plateau corresponds to the equilibrium. The deviation of straight lines from the origin (Figure 9) may be attributed to the difference between the rate of mass transfer in the initial and final stages of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the rate-controlling step [31]. The values of k_p (mg. $g^{-1}.min^{-1}$) obtained from the slope of the straight line (Figure 9) are listed in Table 4. The R^2 value for the initial concentrations of 246.6 and 474.2 mg/l are listed in Table 4. The value of intercept, *C* (Table 4), gives an idea about the boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect [32].

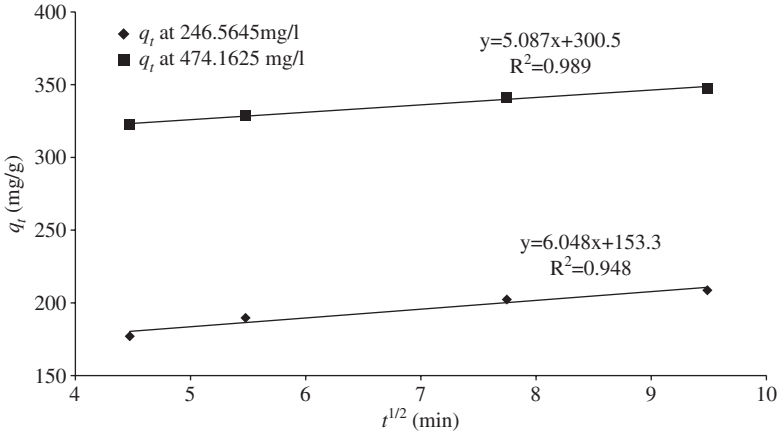

Figure 9: Test of intra-particle diffusion of Pb(II) onto Sesbania sesban L at concentrations of 246.5645 and 474.1625 mg/l.

This value indicates that the adsorption of Pb(II) onto *S. sesban* L. is acceptable for intra-particle diffusion mechanism.

3.4.6 Elovich equation

The Elovich model equation [33] is generally expressed as follows:

$$\frac{dq_t}{dt}=\alpha\exp(-\beta.q_t), \tag{25}$$

where α is the initial adsorption rate (mg/g.min), and β is the adsorption constant (g/mg) during the experiment. To simplify the Elovich equation, Chien and Clayton [33] assumed $\alpha\beta\succ\succ1$; by applying the boundary conditions q=0 at t=0 and $q_t=q_t$ at $t=t$, Eq. 25 becomes

$$q_t=\frac{1}{\beta}\ln(\alpha\beta)+\frac{1}{\beta}\ln(t). \tag{26}$$

If Pb(II) adsorption onto *S. sesban* L. fits the Elovih model, a plot of q_e vs. ln(t) should yield a linear relationship with a slope of 1/β and an intercept of 1/βln($\alpha\beta$). Figure 10 shows a plot of the linearization form of Elovich model at the Pb(II) concentrations of 246.6 and 474.2 mg/l. The slope and intercept of the plots of q_t vs. ln(t) were used to determine the constant β and the initial adsorption rate α. The R^2 values for the concentrations of 246.6 and 474.2 mg/l are listed in Table 4. The correlation coefficient values for the Elovich kinetic model obtained at the Pb(II) concentration of 246.6 and 474.2 mg/l are below 0.87, indicating that the adsorption of Pb(II) onto *S. sesban* L. is not acceptable for this model.

3.5 Mechanism of adsorption

The adsorbent material, *S. sesban* L. biomass can be considered a microporous biopolymer; therefore, pores are large enough to let Pb(II) ions through. The mechanism of Pb(II) adsorption on porous adsorbents may involve the following four steps: (i) diffusion of ions to the external surface of bio-adsorbent, (ii) diffusion of ions into the pores of the bio-adsorbent, (iii) adsorption of the lead ions on the internal surface of the bio-adsorbent, and (iv) interaction between the anionic groups in bioadsorbent (-COOH groups) and the cations in the solution. The anionic nature of *S. sesban* L. plays the key role in the adsorption process. The negatively charged surfaces of the biomass attract the oppositely charged lead cations and bring about stronger complexation.

4 Conclusions

Sesbania sesban L. has been utilized as adsorbent material for the removal of Pb(II) from contaminated water. The ability of *S. sesban* L. to adsorb Pb(II) was investigated by using batch adsorption procedure. The data of the adsorption isotherm were tested using two-parameter models (Langmuir, Freundlich, Temkin, and Dubinin) and three-parameter models (Redlich-Peterson, Toth, Sips, and Khan) using non-linear regression technique. The best fitting model was first evaluated using six different error functions. The examination of all these error estimation methods showed that the Langmuir isotherm model and Redlich-Peterson models provide the best fit for experimental data than other isotherms. The kinetics of adsorption of Pb(II) have been discussed using six kinetic

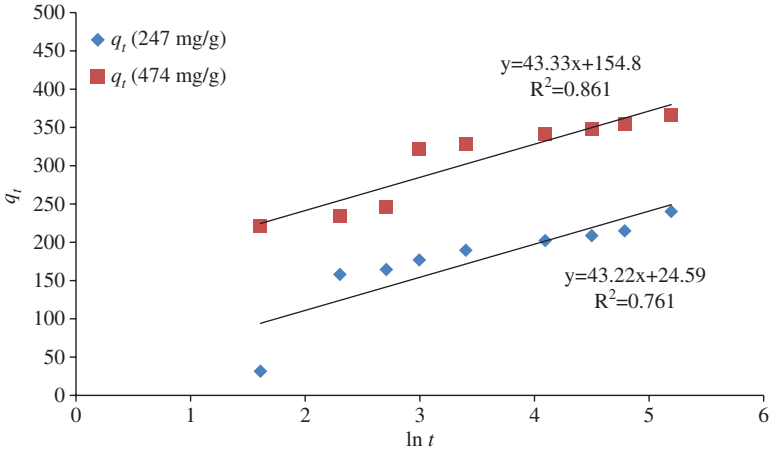

Figure 10: Elovich model of Pb(II) onto *S. sesban* L. at 30°C.

models, i.e., the pseudo-first-order model, the pseudo-second-order model, Batacharia, the Elovich equation, the intraparticle diffusion model, and Bangham equation. The adsorption of Pb(II) onto *S. sesban* L. could be well described by the pseudo-second-order kinetic model.

References

[1] Reed BE, Arunachalam S, Thomas B. *Environ. Prog.* 1994, 13, 60–64.
[2] Nguyen TAH, Ngo HH, Guo WS, Zhang J, Liang S, Yue QY, Li Q, Nguyen TV. *Bioresour. Technol.* 2013, 148, 574–585.
[3] Marin-Rangel VM, Cortes-Martines R, Villanueva RAC, Garnica-Romo MG, Martinez Flores HE. *J. Food Sci.* 2012, 71, 10–14.
[4] Mishra V, Balomajumder C, Agarwal VK. *Clean-Soil Air Water* 2012, 40, 718–727.
[5] Hashem A, Ahmad F, Fahad R. *Adsorpt. Sci. Technol.* 2008, 26, 563–579.
[6] Khalil AA, Sokker HH, Al-Anwar AA, Hashem A. *Adsorpt. Sci. Technol.* 2009, 27, 363–382.
[7] Hashem A, Al-kheraije A. *J. Envir. Protect.* 2013, 4, 280–289.
[8] Hashem A, Azzeer AM, Ayoub A. *Polym-Plast. Technol.* 2010, 49, 1463–1472.
[9] Hashem A, Hussein HA, Sanousy MA, Adam E, Saad EE. *Polym-Plast. Technol.* 2011, 50, 1220–1230.
[10] Hashem A. *Polym-Plast. Technol.* 2006, 45, 35–42.
[11] Volesky B. Biosorption of heavy metals. CRC Press, 1990, 12–23.
[12] Sheng PX, Ting YP, Chen JP, Hong LJ. *Colloid Interface Sci.* 2004, 275, 131–141.
[13] Padmavathy V, Vasudevan P, Dhingra SC. *Process Biochem.* 2003, 38, 1389–1395.
[14] Dimitrova, SV. *Water Res.* 1996, 30, 228–232.
[15] Langmuir IJ. *Am. Chem. Soc.* 1916, 38, 2221–2295.
[16] Freundlish HJ. *Phys. Chem.* 1906, 57, 385–470.
[17] Tempkin MJ, Pyzhev V. *Acta Physiochim. URSS* 1940, 12, 217–222.
[18] Dubinin MM. *Zhurnal Fizicheskoi Khimii* 1965, 39, 1305–1317.
[19] Hasany SM, Chaudhary MH. *Appl. Radiat. Isoptes* 1996, 47, 467–471.
[20] Redlich O, Peterson D. *J. Phys. Chem.* 1959, 63, 1024–1026.
[21] Toth J. *Acta Chim. Hung.* 1971, 69, 311–317.
[22] Vijayaraghavan K, Padmesh TVN, Palanivelu K, Velan M. *J. Hazard Mater.* 2006, 133, 304–308.
[23] Sips R. *J. Chem. Phys.* 1948, 16, 490–495.
[24] Gunay A, Arslankaya E, Tosun I. *J. Hazard Mater.* 2007, 146, 362–371.
[25] Khan AR, Ataullah R, Al-Haddad A. *J. Colloid. Interface Sci* 1997, 194, 154–165.
[26] Trivedi HC, Patel VM, Patel RD. *Eur. Polym. J.* 1973, 9, 525–533.
[27] Ho YS, McKeay G. *Water Res.* 2000, 34, 735–742.
[28] Bhattacharya AK, Venkobachar C. *J. Environ. Eng.* 1984, 110, 110–122.
[29] Tutem E, Apak R, Unal CF. *Water Res.* 1998, 32, 2315–2324.
[30] Weber WJ, Morris CJ. Advances in water pollution research. *Proc 1st Int Conf on Water Pollution Res*, Vol 2. Pregamon Press: Oxford, 1962, p 231.
[31] Poots VJP, McKay G, Healy JJ. *J. Water Pollut. Control Federation* 1978, 50, 926–939.
[32] Nagarethinam K, Mariappan MS. *Dyes Pigments* 2001, 51, 25–40.
[33] Chien SH,Clayton WR. *Soil Sci. Soc. Am. J.* 1980, 44, 265–268.

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