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Kinetic and isotherm modeling of lead(II) sorption onto some waste plant materials

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Peepul leaves were identified as the most potent Pb(II) sorbent ($q_{\max} = 127.34\,\mathrm{mg\,g^{-1}}$), followed in decreasing order by banana peels ($72.79\,\mathrm{mg\,g^{-1}}$), peanut hulls ($69.75\,\mathrm{mg\,g^{-1}}$), coir fibers ($52.03\,\mathrm{mg\,g^{-1}}$), rice stem ($49.57\,\mathrm{mg\,g^{-1}}$), teak saw dust ($40.70\,\mathrm{mg\,g^{-1}}$), discarded tea leaves ($35.89\,\mathrm{mg\,g^{-1}}$), mango leaves ($31.54\,\mathrm{mg\,g^{-1}}$), rice husk ($31.13\,\mathrm{mg\,g^{-1}}$) and grass clippings ($29.05\,\mathrm{mg\,g^{-1}}$). The tested plant materials sorbed Pb(II) optimally at pH 4 or 5, but peepul leaves showed substantial sorption even at lower pH values. Kinetics of Pb(II) sorption by the selected biomass types, excepting peepul leaves, was very fast with >90% sorption occurring within 10 min. The kinetic data of Pb(II) sorption are in good agreement with both pseudo-first-order and -second-order reaction models. However, external diffusion, rather than intra-particle diffusion, seems to be the major mechanism of Pb(II) sorption by the tested plant materials. The isotherm data of Pb(II) biosorption more significantly fitted to Langmuir ($r^2 = 0.96$–0.99) than to Freundlich ($r^2 = 0.88$–0.97) model.

1. Introduction

Of the most common toxic contaminants of industrial wastewaters, heavy metals are known to deleteriously affect all kinds of living organisms [1]. Hence, they must be removed from wastewaters prior to their disposal into a river or sea. The conventional methods of metal removal have several shortcomings, such as, inefficient metal removal at low metal concentrations, high requirements of chemicals and energy, generation of toxic sludge and prohibitively high cost [2–4]. Therefore, efforts are being made to develop efficient and cost-effective technologies for metal removal from industrial wastewaters.

Sorption of metal ions onto biological materials has attracted a great deal of attention during the last two decades for its potential application in metal removal from wastewaters [1]. In this context, a great deal of efforts has been made to evaluate the metal sorption ability of algae, fungi and bacteria [5]. A few plant materials, such as, peat, rice husk, sugar beet pulp, banana pith, saw dust, plant leaves, bark, coir, etc., have also been tested for their metal sorption potential [6]. However, these data cannot be used to precisely compare metal sorption capacity of various biomass types due to varying experimental conditions, such as, pH, initial metal concentration, biomass dose, temperature, etc. The waste biomass derived from different plant species seems particularly attractive for commercial application, as it is cheaply and readily available in large amount, and its surface is rich in cellulose, pectin, lignin and tannin that may provide numerous sites for the binding of metal ions [6,7]. Hence, it is imperative to determine metal sorbing potential of various kinds of waste biomass so as to identify efficient metal accumulators.

The present study deals with the kinetic and equilibrium behavior of Pb(II) sorption by ten common types of waste plant materials, namely, stem and husk of rice, coir fibers, peepul leaves, teak saw dust, peanut hulls, doob grass, banana peels, discarded tea leaves and mango leaves. Pb(II), the metal ion selected for the study, is known to cause renal and neurological damage, blood and brain disorders, and reproductive toxicity in humans [8]. It deleteriously affects the aquatic biota and is one of the most frequently mentioned heavy metal contaminants of aqueous systems [9]. For Pb(II) sorption by the selected biomass types, the pseudo-first-order and -second-order Lagergren models, and intra-particle diffusion model were tested for kinetic modeling, and Freundlich and Langmuir isotherms were used for the equilibrium study.

2. Materials and methods

2.1. Biomass

Stem and husk of rice (*Oryza sativa*), coir fibers from coconut (*Cocos nucifera*), peepul (*Ficus religiosa*) leaves, teak (*Tectona*

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grandis) saw dust, peanut (*Arachis hypogea*) hulls, doob grass (*Cyanodon dactylon*) clippings, banana (*Musa* sp.) peels, discarded tea (*Thea sinensis*) leaves and mango (*Mangifera indica*) leaves were collected and washed several times firstly with tap water and thereafter with Milli-Q water so as to remove dust, soil and other materials adhering to the biomass. Subsequently, the plant materials were dried in a hot air oven at 80 °C overnight and then ground in a mixer followed by sieving to get the biomass particles of 0.1–0.2 mm diameter.

2.2. *Measurement of Pb(II) sorption*

Stock solution (1 g l^{-1}) of Pb(II), prepared in Milli-Q water using the analytical grade $Pb(NO_3)_2$, was appropriately diluted to obtain the selected concentration range for carrying out various experiments. The biomass was added to Pb(II) solution, and kept on a rotary shaker at 25 ± 2 °C for a prefixed time period. Thereafter, the solution was centrifuged at 5000 rpm to separate the biomass. The supernatant was collected in a small plastic vial for Pb(II) analysis using a flame atomic absorption spectrophotometer (PerkinElmer, model 2380). The supernatant was not acidified before analysis as final pH of the solution ranged from 4.5 to 5.5. This particular range does not have pH high enough to cause the precipitation of Pb(II) in the form of hydroxides. The amount of Pb(II) sorbed by the biomass was calculated by the following equation:

$$q = \frac{V(C_0 - C_e)}{1000B} \qquad (1)$$

where q is the amount of Pb(II) sorbed (mg g^{-1}), V is the volume (ml) of the Pb(II) solution. C_0 and C_e are respectively initial and equilibrium concentrations (mg l^{-1}) of Pb(II) in the solution. B is the amount (g) of the test biomass. Four replicates were taken for all the experiments.

2.3. *Pb(II) sorption in relation to pH and biomass concentration*

To study the effect of pH on Pb(II) sorption, 50 ml of 200 mg l^{-1} Pb(II) solution was taken in 150 ml flasks to each of which 50 mg biomass was added. The pH of the solution was initially adjusted within the range 1.0–5.0 using 0.1 N NaOH or HCl. The flasks were kept on a shaker for 4 h under conditions detailed above, and Pb(II) sorption by the biomass was estimated.

Pb(II) sorption was also measured at three biomass concentrations (i.e., 0.1, 1.0 and 10.0 g l^{-1}) of the tested plant materials. For this, 5, 50 or 500 mg of biomass was added separately into 150 ml flasks containing 50 ml of Pb(II) solution (200 mg l^{-1}) whose pH was adjusted to 5. The flasks were kept for 4 h under conditions

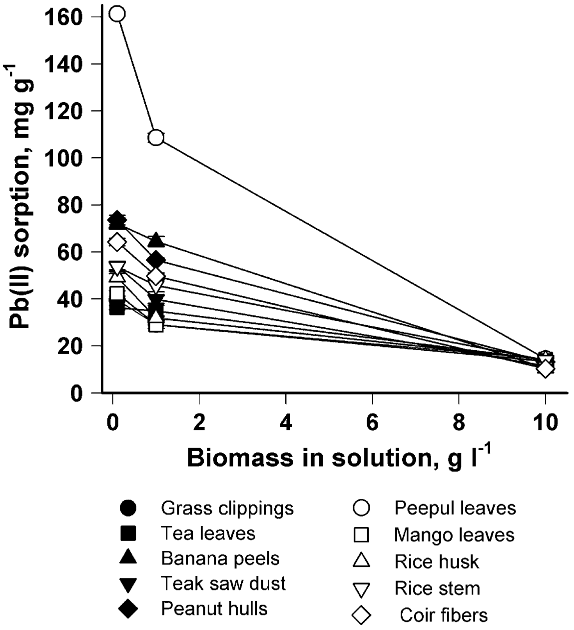

Fig. 2. Effect of biomass concentration on sorption of Pb(II) by various plant materials. All the experiments were conducted at 25 ± 2 °C for 4 h. The metal concentration and pH of the solution were 200 mg l^{-1} and 5, respectively.

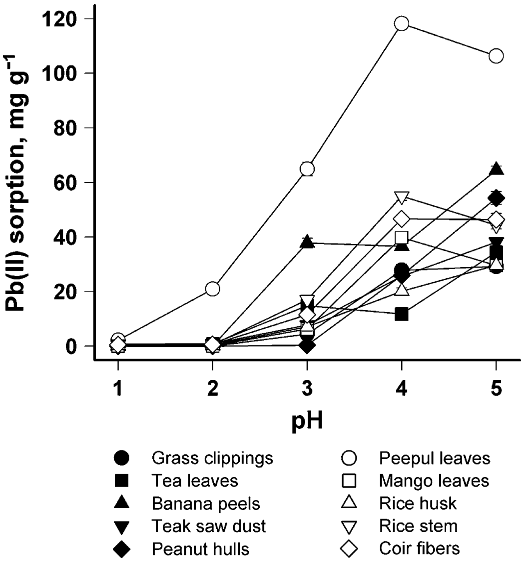

Fig. 1. Effect of pH on sorption of Pb(II) by the test plant materials. All the experiments were conducted at 25 ± 2 °C for 4 h. The metal solution contained 200 mg l^{-1} Pb(II) and 1 g l^{-1} biomass. The vertical bars show standard deviation of means of four replicates.

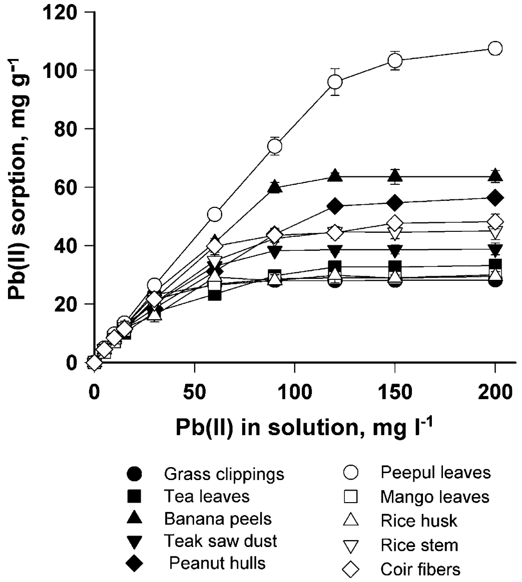

Fig. 3. Pb(II) sorption by test plant materials from solutions containing various concentrations of Pb(II). The experiments were conducted at 25 ± 2 °C for 4 h. The biomass concentration and pH of metal solution for each test biomass were 1 g l^{-1} and 5, respectively.

specified above. Thereafter, the amount of Pb(II) sorbed by the biomass was estimated.

2.4. Kinetic and isotherm modeling of Pb(II) sorption

Time course of Pb(II) sorption by the selected plant materials was studied at three initial concentrations of Pb(II) (i.e., 15, 60 and 120 mg l^{-1}) and at three biomass doses (i.e., 0.1, 1.0, and 10 g l^{-1}). For biomass- and concentration-based kinetics, the metal and biomass concentrations were 150 mg l^{-1} and 1 g l^{-1}, respectively. The pH of the metal solution was adjusted to 5. The metal sorption data obtained at various time intervals were fitted to pseudo-first-order and -second-order reaction models [10], and intra-particle diffusion model [11] using the non-linear regression method and r^2 was calculated to assess the fitness of the models.

Pb(II) sorption by various plant materials was studied at various initial concentrations of Pb(II) (5–200 mg l^{-1}) by adding a fixed amount of biomass (50 mg) into 150 ml flasks containing 50 ml of Pb(II) solution (pH 5). The flasks were incubated at 25 ± 2 °C on a shaker for 4 h. The data obtained from the study were fitted to Freundlich and Langmuir models using the non-linear regression method.

3. Results and discussion

3.1. Pb(II) sorption in relation to pH, and biomass and Pb(II) concentration in solution

The effect of pH on Pb(II) sorption by the selected plant materials was studied only within the acidic range (pH 1–5) as precipitation of this metal ion in the form of hydroxide is known to occur at alkaline pH [2,12]. Pb(II) sorption increased with a rise in pH attaining the maxima at pH 4 (peepul leaves, mango leaves, rice stem and coir fibers) or 5 (grass, tea leaves, banana peels, teak saw dust, peanut hulls and rice husk) (see Fig. 1). Pb(II) sorption by all the tested plant materials, excepting peepul leaves, was too little at extremely acidic pH (1–3). In such conditions, most of the negatively charged sites on the sorbent surface become occupied by hydronium ions (H^3O^+). This makes the surface positively charged, thereby decreasing the binding of metal ions onto it [4]. Peepul leaves sorbed 21 and 65 mg g^{-1} of Pb(II) at pH 2 and 3, respectively. Thus, they seem a better Pb(II) sorbent than other tested plant materials, as they could efficiently sorb Pb(II) even from highly acidic solutions. Many metal-enriched wastewaters, such as, acid mine drainage and wastewaters from metal-related industries, have pH as low as 2

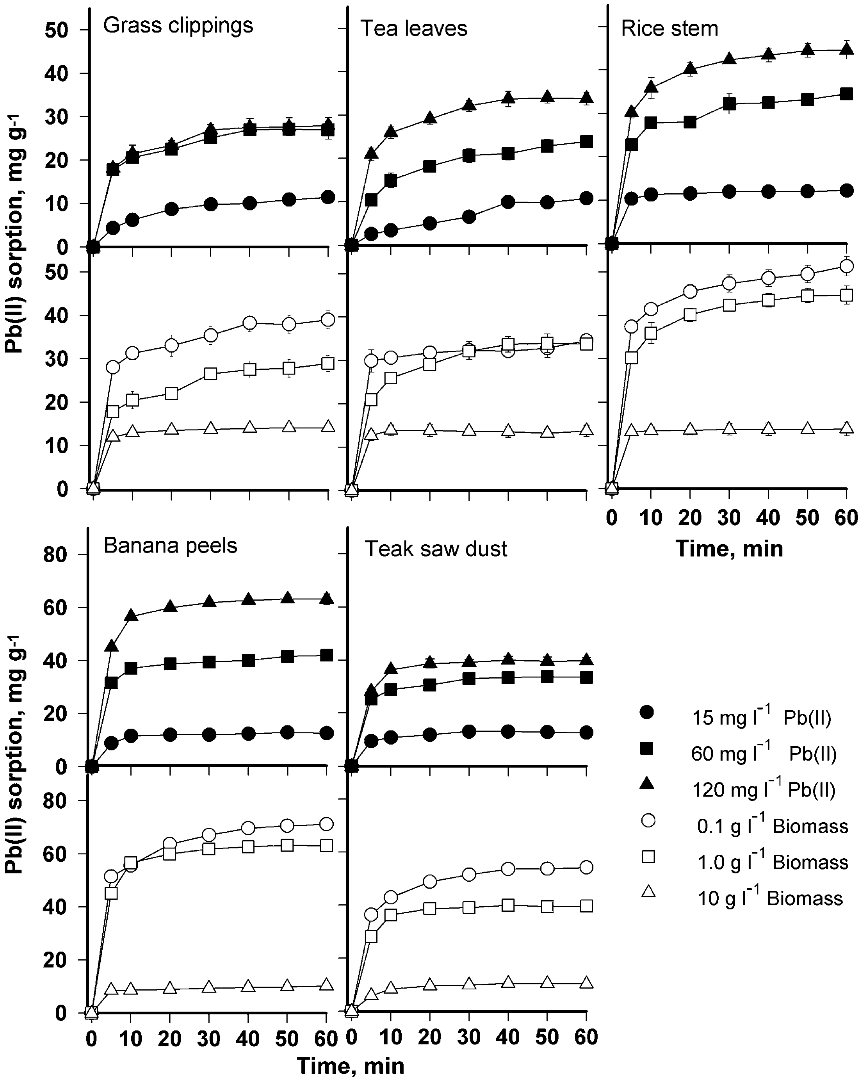

Fig. 4. Time course of Pb(II) sorption by the test plant materials. The experiments were conducted at three different initial concentrations of Pb(II) and at three different biomass doses. For biomass- and concentration-based kinetics, the metal and biomass concentrations were 150 mg l^{-1} and 1 g l^{-1}, respectively.

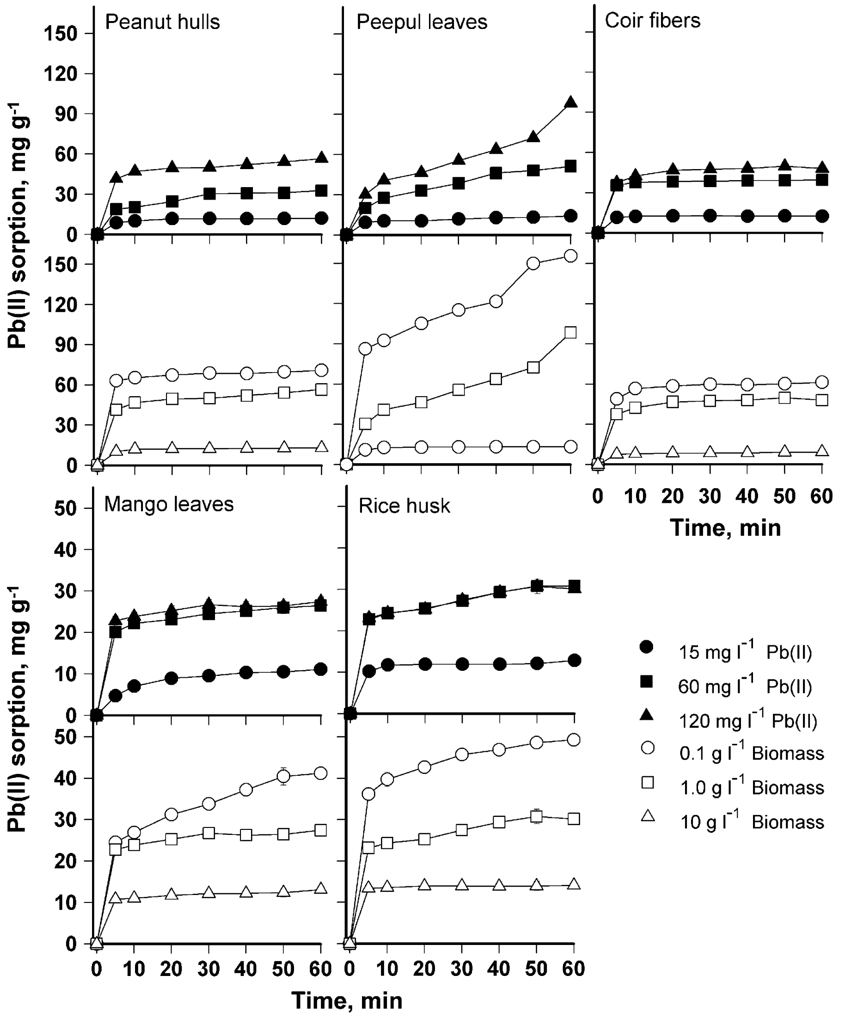

Fig. 5. Time course of Pb(II) sorption by test plant materials. The experimental conditions were as given in Fig. 3.

[13,14], and peepul leaves could very well be used for removing Pb(II) from such waters.

Pb(II) sorption decreased with increase in biomass concentration (Fig. 2). This probably took place due to decreased availability of metal ion per unit biomass. However, Pb(II) sorption increased rapidly with increase in concentration of Pb(II) in the solution, and became saturated at concentrations >120 mg l^{-1} (see Fig. 3). The saturation of Pb(II) sorption is obviously due to the fact that the number of metal binding sites on a known amount of biomass is finite. The test plant materials varied in their Pb(II) sorption ability at any tested concentration of Pb(II) in the solution (see Fig. 3). At 200 mg l^{-1} of Pb(II) in solution, peepul leaves sorbed Pb(II) maximally, followed in decreasing order by banana peels, peanut hulls, coir fibers, rice stem, teak saw dust, tea leaves, rice husk, mango leaves and grass clippings. The magnitude of Pb(II) sorption was not similar for the biomass derived from different parts of the rice plant as its stem has nearly 1.6 times greater Pb(II) sorption ability than the husk. Variations in Pb(II) sorption ability of the tested biomass types seems to be related with the number and nature of metal binding sites on their surfaces [1,7].

3.2. Kinetic modeling of Pb(II) sorption

The kinetics of Pb(II) sorption by various plant materials was studied at three different initial concentrations of Pb(II) and biomass (see Figs. 4 and 5). Pb(II) sorption was very rapid with >90% sorption occurring within 10 min of the process initiation, except for peepul leaves. Both biomass and metal concentration did not significantly affect the time for attaining the equilibrium of Pb(II) sorption by the tested plant materials. An initial rapid Pb(II) sorption was due to the fact that most of the binding sites were free which made possible quick binding of metal ions on the biomass, but subsequent saturation of binding sites led to attainment of the equilibrium.

The time course data of Pb(II) sorption were fitted to the pseudo-first-order and -second-order Lagergren models to find out the order of the reaction. The estimated kinetic parameters are shown in Tables 1 and 2. If regression coefficient (r^2) is taken as the parameter for model fitness, it becomes apparent that both the models very well define the present data. Vilar et al. [10] also showed that both the models could suitably describe the sorption of Cd(II) by the red alga *Gelidium* and its wastes. However, the second-order kinetic model, with slightly higher r^2 values, showed a little superiority over the first-order model in the present case. Similarly, Ho and McKay [15] showed the superiority of the second order model in describing the sorption of metal ions by peat biomass.

The initial rate of Pb(II) sorption by various biomass types has been estimated at three different concentrations of Pb(II) (i.e., 15, 60 and 120 mg l^{-1}) following the pseudo-first-order and the pseudo-second-order Lagergren equations (see Table 3). The first- and the

Table 1
Estimated parameters and regression coefficients of pseudo-first-order and -second-order Lagergren models, and intra-particle diffusion model for Pb(II) sorption at various biomass concentrations

Biomass type	Bio-mass (g l^{-1})	Pseudo-first-order Lagergren model			Pseudo-second-order Lagergren model			Intra-particle diffusion model		
		q_E (mg g^{-1})	k_{1S} (min^{-1})	r^2	q_E (mg g^{-1})	k_{2S} (g mg^{-1} min^{-1})	r^2	I (mg g^{-1})	K_I (mg g^{-1} min$^{0.5}$)	r^2
Grass clippings	0.1	[a]36.53 ± 1.03	0.26 ± 0.04	0.97	39.20 ± 0.87	0.01 ± 0.00	0.99	24.08 ± 3.43	2.02 ± 0.67	0.97
	1.0	26.84 ± 1.06	0.17 ± 0.03	0.95	29.80 ± 1.08	0.01 ± 0.00	0.98	13.38 ± 2.69	2.11 ± 0.59	0.97
	10	13.76 ± 0.13	0.39 ± 0.03	1.00	14.23 ± 0.04	0.07 ± 0.00	1.00	11.54 ± 4.10	0.36 ± 0.62	0.87
Tea leaves	0.1	32.46 ± 0.48	0.49 ± 0.09	0.99	33.33 ± 0.47	0.05 ± 0.01	1.00	28.38 ± 3.42	0.70 ± 0.38	0.91
	1.0	32.78 ± 0.77	0.18 ± 0.02	0.98	36.14 ± 0.05	0.01 ± 0.00	1.00	16.75 ± 2.24	2.51 ± 1.49	0.92
	10	13.66 ± 0.10	0.53 ± 0.05	0.99	13.78 ± 0.18	0.24 ± 0.13	1.00	13.10 ± 1.72	0.08 ± 0.07	0.82
Banana peels	0.1	69.64 ± 1.31	0.22 ± 0.03	0.97	73.12 ± 0.71	0.01 ± 0.00	1.00	43.92 ± 6.73	3.86 ± 1.21	0.95
	1.0	62.98 ± 0.45	0.24 ± 0.01	0.99	65.53 ± 0.43	0.01 ± 0.00	1.00	42.22 ± 5.15	3.14 ± 1.99	0.81
	10	9.85 ± 0.21	0.36 ± 0.08	0.96	10.22 ± 0.17	0.07 ± 0.02	0.98	7.75 ± 1.88	0.30 ± 0.15	0.97
Teak saw dust	0.1	52.39 ± 1.03	0.21 ± 0.02	0.99	56.79 ± 0.45	0.01 ± 0.00	1.00	31.00 ± 6.07	3.38 ± 1.08	0.92
	1.0	39.45 ± 0.15	0.25 ± 0.01	0.99	41.85 ± 0.69	0.01 ± 0.00	1.00	26.70 ± 5.90	1.98 ± 0.89	0.81
	10	10.25 ± 0.09	0.17 ± 0.01	0.99	11.33 ± 0.22	0.02 ± 0.00	1.00	4.68 ± 2.98	0.86 ± 0.63	0.82
Peanut hulls	0.1	68.63 ± 0.67	0.49 ± 0.06	0.99	70.28 ± 0.45	0.02 ± 0.00	1.00	60.99 ± 7.67	1.29 ± 1.40	0.95
	1.0	52.25 ± 1.18	0.29 ± 0.04	0.98	55.36 ± 1.07	0.01 ± 0.00	0.99	37.39 ± 5.78	2.43 ± 0.73	0.95
	10	12.64 ± 0.12	0.33 ± 0.02	0.99	13.18 ± 0.15	0.06 ± 0.01	1.00	9.85 ± 2.49	0.45 ± 0.35	0.88
Peepul leaves	0.1	149.78 ± 9.26	0.08 ± 0.02	0.87	163.27 ± 6.64	0.001 ± 0.00	0.94	56.38 ± 10.10	11.67 ± 2.79	0.93
	1.0	108.07 ± 5.24	0.08 ± 0.02	0.94	124.56 ± 7.98	0.001 ± 0.00	0.95	9.54 ± 4.90	9.07 ± 1.43	0.93
	10	13.39 ± 1.24	0.33 ± 0.01	0.99	13.81 ± 0.59	0.06 ± 0.03	0.99	10.78 ± 3.16	0.36 ± 0.45	0.81
Mango leaves	0.1	37.34 ± 1.79	0.15 ± 0.03	0.94	41.99 ± 1.97	0.01 ± 0.00	0.97	17.19 ± 3.17	3.15 ± 0.39	0.99
	1.0	26.18 ± 0.43	0.38 ± 0.06	0.99	27.23 ± 0.33	0.03 ± 0.01	1.00	21.31 ± 2.65	0.81 ± 0.99	0.92
	10	12.17 ± 0.25	0.41 ± 0.08	0.98	12.65 ± 0.23	0.08 ± 0.02	0.99	9.93 ± 1.56	0.38 ± 0.36	0.96
Rice husk	0.1	46.31 ± 1.18	0.27 ± 0.04	0.98	49.47 ± 0.90	0.01 ± 0.00	0.99	31.47 ± 3.48	2.42 ± 1.49	0.98
	1.0	28.32 ± 0.94	0.29 ± 0.07	0.96	30.23 ± 0.90	0.02 ± 0.01	0.98	19.13 ± 2.45	1.55 ± 1.32	0.98
	10	13.90 ± 0.06	0.64 ± 0.05	0.99	14.06 ± 0.04	0.26 ± 0.03	1.00	13.22 ± 1.12	0.11 ± 0.75	0.82
Rice stem	0.1	48.14 ± 1.05	0.27 ± 0.04	0.98	51.30 ± 0.70	0.01 ± 0.00	1.00	33.04 ± 5.63	2.45 ± 1.09	0.96
	1.0	43.00 ± 0.81	0.22 ± 0.02	0.99	46.49 ± 0.29	0.01 ± 0.00	1.00	26.00 ± 3.20	2.69 ± 0.50	0.92
	10	13.62 ± 0.05	0.69 ± 0.07	0.99	13.75 ± 0.04	0.33 ± 0.05	1.00	13.06 ± 4.89	0.10 ± 0.71	0.87
Coir fibers	0.1	59.87 ± 0.41	0.33 ± 0.02	0.99	62.32 ± 0.49	0.01 ± 0.00	1.00	47.60 ± 9.42	1.95 ± 1.11	0.86
	1.0	47.81 ± 0.66	0.28 ± 0.03	0.99	50.42 ± 0.41	0.01 ± 0.00	1.00	35.04 ± 5.74	2.03 ± 1.69	0.84
	10	8.90 ± 0.17	0.39 ± 0.06	0.99	9.26 ± 0.15	0.10 ± 0.02	0.99	7.20 ± 1.14	0.29 ± 0.72	0.96

[a] Mean ± S.E.

second-order estimated initial rates of Pb(II) sorption were generally higher at 60 and 120 mg l^{-1} of Pb(II) than that at 15 mg l^{-1} of Pb(II) for all the tested biomass types. An initial high concentration of Pb(II) seems to have enhanced the chances of their collision with the binding sites of the sorbent thus resulting in an initial high sorption rate. Table 3 clearly shows that the pseudo-second-order estimated rate of Pb(II) sorption is greater than the pseudo-first-order estimated rate. This is because the pseudo-second-order kinetic model assumes that sorption rate is proportional to the square of number of vacant metal binding sites.

The concentration of biomass greatly influenced the initial rate of Pb(II) sorption by all the tested plant materials (see Table 3). However, the effect of biomass concentration on the initial rate of Pb(II) sorption seems to be rather complex as no general trend was evident. The pseudo-first-order kinetics shows that the initial rate of Pb(II) sorption was the lowest at the highest tested biomass concentration (10 g l^{-1}) of all the tested plant materials, excepting grass clippings and tea leaves. This may be due to the lowest availability of metal ions per unit biomass. The pseudo-second-order kinetics also showed an inverse relationship between biomass concentration and the initial rate of Pb(II) sorption by teak saw dust, peanut hulls, peepul leaves, rice husk and coir fibers. However, the second-order rate kinetics did not show a definite pattern for banana peels, grass clippings, tea and mango leaves, and rice stem at varying biomass concentrations. Thus, the pseudo-first-order kinetic model has greater acceptability than the second-order model in the case of biomass concentration-based kinetics.

A comparison of different biomass types has been made to identify the biosorbent that has the fastest initial Pb(II) sorption rate at 120 mg l^{-1} of Pb(II) and 1 g l^{-1} biomass concentration. The pseudo-first-order rate law gave the following order of decreasing initial Pb(II) sorption rate: peanut hulls > banana peels > coir fibers > mango leaves > teak saw dust > rice stem > peepul leaves > rice husk > tea leaves > grass clippings. However, the pseudo-second-order rate law gave a slightly different trend: coir fibers > banana peels > peanut hulls > rice husk > mango leaves > teak saw dust > rice stem > peepul leaves > tea leaves > grass clippings. Thus, peanut hulls and coir fibers are the fastest Pb(II) sorbents according to the pseudo-first- and -second-order kinetic models, respectively. But both the models suggest grass clippings as the slowest Pb(II) sorbent.

Chemical reaction-based kinetic models successfully predicted the sorption behavior of Pb(II) onto the tested plant material, however, these models do not reflect the importance of diffusion. Thus, to find out the role of diffusion in the process of metal sorption, regression analysis was carried out between q and $t^{0.5}$ [11] for all the tested plant materials at different concentrations of Pb(II) and biomass, and the values of intercept (I), slope (K_I) and r^2 are given in Table 1 and 2. A significant linear relationship was observed between q and $t^{0.5}$ ($r^2 > 0.81$), however, $I \neq 0$, thus, suggesting that intra-particle diffusion was not the rate-limiting step [16]. Thus, external diffusion can be considered as the dominant process in the present case as has been earlier observed for metal sorption by mineral particles [17].

Table 2
Estimated parameters and regression coefficients of pseudo-first-order and -second-order Lagergren models, and intra-particle diffusion model for Pb(II) sorption by plant materials at various initial concentrations of Pb(II) in solution

Biomass type	Pb(II) (mg l^{-1})	Pseudo-first-order Lagergren model			Pseudo-second-order Lagergren model			Intra-particle diffusion model		
		q_E (mg g^{-1})	k_{1S} (min^{-1})	r^2	q_E (mg g^{-1})	k_{2S} (g mg^{-1} min^{-1})	r^2	I (mg g^{-1})	K_I (mg g^{-1} min$^{0.5}$)	r^2
Grass clippings	15	[a] 10.90 ± 0.28	0.09 ± 0.01	0.99	13.19 ± 0.26	0.01 ± 0.00	1.00	1.64 ± 0.48	1.36 ± 1.50	0.97
	60	25.84 ± 0.80	0.19 ± 0.03	0.97	28.30 ± 0.69	0.01 ± 0.00	0.99	14.39 ± 2.51	1.81 ± 1.48	0.95
	120	26.86 ± 0.74	0.19 ± 0.02	0.97	29.43 ± 0.60	0.01 ± 0.00	0.99	14.73 ± 3.10	1.91 ± 1.61	0.94
Tea leaves	15	13.99 ± 2.35	0.02 ± 0.01	0.97	21.16 ± 4.66	0.01 ± 0.00	0.97	0.92 ± 0.28	1.46 ± 1.15	0.96
	60	22.33 ± 0.66	0.11 ± 0.01	0.98	26.17 ± 0.52	0.01 ± 0.00	1.00	5.66 ± 4.95	2.52 ± 1.29	0.96
	120	32.78 ± 0.77	0.18 ± 0.02	0.98	36.14 ± 0.51	0.01 ± 0.00	1.00	16.75 ± 7.24	2.51 ± 1.49	0.92
Banana peels	15	12.58 ± 0.11	0.24 ± 0.01	0.99	13.10 ± 0.15	0.04 ± 0.00	0.99	8.25 ± 1.33	0.66 ± 0.19	0.85
	60	40.94 ± 0.45	0.28 ± 0.02	0.99	42.45 ± 0.25	0.01 ± 0.00	1.00	29.60 ± 8.33	1.72 ± 1.41	0.86
	120	62.98 ± 0.45	0.24 ± 0.01	1.00	65.54 ± 0.43	0.01 ± 0.00	1.00	42.22 ± 7.15	3.14 ± 1.99	0.89
Teak saw dust	15	12.56 ± 0.24	0.25 ± 0.03	0.99	13.38 ± 0.22	0.03 ± 0.01	1.00	8.55 ± 1.58	0.63 ± 0.22	0.82
	60	32.67 ± 0.58	0.27 ± 0.03	0.99	34.66 ± 0.33	0.01 ± 0.00	1.00	23.06 ± 3.99	1.54 ± 0.94	0.90
	120	39.45 ± 0.15	0.25 ± 0.01	1.00	41.85 ± 0.69	0.01 ± 0.00	1.00	26.70 ± 5.90	1.98 ± 0.89	0.81
Peanut hulls	15	11.74 ± 0.16	0.24 ± 0.02	0.99	12.50 ± 0.14	0.04 ± 0.00	1.00	7.92 ± 1.78	0.59 ± 0.28	0.82
	60	30.62 ± 1.33	0.13 ± 0.02	0.95	34.62 ± 1.52	0.01 ± 0.98	0.98	12.42 ± 3.98	2.76 ± 1.99	0.96
	120	52.25 ± 1.18	0.29 ± 0.04	0.98	55.36 ± 1.07	0.01 ± 0.00	0.99	37.39 ± 5.78	2.43 ± 1.73	0.95
Peepul leaves	15	13.14 ± 0.56	0.19 ± 0.02	0.93	14.03 ± 0.45	0.02 ± 0.00	0.97	7.43 ± 1.59	0.83 ± 1.29	0.96
	60	51.28 ± 1.89	0.06 ± 0.01	0.97	56.37 ± 3.54	0.002 ± 0.00	0.98	7.65 ± 2.18	5.79 ± 1.69	0.99
	120	108.07 ± 5.23	0.08 ± 0.01	0.94	124.56 ± 4.88	0.001 ± 0.00	0.95	9.54 ± 4.90	9.07 ± 1.43	0.93
Mango leaves	15	10.51 ± 0.23	0.11 ± 0.01	0.99	12.33 ± 1.62	0.01 ± 0.00	1.00	2.43 ± 1.82	1.23 ± 1.52	0.94
	60	24.92 ± 0.56	0.30 ± 0.05	0.98	26.37 ± 0.44	0.02 ± 0.00	1.00	18.06 ± 4.32	1.13 ± 4.65	0.98
	120	26.18 ± 0.43	0.38 ± 0.06	0.99	27.20 ± 0.33	0.03 ± 0.01	1.00	21.39 ± 6.71	0.79 ± 0.99	0.92
Rice husk	15	12.14 ± 0.14	0.37 ± 0.04	0.99	12.56 ± 0.20	0.08 ± 0.02	1.00	10.01 ± 2.35	0.34 ± 0.30	0.81
	60	28.32 ± 0.94	0.29 ± 0.07	0.96	30.23 ± 0.93	0.02 ± 0.01	0.99	19.69 ± 7.58	1.43 ± 1.32	0.96
	120	28.35 ± 0.96	0.30 ± 0.06	0.96	30.35 ± 1.05	0.02 ± 0.01	0.99	19.13 ± 7.45	1.55 ± 1.32	0.98
Rice stem	15	11.89 ± 0.11	0.39 ± 0.03	0.99	12.29 ± 0.07	0.08 ± 0.01	1.00	9.96 ± 2.18	0.31 ± 0.27	0.85
	60	32.18 ± 0.89	0.22 ± 0.03	0.97	34.89 ± 0.84	0.01 ± 0.00	0.99	19.35 ± 2.94	2.06 ± 1.69	0.92
	120	43.00 ± 0.81	0.21 ± 0.02	0.99	46.49 ± 0.29	0.01 ± 0.00	1.00	26.00 ± 3.20	2.69 ± 1.50	0.92
Coir fibers	15	12.56 ± 0.07	0.47 ± 0.03	0.99	12.79 ± 0.12	0.14 ± 0.03	1.00	11.51 ± 3.23	0.16 ± 0.42	0.86
	60	38.76 ± 0.23	0.49 ± 0.04	0.99	39.57 ± 0.13	0.04 ± 0.00	1.00	34.90 ± 4.09	0.64 ± 0.55	0.86
	120	47.81 ± 0.66	0.28 ± 0.03	0.99	50.42 ± 0.41	0.03 ± 0.00	1.00	35.04 ± 5.74	2.03 ± 0.69	0.84

[a] Mean ± S.E.

3.3. *Isotherm modeling of Pb(II) sorption*

Langmuir and Freundlich isotherms were tested for predicting the equilibrium behavior of Pb(II) sorption onto various biomass types. Pb(II) sorption by the selected biomass types could be more appropriately defined by Langmuir ($r^2 = 0.96–0.99$) than by Freundlich ($r^2 = 0.88–0.97$) model (see Table 4). Several earlier researchers noted the superiority of Langmuir model in predicting equilibrium behavior of metal sorption onto biological materials [1]. The Langmuir model was found superior as it presumes the saturation of metal binding sites. Langmuir parameter $q_{\max}$ predicts the monolayer sorption capacity of the biomass. A high value of $q_{\max}$ is suggestive of high metal sorption capacity of the biomass. In the present study, $q_{\max}$ for Pb(II) sorption was the greatest for peepul leaves and the rest of the biomass types showed the following hierarchy: banana peels > peanut hulls > coir fibers > rice

Table 3
Initial rate of Pb(II) sorption by the test plant materials, as per pseudo-first-order and -second-order Lagergren models, at various biomass and metal concentrations

Biomass type	[a]Initial sorption rate (mg g^{-1} min^{-1})											
	Pseudo-first-order Lagergren model						Pseudo-second-order Lagergren model					
	Biomass (g l^{-1})			Pb(II) (mg l^{-1})			Biomass (g l^{-1})			Pb(II) (mg l^{-1})		
	0.10	1.0	10	15	60	120	0.10	1.0	10	15	60	120
Grass clippings	9.50	4.56	5.37	0.98	4.91	5.10	15.37	7.10	14.58	1.28	8.00	8.66
Tea leaves	15.91	5.90	7.24	0.28	2.46	5.90	55.55	9.14	45.57	3.58	3.42	9.14
Banana peels	15.32	15.12	3.55	3.02	11.46	15.12	26.73	34.35	7.31	6.86	18.02	34.36
Teak saw dust	11.00	9.86	1.74	3.14	8.82	9.86	19.35	17.51	2.57	5.37	12.01	17.51
Peanut hulls	33.62	15.15	4.17	2.82	8.88	15.15	98.78	30.65	10.42	6.25	5.99	30.65
Peepul leaves	12.58	8.43	4.37	2.53	3.17	8.43	21.32	15.51	10.67	4.32	6.35	15.51
Mango leaves	5.60	9.95	4.99	1.16	7.48	9.95	8.82	22.24	12.80	1.52	13.91	22.20
Rice husk	12.50	8.21	8.90	4.49	8.21	8.32	49.47	30.23	14.06	12.56	30.23	30.23
Rice stem	13.00	9.46	9.39	4.64	7.08	9.03	23.68	15.13	62.39	12.08	12.17	17.29
Coir fibers	19.78	13.39	3.47	5.90	18.99	13.38	38.84	25.42	8.58	22.90	62.63	76.27

[a] Calculated by multiplying equilibrium sorption amount with the rate constant for the first-order model or by multiplying square of equilibrium sorption amount with the rate constant for the second-order kinetic model. The equilibrium sorption amount and rate constants are given in Tables 1 and 2 for the first- and the second-order model, respectively.

Table 4
Freundlich and Langmuir isotherms parameters for Pb(II) sorption by various plant materials

Biomass type	Experimental maximum (mg g^{-1})	Freundlich parameters			Langmuir parameters		
		K_F (mg^{1-n} g^{-1} l^n)	n	r^2	$q_{\max}$ (mg g^{-1})	b (l mg^{-1})	r^2
Grass clippings	28.21 ± 1.48	11.16 ± 1.94	0.20 ± 0.04	0.89	29.05 ± 0.57	0.36 ± 0.02	0.99
Tea leaves	33.12 ± 1.51	6.91 ± 1.02	0.33 ± 0.03	0.97	35.89 ± 1.23	0.08 ± 0.01	0.99
Banana peels	63.63 ± 2.05	13.83 ± 1.46	0.34 ± 0.06	0.91	72.79 ± 2.99	0.09 ± 0.01	0.99
Teak saw dust	38.82 ± 2.01	11.47 ± 1.89	0.27 ± 0.04	0.94	40.70 ± 1.79	0.18 ± 0.02	0.97
Peanut hulls	56.42 ± 1.05	8.13 ± 1.59	0.41 ± 0.05	0.97	69.75 ± 5.10	0.04 ± 0.01	0.98
Peepul leaves	107.51 ± 2.11	22.85 ± 4.96	0.37 ± 0.05	0.93	127.34 ± 6.71	0.08 ± 0.01	0.99
Mango leaves	30.02 ± 1.71	8.59 ± 1.99	0.27 ± 0.05	0.88	31.54 ± 1.12	0.15 ± 0.03	0.98
Rice husk	29.51 ± 1.54	8.83 ± 1.75	0.26 ± 0.05	0.91	31.13 ± 1.48	0.16 ± 0.01	0.96
Rice stem	45.12 ± 3.10	10.98 ± 1.99	0.31 ± 0.04	0.95	49.57 ± 1.69	0.10 ± 0.01	0.99
Coir fibers	48.21 ± 2.53	11.28 ± 2.49	0.31 ± 0.05	0.92	52.03 ± 1.67	0.12 ± 0.01	0.99

Mean ± S.E.

stem > teak saw dust > tea leaves > mango leaves > rice husk > grass clippings. The second Langmuir parameter b decreased in the following order: grass clippings > teak saw dust > rice husk > mango leaves > coir fiber > rice stem > banana peels > peepul leaves = tea leaves > peanut hulls. Since, a low value of b reflects a high affinity of the biomass for the metal ions [18], grass clippings and peanut hulls, respectively have the lowest and the highest affinity for Pb(II). However, a good metal sorbent in general should have a low b and a high $q_{\max}$ [18]. Thus, peepul leaf biomass very well fulfills these criteria for the sorption of Pb(II).

The initial rate of sorption, derived from either pseudo-first- or -second-order kinetic model, and $q_{\max}$ for the sorption of Pb(II) by various biomass types did not show any relationship. For example, peepul leaf has the highest $q_{\max}$ but its initial sorption rate is lower than that of coir, banana peels, peanut hulls, sawdust, mango leaves and rice stem.

The Freundlich parameters provide valuable physical information about metal sorption by the biomass. For example, a high value of Freundlich constant K_F suggests easiness in sorption of metal ion onto the biomass. The present study shows that K_F for Pb(II) sorption was the highest for peepul leaves, followed in a decreasing order by banana peels, teak saw dust, coir fibers, grass clippings, rice stem, rice husk, mango leaves, peanut hulls and tea leaves. Several authors report that the biomass types with high K_F often have high $q_{\max}$ as well [17,19], however, this pattern was not observed in the present study. The Freundlich parameter n is a measure of intensity of metal sorption by the biomass. The value of $n < 1$ suggests that sorption of metal ion on the biomass is practically favorable [20]. In the present study, the value of n was <1 for all the selected plant materials, thus suggesting that Pb(II) sorption occurred favorably onto the tested plant materials.

3.4. *Comparison of metal sorbing potential of the tested plant materials with other plants*

Langmuir $q_{\max}$ has been used in most of the earlier investigations for defining Pb(II) sorption potential of different biomass types, and therefore this parameter has been employed in the present study also for comparing the efficacy of the selected materials with other biomass types (Table 5). The tested plant materials show higher values of $q_{\max}$ for Pb(II) sorption than those of many biomass types reported earlier. Peepul leaves stand out as the best Pb(II) biosorbent as they showed the largest $q_{\max}$ (127.34 mg g^{-1}) along with a low value of b (0.08 l mg^{-1}). Moreover, their $q_{\max}$ is comparable to that of many brown algae, which are regarded as the best Pb(II) biosorbents [30].

Table 5
Pb(II) sorption capacity of some plant-derived low cost biosorbents

Biosorbent	Biomass concentration (g l^{-1})	Initial metal concentration (mg l^{-1})	pH	Langmuir $q_{\max}$ (mg g^{-1})	Reference
Sugar beet pulp	2.5	41–517		73.75	[3]
Nopal	2.5	10–51	5.0	29.01	[12]
Peanut hulls	–	–	–	30.04	[21]
Ceratophyllum. demersum	2	2–64	–	45.00	[22]
Saw dust (*Pinus sylvestris*)	1	1–50	5.0	22.22	[23]
Neem leaf powder	1.2	50–150	–	82.00	[24]
Tea leaves	–	–	–	78.70	[24]
Spruce saw dust	–	–	–	224	[24]
Peat	–	–	–	150	[24]
Black gram husk	10	10–800	5.0	49.97	[25]
Grape stalk waste	6.67	31–393	5.5	49.93	[26]
Mustard husk	10	1–5	6.0	30.48	[27]
Saw dust (*Acacia arabica*)	10	1–5	6.0	52.38	[28]
Leaves (*Syzygium cumini*)	3.33	20–100	6.0	32.47	[29]
Grass clippings	1	5–200	5.0	29.05	Present study
Tea leaves	1	5–200	5.0	35.89	Present study
Banana peels	1	5–200	5.0	72.79	Present study
Teak saw dust	1	5–200	5.0	40.70	Present study
Peanut hulls	1	5–200	5.0	69.75	Present study
Peepul leaves	1	5–200	5.0	127.34	Present study
Mango leaves	1	5–200	5.0	31.54	Present study
Rice husk	1	5–200	5.0	31.13	Present study
Rice stem	1	5–200	5.0	49.57	Present study
Coir fibers	1	5–200	5.0	52.03	Present study

4. Conclusions

- Most of the tested plant materials could rapidly sorb Pb(II) from solution with >90% sorption occurring within 10 min.
- Pb(II) sorption attained maxima at pH 4 (peepul leaves, mango leaves, rice stem and coir fibers) or 5 (grass, tea leaves, banana peels, teak saw dust, peanut hulls and rice husk).
- Peepul leaves sorbed Pb(II) maximally followed in decreasing order by banana peels, peanut hulls, coir fibers, rice stem, teak saw dust, tea leaves, mango leaves, rice husk and grass clippings.
- Lagergren pseudo-first-order and -second-order reaction models were in good agreement with the time course data of Pb(II) sorption by various tested plant materials at varying concentrations of metal and biomass. But, the latter model showed greater fitness. Furthermore, external diffusion, rather than intra-particle diffusion, was the dominant mechanism for Pb(II) sorption by all the test plant materials.
- The initial Pb(II) sorption rate depended on the ratio of Pb(II) in solution to biomass concentration and was generally higher at lower biomass and higher Pb(II) concentration in solution. It does not seem to be related with the maximum Pb(II) sorption capacity of the biomass ($q_{\max}$).
- The isotherm data of Pb(II) sorption by all the test biomass types could fit well to Langmuir and Freundlich models. The Langmuir model successfully predicted the maximum sorption capacity and affinity of the test plant materials for Pb(II).
- The present study identifies peepul leaves as an excellent Pb(II) sorbent as it has the highest $q_{\max}$ (127.34 mg g^{-1}) together with a low b (0.08 l mg^{-1}). Peepul leaf biomass could substantially sorb Pb(II) from solution having pH 3, in sharp contrast to other tested plant materials, thus becoming attractive even for the treatment of metal-enriched acidic wastewaters.

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