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Application of mango seed integuments as bio-adsorbent in lead removal from industrial effluent

Tiyasha Kanjilal[a], Swaminathan Babu[b], Kalpana Biswas[a], Chiranjib Bhattacharjee[a,*], Siddhartha Datta[a]

[a]*Chemical Engineering Department, Jadavpur University, Kolkata 700032, India, Tel. +91 96817 61118; email: mailtotiyasha@gmail.com (T. Kanjilal), Tel. + 91 94774 02745; email: kalpscheme@gmail.com (K. Biswas), Tel. +91 9836402118; Fax: +91 33 2414 6203; emails: c.bhatta@gmail.com, cbhattacharyya@chemical.jdvu.ac.in (C. Bhattacharjee), Tel. +91 98301 08902; emails: sdatta@chemical.jdvu.ac.in, sdatta_che@rediffmail.com (S. Datta)*
[b]*Department of Biotechnology, Lovely Professional University, Jalandhar, Phagwara, Punjab 144411, India, Tel. +91 84274 37372; email: 4153.swaminathan@gmail.com (S. Babu)*

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ABSTRACT

Utilization of biological waste in treatment of industrial effluents is an emerging field of research. In present context of waste management, bio-adsorbent-based techniques are well-established as inexpensive and eco-friendly approach for cleaning up contaminated effluents from various industries and as a part of sustainable process developments. Mango seed integuments have been used in this study as biological waste. The main objective of this study was based on the removal of heavy metal lead (Pb) (II) from paint industry effluent using the mango seed integuments. Efficiency of the process was optimized with variation of the process parameters such as adsorbent dosage, contact time, initial [Pb(II)] concentration, and adsorbent nature. The nature of adsorption was also assessed using standard isotherms. This work showed the potential of the mango seed integuments as bio-adsorbent for removal of lead ions from paint industry effluent.

Keywords: Bio-adsorbent; Mango seed integuments; Lead removal; Paint industry effluent; Adsorption; Response surface methodology

1. Introduction

Pollution due to anthropogenic activities is the greatest problem to the present ecosystems. In the last two millennia or so, the human population growth and indiscrete uses of earth's non-renewable resources have brought about rapid change of the earth rather undesirably. The heavy metal pollution among them is a serious threat to the environment [1]. These contaminants are discharged in aquatic system from various industries including paint and electroplating industries, textiles, refineries, mining, and so on [2].The aqueous metal ions are known to be toxic in nature, non-biodegradable, and more likely to accrue in human body, thus causing a number of health problems, diseases, and disorders. Among the toxic and hazardous metal ions are copper, lead, mercury, cadmium, and chromium [3]. Stringent contaminant limit has been put into practice by World Health Organization to counter this predicament. Permissible

*Corresponding author.

concentrations for copper and lead in drinking water, for instance, should be as low as 2 and 0.01 ppm, respectively [3]. Accordingly, innovative economic processes for water and waste water treatment are continuously developing. This study aims removal of Pb(II) from paint industry effluent using an eco-friendly, low-cost, easily accessible bio-adsorbent.

Lead can be absorbed through ingestion into the gut, through inhalation, and through the skin [4]. Major health aspects due to Pb(II) poisoning are reported as nervous and renal breakdown, weakness, headache, brain damage convulsion, behavioral disorder, and constipation [2]. Conventional techniques for removing dissolved heavy metals include chemical precipitation, carbon adsorption, electrolytic recovery, ion exchange, chelation, and solvent extraction or liquid membrane separation [5–8]; all exhibit several disadvantages, such as high cost, incomplete removal, low selectivity, high energy consumption [9], and generation of toxic slurries that are difficult to eliminate [10,11]. Emphasis is pivoted particularly in utilization of abandoned agro-waste and natural waste products. The advantages of adsorption over other conventional approaches include minimum cost, high efficiency, minimization of chemical and biological sludge, and renewal of adsorbent, and possibility of metal recovery [2].

In order to reduce the cost of an adsorption system, some attempts have been made to find low-cost alternative adsorbents. A wide variety of materials such as *Aspergillus niger* biomass, algal biomass, *Spirogyra rhizopus* biomass, rice husk, bark, wheat shell, citric acid-esterifying wheat straw, dehydrated wheat bran, carbonized press mud, tree fern, apple pomace and wheat straw, coir pith, cotton, shell of bittim, banana stalk waste, dolomitic sorbents, chitosan, wood sawdust, palm kernel fiber, jute fiber, waste of sugarcane, perlite, raw kaolin, pure kaolin, calcined raw kaolin, calcined pure kaolin, NaOH-treated raw kaolin, palygorskite, zeolite, Leca (clay), and fly ash have been investigated with varying degrees of success [12–37]. Mango seed kernel has been studied as an adsorbent for the removal of methylene blue and safranine dye from its aqueous solutions [38,39].

Mango (*Mangifera indica* L.), belonging to the family Anacardiaceae, is one among the most cultivated fruit in the world. Quite a lot of mango wastes are produced annually from factories. Because mango is a seasonal fruit, and about 20% of fruits are processed for products including puree, nectar, leather, pickles, and canned slices, among others, that have worldwide popularity [40].

In this study, attention is being devoted to the utilization of the agricultural solid waste since most agricultural solid wastes are inexpensive, abundant, and easily available, and consequently, the fundamental focus is on the feasibility of low-cost materials that were derived from agricultural wastes for the removal of heavy metal from industrial effluents.

Objective of this study was to investigate the feasibility of mango seed integuments as bio-adsorbent in removal of Pb(II) from industrial effluents. Emphasis is given on the effect of operating variables and their interactive effect on overall removal efficiency and optimization of the process condition to maximize the overall removal percent of Pb(II) ions from aqueous solution using response surface methodology.

2. Materials and methods

2.1. Collection and preparation of adsorbent

Ripe mango seeds of Alphonso variety as by-products were collected after mango pulp processing, from Tai Industries limited, Kolkata, India. The seed obtained after processing (removal of epicarp and mesocarp) is the endocarp with seed inside it, and for the present study, only the endocarp (integument) is used; the seed and seed cover inside were removed manually. The integuments were used in order to study Pb(II) adsorption.

The raw integuments (untreated) and its immersion in NaOH (treated) were studied individually, as the potential adsorbents, in batch mode for different process parameters and isothermal experiments. The integuments were washed with distilled water and then immersed in an HCl solution (0.01 N) to remove impurities for 24 h. They were then rinsed with distilled water. Next, few of the integuments were dried in an oven at 70°C for 5 d to reach a constant weight. In order to powder the matters, the dried integuments were chopped and then grinded using a blender. The powder was then screened in a sieve with a nominal size of 110 μm and labeled as the untreated sample. The remaining HCl-treated integuments (but not dried in oven) was immersed in 1 N NaOH solution for 48 h after washing it with distilled water. Next, they were rinsed again with distilled water and subsequently dried in oven at 70°C for 5 d, and further, they were powdered by chopping and grinding. The powder was then screened using sieve (110 μm) and labeled as the alkali-treated sample, and further, the sieved mango seed integuments samples are separately used to treat a batch of effluent containing Pb(II).

2.2. Reagents

Lead Nitrate (A.R. grade), hydrochloric acid, and sodium hydroxide were obtained from Merck, Mumbai, India. Industrial effluent was collected from a paint industry nearby Kolkata.

A stock solution of Pb(II) ions (1 g/L) was prepared by dissolving $Pb(NO_3)_2$ in deionized water. All working solutions were prepared by diluting the stock solution with deionized water.

2.3. Analytical technique

Atomic adsorption spectrophotometer (AAS- spectra A Analyst 200, Perkin Elmer, USA) was used to quantify the metal ions in experimental reaction mixtures. The procedure is based on flame absorption (all the measurements were carried out in air/acetylene flame), and it depends upon the fact that metal atoms absorb strongly at discrete characteristic wavelengths, which coincides with the emission spectra lines of the particular metal. For lead metal ion, the characteristic wavelength was found to be 283.3 nm. AAS was used for its high degree of freedom from the interference of its environment, that is, presence of other elements; traces of one element can be accurately determined in presence of high concentration of other elements. The method is also almost independent of the flame temperature, since we are usually dealing with atoms in an unexcited or ground state.

2.4. Bio-adsorption study

Batch adsorptions for different parameter were carried out to study the adsorption efficiency of Pb(II) on adsorbent. Batch samples of aqueous Pb(II) solution with alkali-treated and untreated mango seed integuments were prepared.

The adsorption efficiency was studied by varying pH of batch from 3 to 9. The flasks were kept in the BOD incubator with rotary shaker under constant process parameters (rpm: 80, temperature: 30˚C, time: 300 min, Pb(II) conc.: 0.05 g/L).

The adsorption efficiency was studied by varying temperature of batch from 20 to 70˚C. The constant process parameters were maintained (rpm: 80, pH: 7, time: 300 min, Pb(II) conc.: 0.05 g/L).

The adsorption efficiency was studied by varying exposure time of batch (30 min, 60 min, 90 min, 120 min, 150 min, 180 min, and 200 min).The constant process parameters were maintained (rpm: 80, pH: 7, temperature: 30˚C, Pb(II) conc.: 0.05 g/L).

The adsorption efficiency was studied by varying the initial Pb(II) ion concentration in the batch (0.01, 0.02, 0.03, 0.04, and 0.05 g/L). The constant process parameters were maintained (pH: 7, rpm: 80, temperature: 30˚C, time: 300 min).

The adsorption efficiency was studied by varying the amount of mango seed integuments (alkali treated and untreated) from 0.5 to 3 g in the batch. The constant process parameters were maintained (rpm: 80, pH: 7, temperature: 30˚C, Pb(II) conc.: 0.05 g/L, time: 300 min).

The adsorption efficiency was studied by varying the agitation speed (40, 60, 80, 100, and 120 rpm). The constant process parameters were maintained (pH: 7, temperature: 30˚C, Pb(II) conc.: 0.05 g/L, time: 300 min).

The batch samples after treatment were filtered using Whatmann filter paper, and then, the concentration of Pb(II) in the filtrate was measured using AAS.

The results were expressed as the removal efficiency *(E)* of the adsorbent toward metal ions or the % removal, which was quantified using the following equation:

$$\%E = 100 \times (C_0 - C_f/C_0) \quad (1)$$

where C_o and C_f are taken to be the initial and final equilibrium concentration (g/L) of metal ions in solution, respectively.

2.5. Determination of point zero charge (pH_{pzc})

The charge on all functional groups of the adsorbent approaches zero at the point of zero charge (pH_{pzc}). To determine pH_{pzc}, 0.1 g of mango seed integument (alkali treated and untreated) were added to 0.05 liter of KNO_3 solution (0.01 N), and the initial pH was adjusted to be between 2 and 10 using KOH (0.01 N) and HNO_3 (0.01 N) solution. The flasks were kept in shaker for 48 h. The mixture was filtered, and the pH of the solution was measured in order to calculate the final pH. The intersection point of the obtained curve indicated the amount of point zero charge.

2.6. FTIR and FESEM analysis

The batch sample of Pb(II) solution and mango seed integuments (alkali treated and untreated) were kept under constant process parameters (30˚C, pH: 7, time: 300 min, 80 rpm, 0.05 g/L Pb(II) conc.). Then the samples were taken for analysis in FTIR (ATR 8200 h/8200HA) and FESEM (JOEL JSM 6700F).

2.7. Adsorption isotherm

One of the objectives in this study was to determine the best-fitted adsorption isotherm for Pb(II) adsorption on mango integuments. Bio-adsorption isotherms are the most important information for analyzing and designing a bio-adsorption process [41]. To examine the relationship between the amount of the adsorbate adsorbed (q_e) to its concentration in the aqueous phase (C_e) at equilibrium, the adsorption isotherm model is employed for fitting the data. In the present investigation, the results of Pb(II) adsorption studies were fitted to model of Langmuir and Dubinin–kaganer–radushkevich (DKR) isotherm with varying initial Pb(II) ion concentration in the batch.

2.8. Experimental design procedure

The experimental working conditions were selected in the subsequent ranges:

Contact time 30–180 min, adsorbent loading weight 0.5–3 g/L, and initial metal ion concentration 0.01–0.05 g/L. A total of 20 experimental runs were conducted with six center points. Experiments were performed according to face-centered central composite design (FCCD) formulated through Design Expert® 8.1 Software (Stat-Ease, Inc., Minneapolis, USA) to determine the effect of various operational parameters, viz. initial metal ion concentration, contact time, and adsorbent loading weight on the removal percent of Pb(II). In order to examine the effects of individual parameters as well as their relative effects on the response variable, a general second-order polynomial model was selected and is deduced by Eq. (2).

$$y = b_o + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} b_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=1}^{3} b_{ij} X_i X_j \quad (2)$$

where "y" is the response variable, b_o is the constant, $b_i$is the linear coefficient, $b_{ii}$the quadratic coefficient, $b_{ij}$the interaction coefficient, and X_i is dimensionless coded variables (X_1depicted for contact time, X_2 for adsorbent loading weight, and X_3 for initial metal ion concentration). The regression of Eq. (2) was considered for optimization to maximize "y" using numerical optimization program of the same design software where the responses for each combination which have been determined experimentally were given as input for optimization. Response surface methodology was used to maximize the removal of Pb(II). To ascertain the reproducibility of the data, all experimental runs were conducted in triplicate.

3. Results and discussions

3.1. Effect of different parameters

3.1.1. Determination of point zero charge (pH_{pzc})

The curve for both treated and untreated mango integuments did not intersect in the pH range of 2–10, so the point zero charge for the mango integuments could not be determined, but in the pH range of 5–7, it was seen that there is very less variation in charge; hence, it was taken as the optimum value, and further, it was verified that whether in that pH (say pH 7), the percentage adsorption of Pb(II) is maximum or not (Fig. 1).

3.1.2. Effect of pH

The adsorption capacity of mango integuments increased with increase in pH, and it is seen that at pH 7, there was maximum adsorption of Pb(II) by mango integuments, and it was taken to be the optimum pH for all other parameters. May be it is that at that pH as the net charge is approximately zero (from pH_{pzc}), adsorption is taking place due to the formation of hydrogen bonds and Van der Waals force of interaction. And also it is clear from the plot that the treated mango integuments have a higher adsorption capacity of Pb(II) than the untreated mango integuments in the pH range of 3–9 (Fig. 2).

3.1.3. FTIR analysis

The FTIR spectrum of samples indicated weak and broad peaks in the region of 4,000–500 cm^{-1} (Fig. 3).

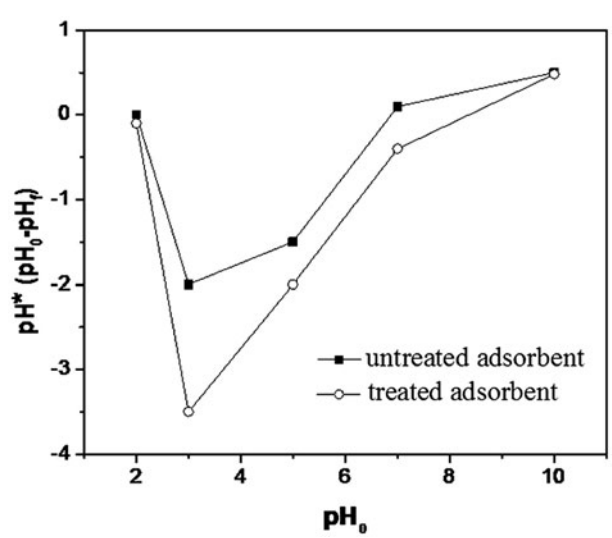

Fig. 1. Effect of point zero charge.

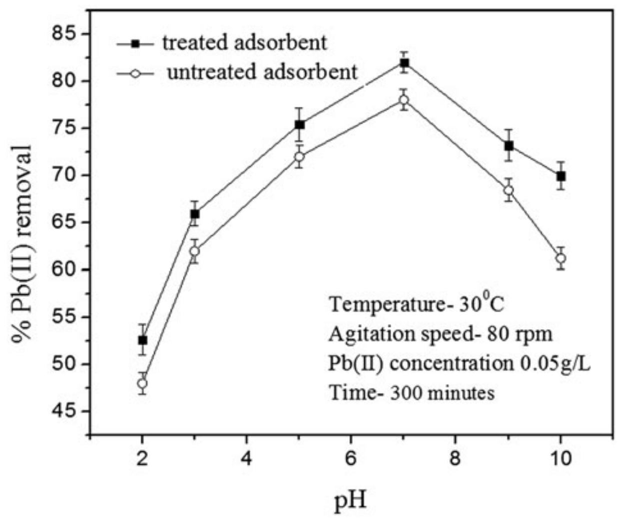

Fig. 2. Effect of pH on the removal of Pb(II) ions using mango seed integuments.

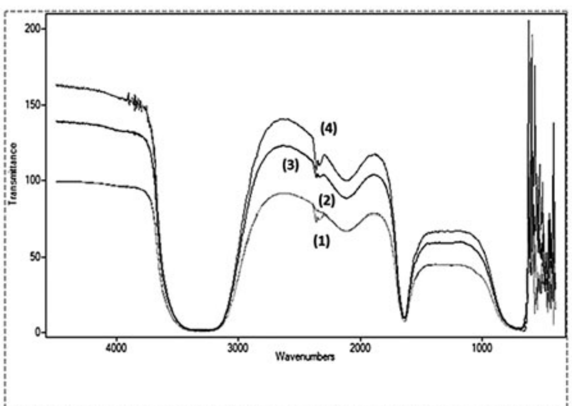

Fig. 3. Effect of FTIR analysis showing the surface chemistry of mango seed integuments. (1) Untreated mango integument before adsorption, (2) Treated mango integument before adsorption, (3) Untreated mango integument after adsorption, (4) Treated mango integument after adsorption.

The FTIR bands can be assigned to the presence of carboxyl, lactones, and phenols groups [39]. The FTIR spectrum of treated and untreated mango integuments indicated the strong peak of hydroxyl (O–H) group at wave number 3,329 cm^{-1}. The adsorption bands around 2,360 and 2,334 cm^{-1}(two medium-sized peaks) corresponds to primary and aliphatic amines. The peak around 2,100 cm^{-1} denotes the presence of alkyne group. The Adsorption band around 1,634 cm^{-1} indicates the alkene group. An adsorption band around 714 cm^{-1} denotes aldehydes and ketonic group. The peak at 599 cm^{-1} was attributed to aromatic C–H bending. The mango integuments are composed of cellulose, lignin, and hemicelluloses. The treatment of mango integument by NaOH shows the high lignin content in mango seed, consequently producing cellulose acetate ($C_6H_{10}O_5$) [42].

3.1.4. Effect of temperature

From the plot (Fig. 4), it is clear that the rise in temperature causes reduction in the percentage removal of Pb (II); it might be because of breakage of bonds due to higher temperature and the rise in the intermolecular collision. And it is seen that the treated mango integuments remove more lead as compared to the untreated mango integuments and both of them behave in a similar way with the rise in the temperature. From the plot, it is also clear that the percentage removal of Pb(II) is maximum at a temperature of 30˚C; hence, it is considered to be the optimum temperature for all the parameters.

3.1.5. Effect of contact time

It is seen (Fig. 5) that initially adsorption increases slowly as it takes time for acclimatization and later the adsorption increases exponentially and reaches a maximum value (at 120 min) and as the time increases adsorption decreases, due to desorption (may be due to competition between the Pb(II) ions). In this case, it can be interpreted that desorption in case of untreated is gradual and keeps on increasing with time, but in

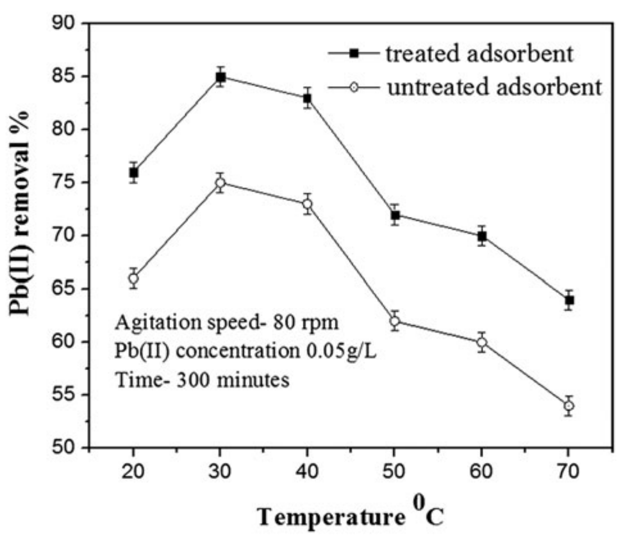

Fig. 4. Effect of temperature on the removal of Pb(II) ions using mango seed integuments.

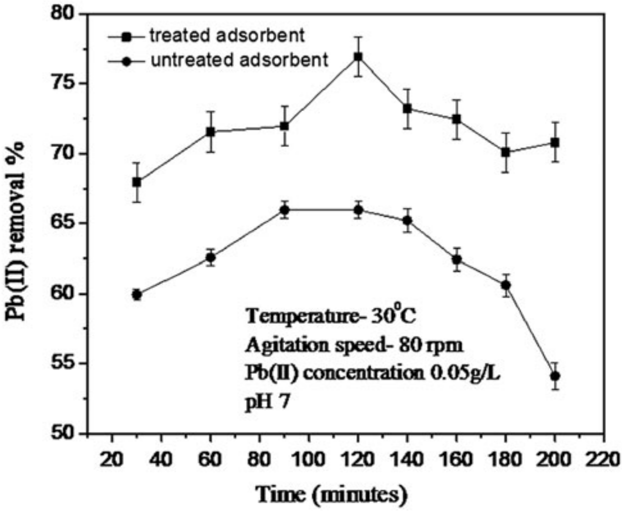

Fig. 5. Effect of contact time on the removal of Pb(II) ions using mango seed integuments.

case of treated, it is slightly abrupt, but later, desorption is lesser than untreated (from 160 to 180 min).

3.1.6. Effect of initial lead(II) concentration

The plot (Fig. 6) shows that with the increase in concentration of initial Pb(II) ions, the adsorption increases and also depicting that the treated mango integuments can remove higher percentage of Pb(II) than the untreated mango integuments. But at higher concentration, the plot becomes constant which infers that all the adsorption sites are occupied and no more Pb(II) ions can be adsorbed.

3.1.7. Effect of adsorbent loading weight

The dependence of Pb(II) adsorption on adsorbent dose was studied by varying the amount of adsorbents from 0.5 to 3 g, while keeping other parameters (concentration and contact time) constant. It can be deduced that the percent removal of lead increases with increasing adsorbent doses from 0.5 to 1.5 g (Fig. 7). It must be also noted that there were decreases in removal percentages when adsorbent dose was increased from 2 to 3 g. The reason for such behavior can be intramolecular interaction between adsorbent (not yet determined) and the steric hindrance by the adsorbent molecule to the adsorbate molecule

3.1.8. Effect of agitation speed

Optimum agitation is required for better adsorption and higher removal of Pb(II), and it is clear from the results obtained. As the agitation speed is increased from 40 to 80 rpm, the percentage removal of Pb(II) also increased, but after that, as the agitation is increased further to higher speed, the adsorption decreased because due to a very higher agitation speed, the Pb(II) could not get adsorbed on mango integuments. Also in this case, the treated mango integuments show higher percentage removal of Pb(II) than the untreated mango integuments. From the plot (Fig. 8), it is determined that at an optimum agitation

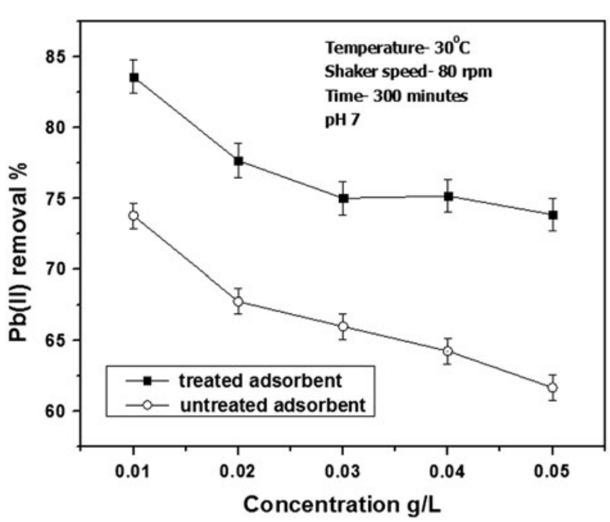

Fig. 6. Effect of initial Pb concentration on the removal of Pb(II) ions using mango seed integuments.

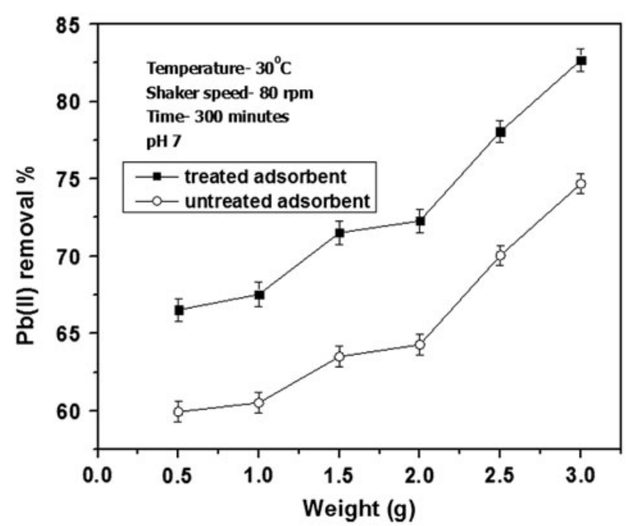

Fig. 7. Effect of adsorbent loading weight on the removal of Pb(II) ions using mango seed integuments.

speed, the adsorption and removal of Pb(II) by mango integuments is maximum and that optimum speed is 80 rpm.

3.1.9. FESEM analysis

Field emission scanning electron micrographs were viewed so as to confirm the adsorption of Pb(II) on mango integuments, and the results obtained were positive. From Fig. 9, it was evident that the FESEM images of mango integument samples showed considerable numbers of holes and spots where there is a good possibility for Pb(II) to be trapped and adsorbed into these spaces.

3.2. Adsorption isotherm

The observed data of adsorption were fitted in standard isotherms. The data plot satisfied the Langmuir and DKR isotherm model of Pb(II) ions on the adsorbent surface. The adsorption isotherms were obtained in sufficient time of 300 min at different initial concentration (0.05–0.25 g/L).

The Langmuir model is expressed based on the assumption of monolayer adsorption on to adsorbent surface, finite capacity adsorption for adsorbate, and the occupation of a metal ion on one site [43]. The Langmuir model is expressed as:

$$C_e/Q_e = (1/q_m K_L) + (C_e/q_m) \quad (3)$$

where q_m(mg/g) is the maximum amount of metal ion per unit mass of the adsorbent, forming a complete

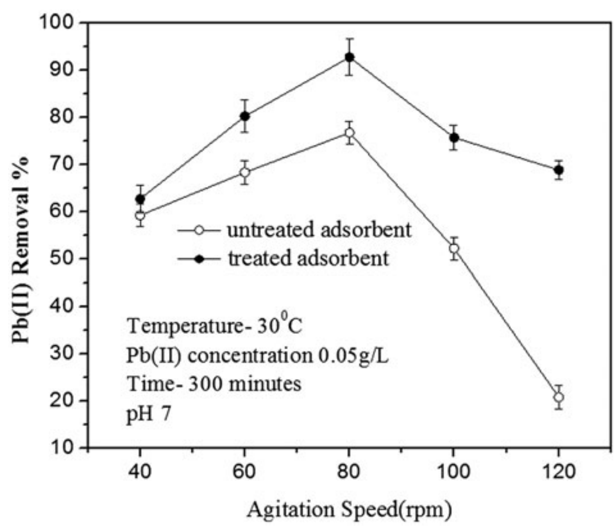

Fig. 8. Effect of agitation speed on the removal of Pb(II) ions using mango seed integuments.

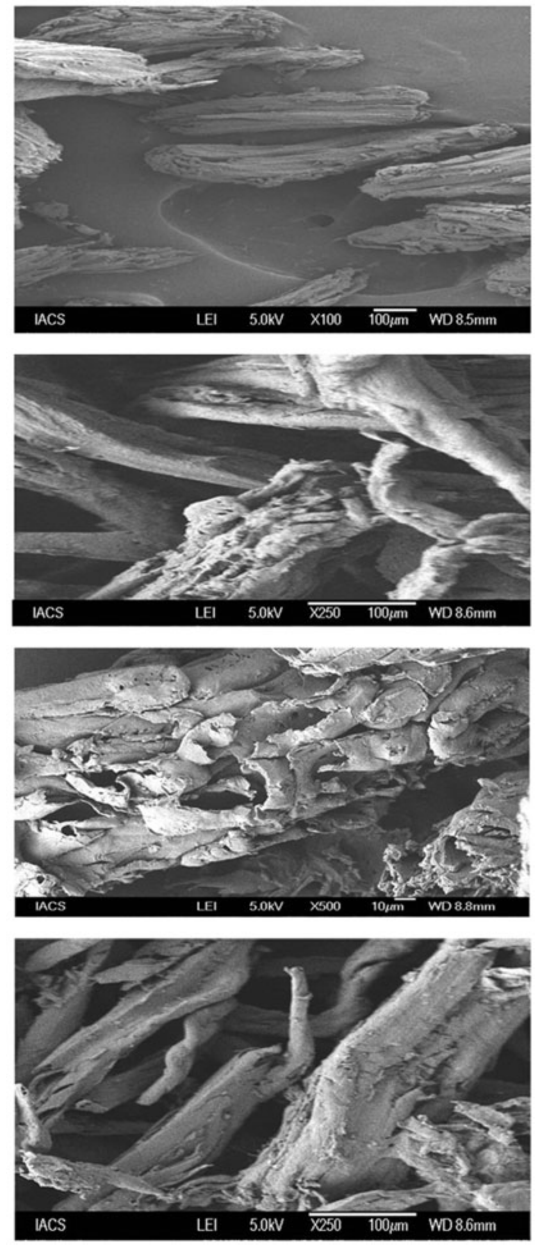

Fig. 9. Micrographs of mango seed integuments before and after Pb(II) ions adsorption over it. (a) Untreated mango integuments before adsorption, (b) Treated mango integuments before adsorption, (c) Untreated mango integuments after Pb(II) adsorption, (d) Treated mango integuments after Pb(II) adsorption.

monolayer on the surface and K_L (l/g) is the Langmuir constant which signifies the energy of adsorption.

The plots (Fig. 10(a) and (b)) of $1/Q_e$ vs. $1/C_e$ for both alkali-treated and untreated mango seed integuments after adsorption of Pb(II) ions on it were drawn. From the slope and intercept q_m and K_L can be calculated.

An important feature of the Langmuir adsorption is expressed in terms of R_L, a dimensionless separation factor [44]. R_L indicates the behavior of the process (Table 1).

$R_L > 1$, unfavorable process

$R_L = 1$, linear process

$0 < R_L < 1$, favorable process

$R_L = 0$, irreversible process

It is expressed as:

$$R_L = 1/(1 + K_L C_O) \quad (4)$$

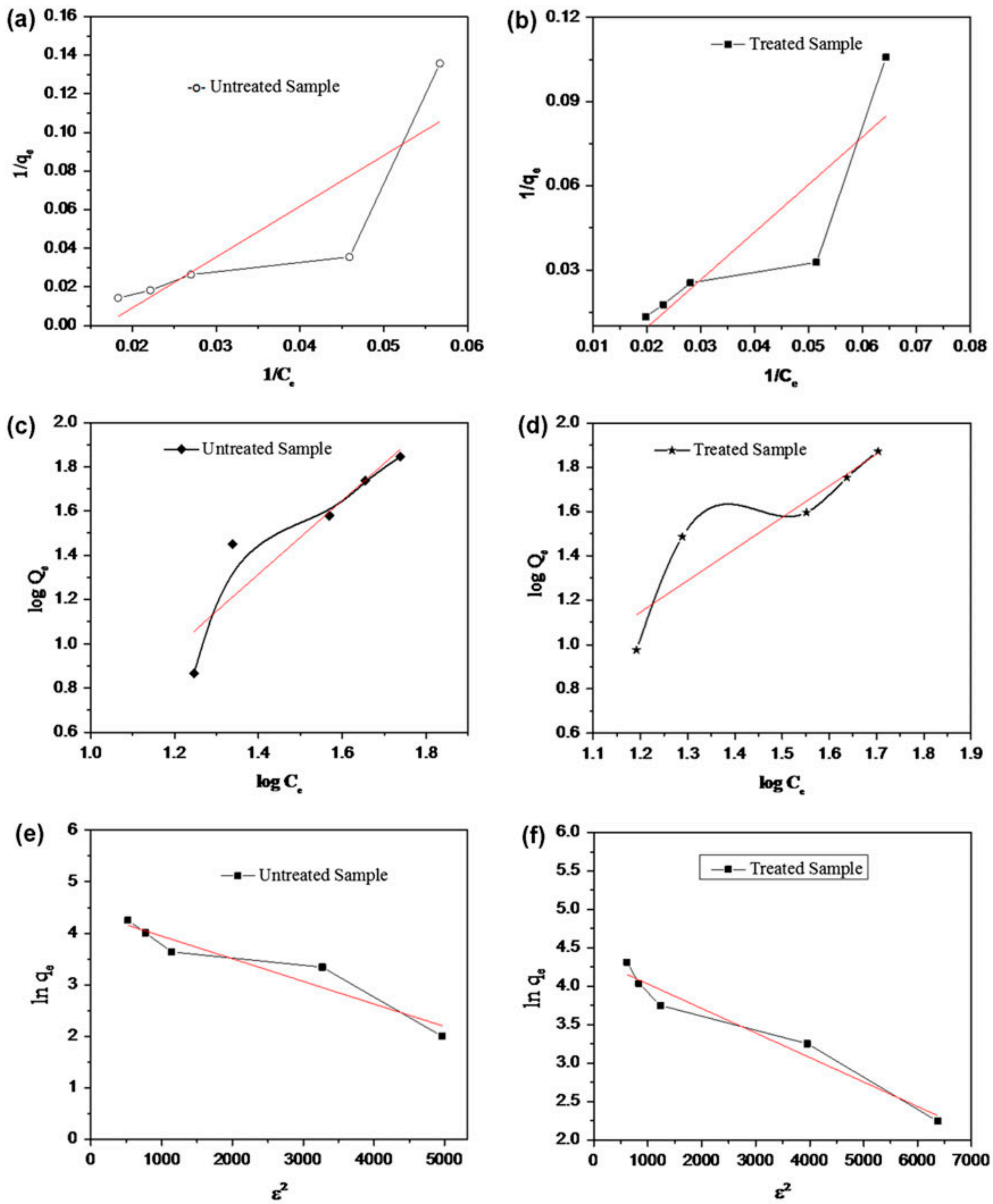

Fig. 10. Adsorption isotherms. (a) Langmuir isotherm for untreated mango seed integuments, (b) Langmuir isotherm for treated mango seed integuments, (c) Freundlich isotherm for untreated mango seed integuments, (d) Freundlich isotherm for treated mango seed integuments, (e) DKR isotherm for untreated mango seed integuments, (f) DKR isotherm for treated mango seed integuments.

Table 1
Langmuir isotherm

	Untreated mango seed integument		Treated mango seed integument	
		S.D		S.D
K_L (l/mg)	−0.04346	0.03395	−0.02447	0.02262
q_m (mg/g)	2.62996	0.9155	1.69898	0.54866
R^2	0.64452		0.68226	
R_L	1.0111		1.00704	

where C_o is the highest initial Pb(II) concentration.

As R_L values for both alkali-treated and untreated mango seed integuments (after adsorption) are almost equal to 1, the process is favorable.

The Freundlich model is expressed considering the interactions between adsorbed molecules in a heterogeneous system. This model is expressed as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{5}$$

where K_f (mg/g) is Freundlich constant which represents bonding energy and "n" is the heterogeneity factor which indicates the feasibility of the adsorption process. For $n > 1$, it is favorable adsorption process (Table 2).

Table 2
Freundlich isotherm

	Untreated mango seed integument		Treated mango seed integument	
		S.D		S.D
K_f (mg/g)	−1.02987	0.64531	−0.56902	0.5204
$1/n$	1.67419	0.42435	1.42785	0.34974
R^2	0.78454		0.79662	

The plots (Fig. 10(c) and (d)) of log q_e vs. log C_e help us in determining the intercept (K_f) and slope (n).

As the "n" values for alkali-treated and untreated mango seed integuments (after adsorption) are less than 1, the process is not favorable.

The DKR isotherm helps in predicting the nature of adsorption by determining the apparent energy of adsorption. This model does not assume a homogenous surface or constant sorption potential [45]. DKR isotherm is expressed as:

$$\ln(q_e) = \ln(X_m) - \beta\varepsilon^2 \tag{6}$$

where X_m (mg/g) is the maximum sorption capacity, β (mol^2/kJ^2) is the activity coefficient related to mean sorption energy, and ε is the Polanyi potential which is expressed as:

$$\varepsilon = \mathrm{RT}\ln(1 + 1/C_e) \tag{7}$$

where R (kJ/kmol K) is the gas constant.

The plots (Fig. 10(e) and (f)) of ln (q_e) vs. ε^2 give the slope β and intercept X_m. And the adsorption energy (E) is calculated using the relation:

$$E = (-2\beta)^{-1/2} \tag{8}$$

For,

(1) Physio-sorption, $E < 40$ kJ/mol
(2) Chemisorption, $E > 40$ kJ/mol
(3) Chemical ion exchange, 8 kJ/mol < E < 16 kJ/mol
(4) Physical adsorption, $E < 8$ kJ/mol

Hence, we can infer that the mango seed integuments follow both Langmuir and DKR isotherm (Table 3) and there is monolayer formation with physic-adsorption process.

Table 3
DKR isotherm

	Untreated mango seed integument		Treated mango seed integument	
		S.D		S.D
β (mol^2/kJ^2)	−0.000449756	0.0000639329	−0.000318837	0.0000365133
X_m (mg/g)	4.40419	0.17515	4.34968	0.12526
R^2	0.92379		0.94953	
E (kJ)	33.342		39.6	

Table 4
Experimental ranges and levels of factors for response surface study

Uncoded factors	Coded factors[a]	Units	Uncoded values	Coded values
W	X_1	g/L	0.5	−1
			1.5	0
			3	+1
T	X_2	minute	30	−1
			105	0
			180	+1
C_0	X_3	g/L	0.5	−1
			1.75	0
			3	+1

[a]$X_1 = (w - 1.5)/2$.
$X_2 = (t - 105)/2$.
$X_3 = (C_0 - 1.75)/2$.

Table 5
Experimental design matrix

Sl No.	t (min)	w (g/L)	C_0 (g/L)	R (%)
1	30	1.75	30	53.20
2	30	3.00	10	61.09
3	30	3.00	50	64.39
4	30	0.5	10	44.68
5	30	0.5	50	67.92
6	105	1.75	30	59.25
7	105	1.75	30	59.25
8	105	1.75	10	59.40
9	105	0.5	30	54.70
10	105	1.75	30	59.25
11	105	1.75	30	59.25
12	105	1.75	30	59.25
13	105	1.75	30	59.25
14	105	1.75	50	74.65
15	105	3.00	30	60.87
16	180	3.00	50	71.00
17	180	1.75	30	59.40
18	180	3.00	10	64.30
19	180	0.5	10	48.60
20	180	0.5	50	74.91

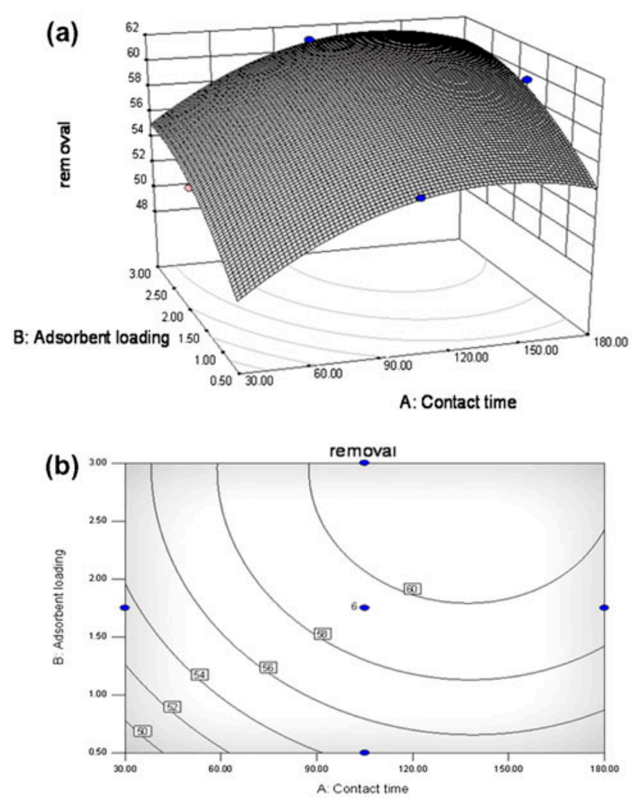

Fig. 11. Central composite design model showing the effect of contact time and the adsorbent loading weight on the removal percent of Pb(II). (a) In three-dimensional format. (b) In contour format.

3.3. Experimental design analysis

As per the results obtained till now, it is clear that the alkali-treated mango integuments show more efficient removal of Pb(II) ion from the effluent. Thus, considering the different process controlling parameters for alkali-treated mango seed integument, such as dose of bio-adsorbent (w) was varied within the range of 0.5–3.0 g, initial metal ion concentration (C_0) was investigated in the range of 0.01–0.05 g/L, and contact time (t) observed up to 180 min. Contact time (t), adsorbent loading weight (w), and initial metal ion concentration (C_0) were varied as process variables according to the “FCCD” (Tables 4 and 5) for optimization of the Pb(II) removal percent (E) as response. FCCD was created by entering factors “w”, “t”, and

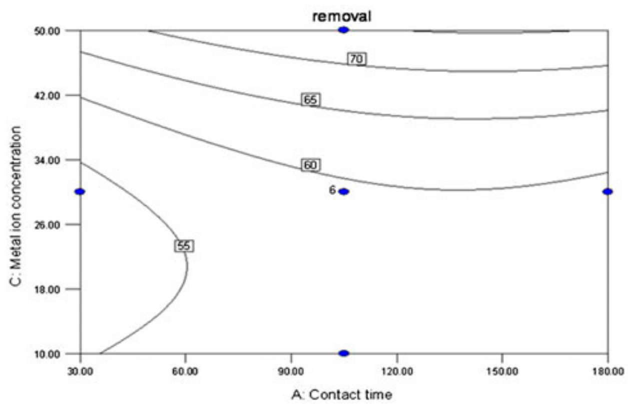

Fig. 12. Central composite design model showing the effect of contact time and the metal ion concentration on the removal percent of Pb(II).

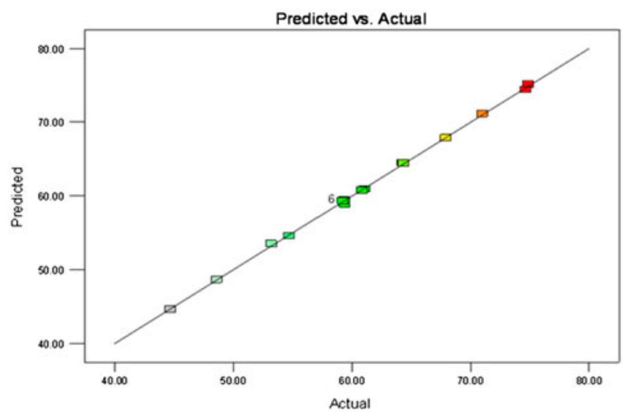

Fig. 13. Plots of the model predicted values with actual experimental values.

"C_0" in terms of ±1 level to perform RSM and to predict the effect of process variables on Pb(II) removal.

According to statistical model fit summery (Table 5), a quadratic model was taken as the best-fitted model with lower standard deviation (0.24) and lowest PRESS value (4.39), the higher adjusted and the predicted R^2 value (0.99) and adequate precision >4 in comparison to other models.

According to ANOVA, model insignificant terms (p-value > 0.05), are neglected, and the final equation in coded form is expressed as.

$$R(\%) = 59.32 + 2.69X_1 + 3.08X_2 + 7.48X_3 + 0.81X_1X_3 - 4.94X_2X_3 - 3.13X_1{}^2 - 1.65X_2{}^2 + 7.59X_3^2 \quad (9)$$

It is evident from Eq. (4) that X_1, X_2, and X_3 have linear correlation with the percent removal of lead ions. The quadratic relation of X_1 and X_2 has negative effect and the interactive effect of X_2 and X_3 also has negative effect on $R\%$. The removal of Pb(II) from the aqueous solution increased with increasing "t", "w", and "$C_{0''}$ values with significant contribution of C_0. Effect of varying contact time (t) and adsorbent loading weight (w) on Pb(II) removal is shown in response surface plot (Figs. 11(a) and (b) and 12)

The Fig. 13 illustrates the predicted removal (%) vs. actual removal plot which proves the significance of the model for maximization of the Pb(II) removal. Numerical optimization depicts the optimum arrangement of all three parameters to achieve maximum removal percent (75.23%) of Pb(II) ion from aqueous solution. Optimum point obtained at contact time of 118.77 min, adsorbent loading weight 0.77, and metal ion concentration of 49.87 with desirability factor of 0.97.

4. Conclusion

The bio-adsorption of Pb(II) ions from aqueous solution onto mango integuments has been investigated in this article. Bio-adsorption tests were carried out as a function of contact time, bio-adsorbent dose, and metal concentration. Experimental results indicate that mango integuments were effective in removing Pb(II) ions from aqueous solutions. Initial metal ion concentration was the most significant factor controlling the percent removal of the metal ions from aqueous solution. The interactive effect of contact time and the adsorbent loading weight was found having no significant effect on the removal efficiency. Under the optimum combination of the variables, maximum removal achieved was 75.23% with initial metal ion concentration of 49.79 g/L, adsorbent loading weight of 1.62 g/L, and contact time of 118.7 min. The percentage of removal illustrated positive linear correlation with all three variables. Quadratic relation of initial metal ion concentration only showed positive effect, but the other two presented negative effect on the removal efficiency. The model fit summery shows the significance of the model and suggests the potency of using mango seed integuments as the bio-adsorbent of lead ions from aqueous solution. From the results, it can be concluded that abundantly available mango seed integuments can be used as efficient adsorbent for lead ions removal.

Symbols	Representation	Units
C_0	initial dye concentration	g/L
C_t	final dye concentration	g/L
C_e	equilibrium concentration of metal solutions	g/L
K_f	freundlich biosorption constant	
n	heterogeneity factor	
q_m	amount of metal ion per unit biosorbent mass	mg/g
Q_e	adsorbed amount of Pb(II) per gram of bio-adsorbent at equilibrium	
K_L	langmuir biosorption constant	1/g
R	gas constant	kJ/kmol K
R^2	correlation coefficient	
R_L	separation factor	
X_m	maximum sorption capacity	mg/g
β	activity coefficient	mol^2/kJ^2
ε	polanyi potential	
E	adsorption energy	kJ
w	adsorbent loading weight	g
t	contact time	minutes
y	response variable	
b_o	constant term	
b_i	linear coefficient	
b_{ii}	quadratic coefficient	
b_{ij}	interaction coefficient	
X_i	dimensionless coded variables	

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