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Multi-variant sorption optimization for the uptake of Pb(II) ions by Jamun Seed Waste

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In the present study, jamun seed waste has been explored for the removal of Pb(II) ions from aqueous solution. The multi-variant sorption optimization was achieved by the factorial design approach. 99.91% of Pb(II) ions was removed from aqueous solution. The results predicted by the model were in good agreement with the experimental results (the values of R^2 and $R^2_{adj.}$ were found to be 99.89% and 99.95%, respectively). Langmuir and D-R isotherm studies were carried out to find adsorbent's capacities (183.9 ± 0.31 mg/g and 184.5 ± 0.16 mg/g respectively), sorption free energy 13.17 ± 0.16 and RL values in the range of 0.05–0.77, suggested the favorable chemical and/or ion exchange nature of the sorption process. The FT-IR study was carried out for unloaded and Pb(II) ions loaded jamun seed, indicated, Pb(II) ions associated with nitrogen and oxygen of jamun seed containing moieties during the adsorption process. The proposed method was successfully validated and applied for the treatment of Pb(II) ions contaminating drinking water.

Keywords: Optimization, Pb(II) ions removal, Jamun seed waste, Response surface methodology, Factorial design approach.

INTRODUCTION

Heavy metal ions are conservative contaminants that are not easily biodegradable chemically or biologically. They are therefore permanent chemical overload in the environment[1]. Heavy metals are major pollutants of some ground and surface waters and are often present in industrial or urban wastewaters. Removal of trace amounts of heavy metal ions from wastewater and drinking water is of great importance due to their high toxicity[2–4]. Lead is a heavy metal which has been introduced into natural water from a variety of sources such as lead storage batteries, lead smelting, tetraethyl lead manufacturing, mining, plating, ammunitions and the ceramic glass industries[5]. Lead has been a major focus in wastewater treatment because it is associated with many health hazards[6]. The major bio-chemical effect of Pb(II) ions is its interference with heme synthesis, which leads to hematological damage. Thus, it is imperative that lead is removed from an effluent before being discharged into the sewage system or into the aquatic environment. The permissible limit of lead in drinking water is 0.05 mg/l[7]. Above the tolerance limit it is toxic. In children, lead causes a decrease in intelligent quotient score, retardation of physical growth, hearing impairment, impaired learning, as well as decreased attention and classroom performance. In individuals of all ages, lead can cause anaemia, kidney failure, brain diseases and impaired function of peripheral nervous system, high blood pressure, reproduction abnormality, developmental defects, abnormal vitamin-D metabolism, colic-like abnormal pains, dementia, madness and in some situations, death[8]. Lead as a Pb^{2+} ion has a strong affinity for thio group and phosphate ion containing enzymes, ligands and biomolecules, thereby, inhibiting the biosynthesis of haeme units, affecting membrane permeability of kidney, liver and brain cells of human being. These result in either reduced functions or complete breakdown of these organs. Lead forms complexes with oxo-groups in enzymes to affect virtually all steps in the process of heamoglobin synthesis and porphyrin metabolism[8]. Adsorption is one of the easiest, safest and most cost-effective methods for the removal of these heavy metal ions. Abundantly available agricultural wastes such as orange peel[9] fruit peels[10], olive tree pruning waste[11], orange waste[12], pomegranate peel[13], pine cone activated carbon[14], grape waste[15], seaweeds[16], alginic acid[17], Cassia grandis seed[18], tree fern[19] and Grewia asiatica seed[20] have been reported sorbent for the removal of toxic heavy metal ions from aqueous solutions. This research investigated the removal efficiency of jamun seed waste for Pb(II) ions from an aqueous system and the multi-variant sorption optimization with respect to agitation time, temperature. Sorbent dose pH and the initial Pb(II) ions concentration was monitored using the Response Surface Methodology (RSM) approach. The conventional batch adsorption method is time-consuming as it requires a large number of experiments to determine the optimum value. A major disadvantage of the conventional method is that it uses a variation of only one parameter at a time, keeping the other parameters constant, and thus, the cumulative effect of all the affecting parameters at a time cannot be studied which leads to unreliable results[21]. However, in RSM, the interactions of two or more variables can be studied simultaneously. It results in higher percentage yields, reduced process variability, less treatment time and minimum costs. A possible sorption mechanism of Pb(II) ions onto jamun seed surface was also investigated[22].

MATERIALS AND METHODS

Adsorbate: Pb(II) ions

Stock solution of Pb(II) ions was prepared (1000 mg/l) by dissolving a required amount of lead nitrate $Pb(NO_3)_2$

(Merck) in distilled water. The stock solution was diluted with distilled water to prepare the working solutions (10–100 mg/l) with different pH (2.0, 5.5 and 9.0). HCl, acetate buffer and NaOH were used to maintain pH 2.0, 5.5 and 9.0 respectively. CH_3COOH, CH_3COONa, NaOH and HCl, were used of Merck (Darmstadt, Germany).

Adsorbent: jamun fruit seed

Jamun (Syzgium cumini L.) is an evergreen tropical tree in the flowering plant family Myrtaceae, native to India and Indonesia. It is also grown in other areas of Southeast Asia including Malaysia, Myanmar, Pakistan and Afghanistan. Jamun is a fast growing plant that can attain the height of about 30 m after about 30 years of growth. Jamun tree starts flowering in March and April. This is followed by fruiting (a berry) which appears in May–June[23]. Flesh of fruit was removed by eating and seed was washed with distilled water and dried in an oven at 100°C for 12 hours. The dried seed was ground and screened to uniform material for the batch experiments.

Batch experiments

The retention of Pb(II) ions onto jamun seed was conducted by performing batch experiments in a thermostated shaker at controlled temperature of 30°C for a period of 10–180 min at 150 rpm using a 250 ml conical flask containing different weighted amount of adsorbent (10–100 mg) and 10 ml of Pb(II) ions solution of different concentration (10–50 mg/l) and pH (2, 5.5 and 9). The residual concentration of Pb(II) ions in the solution was analyzed by Perkin Elmer Atomic Absorption Spectrophotometer. The % removal and sorption capacity were calculated by eq. 1 and eq. 2 respectively.

$$\%\ \text{Removal} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

$$q_e = \frac{C_o - C_e}{m} \times V \qquad (2)$$

Where C_o and C_e are the initial and equilibrium concentrations (mg/l) of Pb(II) ions solution respectively. Where q_e is sorption capacity (mg/g), V is the volume of solution (l) and m is adsorbent dose (g). All the batch experiments were done in duplicate and random order to evaluate pure error and minimize the effect of possible uncontrolled variables.

Mathematical and statistical procedure

Multi-variant sorption optimization for the sorption of Pb(II) ions onto the jamun seed was performed using Draper-Lin small composite design, RSM. The design contained eighteen batch experiments. Each experiment was performed at the different level of independent variables. The range and level of independent variables are summarized in Table 1. Response function (% removal) with two independent variables (X_i and X_j) is shown by eq. 3.

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_{II}X_1^2 + B_{12}X_1X_2 + B_{13}X_1X_3 + B_{14}X_1X_4 + B_{22}X_2^2 + B_{23}X_2X_3 + B_{24}X_2X_4 + B_{33}X_3^2 + B_{34}X_3X_4 + B_{44}X_4^2 \qquad (3)$$

where Y is the predicted dependent response (% removal), X_1-X_4 are the independent variables, B_0 is the intercept (or constant term), B_1-B_4 are the first order coefficients. B_{12}-B_{34} are the interaction coefficients and B_{II}-B_{44} are the (pure) second-order coefficients. The response function coefficients were determined by regression using Statgraphics plus 5.1 computer program[20].

Table 1. Levels of factors used in experimental design for removal of Pb(II) ions by jamun seed

Independent variable	Range	Coded levels		
		−1	0	+1
Amount (mg)	A (X_1)	10	55.0	100
Concentration (mg/l)	B (X_2)	5	27.5	50
pH	C (X_3)	2	5.5	9
Time (min)	D (X_4)	10	95	180

RESULTS AND DISCUSSION

Experimental design

The traditional sorption optimization is a uni-variant sorption optimization which has drawbacks of results reliability, time and cost factor as well. An alternate is RSM, which has advantages of results reliability, time, cost and prediction of optimum response[24]. Draper-Lin composite design was used to develop a correlation between the observed and predicted % removal of Pb(II) ions form the aqueous solution. The design of 18 experiments is summarized in Table 2 with the results of the experimental and predicted values of the % removal Pb(II) ions.

Table 2. Experimental design and results for the % removal of Pb(II) ions by jamun seed

Trail	Coded values				% Removal (Experimental)	% Removal (Predicted)
	A	B	C	D		
1	-1	-1	+1	-1	88.86	89.06
2	-1	-1	-1	-1	19.87	20.00
3	0	+1	0	0	98.43	98.77
4	+1	+1	-1	-1	6.87	6.50
5	+1	+1	+1	-1	96.12	96.32
6	0	0	0	-1	96.79	97.12
7	-1	+1	+1	+1	89.68	89.88
8	+1	0	0	0	96.04	96.38
9	0	0	+1	0	90.78	89.97
10	+1	-1	+1	+1	77.30	77.50
11	0	0	-1	0	25.54	27.02
12	+1	-1	-1	+1	56.92	56.55
13	-1	+1	-1	+1	18.78	18.41
14	0	-1	0	0	90.34	90.68
15	-1	0	0	0	95.99	96.33
16	0	0	0	+1	93.40	93.73
17	0	0	0	0	96.34	96.10
18	0	0	0	0	96.34	96.10

Statistical analysis and model adequacy

Verification of model adequacy is an important part of the data analysis as the model would give misleading results if it is an inadequate fit. The residual plots were examined to approximate the model[20,25]. Regression analysis was performed to fit the response function of Pb(II) ions sorption onto jamun seed surface.

Interpretation of the regression analysis

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using the analysis of variance (ANOVA). ANOVA is a statistical technique that subdivides the total variation in a set of data into component parts associated with specific sources of variation for testing hypothesis on the parameters of the model. P-value is defined as the smallest level of significance leading to the rejection of null hypothesis. In general, the larger the magnitude of F and smaller the value of P, the more significant is the corresponding coefficient term[26]. According to Table 3 the F statistics values for at least 10 terms were higher than 50. The order of F-ratios of main variables was as; pH (3991) > Concentration (13.18) > time (2.31) > amount (0.00). The large value of F indicates that most of the variation in the response can be explained by the regression equation. The associated P-value is used to estimate whether F statistics is large enough to indicate statistically significant[27]. If P-value is lower than 0.05, it indicates the statistical significance of the model[28]. The effect of all the terms (except time) such as concentration, pH, and adsorbent amount were found to be highly significant because P values were less than 0.05. The highest values of *F*-ratio with lowest value of P (0.00) for pH indicate the significance of this term for Pb(II) ions removal by jamun seed surface. It was observed from ANOVA study that the coefficient for the linear (P = <0.005) and interaction (P = <0.005) effects were highly significant and thus confirm the applicability of the predicted model. In addition, a positive sign of the coefficient represents a synergistic effect whereas a negative sign indicates an antagonistic effect. It has been found that concentration and interaction term concentration and time, concentration and pH, amount and time, amount and pH have an antagonistic relationship with the removal process, which means that; with the increase of these factors the uptake of Pb(II) ions decreases. Whereas terms; amount, pH, time and interaction terms concentration and amount, pH and time have a synergistic effect on the sorption of Pb(II) ions. Thus with the increase of these variables the uptake of Pb(II) ions will increase. Finally, a regression equation was prepared using the values of coefficients as shown by eq. 4.

$$Y = -57.5534 + 0.0715585X_1 + 0.136365X_2 + 43.6578X_3 + 0.0731572X_4 + 0.000126716X_1^2 - 0.00549536X_1X_2 - 0.024019X_1X_3 + 0.00208732X_1X_4 - 0.002712X_2^2 + 0.112343X_2X_3 - 0.00129545X_2X_4 - 3.06915X_3^2 - 0.0281328X_3X_4 - 0.0000923185X_4^2 \quad (4)$$

Interpretation of residual graphs

The residual is the difference between the observed and the predicted values from the regression to obtain the normal distribution. Durbin-Watson statistic test is a powerful statistical means that generates normal probability plot and performs a hypothesis test to examine whether the observations follow the normal distributions. Figure 1a plot shows the normal probability versus studentized residuals for the removal of Pb(II) ions by jamun seed. This plot is intended to determine whether or not the residuals follow the assumed normal distribution. It is scaled in such a way that if the residuals follow a normal distribution, the points will lie approximately along a straight line. Any consistent deviation from a straight line would be the sign of not normal behaviour, which can often be corrected by transforming the values of % removal. Hence this plot indicates that all points

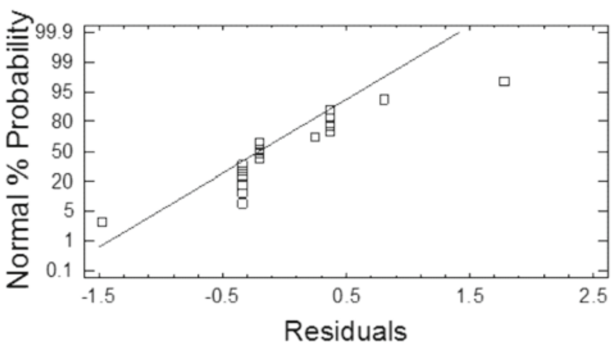

Figure 1a. Plot for normal % probability versus residuals for the % removal of Pb(II) ions by jamun seed waste

Table 3. ANOVA and estimated regression coefficients of Pb(II) ions removal by jamun seed

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value	Regression coeff.
Constant	–	–	–	–	–	-57.553
A:amount	0.001	1	0.001	0.000	0.980	0.072
B:con	32.724	1	32.724	13.180	0.036	0.136
C:pH	9907.020	1	9907.020	3991.650	0.000	43.658
D:time	5.743	1	5.743	2.310	0.226	0.073
AA	0.166	1	0.166	0.070	0.813	0.000
AB	49.534	1	49.534	19.960	0.021	0.005
AC	114.489	1	114.489	46.130	0.007	-0.024
AD	101.991	1	101.991	41.090	0.008	0.002
BB	4.757	1	4.757	1.920	0.260	-0.002
BC	626.155	1	626.155	252.290	0.001	0.112
BD	9.821	1	9.821	3.960	0.140	-0.001
CC	3567.500	1	3567.500	1437.390	0.000	-3.069
CD	560.388	1	560.388	225.790	0.001	-0.028
DD	1.123	1	1.123	0.450	0.549	0.000
Lack-of-fit	6.275	2	3.138	2.680	0.391	–
Pure error	1.170	1	1.17045	–	–	–
Total error	7.446	3	2.48193	–	–	–
Total (corr.)	18170.700	17	–	–	–	–

lie almost along the straight line so residuals follow the normal distribution. Figure 1b plots the residuals versus predicted values. The residual is the difference between the observed and the predicted values. All the residuals are scattered randomly around zero and all points were found in the range of +1.5 to −1.5, showing that the errors have a constant variance and confirmed the fitting of the model. Figure 1c shows the plot for observed versus predicted values of percent removal of Pb(II) ions by jamun seed. The experimental values are measured from a particular run and the predicted values were evaluated from the CCD model. Values of R^2 and $R^2_{adj.}$ were found to be 99.89% and 99.95% respectively, indicating a close agreement between the predicted and observed values as shown in Table 2.

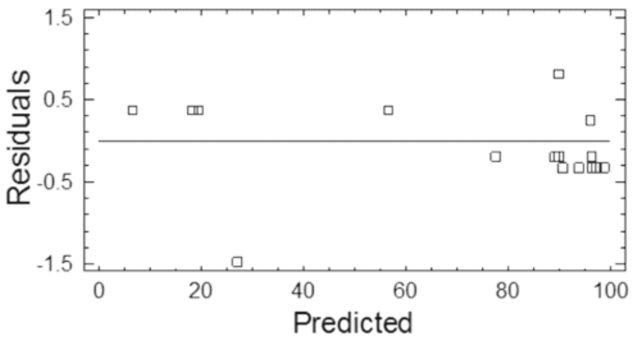

Figure 1b. Plot for residuals versus predicted % removal of Pb(II) ions by jamun seed waste

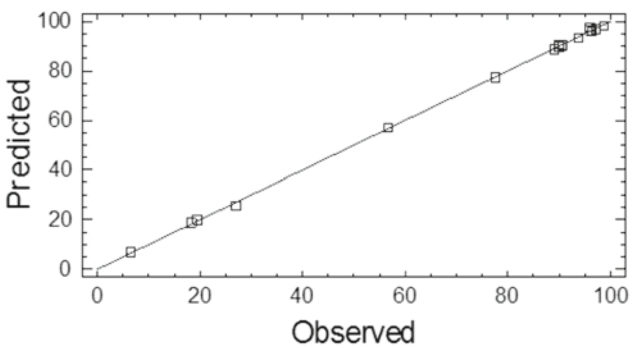

Figure 1c. Plot for observed versus predicted removal of Pb(II) ions [%] by jamun seed waste

Interpretation of response surface plots

Figures 2(a–f) show graphical representations of regression equations. Each 3D plot shows the combined effect of any two independent variables keeping other variables at their respective optimum values. The effect of each variable is dependent on each other. Figure 2a shows the combined effect of Pb(II) ions concentration and the agitation time on % removal of Pb(II) ions by jamun seed at optimum adsorbent dose (53 mg) and pH (8). The % removal slightly decreases with an increase of Pb(II) ions concentration while potentially increases with an increase of pH of Pb(II) ions solution and become maximum at pH 8. Figure 2b shows the combined effect of the adsorbent dose and the agitation time on the % removal of Pb(II) ions by jamun seed at optimum Pb(II) ions concentration (28 mg/l) and pH (8). The % removal slightly decreases with the increase of adsorbent dosage. The effect of agitation time depends on the adsorbent dose the % removal of Pb(II) ions decreases with an increase of agitating time at about adsorbent dosage of 10 mg while increases with an increase of agitation time at about adsorbent dose of 100 mg. Figure 2c shows combined effect of adsorbent dose and Pb(II) ions concentration on the % removal of Pb(II) ions by jamun seed at optimum agitation time (90 min) and pH (8). The % removal increases with increasing adsorbet dose and Pb(II) ions concentration. Figure 2d shows the combined effect of Pb(II) ions concentration and the agitation time on the % removal of Pb(II) ions by jamun seed at optimum adsorbent dose (53 min) and pH (8). The % removal increases with the increase of Pb(II) ions concentration and the agitation time. Figure 2e shows the combined effect of adsorbent dose and pH of Pb(II) ions solution on the % removal of Pb(II) ions by jamun seed at optimum Pb(II) ions concentration (28 mg) and the agitation time (90 min). The % removal slightly increases with increasing adsorbent dose while potentially increases with the increase of pH of Pb(II) ions solution and become maximum at pH 8. Figure 2f shows the combined effect of pH of Pb(II) ions solution and the agitation time on the % removal of Pb(II) ions by jamun seed at optimum Pb(II) ions concentration (28 mg) and adsorbent dose (53 mg). The % removal potentially increases with the increase of pH of Pb(II)

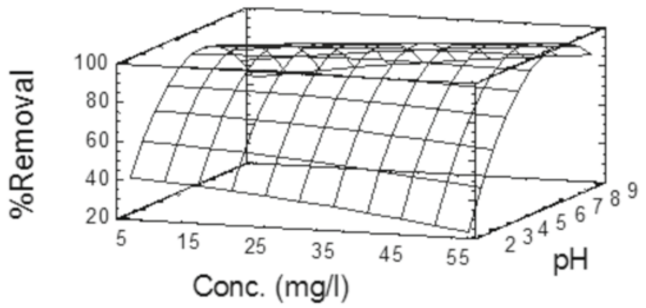

Figure 2a. Combined effect of intial Pb(II) ions concentration and pH of adsorbate solution for the removal of Pb(II) by jamun seed waste

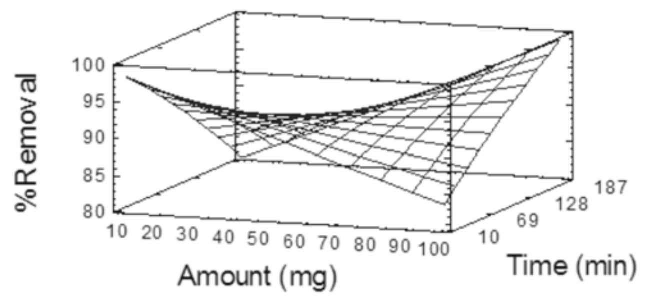

Figure 2b. Combined effect of adsorbent dose and agitating time for the removal of Pb(II) ions by jamun seed waste

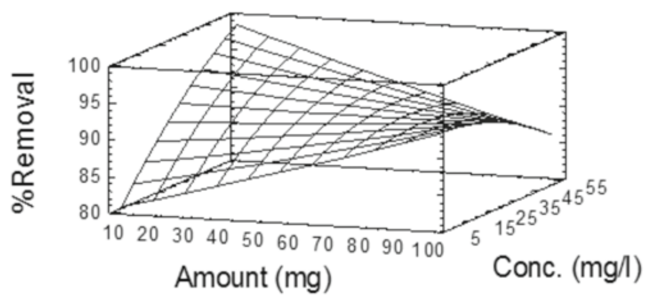

Figure 2c. Combined effect of adsorbent dose and initial Pb(II) ion concentration for the removal of Pb(II) ions by jamun seed waste

ions solution and become maximum at pH 8 while the agitation time has no significant effect along with pH.

Pareto Chart

Fig. 3 shows a Pareto chart of the estimated effects in the decreasing order of magnitude. The length of each bar is proportional to the standardized effect, which is the estimated effect divided by its standard error. This is equivalent to computing a Student's *t*-test values for each effect. The vertical line can be used to judge which effects are statistically significant. It was observed that for a 95% confidence level and eight freedom degrees, the *t*-value was equal to 3.18. Any bars which extend beyond the *t*-value are statistically significant at the 95.0% confidence level. In this case, 8 effects are significant.

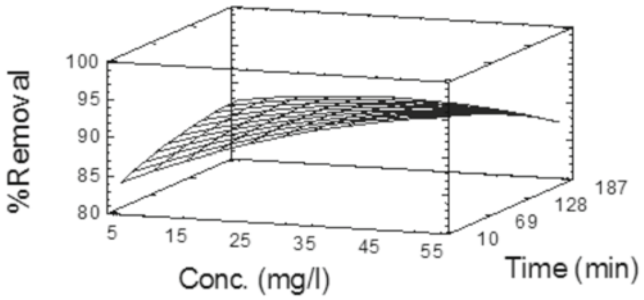

Figure 2d. Combined effect of initial Pb(II) ions concentration and agitating time on the removal of Pb(II) ions by jamun seed waste

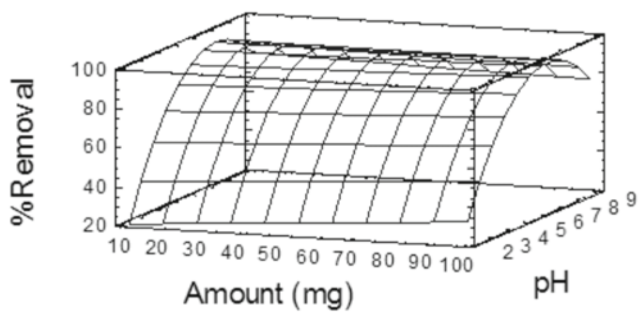

Figure 2e. Combined effect of adsorbent dose and pH of adsorbate solution on the removal of Pb(II) ions by jamun seed waste

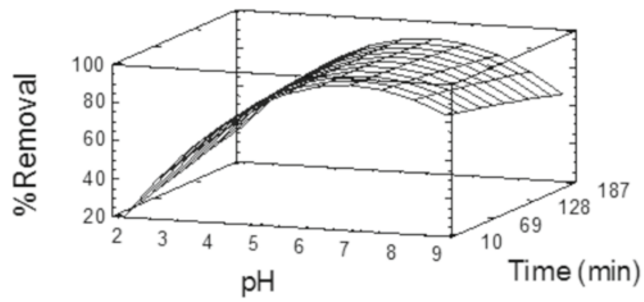

Figure 2f. Combined effect agitating time and pH of adsorbate solution on the % removal of Pb(II) ions by jamun seed waste

FT-IR spectral Study

Figure 4(A, B) shows the FT-IR spectra for jamun seed unloaded (A) and Pb(II) ions loaded (B). Spectrum-A exhibits the characteristic signals at 3500–3200 cm^{-1} broad (for carboxylic acid), 2925.31 $cm^{-1}$and 2843.59 cm^{-1} (for saturated hydrocarbons), 1736.21 $cm^{-1}$and 1625.88 cm^{-1} (for carbonyl group), 1233.60 $cm^{-1}$and 1028.03 cm^{-1}(C-O and C-N

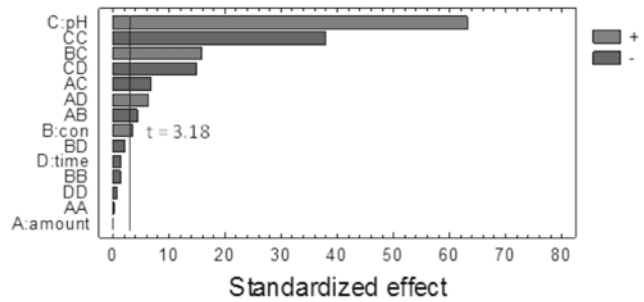

Figure 3. Standardized pareto chart for the removal of Pb(II) ions by jamun seed waste

stretching). Spectrum-B for Pb(II) loaded jamun seed, the noticeable decrease in the intensities of peaks at 3313.51 cm^{-1} (medium) to 3313.51 cm^{-1} (weak), 1736.21 cm^{-1} (medium) to 1736.21 cm^{-1} (weak), 1625.88 cm^{-1}(medium) to 1625.88 cm^{-1}(weak), 1233.60 cm^{-1}(medium) to 1233 cm^{-1}(weak) and 1028.03 cm^{-1}(strong) to 1028.03 cm^{-1}(weak), confirm the participation of O–H, C=O, C–O and C–N, respectively for the uptake of Pb(II) ions from aqueous medium by jamun seed[29].

Isotherm study

Several isotherm models have been used for describing sorption equilibrium. The study of isotherm was carried out by varying initial metal ion concentration at 30°C and pH 8.0. Amount of sorbent used was 53 mg and the mixture was agitated for 90 min. In order to evaluate the sorption capacity and nature of sorption of Pb(II) onto the surface of jamun seed, Langmuir and Dubinin--Radushkevich (D-R) models are evaluated using eq. 5 and 6 respectively.

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{5}$$

$$\ln C_{ads.} = \ln K_{D-R} - \beta\varepsilon^2 \tag{6}$$

where C_e is the equilibrium Pb(II) ions concentration (mg/l) and $C_{ads.}$ is the amount of Pb(II) ions on jamun seed surface (mg/g), Q and b are the Langmuir constants related to the monolayer sorption capacity (mg/g) and free sorption energy (l/g) respectively. ϵ is Polanyi potential and is equal to RT ln $(1+1/C_e)$, T is temperature and R is general gas constant and β is the slope of Langmuir isotherm which is related to the sorption energy per mole of the sorbent. The Langmuir sorption isotherm describes monolayer sorption without interaction between sorbed molecules[30]. The Langmuir constants, Q and b were calculated respectively from the slope and from the intercept of the plot between $Ce/C_{ads.}$ and C_e. The isotherm showed good fit to the experimental data with correlation coefficient of 0.971. The sorption capacity of jamun seed was found to be 183.9 ± 0.31 mg/g. The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor R_L, it describes the type of isotherm which is expressed mathematically by eq. 7.

$$R_L = \frac{1}{1+bC_i} \tag{7}$$

Table 4. Langmuir and D-R isotherm parameters

Langmuir			D-R		
Capacity (mg/g)	R_L	R^2	Capacity (mg/g)	Energy (kJ/mol)	R^2
183.9 ± 0.31	0.05–0.77	0.971	184.5 ± 0.16	13.17 ± 0.16	0.991

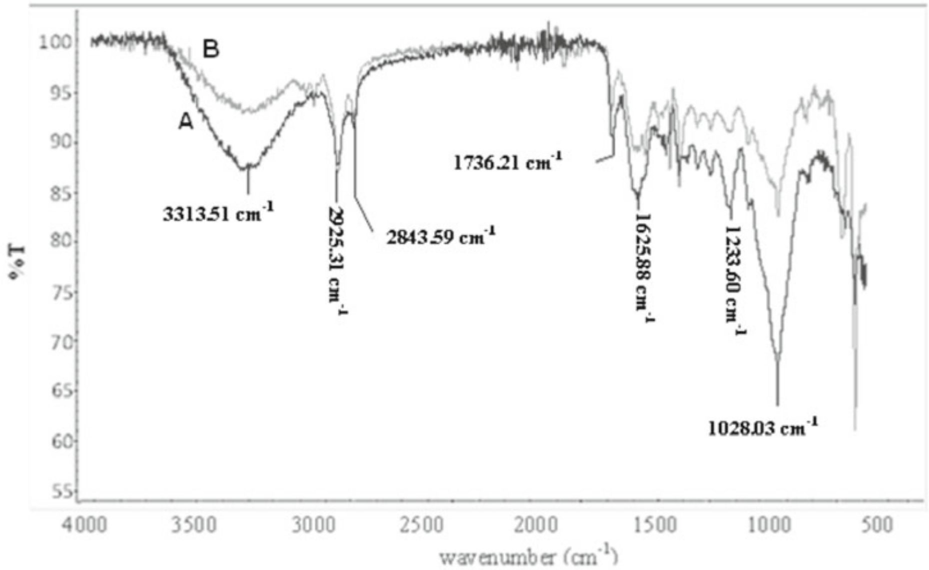

Figure 4. (A, B) FT-IR spectra; jamun seed unloaded (A) and Pb(II) ions loaded (B)

where b is the Langmuir constant and C_i is the initial Pb(II) ions concentration. According to the value of R_L, the isotherm shape can be interpreted as; $R_L = 0$, irreversible; $R_L > 1$, unfavorable; $R_L = 1$, linear and $0 < R_L < 1$, favorable[31]. The R_L values calculated for the sorption of Pb(II) ions onto jamun seed surface were in the range of 0.05–0.77, indicating the favorable nature of sorption.

D-R isotherm assumes no homogeneous surface of the sorbent material, a good linear relationship with correlation coefficient of 0.991 was obtained in a plot of $\ln C_{ads}$ versus ϵ^2. The applicability of the isotherm model for Pb(II) ions sorption, showed that there is a possibility of heterogeneous energetic distribution of active sites on the surface of the sorbent. The sorption capacity 184.5 ± 0.16 mg/g, sorption free energy (E) 13.17 ± 0.16 kJ/mol have been calculated (Table. 4). Magnitude of E between 8 and 16 kJ/mol indicates the process of sorption proceed via chemisorption or ion exchange, while for values of E < 8 kJ/mol, the sorption process is of a physical nature[30].Therefore Pb(II) ions were predominantly sorbed onto jamun seed surface by chemisorption and/or ion exchange.

Possible mechanism of adsorption

Based on the FT-IR study, pH dependent sorption observations and mean free energy of sorption calculated from D-R sorption isotherm, following mechanisms may be proposed.

Where R is the matrix of jamun seed. Based on the electron donating nature of the nitrogen (amine) and oxygen (alcohol and carboxyl) of jamun seed and the electron-accepting nature of Pb^{2+} ion, the ion exchange mechanism could preferentially be considered. The divalent Pb^{2+} may attach with nitrogen and oxygen of jamun seed containing moieties during adsorption process.

Method validation

Optimum sorption conditions determined from mathematical model were validated by conducting sorption experiment at optimum conditions predicted by model and comparing experimental and predicted removal values. Table 5 shows a good agreement between calculated and predicted values for Pb(II) ions removal from aqueous solution.

Table 5. Model validation for Pb(II) ions removal

Adsorbent dose (mg)	pH	Initial conc. (mg/l)	Time (min)	% Removal	
				Predicted	Experimental
53	8	28	90	100	99.91

Applications of the method

The proposed sorbent and model applied successfully for the treatment of Pb(II) ions contaminated drinking water by batch process at optimum conditions. Table 6 shows the % removal of Pb(II) ions from the drinking water samples collected from various cities of Pakistan.

Table 6. Application of proposed method for the removal of Pb(II) ions from drinking water

*Sample	Initial conc. (mg/l) of Pb(II) ions	% Removal of Pb(II) ions	RSD
S1	3.58	98.09	1.30
S2	2.13	91.11	1.90
S3	2.50	91.33	1.50
S4	2.90	89.65	0.93

*S1 Wastewater sample Collected from site area in Karachi, Pakistan
*S2 Wastewater sample Collected from site area in Hyderabad, Pakistan
*S3 Wastewater sample Collected from site area in Kotri, Pakistan
*S4 Wastewater sample Collected from site area in Faisalabad, Pakistan

CONCLUSIONS

Waste (seed) of fresh fruit jamun was found to be a potential sorbent for the treatment of Pb(II) ions contaminated drinking water. A 2^4 full factorial Draper-Lin composite design predicted the results with high correlation (R^2 = 99.89% and $R^2_{adj.}$ = 99.95%) between the

$$2RCOOH + Pb(II) \rightarrow Pb(OOCR)_2 + 2H^+$$

$$2ROH + Pb(OH)^+ \rightarrow Pb(OR)_2 + 2H^+$$

Amines-N: + Pb(II) → Amine-N: - - - - Pb(II) - - - - :N-Amine (electrostatic attraction)

Figure 5. Possible sorption mechanism for the uptake of Pb(II) ions

experimental and predicted values. ANOVA suggested that the tested model describes sorption data adequately. The uptake of Pb(II) ions by jamun seed was very sensitive to the pH of metal ion solution and was found to follow both Langmuir and D-R isotherm, suggesting the monolayer sorption as well as heterogeneous energetic distribution of active sites. FT-IR study shows the involvement of carboxyl, hydroxyl and amine groups in the sorption of Pb(II) ions. It was therefore concluded that jamun seed waste could be used as an effective, low-cost and green alternative bio-sorbent material for effective treatment of Pb(II) ions contaminated water. By commercializing this method solid waste, jamun seed could be managed well.

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