Optimization and equilibrium studies of Pb(II) removal by *Grewia Asiatica* seed: a factorial design approach

Ali N. Siyal[1], Saima Q. Memon[2*], Mazhar I. Khaskheli[3]

[1] *M.A. Kazi Institute of Chemistry University of Sindh, Jamshoro, Pakistan*
[2,3] *University of Sindh, Institute of Advance Research Studies in Chemical Sciences, Jamshoro, Pakistan*
[*]*Corresponding author: e-mail: msaima77@gmail.com*

This study aims to explore the efficiency of an agro waste material for the remediation of Pb(II) contaminated water. A factorial design approach is adopted to optimize removal efficiency and to study the interaction between effective variables. A face-centered Draper-Lin composite design predicted 100% removal efficiency at optimum variables; pH 8, initial concentration of Pb(II) ion 12mg/L , sorbent dose 200mg and agitation time 110 min. Regration coefficient ($R^2 = 99.9\%$) of a plot of the predicted versus the observed values and p value (>0.05) confirms the applicability of the predicted model. Langmuir and Dubinin–Radushkevich (D–R) isotherm models were applicable to sorption data with the Langmuir sorption capacity of 21.61 ± 0.78 mg/g. The energy of sorption was found to be 13.62 ± 0.32 kJ/mol expected for ion-exchange or chemisorption nature of sorption process. Characterization of *Grewia* seed suggested a possible contribution of carboxyl and hydroxyl groups in the process of biosorption. The present study shows that *Grewia* seeds can be used effectively for the remediation of Pb(II) contaminated water.

Keywords: Optimization; Pb(II) removal; *Grewia* seed waste; Response Surface Methodology; Factorial design; Equilibrium Studies; Biosorption

INTRODUCTION

Contamination of water bodies due to increasing industrialization is becoming a serious environmental threat. Pollution by heavy metal ions such as lead is one of major environmental issues around the world due to their possible toxic effects and non-biodegradable nature. Lead is recognized as a longstanding environmental contaminant. Ceramic, glass, production of lead additives for gasoline, lead storage batteries, lead smelting, mining, printing, tanning, plating and finishing industries are mainly responsible for the introduction of lead into natural water bodies[1]. The permissible limit of lead in drinking water is 0.05 mg/L, exceeding this limit may cause adverse health effects. As Pb^{2+} ion has an ability to react with Mercapto group and Phosphate ion of enzymes, ligands and biomolecules, thereby it inhibits the biosynthesis of haeme units, affecting membrane permeability of kidney, liver and brain cells, it results either in reduced functions or complete breakdown of these organs[2,3]. In view of its toxicity and in order to meet regulatory discharge standards, it is essential to remove this toxic metal from wastewater prior to discharge into fresh water bodies. Extensive research has been dedicated to identify new, effective and economical methods for its removal from aqueous solution[4].

Removal by adsorption is considered as the most favorable and effective method because of its high efficiency even at low concentrations. Number adsorbents including agricultural waste materials have been utilized. Agriculture waste materials contain proteins, polysaccharides and lignin containing multi-functional groups such as hydroxyl, carbonyl and carboxyl play vital role for metal uptake purpose[5-7]. Abundantly available agricultural wastes sorbent such as; apple peel, modified orange waste, banana, tea leaves, cactus leaves, palm shell activated carbon, almond shells, coconut shell, brown seaweed, olive tree pruning waste, pine cone, pine needles[8-13], have been reported for the removal of the toxic metals from aqueous solutions. A large number of reports in literature use batch adsorption experiments for the removal purpose. A conventional batch sorption method is time consuming as it requires a large number of experiments to determine the optimum value. A major disadvantage of 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 could lead to unreliable results[14]. However, in Response Surface Methodology (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[15,16].

The objective of this research is to investigate the lead removal efficiency of Grewia seed from aqueous media and to maximize the removal by studying the combined effects of contact time, initial concentration of Pb(II) ions, pH and sorbent dosage using RSM approach. Equilibrium sorption behavior and possible sorption mechanism of Pb(II) on Grewia seed surface is also investigated.

Grewia (Grewia Asiatica) is a summer fruit, originated in Southern India, Pakistan, Bangladesh, Nepal, Sri Lanka, Philippines, Thailand, Laos, Cambodia and Vietnam. Fully ripen Grewia is reddish maroon in color. To the best of our knowledge this waste has not been used before for any remediation purpose.

MATERIALS AND METHODS

Sorbate: Pb(II) ion solution

A stock solution of Pb(II) was prepared (1000 mg/L) by dissolving appropriate amount of lead nitrate $Pb(NO_3)_2$ (Merck) in distilled water. The stock solution was diluted with distilled water to the obtained working solutions (10–100 mg/L). The initial pH of the solutions was

maintained at 2.0, 5.5 and 9.0 with HCl, Acetate buffers, and NaOH respectively. CH₃COOH, CH₃COONa, NaOH, HCl, were used of Merck (Darmstadt, Germany).

Sorbent: Grewia asiatica fruit seed:

The seeds of Grewia asiatica fruit were collected from a local market and from the fresh juice sellers. It is reported that the use of untreated biomass as the biosorbent can lead to high chemical oxygen demand (COD) due to the release of soluble organic compounds contained in these materials. Also these materials discharge color in the treated water[17]. We found that Grewia asiatica fruit seed did not release any color into the system at any pH (acidic, neutral or basic), hence can be used without any treatment. However, COD was found to be little greater than the WHO recommended level, therefore the sorbents were washed many times with de-ionized water till the effluent's COD got within the range of WHO recommended safe limit. The washed sorbent was air dried and kept in an incubator at 60ºC for 24 hours, then ground and screened to a uniform material for the complete set of sorption.

Batch sorption experiments:

Batch sorption experiments were carried out as reported earlier[27] by agitating different weighted amounts of Grewia seeds (10–200 mg) with 20 mL solution of Pb (II) ion for specified time (10–180 min) at 150 rpm. Initial concentrations of Pb (II) ion used were in the range of 10–100 mg/L maintained at pH 2–9, while the temperature was kept constant at 30ºC. The residual concentration of Pb(II) ions was analyzed by using Perkin Elmer Atomic Absorption Spectrophotometer (AAS) after filtering the sorbent with the Whatmen filter paper.

Removal efficiency of Pb(II) ions by *Grewia* seed surface can be calculated by the following equation:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of Pb(II) ion solution respectively. The amount of metal ions sorbed at equilibrium per unit mass of the sorbent (lead sorption capacity) was determined according to the following equation:

$$q_e = \frac{C_0 - C_e}{m} \times V \qquad (2)$$

where q_e is the metal uptake at equilibrium or sorption capacity (mg of metal ions/g of the sorbent), V, the liquid volume (L) and m is the amount of the sorbent sample on a dry basis (g). Each experiment was carried out twice to check the reproducibility of the results and sorbent free blanks were used as control.

Fourier Transform- Infrared spectroscopic (FT-IR) study

The samples of sorbents (free and metal treated) were dried overnight to remove any water retained which could interfere with an observation of hydroxyl groups on the surface. The samples were then scanned into transmission mode using a Fourier Transform infrared (FT-IR) spectrometer (Thermo Nicolet IS-10 with diamond accessory). The IR spectra of control and metal treated sorbents were recorded through a wavelength range of 400 to 4000 cm⁻¹.

Removal of Pb(II) from environmental water samples

Lead contaminated drinking water samples were collected in plastic bottles from different areas of Pakistan. The collected samples were filtered and the initial lead concentration was determined using AAS. After an addition of specified (Table 5) amounts of standard Pb(II) the same procedures described above were used to calculate % recovery of Pb(II) ions.

Mathematical and statistical procedure:

For the modeling of removal efficiency of lead from an aqueous solution, a design of 18 experiments was formulated using Face Centered Draper-Lin small composite design. The range and level of the experimental variables investigated in this study are shown in Table 1. Each parameter was coded at three levels: -1, 0 and +1. The response function describing the variations of dependent variable (percent removal efficiency) with four independent variables can be written as follows:

$$Y = B_0 + B_1X_1 + B_2X_2 + B_3X_3 + B_4X_4 + B_{11}X_1^2 + B_{12}X_1X_2 + B_{13}X_1X_3 + B_{14}X_1X_4 + B_{22}X_2^2 + B_{23}X_2X_3 + B_{24}X_2X_4 + B_{33}X_3^2 + B_{34}X_3X_4 + B_{44}X_4 \qquad (3)$$

where Y is the measured response variable, *X1–X4* 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_{11}-B_{44} are the (pure) second-order coefficients.

All the experiments were done in duplicate and random order to evaluate pure error and minimize the effect of

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

Independent variable Range	Coded levels		
	−1	0	+1
Amount (mg), A(x₁)	10	55	100
Concentration (mg/L), B (x₂)	5	27.5	50
pH, C (x₃)	2	5.5	9
Time (min.), D (x₄)	10	95	180

possible uncontrolled variables.

The response function coefficients were determined by regression using *Statgraphics plus 5.1* computer program.

RESULTS AND DISCUSSION

Experimental design

Traditional batch removal experimental method uses optimization of one factor at a time approach which can hardly establish a relationship among all the experimental input factors and the output response. Though this approach can be useful in finding predominant factor; it is difficult to observe an optimum value of the working parameters as no interaction among them is considered. To solve this problem and to obtain a probable optimum values, design of experiment (DOE) offers a better alternative to study the effect of variable and their response with a minimum number of experiments[18]. Draper-Lin composite design, used in the present study develops a correlation between aqueous solution variables to the sorption efficiency of Pb (II) on *Grewia* seed. The design of the experiment is given in Table 2, together with the experimental and predicted results for the removal of

Table 2. Experimental design and results for percentage removal and sorption capacity of Pb(II) by *Grewia* seed

Trail	Coded values				% Removal (Experimental)	% Removal (Predicted)	Capacity (mg/g)
	A	B	C	D			
1	-1	-1	+1	-1	81.66	81.69	4.080
2	-1	-1	-1	-1	22.38	22.41	1.120
3	0	+1	0	0	80.52	80.41	7.320
4	+1	+1	-1	-1	20.64	20.66	1.030
5	+1	+1	+1	-1	66.01	66.03	3.30
6	0	0	0	-1	73.83	73.72	3.690
7	-1	+1	+1	+1	74.12	74.15	37.06
8	+1	0	0	0	74.49	74.38	2.050
9	0	0	+1	0	79.00	78.87	3.950
10	+1	-1	+1	+1	84.50	84.53	0.420
11	0	0	-1	0	18.90	18.81	0.950
12	+1	-1	-1	+1	18.78	18.80	0.100
13	-1	+1	-1	+1	4.260	4.28	2.130
14	0	-1	0	0	95.62	95.51	0.870
15	-1	0	0	0	84.62	84.52	23.27
16	0	0	0	+1	73.00	72.89	3.650
17	0	0	0	0	81.69	80.99	4.090
18	0	0	0	0	79.64	80.99	3.980

pb(II). The maximum percent sorption and capacity of Pb (II) was found to be 95.62% and 37.06 mg/g respectively. Table 2 shows a very close agreement between the predicted and the experimental values indicating the applicability of a model for sorption of Pb (II) ions by *Grewia* seed surface.

Statistical analysis

The model adequacy check is an important part of the data analysis procedure as the approximating model would give poor or misleading results if it were an inadequate fit. Residual plots were examined to approximate the model[19]. Regression analysis was performed to fit the response function of the sorption of Pb(II) on Grewia 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). In general, the larger the magnitude of F and the smaller the value of P, the more significant is the corresponding coefficient term[20]. According to Table 3 the F Statistics values for at least 10 terms are higher than 50. The order of F-ratios of the main variables is as: pH (11121.04) > The concentration (140.6) > amount (63.32) > time (4.2). 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[21]. The values of P are lower than 0.05, which indicates that the model is statistically significant[22]. The effect of terms; concentration, pH, and the sorbent amount were found to be highly significant because the P values were less than 0.05. The highest values of F-ratio with the lowest value of P (0.00) for term pH indicate the significance of this term for lead removal efficiency of *Grewia* seed. It was observed from the ANOVA study that the coefficients for the linear (P = <0.005) and interaction (P = <0.005) effects were

highly significant and thus confirm the applicability of the predicted model.

Variables; concentration, and interaction terms; concentration and time, concentration and pH, amount and time, amount and pH have an antagonistic relationship with the removal process i.e.. That means with the increase of these factors the uptake of Pb(II) 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). Thus with the increase of these variables the uptake of Pb(II) will increase. Finally, a regression equation was prepared using the values of coefficients, which is as follows:

% Removal = -41.3461 + 0.0870671*amount - 0.747376*con + 37.4345*pH + 0.244724*time - 0.000763839*amount^2 + 0.000705679*amount*con - 0.0143333*amount*pH - 0.000591765*amount*time + 0.0137565*con^2 - 0.0155238*con*pH - 0.00313961*con*time - 2.62488*pH^2 + 0.013*pH*time - 0.00106419*time^2   (4)

A very low value of standard deviation (0.900) between the experimental and predicted results shows that Eq. (3) adequately represents the actual relationship between the response and significant variables. The high value of R^2 (99.98%) and R^2 (adjusted) (99.91%) indicates a high dependence and correlation between the observed and the predicted values of response.

Interpretation of residual and response surface plots

The normality of the data can be checked by plotting the normal probability plot (NPP) of the residuals. The residual is the difference between the observed and the predicted value (or the fitted value) from the regression. Fig. 1(a) plots the residuals versus the fitted values (predicted response) and it could be seen that the experimental points are reasonably aligned suggesting normal distribution. Fig. 1(b) is a plot of residuals in the order of the corresponding observations. The residuals appear to be randomly scattered about zero.
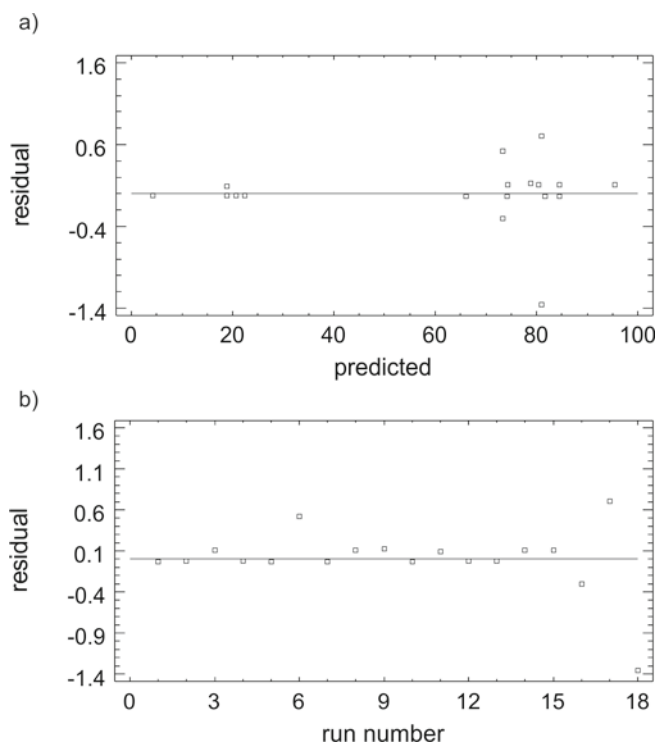
The 3D response surface plots (Fig. 2a–2c) are also

a)

b)

Figure 1. Validation of model for the uptake of Pb(II) by *Grewia* asiatica seed a) plot of residuals vs calculated values, b) plot of residuals vs run order

plotted. Fig 2a–2c represents an infinitive number of combinations of two test variables with the other two maintained at their respective optimum value. Fig. 2a clarifies the combined effect of initial concentration of Pb(II) and sorbent dose on the sorption of lead(II) at constant pH (8) and time (110 min). Removal was found to be good even at low sorbent amounts and minimum lead concentration (10 mg/L). Fig. 2b shows the interactive effect of time and initial concentration of Pb(II) and a rapid uptake values of lead at lower initial concentrations can be seen. The three dimensional response surfaces of the combined effect of sorbent amount and time on sorption of lead(II) at constant pH (8) and initial lead concentration (10 mg/L) is shown in Fig. 2c. A maximum sorption of lead ~99 % was determined at optimum values.

Student's t Test

In order to determine whether the calculated effects were significantly different from zero, Student's t test was employed. It was observed that for a 95% confidence level and eight degrees of freedom, the t value was equal to 3.19. The evaluations are illustrated by means of Pareto charts in Fig. 3. The vertical line indicates the minimum statistically significant effect magnitude for a 95% confidence level. The values shown in the horizontal columns are Student's t test values for each effect. All the values presenting an absolute value higher than 2.3, which are located right of the line, are significant.

Interpretation of effect of pH

The ANOVA studies suggested the pH as a most significant variable for the sorption of Pb(II) by *Grewia* seed, the same can be confirmed from its main effect plot (Fig 4).

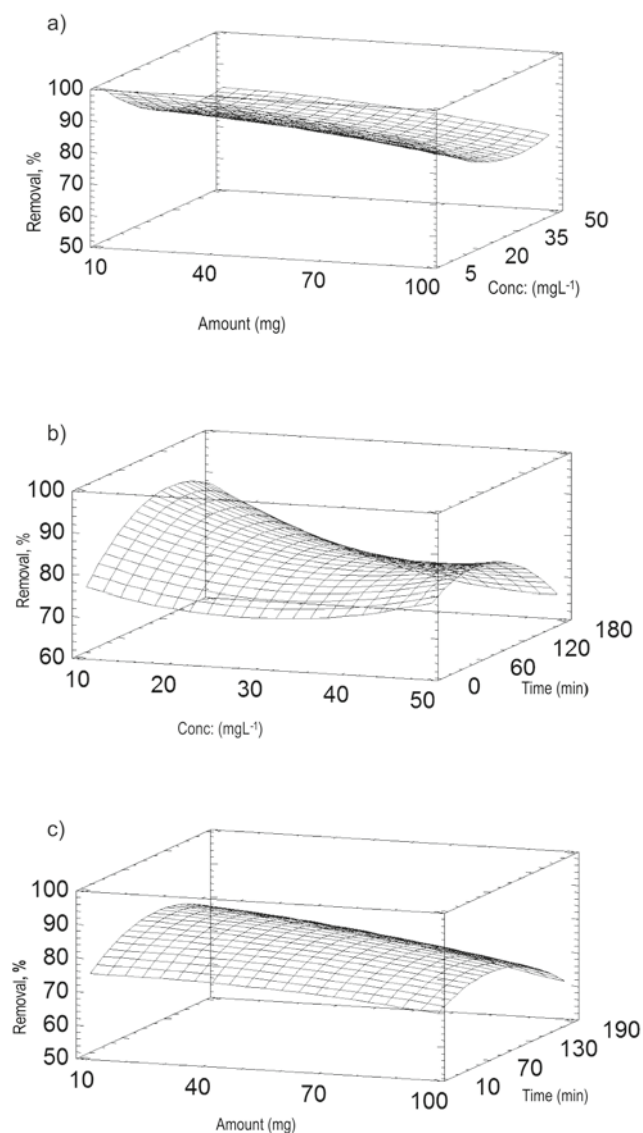In order to interpret the effect of pH on the sorption of Pb(II) ions on an sorbent surface, knowledge of Pb(II)

a)

b)

c)

Figure 2. . Three dimensional response surface plot for uptake of of Pb(II) by *Grewia* seed: a) effect of amount of *Grewia* seed and initial Pb(II) ion concentration, b) effect of initial Pb(II) concentration and agitation time, c) effect of amount of *Grewia* seed and agitation time

speciation and the sorbent surface characteristics is essential. *Agro* materials usually contain carboxylic, phenolic and amine groups which possess the capability of capturing heavy metal ions. It can be speculated that carboxylic or other compounds are the active ion exchange sites. Up to pH 7 the main species of Pb(II) is Pb^{2+} (>80%) and at pH 8 the dominant species of Pb(II) ions would be Pb^{2+}(~50%), $Pb(OH)^{+}$(~45%),$Pb3(OH)_4^{2+}$ (~3%), and
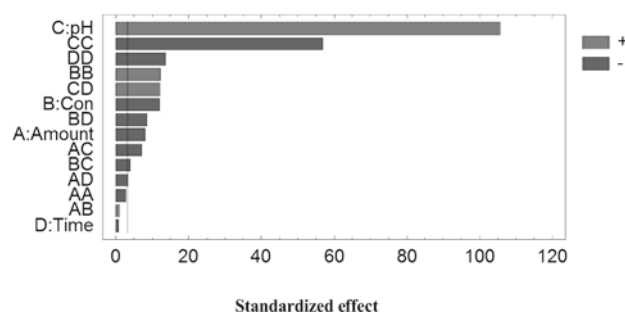

Figure 3. Pareto chart of statistical effects on the removal of Pb(II) ions
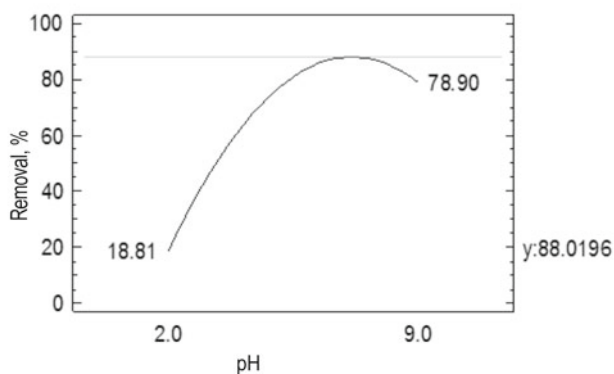
Figure 4. Main effects plot for % uptake of Pb(II) by *Grewia* seed surface

Pb(OH)$_2$ (~1%)[23]. As pH of sorbate solution increases the groups at the surface become dissociated resulting a negative character to the surface which could trap the positively charged Pb(II) species. At lower pH, the H$^+$ ions compete with Pb(II) cations for the exchange sites on *Grewia* seed surface. The amount of adsorbed Pb(II) ions increased with an increase in pH up to pH 7–8 attains the maximum value of ~88% and then decreased with a further increase of pH (Fig. 4). The decrease of ~10% at pH 9 may be due to an increase in neutral species (Pb(OH)$_2$) of Pb(II) at this pH. Similar behavior has been reported earlier in literature[24,25].

Interpretation of FT-IR spectra

In order to study the role of the functional groups present on the surface of *Grewia* seed sorbent, FT-IR spectrum of free seed was recorded (Fig 5a). The FT-IR spectrum of the free seed exhibit the presence of alcohol, amine and carboxylic acid evident from strong broad bands in the region of 3500–3200 and those at; 3109cm^{-1}, 3019 cm^{-1} bands at 2927cm-1, 2843cm^{-1} bands, confirm the presence of alkenyl and alkyl groups respectively. The band at 1752.cm^{-1}, 1627.cm^{-1} indicates the presence of carbonyl and carboxyl moieties, respectively. While the bands at 1239.cm^{-1}, 1021.cm^{-1}, 690.cm^{-1} support the presence of amine, carboxylic acid and acid chloride respectively. The FT-IR spectrum of Pb(II) loaded seed was also recorded (Fig 5b). A noticeable decrease in intensities; 3293cm^{-1} (medium) to 3293cm^{-1} (weak), 1627cm^{-1} (medium) to 1627cm^{-1} (weak) and 1021(strong) cm^{-1} to 1021(weak) can be seen in Fig 5a–5b, indicating the involvement of O–H, C=O and C–O respectively for Pb(II) uptake by *Grewia* seed. Also, disappearance of peak at 1239 further confirms the involvement of C-O of alcohol[26].

Study of sorption equilibrium

Various isotherm models have been utilized for the description of sorption equilibrium for the contaminated treatment. In order to evaluate the sorption capacity and the nature of sorption of Pb(II) onto the surface of Grewia seed surface, Langmuir and Dubinin–Radushkevich models are evaluated using the following equations[27], respectively in the concentration range of 4.83×10^{-5}-4.83×10^{-4} molL^{-1}.

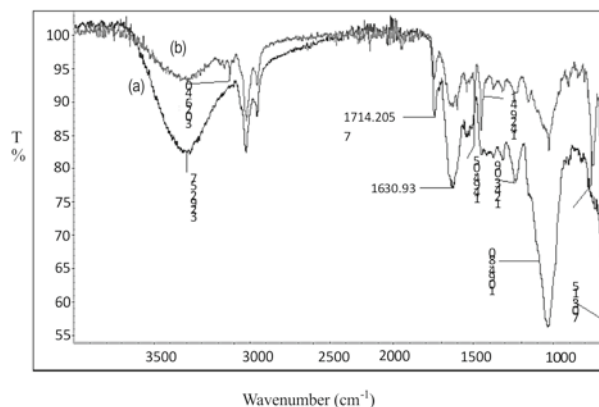$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{5}$$

Figure 5. FT-IR: (a), Free *Grewia* seed; (b), Pb(II) loaded *Grewia* seed

$$lnC_{ads} = lnK_{D-R} - \beta\varepsilon^2 \tag{6}$$

where C_e is the equilibrium concentration of pb(II) in solution (mol/L) and C_{ads} is the amount of Pb(II) on *Grewia* seed surface (mol/g), Q and b are the Langmuir constants related to the monolayer sorption capacity (mg/g) and free sorption energy (L/mg), respectively. ε is Polanyi potential and is equal to RT ln (1+1/C_e), T is temperature and R is general gas constant; β is related to the mean free energy of sorption per mole of the sorbent when it is transferred from an infinite distance in the solution to the surface of the solid.

The study of isotherm was carried out by varying the initial metal ion concentration at 30°C and pH 8.0. The amount of sorbent used were 20 mg and the mixture was agitated for 110 min.

The Langmuir sorption isotherm describes a monolayer sorption without an interaction between the sorbed molecules[27]. The isotherm constants Q and b are calculated from the slope and intercept of the plot between *Ce/Cads* and *Ce*, respectively. The isotherm showed good fit to the experimental data with good correlation coefficients (0.98). The sorption capacity of *Grewia* seed was found to be 21.61±0.78 mg/g.

The essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor R_L, which describes the type of isotherm and is defined as:

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

where b is the Langmuir constant and C_i is the initial concentration of Pb(II) ions.

According to the value of R_L, the isotherm shape can be interpreted as $R_L > 1$, unfavorable; $R_L = 1$, linear; $R_L = 0$ Irreversible and $0 < R_L < 1$ favorable[27]. The RL values calculated for the sorption of Pb(II) on *Grewia* seed surface was in the range of 0.004–0.08 through the investigated range of concentrations showing the favorable nature of sorption.

D-R isotherm assumes no homogeneous surface of the sorbent, a good linear relationship with correlation coefficient of 0.99 was obtained in a plot of ln C_{ads} vs ε^2. The applicability of this isotherm model to the lead sorption shows that there is a possibility of heterogeneous energetic distribution of active sites on the surface of the sorbent. The estimated values of mean sorption

Table 3. Analysis of Variance and Estimated regression coefficients of Pb(II) removal by *Grewia* seed

Source	Sum of Squares	Mean Square	F-Ratio	P-Value	Regression co-eff.
Constant					-41.346
A:amount	51.35	51.35	63.32	0.0041	0.0870
B:con	114.0	114.0	140.6	0.0013	-0.7470
C:pH	9019	9019	11121	0.0000	37.43
D:time	0.3410	0.3410	0.4200	0.1628	0.2450
AA	6.038	6.038	7.450	0.0520	-0.0008
AB	0.8170	0.8170	1.010	0.3895	0.0007
AC	40.77	40.77	50.27	0.0058	-0.0143
AD	8.197	8.197	10.11	0.0501	-0.0006
BB	122.4	122.4	150.9	0.0012	0.0138
BC	11.96	11.96	14.74	0.0312	-0.0155
BD	57.69	57.69	71.13	0.0035	-0.0031
CC	2609	2609	3218	0.0000	-2.625
CD	119.7	119.7	147.6	0.0012	0.0130
DD	149.2	149.2	184.0	0.0009	-0.0011
Total error	2.433	0.8110			
Lack-of-fit	0.3150	0.1580			
Pure error	2.117	1	2.118		
Total (corr.)	14785	17			

R^2 = 99.98 %, R^2 (adjusted for d.f.) = 99.91%, s = 0.9006

energy (E), calculated from slop of the plot (β) were 13.62±0.32 kJ/mol. The magnitude of *E* between 8 and 16 kJ/mol indicates the process of sorption to proceed via chemisorption or ion exchange, while for the values of *E* < 8 kJ/mol, the sorption process is of physical nature[28]. Hence, it is very likely that Pb(II) ions are sorbed on Grewia seed, predominantly by chemisorption or ion exchange[29].

Validation

The optimum sorption conditions determined from mathematical model were validated by conducting sorption experiment at optimum conditions predicted

Table 4. Model validation for Pb(II) removal by *Grewia* seed

Amount of adsorbent A (mg)	pH B	Initial Concentrations C (mg/L)	Time D (min)	% Removal	
				Predicted	Experimental
200	8	12	110	100	99.91

by model and comparing experimental and predicted removal values. Table 4 shows a good agreement between the calculated and the predicted values for lead (II) removal.

Sorption mechanism

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

$$2\ RCOOH + Pb^{2+} \rightarrow Pb(OOCR)_2 + 2H^+ \qquad (8)$$

$$ROH + Pb(OH)^+ \rightarrow Pb(OH)(OR) + H^+ \qquad (9)$$

where *R* is the matrix of the *Grewia* seed. Based on the electron donating nature of the oxygen containing alcohol and carboxyl groups in *Grewia* seed and the electron-accepting nature of Pb^{2+} ions, the ion exchange mechanism could preferentially be considered. For instance, a divalent heavy metal ion such as Pb^{2+} may attach itself to two adjacent hydroxyl groups which could

donate two pair of electrons to the metal ion, forming four coordination number compounds and releasing two hydrogen ions into solution.

Applications of the method

The proposed Sorbent was successfully applied for the removal of Pb (II) from drinking water samples. Samples were collected from different areas of Pakistan. The removal of Pb (II) ions was investigated by the method as mentioned in the experimental section after an addition of 10 μg of standard Pb(II) ion solution. Table 5 shows the efficiency of *Grewia seeds* for the removal of Pb (II) ions from the real water systems at different concentration of lead ions.

CONCLUSIONS

Waste (seed) of fresh summer fruit Grewia was found to be a potential sorbent for the uptake of Pb(II) from aqueous systems without increasing system's COD. A 2^4 full factorial Draper-Lin composite design predicted the results with high correlation between the experimental and predicted values (R^2 = 99.9%) with removal of ~ 95%. Analysis of variance suggested that the tested model describes sorption data adequately with p values less than 0.05 for most of main as well as interaction terms. The uptake of Pb(II) by *Grewia* seed was very sensitive to the pH of metal ion solution and was found to follow both Langmuir and D–R isotherm over the entire tested concentration range (4.83×10^{-5}-4.83×10^{-4} molL^{-1}), suggesting the monolayer sorption as well as heterogeneous

Table 5. Removal of Pb from drinking water samples

*Sample	Initial Conc: of Pb(II) mg/l	*Conc: after addition mg/l	% Recovery	RSD (%)
S1	2.580	12.58	87.98	1.1
S2	2.740	12.74	79.99	2.7
S3	1.10	11.10	95.71	1.9
S4	2.390	12.39	84.65	3.1

* Amount of Pb(II) added = 10μg
*S1:- Hand pump water (Choudhary Mohammad Sadiq Chak 147, Taluka Sadiqabad, Distt: Rahimyar Khan).
*S2:- Hand pump water (Basic Health Unit Manthar, Taluka Sadiqabad, Distt: Rahimyar Khan).
*S3:- Tap water (Institute For Advanced Research Studies in Chemical Sciences, University Of Sindh, Jamshoro)
*S4:- Hand Pump (Madarssa Dar-ul-uloom Manthar Taluka Sadiqabad Distt: Rahimyar Khan).

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 is therefore concluded that *Grewia* waste could be used as an effective, low-cost and green alternative biosorbent material for lead removal from aqueous solution.

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