Biosorption of Heavy Metals onto the Bark of Prosopis Spicigira: A Kinetic Study for the Removal of Water Toxicity

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Abstract: The main objectives of this study are to investigate the lead (II), cadmium (II), copper (II) and chromium (VI) biosorption from aqueous solution by *Prosopis spicigira* bark, study the influence of contact time, pH, sorbent dose and initial metals concentration on biosorption process performance and determine appropriate adsorption isotherm and kinetics parameters of metals biosorption on *Prosopis spicigira* bark. The results of this study showed that biosorption of heavy metals like lead (II), cadmium (II), copper (II) and chromium (VI) ions by *Prosopis spicigira* bark reached to equilibrium after 30 min and after that a little change of metals ions removal efficiency was observed. The optimum pH for maximum removal (82.5 %) was 4. The biosorption of metals by *Prosopis spicigira* bark decreased at the higher initial metal concentration and lower sorbent doses. The obtained results showed that biosorption of metals by *Prosopis spicigira* bark follows both Freundlich and Langmuir isotherm equation with correlation coefficients equal to 0.9522 and 0.9943 respectively. In addition, the kinetics of the biosorption process follows the pseudo second-order kinetics model with a rate constant values of 0.54812, 0.3423, 0.1859, 0.2653 g/mg.min for lead (II), cadmium (II), chromium (VI) and copper (II), ions respectively. The results indicate that *Prosopis spicigira* bark can be employed as a low cost alternative to commercial sorbents in the removal of lead (II), cadmium (II), copper (II) and chromium (VI) ions from wastewater.

Key words: *Prosopis spicigira* · Batch biosorption · Heavy metals · Langmuir isotherm · Commercial sorbents

INTRODUCTION

Heavy metals are toxic even at minor concentrations [1]. This term is generally used for metals and metalloids having higher density than water [2]. However, chemical properties are more important than density. The major sources of heavy metal pollution in urban areas of Pakistan are anthropogenic, while contamination from natural sources such as brush burning, windblown dusts and weathering of minerals deposits predominates in rural areas. Anthropogenic sources of pollution include electroplating, pulp and paper mills, fertilizer plants, steelwork foundries, petroleum refineries, aircraft plating, motor vehicles finishing, non-ferrous metal works, mining and metal processing. In these days, urban areas with high population, traffic and industries is the hub of toxic chemicals. Among the heavy metals, the most serious effect of pollution is presently associated with lead (Pb) emission [3, 4].

When these metals contaminate the agricultural soils, these are taken up by the plants and ultimately add up in their tissues [5]. Animals that use such pollutant affected plants and drink contaminated waters, as well as aquatic organisms take heavy metals into their body, which are

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accumulated in their tissues and milk, if lactating [6]. Humans are, in turn, exposed to heavy metals by eating these contaminated plants and animals as food. In short, all the organisms, living in an ecosystem, are differently affected through their food chain cycles.

Peoples living near industrial sites of heavy metal mining and processing are exposed, through air, by suspended particulate matters [7]. Several analytical techniques have been devised for the treatment of water containing heavy metals including chemical precipitation, Cementation process, Ion exchange resins and the use of micro organisms. But incomplete removal of toxic metals, excessive time consumption, pretreatment and long contact time requirements are the major hurdles for application of these methods. Lack of specificity, Generation of toxic sludge, sophisticated conditions requirement and inability to give better results at low metal concentrations are the main disadvantages of these methods. In present study, biosorption capacity of *Prosopis spicigira* bark was investigated for the removal of heavy metals from aqueous solutions. The effect of sorbent amount, solution pH, particle size, metal concentration, shaking time, shaking speed and number of pores were also investigated.

MATERIALS AND METHODS

Experimental Design

Preparation of *Prosopis spicigira* Sample: *Prosopis spicigira* is a species of flowering tree in the pea family. Flowers are small and creamy yellow. *Prosopis spicigira* bark was collected locally, washed with distilled water and sun dried followed by drying in oven at 110ºC to a constant weight. The dried sample was ground with mortar and pestle, particles of different sizes were separated using sieves (No. 100 and 200) and stored in plastic air tight bottles to avoid moisture absorption.

Chemicals and Reagents: All chemicals and reagents used in this research work were of analytical grade. The stock solutions containing the 1000 mg/L concentration of Pb^{+2}, Cd^{+2}, Cr^{+6} and Cu^{+2} were prepared by dissolving the Lead nitrate, Cadmium Nitrate, Potassium dichromate and Copper sulphate in distilled water and were used in experiment. Initial pH of solutions was adjusted to 4.0 by using 1N HCl or 1N NaOH before putting sorbent into solutions.

Instruments: The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biomass. The biomass samples were

examined, using IR Prestige-21 Forier Transform Infrared Shimadzu spectrometer, within range of 400-4000 cm^{-1}. All analysis were performed using, KBr as back ground material. In order to form pellets, 0.002 g of biomass was mixed with 0.3 g Kbr and pressed at 6-8 bar pressure. The surface structure and particle size distribution of biosorbent was examined using Hitachi Scanning Electron Microscope (SEM).

A variable orbital shaker OS-752 (20-500 rpm) was used for batch experimentation. It has the capacity of holding nine Erlenmeyer flasks simultaneously. It was equipped with thermostatically controlled, heating water bath. Shimadzu (AX 200) electronic balance with weighing capacity 0.1 mg to 200 mg was used to measure weight of sorbent. pH of solution was measured using HM-30V pH meter.

The filtrate was analyzed, using AA-6300, Shimadzu Atomic Absorption Spectrophotometer, to determine the quantity of residual metals. The quantity of adsorbed metal was found by material balance. The metal uptake, q_t was determined using the following equation:

$$q_t = V(C_o - C_f)/m \qquad (1.1)$$

where, 'C_o' and 'C_f' are the initial and final concentration of metal in solution (mg L^{-1}), 'V' is volume of solution and 'm' is mass of biosorbent (g).

Chemical Analyses: Air dried, platinum coated samples of the *Prosopis spicigira* bark powder were observed by using an analytical scanning electron microscope (JOEL JSM-6360A). The interactions of this powder with Cu (II), Pb (II), Cr (VI) or Cd (II) were monitored by FTIR. For this purpose, the untreated control powder and metal loaded samples were completely dried and blended with KBr to obtain a pellet. The FTIR spectra were collected at resolution of 4 cm^{-1} in the transmission mode (4,000–400 cm^{-1}) using a Shimadzu Prestige-21 FTIR spectrophotometer. Metal content in the supernatant were analyzed by AA-6300, Shimadzu Atomic Absorption Spectrophotometer.

Batch Biosorption Studies: It was done in the Erlenmeyer flask with working volume of 100 ml. Dried biomass was added at different concentrations in Erlenmeyer flasks and metal concentrations (Lead, chromium, cadmium and copper) were kept near to 50 mg/L separately for each metal at pH 4.0 using dilute HNO$_3$ and were agitated at 100 rpm at room temperature. Five ml samples were drawn at different times (10, 20, 30, 60 and 120 mins), filtered using whatman filter paper no. 42 and metal content in the

supernatant were analyzed by AA-6300, Shimadzu Atomic Absorption Spectrophotometer. Similarly, time course biosorption experiments were carried out at varying pH, biomass concentration (1, 2, 3, 4 and 5 g of 100 ml of metal solution) and with varying metal ion concentration (3, 6, 9, 12 and 15 ppm).

Specific metal removal (q) by sorbent (mg/ g) was calculated by the relation given below:

$$q = V \times (C_i - C_f) / 1000 \, W \qquad (1.2)$$

where 'V' is the volume of the metal solution, C_i represents the initial concentration (mg /L), C_f is the final concentration of metal in the solution and 'W' is the mass of sorbent (g).

Similarly biosorption efficiency 'R' (%) can be calculated as,

$$R = C_i - C_f / C_i \times 100 \qquad (1.3)$$

RESULTS AND DISCUSSION

Characterization of *Prosopis spicigira*
FTIR Analysis: FTIR spectra are valuable tools for analyzing the functional groups that may be playing a role in the biosorption process. The functional groups on the native *Prosopis spicigira* bark are shown in the Fig. 1. The major peak observed at around 3,489 cm^{-1} was assigned to the –OH stretching vibration. This peak shifted from 3,489 to 3,436 cm^{-1} and thus revealed the possible involvement of hydroxyl groups in Cd (II) biosorption onto *Prosopis spicigira* bark powder. The peak located around at 2,355 cm^{-1} can be attributed to the N–H or the C=O stretching vibrations. The peak shifted from 2,922 to 2,913 cm^{-1} and indicated the possible involvement of oxygen or nitrogen in Pb (II) biosorption. The peaks shift from 1,444 to 1,433 cm^{-1} (Cu^{-2} and Cr^{-4}) can be assigned to aliphatic and aromatic (C–H) groups in the plane deformation vibration of methyl, methylene and methoxy groups. The peak located at 1,317 cm^{-1} could be assigned to C–N stretching in aromatic amines. This peak shifted from 1,317 to 1,311 cm^{-1} (for Cu^{-2} and Pb^{-2}) and 1,246 to 1,237 cm^{-1} (for Cd^{-2}) and thus revealed the possible involvement of aromatic amines in metal biosorption. It was also observed that the peaks shifted from 1,153 to 1,148 cm^{-1} (Cr^{-4} and Cd^{-2}) suggesting the role of the C–H stretching in amide III. The band 1,031 cm^{-1} in metal free powder was assigned to C–N stretching in –CO–NH–. This peak shifted from 1,078 to 1,024 cm^{-1} thus suggesting a possible involvement of the amino groups in Pb-II biosorption onto *Prosopis spicigira* bark

powder. The FTIR study thus revealed the possible involvement of the major functional groups such as hydroxy, carboxyl and amino groups in metal ion biosorption by Prosopis Spicegera bark powder.

Scanning Electron Micrograph: Fig. 2 (a) shows the SEM micrograph image of *Prosopis spicigira* bark. It clearly indicates large number of pores and highly irregular surface which makes adsorption process of metals possible. The heterogeneous structure of raw sorbent can be seen in Figure 2 (b) SEM micrograph image of *Prosopis spicigira* bark. It is clear from figure that more number of pores is present on surface providing more sites for metal ions adsorption.

Optimization of Biosorption Parameters
Effect of Metal Concentration on Removal Efficiency: Initial metal concentration is one of the effective factors on adsorption efficiency. The experiments were done with variable initial lead, cadmium, chromium and copper concentrations (3, 6, 9, 12 and 15 mg/L) and constant temperature (30°C), pH (4), agitation speed (100 rpm), contact time (20 min) and 2 g of sorbent dose (2 g/100 ml). The experimental results of the effect of initial metals concentration on removal efficiency were presented in Fig. 3. It is shown that heavy metals ions (Pb^{+2}, Cd^{+2}, Cr^{+6} and Cu^{+2}) removal efficiency decreased with the increase in initial metal concentration. In case of low metal concentrations, ratio of the initial number of moles of metal ions to the available surface area of sorbent is large and subsequently the fractional adsorption becomes independent of initial concentration [8]. However, at higher concentrations, the available sites of adsorption become fewer and hence percentage removal of metal ions which depends upon initial concentration, decreases. Hence the adsorption rate is a function of initial metal concentration [9, 10].
Another factor which may decrease the adsorption efficiency is the agglomeration of adsorbent particles at higher concentrations as total surface area available for adsorption becomes smaller [11].

Effect of pH on Removal Efficiency: The pH of aqueous solution is clearly an important parameter that controls the adsorption process. The experiments of this stage were done under conditions of constant temperature (30°C), agitation speed (100 rpm), contact time (20 min), sorbent dose (2g/100 ml) and initial metals concentrations (6 mg/L). pH of solution was changed and the metals removal was investigated. The experimental results of this stage are presented in Fig. 4. As it is shown, the optimum

Table 1: Functional groups responsible for adsorption of metals

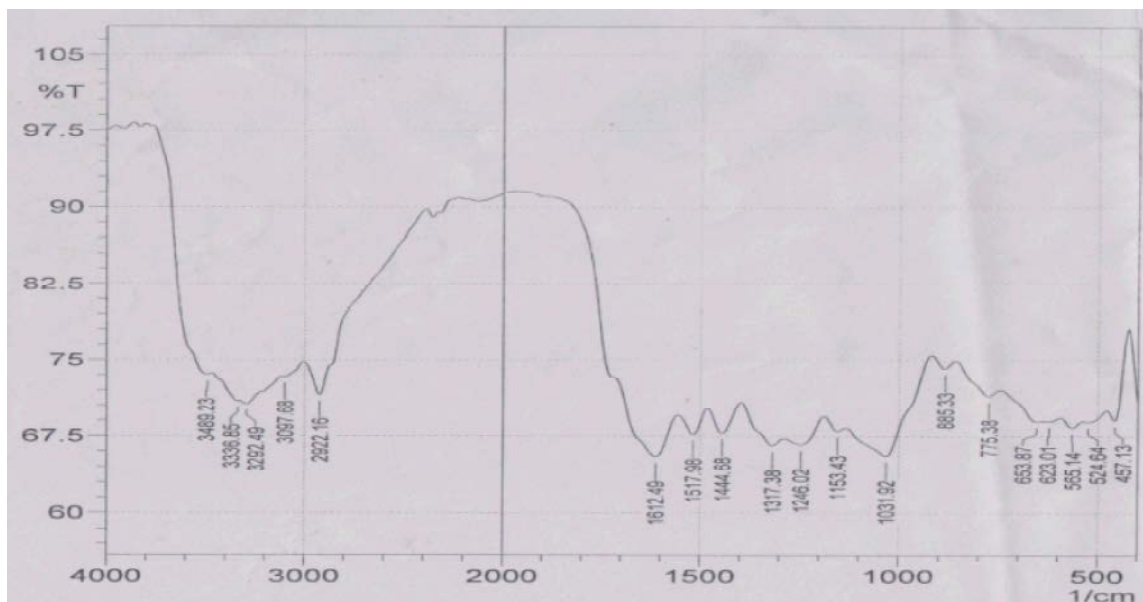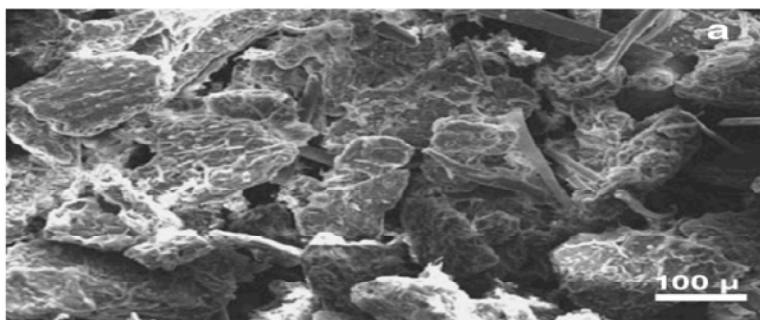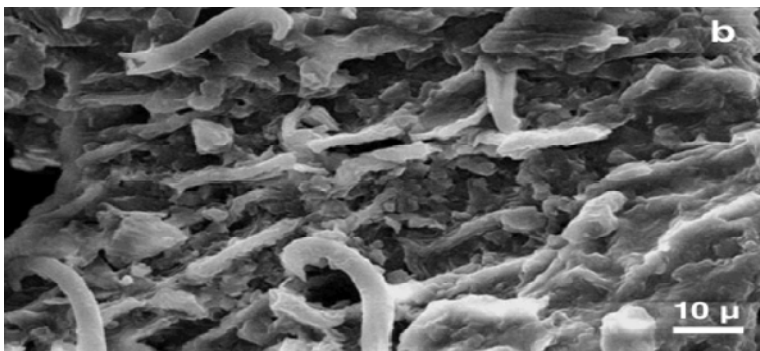| Functional group	IR frequency Range (cm^{-1})	Metals Removed
-OH	3,489	Cd (VI)
N-H or C=O	2,355	Pb (II)
C-H	1,444	Cu^{-II} and Cr^{-VI}
C–N	1,317	Cu (II), Pb (II), Cd (VI)

Fig. 1: FTIR spectrograph of native *Prosopis spicigira* bark

Fig. 2a: Scanning electron micrographs of *Prosopis spicigira* bark powder before biosorption of metal ions magnification ×150, bar represents 100μm

Fig. 2b: Scanning electron micrographs of *Prosopis spicigira* bark powder before biosorption of metal ions magnification ×1,000, bar represents 10μm
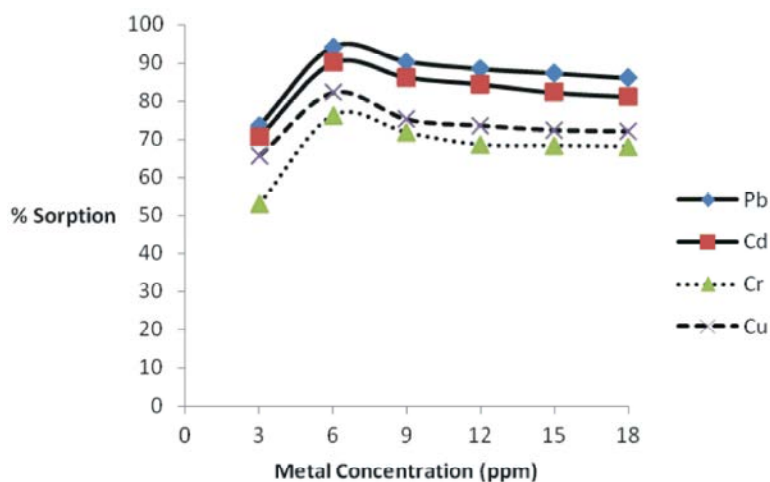
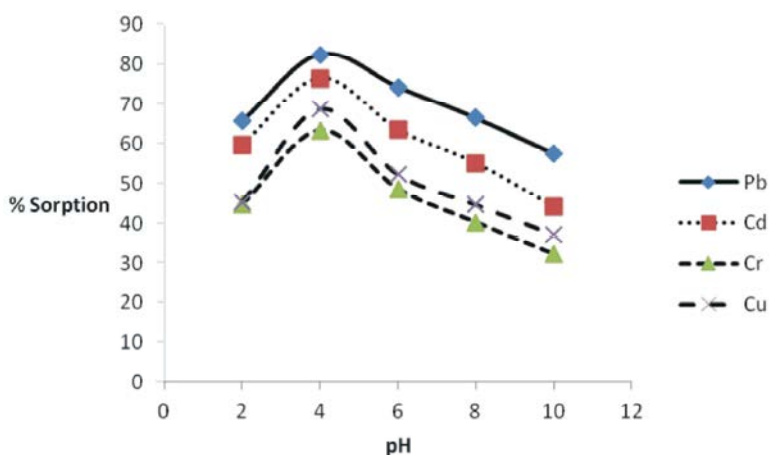Fig. 3: Effect of metal concentration on % adsorption

Fig. 4: Effect of pH on % adsorption

pH of solution was observed at pH of 4 and by increasing pH, a drastic decrease in adsorption percentage was observed. This might be due to the weakening of electrostatic force of attraction between oppositely charged sorbate and sorbent that ultimately leads to the reduction in adsorption capacity. Less adsorption at low pH (<4) may be attributed to the presence of H_3O^+ ions in the solution, which compete with metal ions and thus hinders their approach to protonated binding sites of sorbent surface [12]. The increase in adsorption with increase of pH (Up to pH 4) may result owing to more electrostatic interactions between negatively charged binding sites available on the *Prosopis spicigira* bark surface and the metal cationic species, which thus decrease the stability of metal ions in solution. At higher pH, oxygen of each negatively charged binding sites available onto *Prosopis spicigira* bark matrix (-C=O or -OH groups of polyphenols) behaves as strong Lewis base

and may result in complexation of metal ions. A further increase of pH decreases the solubility of metal ions due to formation of their hydroxides in solution [13] which may result in suppression of adsorption efficiency of *Prosopis spicigira* bark.

Effect of Sorbent Dose on Removal Efficiency: At this stage, experiments were done under conditions described at previous stage with constant pH of 4 and variable sorbent dose (1, 2, 3, 4 and 5 g/100 ml). The effect of sorbent dose on adsorption of metal ions by *Prosopis spicigira* bark was presented in Fig. 5. It indicates that metals removal efficiency increased with increase in sorbent dose, since contact surface of sorbent particles increased [14, 15]. It would be more probable for metal ions to be adsorbed on adsorption sites and thus adsorption efficiency increased.
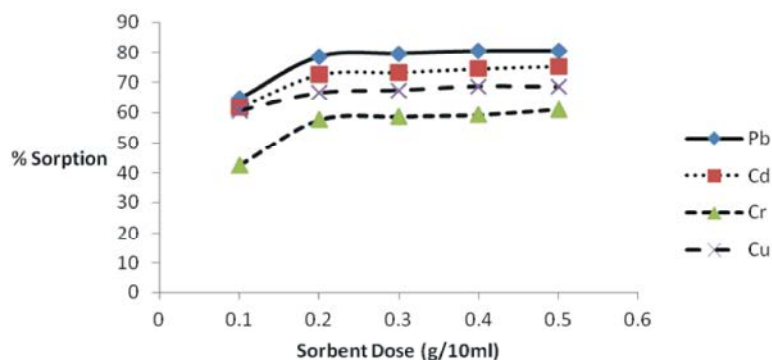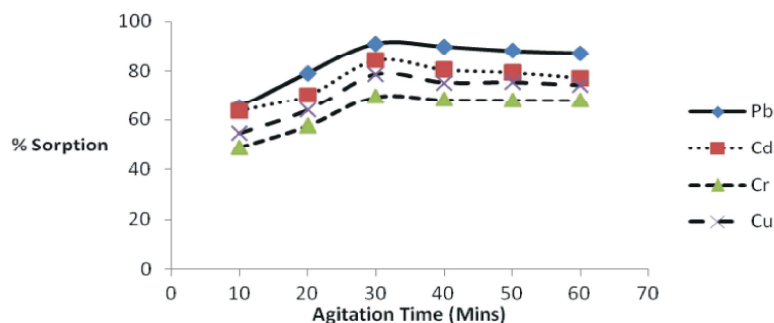
Fig. 5: Effect of sorbent dose on % adsorption

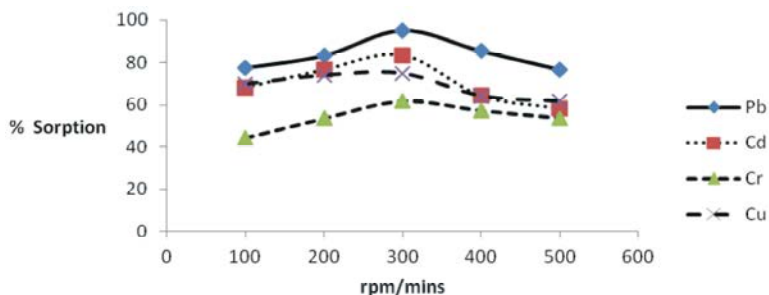Fig. 6: Effect of contact time on % adsorption

Fig. 7: Effect of shaking speed on % adsorption

Effect of Contact Time on Removal Efficiency: Contact time is one of the effective factors in batch adsorption process. In this stage, all of the parameters except contact time, including temperature (30°C), sorbent dose (5 g/100 ml), pH (4), initial metals concentration (6 mg/L) and agitation speed (100 rpm), were kept constant. The effect of contact time on Cu (II), Pb (II), Cr (VI) or Cd (II) adsorption efficiency showed in Fig. 6. As it is shown, biosorption rate initially increased rapidly and the optimal removal efficiency was reached within about 30 min. to 91 %. This was due to the availability of more active sites initially [16]. There was no significant change in equilibrium concentration after 30 min. up to 60 min. and after 30 mins, the biosorption phase reached to equilibrium. This is due to the saturation of active sites and the repulsion between adsorbed molecules and those in the bulk phase [17]. The order of

removal efficiency remained $Pb^{+2} > Cd^{+2} > Cu^{+2} > Cr^{+6}$ throughout the entire range of contact time investigated. This order may be correlated with atomic mass of metals and solubility of their salts in water. The greater the atomic mass, the greater is the removal efficiency because metals with higher atomic mass will have more probability to come into contact with the sorbent surface. More soluble substances in water prefer to remain in aqueous solution than to be adsorbed on the sorbent surface.

Effect of Shaking Speed on Removal Efficiency: At this stage, the experiments were done under conditions described at previous stage with constant pH of 4 and variable shaking speed (100, 200, 300, 400 and 500 rpm). The effect of shaking speed on adsorption of metal ions by *Prosopis spicigira* bark was presented in Fig. 7.

Table 2: Freundlich isotherm parameters

Metals	Multilayer adsorption capacity (C_m)	Characteristic constant (n)	R^2
Pb	0.736	2.7196	0.9522
Cd	0.788	2.0820	0.9674
Cr	0.9485	1.1281	0.9886
Cu	0.6836	6.644	0.9138

Table 3: Langmuir isotherm parameters

Metals	Slope	Intercept	Langmuir constant(b)	Q(mol/g)	Separation factor (R_L)	Correlation coefficient(R^2)
Pb	0.281	-0.087	3.2523	3.5587	0.0397	0.994
Cd	0.308	-0.157	2.1182	3.2457	0.064	0.956
Cr	0.501	-0.597	0.5161	1.994	0.222	0.940
Cu	0.266	-0.067	2.3289	3.7509	0.0595	0.986

Table 4: D-R isotherm parameters

Maximum adsorption capacity	Polanyi adsorption potential	β	Correlation coefficient (R^2) (X_m mmol/g)	(ε)
Pb	-13.38	33.12	0.002	0.851
Cd	-13.65	30.99	0.003	0.668
Cr	-16.41	29.90	0.006	0.689
Cu	-11.84	30.37	0.001	0.314

As illustrated in figure metals removal efficiency increased with increase in shaking speed up to 300 rpm This may be due to the reason that by increasing the agitation speed, the diffusion rate of metal ions from the bulk liquid to the sorbent particles becomes higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer [18]. Further increase in shaking speed leads to decrease in adsorption.

Apparent equilibrium constant (K_c) for the process has been described as:

$$K_C = \frac{C_{ad}}{C_{aq}}$$ (1.4)

where 'C_{ad}' and 'C_{eq}' are the adsorbed (mg.g^{-1}) and equilibrium metal ion concentrations (mgL^{-1}), respectively.

Adsorption Isotherms: The distribution of metal ions between liquid phase and solid phase can be described by several isotherm models such as Langmuir, Freundlich and Dubinin–Radushkevich (D-R). The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. However, the Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption and Dubinin–Radushkevich (D-R) isotherm assumes a heterogeneous surface, too. In order to find the most appropriate model for lead, cadmium, chromium and copper adsorption, the data were fitted to each isotherm model. The obtained isotherm parameters and correlation coefficients (R^2) are presented in Table 2. The experimental and predicted isotherms for *Prosopis spicigira* bark at 30±1 °C are given in Fig. 8. The results showed that the Langmuir adsorption isotherm was the best model for metals (Pb^{+2}, Cd^{+2}, Cr^{+6} and Cu^{+2}) adsorption on Prosopis Spicegera bark with R^2 of 0.997 as shown in Fig. 9. Langmuir isotherm model parameters are given in Table 4. The essential features of Langmuir adsorption isotherm can be expressed in terms of a dimensionless constant called separation factor or equilibrium parameter (R_L), which is defined by the following relationship:

$$R_L = \frac{1}{1 + bC_o}$$ (1.5)

where, C_0 is the initial metals concentration (mg/L). The R_L value indicates the shape of the isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 0$) or unfavorable ($R_L > 1$). Through the above mentioned equation, R_L value for investigated Pb^{+2}, Cd^{+2}, Cr^{+6} and Cu^{+2} sorbent system is found to be 0.0397, 0.064, 0.222 and 0.0595 respectively. From the value of R_L, it is confirmed that *Prosopis spicigira* bark is desirable for biosorption of lead, cadmium, chromium and copper from wastewater under the conditions used in this study. For Freundlich isotherm, as it was shown in Table 2, n is equal to 2.7196, 2.0820, 1.1281 and 6.644. The situation n > 1 is most common and may be due to a distribution of surface sites or any factor that cause a decrease in sorbent-sorbate interaction with increasing surface density and the values of n within the range of 2-10 represent good biosorption.

Table 5: Morris–Weber parameters

K, first order rate constant (min^{-1})		$R_{id,}$ intra-particle diffusion rate constant (mol g^{-1} min^{-1})
Pb	0.0073	1.3349
Cd	0.0051	1.2195
Cr	0.0076	1.187
Cu	0.0006	1.1706

Table 6: Kinetic adsorption parameters

Metals	Slope	Intercept	R^2	K_1	K_2
Pb	0.0032	0.6087	0.5451	0.00171	0.54812
Cd	0.0022	0.5998	0.3628	0.00171	0.3423
Cr	0.0033	0.4805	0.5487	0.00171	0.1859
Cu	0.0002	0.6144	0.0113	0.00171	0.2653

Table 7: Parameters of Pseudo- second order model

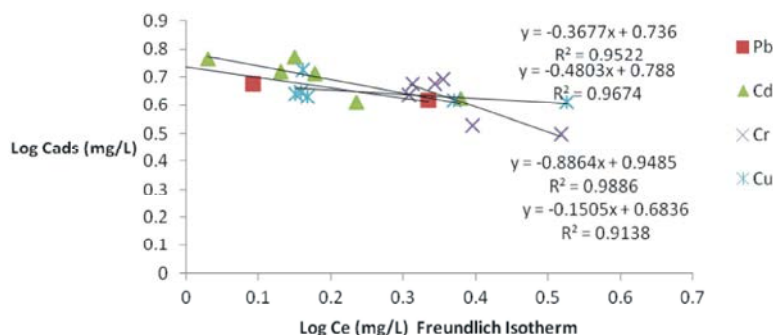| $K_{2,ads}$	h (mg/g.min)	R^2
2.924	17.66	0.973
3.54	10.96	0.962
3.931	21.99	0.958
4.653	-4.609	0.982

Fig. 8: Freundlich isotherms of Pb (II), Cd (II), Cr (VI) and Cu (II)
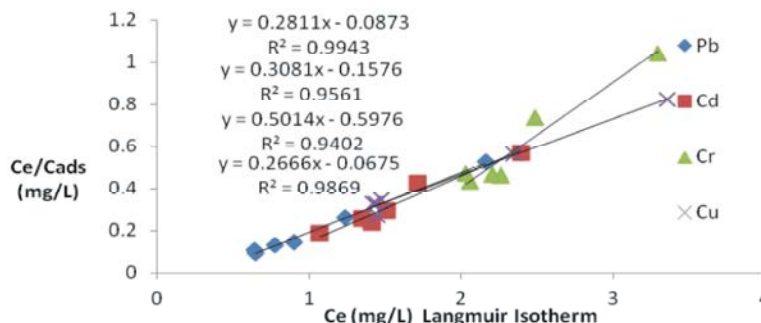

Fig. 9: Langmuir isotherms of Pb (II), Cd (II), Cr (VI) and Cu (II)

Kinetics of Adsorption: In order to define the adsorption kinetics of heavy metal ions, the kinetics parameters for the adsorption process were studied for contact times ranging from 10 to 60 min. by monitoring the removal percentage of Cu (II), Pb (II), Cr (VI) or Cd (II). The data were then regressed against the Lagergren equation (Eq. 1.6), which represents a first-order kinetics equation and against a pseudo-second-order kinetics equation (Eq. 1.7).

$$\text{Log }(q_e - q) \quad Log(qe) - \frac{K_{1ad}}{2.303}t \tag{1.6}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{1.7}$$

where, q_t is the metal uptake per unit weight of sorbent (mg/g) at time 't', 'q_e' is the metal uptake per unit weight of sorbent (mg/g) at equilibrium and 'k_1' (min^{-1} and k_2 (g/mg.min) are the rate constants of the pseudo-first-order
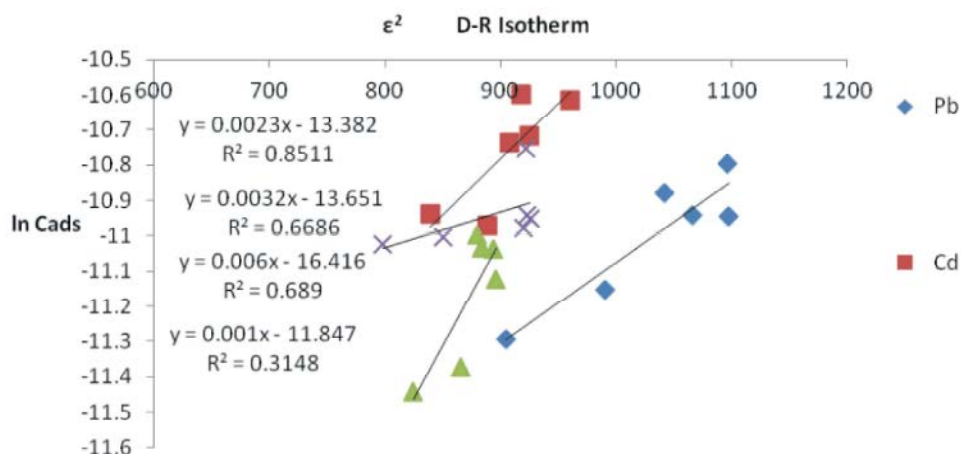
Fig. 10: D-R isotherms of Pb (II), Cd (II), Cr (VI) and Cu (II)
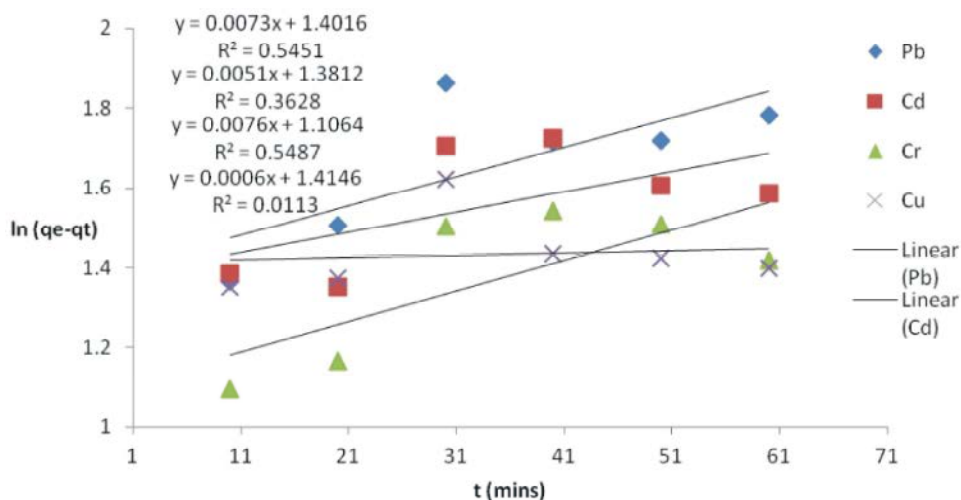

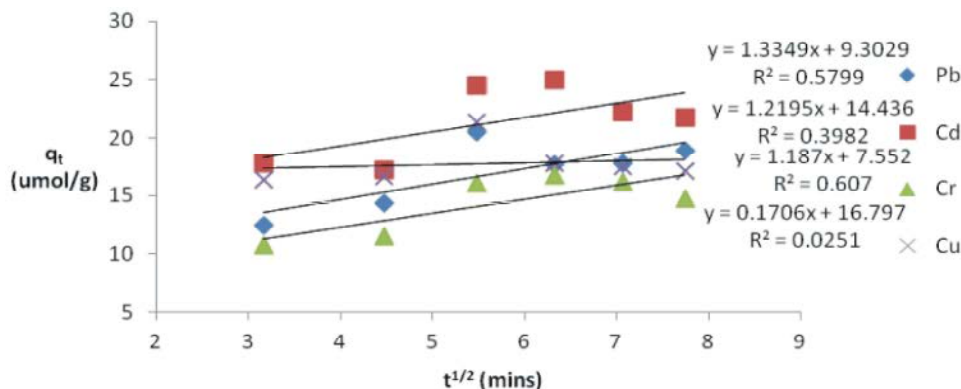Fig. 11. Pseudo First Order Model for Adsorption of Pb (II), Cd (II), Cr (VI) and Cu (II)

Fig. 12: Morris Weber plot for Adsorption of Pb (II), Cd (II), Cr (VI) and Cu (II)

and pseudo-second-order kinetics equations, respectively. The slopes and intercepts of these curves were used to determine the values of K_1 and K_2, as well as the equilibrium capacity (q_e). The first and second order kinetics constants are presented in Table 5. The results indicated that the adsorption process follows pseudo-second-order model. The plot of t/q_t versus $1/q_e$ gives a straight line as shown in Fig. 13.
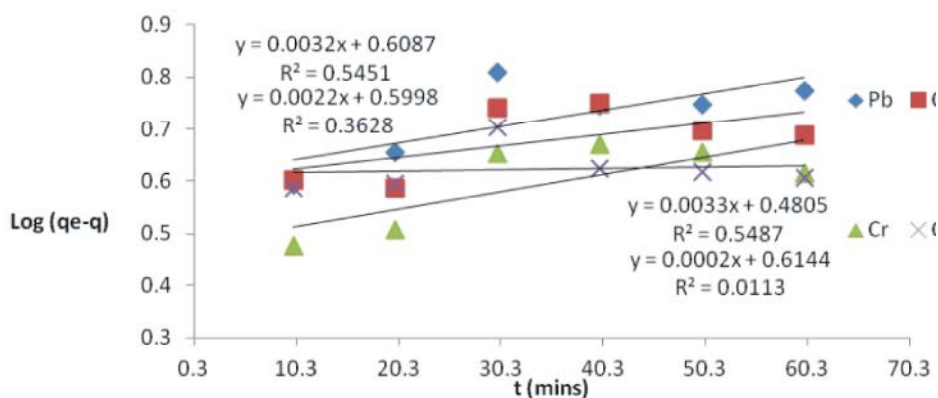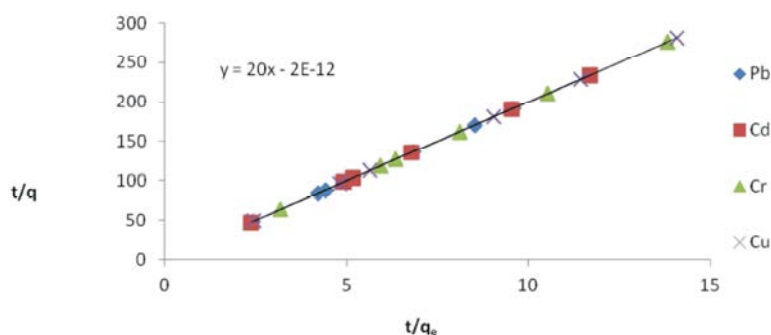
Fig. 13: Pseudo First Order Model

Fig. 14: Pseudo Second Order Model for Adsorption of Pb (II), Cd (II), Cr (VI) and Cu (II)

CONCLUSION

The present study on heavy metal adsorption by *Prosopis spicigira* bark powder revealed that the maximum specific uptakes for Cu (II), Pb (II), Cr (VI) and Cd (II) were 48.40±0.5, 45.9 ± 0.5, 35.56 ± 0.6 and 38.65 ± 0.7 mg g^{-1}at pH 4.0, when 6 mg L^{-1} of the metal solutions were used at 30°C. Both Freundlich and Langmuir isotherms fitted well to the adsorption data. The dimensionless separation factors, R_L, were favorable on lower as well higher metal ion concentrations and the surface coverage (θ) values suggested that the *Prosopis spicigira* bark powder has a high affinity for the metal ions. Kinetic studies fitted to the pseudo-second-order equation indicating that chemical reactions may be playing a role in the metal adsorption process. Scanning electron micrographs confirmed porous nature of the *Prosopis spicigira* bark powder and its suitability for heavy metal ion adsorption. FTIR studies indicated the possible involvement of hydroxyl, carboxyl and amino groups in metal ion adsorption process. Through this study the potential of a new cost-effective and abundantly available natural sorbent for the removal of a variety of heavy metal ions from aqueous solutions was identified. These laboratory studies suggested that an effective alternative to other cost-intensive methods such as solvent extraction, chemical oxidation, or active carbon adsorption could be developed.

Prosopis spicigira bark is a cheap material so its utilization in industrial wastewater treatment plants would be convenient. Meanwhile it is possible to increase the treatment efficiency by pretreatment with some chemicals such as acids, bases and detergents. Finally we recommend to evaluate the effect of pretreatment processes for this type of treatment and to investigate the probable changes of adsorption efficiency in conditions of encountering the various metals in actual wastewaters.

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