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Biosorption of some toxic metals by pine nut shell from contaminated waste water

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Key words: Heavy metals, Adsorption, Pine nut shell, Biosorption, Contaminated water

Abstract

Adsorption is a cost effective method to remove heavy metals from industrial effluents. This study uses batch adsorption techniques to determine the potential of pine nut shell (PNS) and its thermally treated form i.e. pine nut shell ash (PNSA) as an adsorbent for removal of Cu(II), Pb(II) and Cr(VI). PNS proved to be an appreciable sorbent for the removal of Cu, Pb and Cr metal ions (86%, 93% and 80%) respectively from aqueous solution. The chemical (HNO_3 and K_2CO_3) and thermal activation (873 K for 6 hours) of pine nut shell increased the removal efficiency for toxic metal ions. Metal ion concentration of 9 ppm, 0.5 gram sorbent dose, 20 min agitation time, agitation speed of 100 rpm and 4pH were optimized conditions for sorption process. The sample was characterized by SEM & FTIR. Freundlich, Langmuir and Dubinin–Radushkevich (D-R) sorption isotherms was used to assess the sorption capacity. Adsorption isotherm parameters of Cu(II), Cr(VI) and Pb(II) onto PNS have been found to be 1.12, 1.23, 1.08 mmol g^{-1} by Freundlich, 0.031, 0.028, 0.026 mmol g^{-1} by Langmuir and 0.37, 0.39,0.36 mmol g^{-1} by D–R isotherms respectively. While the mean energy of sorption process 11.18, 15.81, 10.0 kJ mol^{-1} for Cu (II), Cr(VI) and Pb(II) is calculated by D–R isotherm. This study concluded that, the sorption process by pine nut shell under optimized conditions is stable, spontaneous, and exothermic and can be effectively used in adsorption of toxic metals from contaminated water.

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Introduction

Water pollution is the global issue which causes at least 5 million deaths per year due to waterborne diseases (Abia *et al.*, 2003). Heavy metals are the major class of water pollutants originated from urbanization, pesticides, municipal, industrial, agriculture uses and coal burning (Hamid *et al.*, 2016). Some heavy metals like Cu, Pb, Cr, Ti and Ag are toxic in aquatic ecosystem and directly or indirectly create human health issues (Khan *et al.*, 2015; Shakeel *et al.*, 2015; Asghar *et al.*, 2016). Slightly increased levels of these heavy metals pollutants may promote variety of sub-lethal or toxic effects in aquatic organisms (Jalali *et al.*, 2002; Tabari *et al.*, 2010; Tchounwou *et al.*, 2012; Khan *et al.*, 2015b). The absorption of heavy metals in plants tissue and bioaccumulation in the aquatic animal tissue pass on to human through food chain leading to symptoms of cellular disorders, toxicity and eventually death (Nadeem *et al.*, 2009; Asghar *et al.*, 2015; Khan *et al.*, 2015).

Regarding the toxic effects of heavy metals, it is essential to remove them from wastewater using conventional methods i.e. Electro-dialysis, Ion exchange, Reverse osmosis, Ultra-filtration, Chemical precipitation and Phytoremediation (Matheickal *et al.*, 1999; Barakat, 2011). All of these techniques involve expensive reagent and laborious methodologies therefore less important (Xia and Liyuan, 2002; Hegazi, 2013). The need of trouble-free, efficient, economic and eco-friendly techniques for enhancement of wastewater treatment is still necessary (Mahmud *et al.*, 2016). This need develops new technique known as biosorption, which was based on the ability to bind metals by taking in consideration numerous biological materials. By this technique it is easy to avoid the production of toxic sludge, possibly recover the metal concentration and regenerate the biomass (Qaiser *et al.*, 2007; Mahmud *et al.*, 2016).

The uptake efficiency of biosorbents has been proved to be better than that of commercially available ion exchange resins. Moreover, biosorbent materials are economical, easy to prepare and available in excess (Choi *et al.*, 2009).

Several types of biosorbents are employed including the seaweeds, nut shells and industrial waste products e.g. yeast (Rahimizadeh and Liaghatb, 2015). Senthil-Kumar and Mysore (2011) employed cashew nut shell (CNS) as a biosorbent for the elimination of Cu ions from aqueous solutions. Murthy *et al.* (2012) treated coconut shell powder as adsorbent to remove copper ions from aqueous solutions. Abdolali *et al.* (2016) used multi-metal binding biosorbent made up of tea wastes, maple leaves and mandarin peels for removal of Cd (II), Cu (II), Pb (II) and Zn (II) in waste water.

In this study, the biosorption of Pb, Cu and Cr on to pine nut shell (Family: Pinaceae, Genus: *Pinus*) and pine nut shell ash was investigated. The main objective of present study is to investigate the sorption capacity of PNS for the removal of heavy metals from aqueous solutions. Sorbent was modified thermally and chemically to evaluate any improvement in sorption capacity. Analysis of data by various sorption isotherms i.e. Langmuir, Freundlich and D.R. reveal the feasibility of sorption process.

Material and methods

All chemicals were of analytical grade and purchased form Sigma alderich and Merck (Germany) via local distributor

Collection and Pretreatment of Sample

Pine nut shells were collected from local dry fruit market of Sargodha, Pakistan. The shells were cleaned out of edible materials, washed thoroughly for three times and soaked overnight in distilled water to remove particulate matter and other waste soluble residues. They were then subjected to sun-dried followed by oven drying in an electric oven (IRMECO) at 110°C for 3 hours to attain constant weight. One Kg of pine nut shells were sub-sampled, grinded and sieved to get homogenous particle size by passing through the sieves having 50, 100 and 200 µm mesh sizes respectively. The sieved material was stored in an air tight plastic container to uphold damp free conditions. Selected sorbent was washed with ample amount of deionized water and then dried at 383 K for 3 hours. 100g of uniform particle sized sorbent was soaked in 0.1 M HNO_3 for 2 hours to achieve chemical activation and to increase the surface area. Soaked material was then dried at 383 K for 2 hours.

Acid treated sample was again soaked in 1M K_2CO_3 for basic pretreatment. The treated biosorbent was repeatedly washed with deionized distilled water (DDW) in each case, until a pH of 7 was reached. The chemically treated and thoroughly washed sorbent was then subjected to drying at 383 K for 24 hours and stored for sorption studies.

FTIR studies

Infrared spectra of Pine nut shell and pine nut shell ash were obtained after drying the biomass at 110° C for 24 h. The finely powdered samples were encapsulated with potassium bromide to prepare translucent sample disks, and the spectra were recorded using a Fourier transform infrared spectroscope (IR prestige-21 SHIMADZU).The spectra were measured within the range of 500–4000 cm^{-1}.

Optimization of Sorption Parameters

Metal ion concentration of 9 ppm, 0.5 gram sorbent dose, 20 min agitation time, agitation speed of 100 rpm and pH 4 were adopted as optimized conditions for sorption process.

Batch Sorption Studies

In all sets of experiments, fixed volume of Cu (II), Cr (VI) and Pb (II) solutions (100 mL of 100 mg/L) were taken in each 250 mL conical flasks. The initial pH of each metal solution was adjusted to the required pH value using 0.1 N NaOH and 0.1N HCl. Solutions were agitated in orbital shaker at different RPM and for different time intervals. After 24 hours, samples were filtered with filter paper (Whatman No. 40, ashless) and stored in plastic sample bottles at 4˚C till AAS analysis. Metal concentrations were determined using AA-6300 SHIMADZU Atomic Absorption Spectrophotometer. Maximum metal sorption capacity (q) was determined by decrease in metal concentration in the solution after addition of different amounts of sorbent. The initial concentration, C_i (mg/L) and equilibrium metal concentrations, C_e (mg/L) respectively, were determined.

The following equations were used to compute the percent metal uptake and sorbent uptake capacity at equilibrium q_e (mg/g) respectively:

$$\%\ \text{Sorption} = \frac{(\text{Ci}-\text{Ce})}{Ci} \times 100$$

$$qe = \frac{(\text{Ci}-\text{Ce})}{1000} \times \frac{\text{V}}{W}$$

Where V is the volume of the solution in mL and W is the mass of the sorbent in g. All the data shows the mean of three independent experiments. All results were computed by using mean ± SD. Statistical analyses were performed and correlation coefficient R^2 values of the linear form of Langmiur, Frendlich, D-R models and of Webber-Morris model were also determined.

Sorption Isotherms

The experimental sorption particulars usually evaluated by utilizing three isotherm models i.e. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models. Freundlich isotherm describes equilibrium on heterogeneous surfaces and the isotherm is described by the following equation

$$\log C_{ads} = \log C_m + 1/n \log C_e$$

Where, C_{ads} (mol/g) and C_e (mol/L) are sorbed and equilibrium concentrations of sorbate onto sorbent surface and in solution at equilibrium. C_m (mmol/g) represents the multilayer sorption capacity of sorbent. 1/n is Freundlich constant and was calculated from the slope and intercept of the Freundlich plots. Langmuir isotherm was linearized form of relationship.

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

Where Q (mmol/g) is the monolayer sorption capacity of sorbent and b (L/mol) is a constant related to the free energy of sorption and is independent of temperature. The Dubinin-Raduskevich (D-R) isotherm was calculated with following relationship

$$\ln C_{ads} = \ln X_m - \beta\varepsilon^2$$

Results and discussion

Heavy metal pollution is increasing in the aquatic environment form industrial influents, domestic usage, commercial usage and agriculture (Hamid *et al*., 2016; Khan *et al*., 2016). Various biosorbants are used for the remediation. In the present investigation, pine nut was employed for the adsorption of some heavy metals in the contaminated water.

FTIR technique was used to examine the surface groups of the adsorbent and to identify those groups responsible for dye adsorption. Adsorption in the IR region takes place because of rotational and vibrational movements of the molecular groups and chemical band of a molecule (Cardoso *et al*., 2011; Simonescu, 2012).

Significant differences are present in the spectra of pine nut shell and pine nut shell ash; both demonstrate number of peaks responsible for sorption. Broad band for Pine nut shell spectra in the region ~ 3502 cm^{-1} in PNS spectrum, in Fig. 1 may be assigned to–OH stretching vibration mode of chemisorbed water or may be due to binding of –OH group with polymeric structure of Pine nut shell. Peak obtained at ~1722 cm^{-1} may be due to –COOH group.

The small peaks observed in the region of ~ 1508-1444 cm^{-1} are attributed to ether and carboxylate groups. Finally, the broad bands at ~ 1259 and 1028 cm^{-1} are expected to be due to overlapping of C-O-C stretching, C-O stretching and -OH bending modes of ether, phenolic and alcoholic groups and a small peak position at ~ 889 cm^{-1} may be due to Si-O-Si linkage (Burneau *et al*., 2000).

The spectrum of pine nut shell ash, Fig. 2 demonstrates a sharp peak at ~ 1475cm^{-1} responsible for NO_2 stretching. The effect of initial metal ion concentration is the most important parameter in sorption experiment which sets the base for the rest of the process. It predicts which concentration of sorbate is to be kept constant for further experiments.

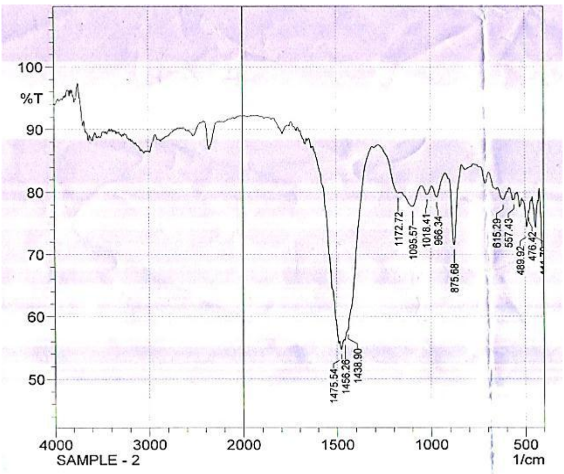

Fig. 1. FTIR spectra of PNS showing the attached compounds.

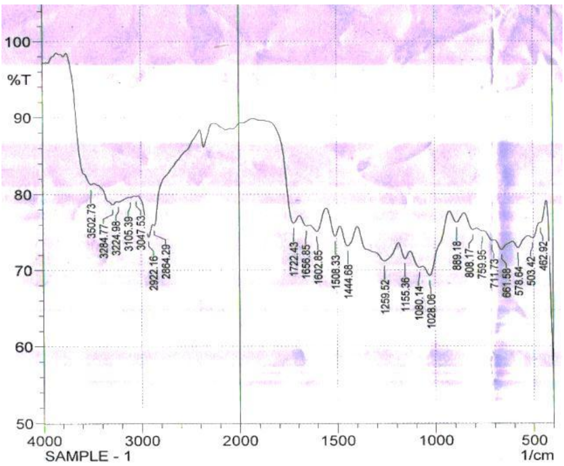

Fig. 2. FTIR spectra of PNSA showing attached compounds.

The concentration range of metal ion solution was selected between 3 to 15 mg/L. Solutions were taken by using 0.5 g of adsorbent under optimum conditions. Fig.-3 shows that sorption increases by increasing initial metal ion concentration (C_i) for all metals. Maximum removal of metal ions was found at 9 ppm while after that concentration, the removal becomes almost constant. The reason of increased sorption capacity is more concentration of metal makes available more amount of sorbate to adsorb on the surface of sorbent. Equilibrium establishes at 9 ppm concentration of metal ions and removal efficiency becomes constant after that concentration. So, optimum value of 9 ppm was adopted for further experiments (Fig. 4).

It is further raveled that percent sorption increases by increasing the contact time eventually attains equilibrium value after 20 min. The increase in extent of % sorption value with increasing shaking time is due to the availability of more vacant sites and high value of concentration gradient of metal ions on the surface of sorbent and aqueous solution. After lapse of time, occupation of sorbent surface with metal ions becomes difficult due to repulsion between metal ions adsorbed onto sorbent and in bulk solution. Besides, during initial stage of adsorption mesopores gets saturated with metal ions, furthermore, metal ions have to adsorb into deeper pores encountering much more repulsion (Saeed *et al.*, 2005), so no increase in % removal results during later period of time after attaining an equilibrium state.

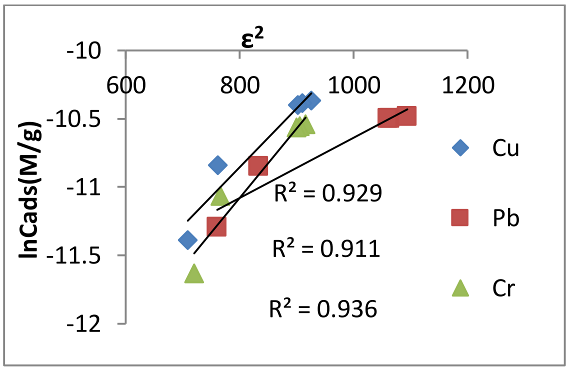

Fig. 3. Linearized D-R adsorption isotherms of Cu, Pb and Cr by PNS. Experimental conditions: temperature: 30° C; sorbent dose: 0.5 g; agitation rate: 100 rpm; sorbate concentration 9: g/L; pH: 4.

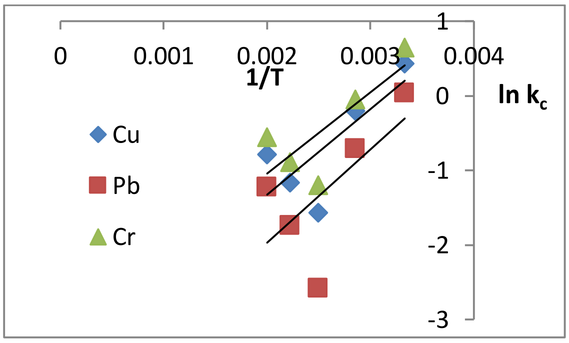

Fig. 4. Relation between Temperature and Equilibrium Constant k_c.

The adsorption of Cu, Pb and Cr metal ions was studied over the range 2-8 pH at shaking speed of 100 rpm, contact time of 20 min, sorbent dose of 0.5 g and sorbate concentration of 9 ppm.

The adsorption efficiency of PNS and PNSA increased with the increase in pH up to 4 but further increase of pH decreased the sorption. Hence, pH value of 4 was taken as the optimal pH value for further adsorption experiments. Less sorption at low pH value may be attributed to the presence of H^+ and H_3O^+ ions in the solution, which hinders the metal ions approach to protonated binding sites of the sorbent surface.

The increase in sorption with increase of pH up to 4 may result owing to more electrostatic interactions between the negatively charged binding sites. Available onto pine nut shell matrix (C=O or OH groups of polyphenols) behave as strong Lewis base and may result in complexation of metal ions (Namasivayam and Yamuna, 1995). Further increase in pH decreases the solubility of metal ions due to formation of their hydroxides in solution, which may result in suppression of sorption efficiency of PNS and PNSA (Fig. 5).

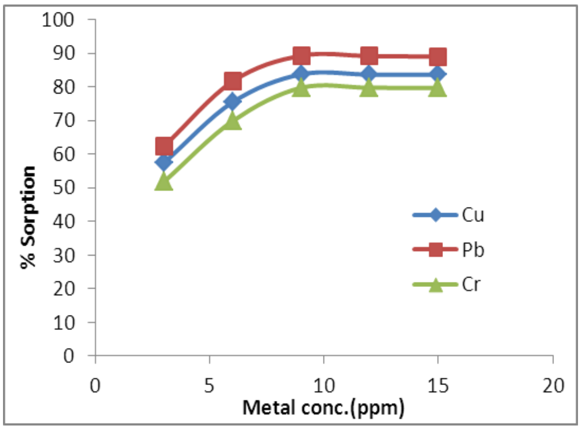

Fig. 5. Effect of metal ion concentration on % removal for PNS.

Effect of sorbent dose on removal efficiency was conducted by batch sorption experiments using variable amount of sorbent (0.1-1 g) and set optimum conditions.

The percent (%) removal value increased as sorbent amount was increased from 0.1-0.5 g, with maximum % removal values of selected metal ions i.e 86% for Cu, 94% for Pb and 81% for Cr. On further increase in sorbent amount, removal values remain unchanged (Fig. 6-7). Sorption density decreased due to unsaturation of more sorption sites as the amount of sorbent is increased.

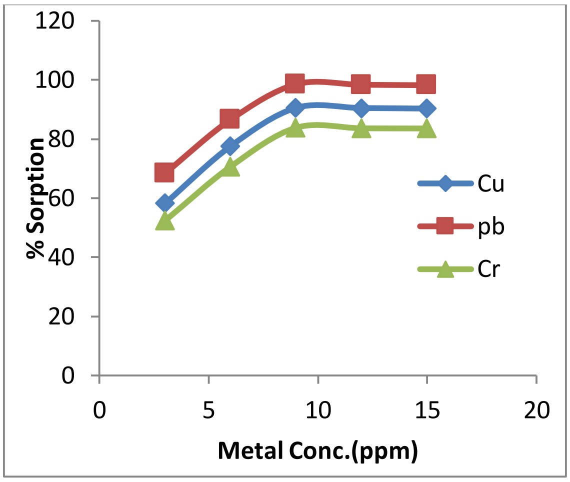

Fig. 6. Effect of metal ion concentration on % removal for PNSA.

At sorbent dose ≈ 0.5 g, sorbent dose becomes saturated with metal ions, still concentration of residual metal ions in the solution is high and maximum sorption value was observed at sorbent amount of 0.5 g. So 0.5 g sorbent dose was selected as optimized value for further studies.

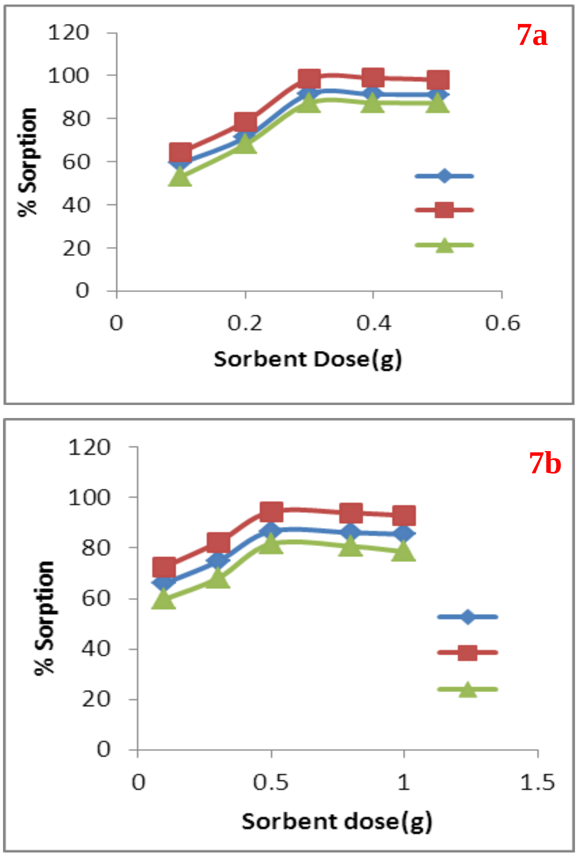

Fig. 7 (a,b). Effect of sorbent dose on % removal for PNS and PNSA.

After that % removal value of metal ions becomes almost constant and not affected by increasing sorbent dose and attains an equilibrium state, in accordance with earlier reports of metal ion biosorption (Nouri *et al.*, 2009).

Sorption Isotherms

Sorption isotherms depict the certain relationship between the degree of accumulation of sorbate onto surface of sorbent at constant temperature and concentration of sorbate. The values of n computed from the slope of the plots (0.622 ± 0.02, 0.338 ± 0.04, 0.734 ± 0.03 for Cu, Pb and Cr respectively) indicate better sorption at low concentration of (Table 1).

Langmuir isotherm determines the sorption of sorbate onto saturated mono layers of sorbent at specific homogeneous sites. The values of Q (monolayer sorption capacity) are analyzed from the slope of linear plots (Table 2). The metal ions i.e. Cu, Cr and Pb were taken to the atomic absorption spectrometer to exhibit their light absorption ability.
Initial metal ion concentration depicts the absorption ability of sample before adsorption of metal ions on pine nut shells. Equilibrium metal ion concentration shows the absortion ability of sample after the adsorption of metal ions onto PNS. Table indicates that before the sorption of metal on sample, the concentration of radiations passed is high whereas after making solution of sample with metals, the concentration of radiations passed decreases. It shows that the sample adsorbs the metal ions from solution in noticeable amount i.e. 87%, 92% and 81% respectively for Cu (II), Pb (II) and Cr (VI) which can ultimately purifies the sample.

Dubinin-Raduskevich (D-R) isotherm was projected by Dubinin and coworkers for vapours in micro-porous solids where a sorption phenomenon obeys pore filling mechanism onto the non-uniform surface. The most important parameter in D-R equation is characteristic energy determination.

The Polanyi sorption potential ε is the amount of energy required to pull a sorbed molecule from its sorption site to infinity may be evaluated by using relationship

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right)$$

Table 1. Freundlich Parameters for Cu, Pb and Cr onto PNS.

Metal Ion	Log C_e	Log C_{ads}	C_m (mmol g^{-1})	1/n	R^2
Cu (II)	0.152834	0.895202	1.125	0.622	0.934
Pb (II)	-0.18128	0.968383	1.233	0.338	0.919
Cr (VI)	0.254184	0.89229	1.080	0.734	0.941

Where "R" is a gas constant in kJ mol^{-1} K^{-1}, "T" is the temperature in Kelvin, C_e (mol L^{-1}) is as mentioned earlier. In Fig. 3 the plots of ln C_{ads} versus ε^2 yield coefficient of determinations close to unity and the results of X_m computed from the slope and intercept of respective plots. The values of R2 close to unity validate the system for the sorption phenomena.

Kinetics of Sorption

The kinetic study for the uptake of metal ions onto PNS and PNSA was carried out by applying linearized form of Lagergren equation i.e. ln (q_e - qt) = ln q_e – k_t and Morris-Weber equation i.e.

$$q_t = R_{id}\sqrt{t}$$

Where q_t is sorbed concentration (µmol g^{-1}) of metal ions at time t and R_{id} (µmol$g^{-1}$$min^{-1}$) is intraparticle diffusion rate constant. R_{id} is evaluated from the slope of the corresponding plots between $t^{1/2}$ and qt. Value of R_{id} is 4.84, 3.75 and 4.33 for Cu, Pb and Cr respectively as plot drawn in Fig. 18. The results show first order kinetics and partial intra-particle diffusion during sorption mechanism.

Table 2. Langmuir Parameters for Cu, Pb and Cr onto PNS.

Metal Ions	C_e(M/L)	C_e/C_{ads}(M/g)	Q (mmol g^{-1})	b	R_L	R^2
Cu (II)	5.698×10^{-06}	0.180980584	0.031	1.042	0.093	0.942
Pb (II)	1.988×10^{-06}	0.070849597	0.028	2.714	0.035	0.942
Cr (VI)	6.103×10^{-06}	0.230087959	0.026	0.116	0.1165	0.942

In Lagergren equation, K is the first order rate constant (min^{-1}), while qe and qt are the equilibrium and sorbed concentrations (µmol g^{-1}) of metal ions at time "t". In linear plots of ln (qe - qt) versus t, the value of k are 0.020, 0.006 and 0.026 for Cu, Pb and Cr respectively. These values indicate that this model fits with the system for adsorption process.

Applications to Real Wastewater Samples

Waste water samples from different industries, as mentioned earlier were passed through filtration using whatmann glass filter paper (0.45µm) to remove toxic insoluble particulate matters. These filtered samples (100 ml each) were mixed up with 9 ppm solutions of Cu, Pb and Cr. Quantitative determination of Cu, Pb and Cr was carried out by AAS. Samples were mixed with 0.5 g of pine nut shell (PNS) and pine nut shell ash (PNSA) at 4 pH and agitated at the rate of 100 rpm for 20 mins.

By AAS analysis, it was demonstrated that PNS removed 86%, 93% and 80% Cu, Pb and Cr ions respectively from contaminated wastewater samples. The results of AAS analysis are demonstrated in Table 3 which exhibits the high efficiency of pine nut shell for the removal of Cu, Pb and Cr from wastewater.

Table 3. D-R Parameters for Cu, Pb and Cr onto PNS.

Metal Ions	log Cads (M/g)	ε^2	X_m (mmol g^{-1})	E (kJmol^{-1})	R^2
Cu (II)	-4.5018683	925.3405	0.370	11.18	0.929
Pb (II)	-4.55170775	1093.693	0.390	15.81	0.911
Cr (VI)	-4.57633808	914.8569	0.390	10.00	0.936

Table 4. Sorption (%) of metal ions on the PNS at optimum conditions.

Metal Ion	Initial concentration C_i (M/L)	Equilibrium metal concentrations C_e (M/L)	$C_{ads} = C_i\text{-}C_e$ (M/g)	Sorption (%)
Cu (II)	3.718×10^{-05}	2.616×10^{-06}	3.256×10^{-05}	87.586
Pb (II)	3.718×10^{-05}	4.502×10^{-06}	2.769×10^{-05}	92.142
Cr (VI)	3.262×10^{-05}	2.362×10^{-06}	2.652×10^{-05}	81.288

Conclusions

The present investigation is based on this method in which very toxic metals i.e. Cu (II), Pb (II) and Cr(VI) have been selected. A wide variety of sorbents was being considered as adsorbents of heavy metals for treatment of industrial and domestic wastewater. Pine nut shell proved to be an appreciable sorbent for the removal (86%, 93% and 80%) of Cu, Pb and Cr metal ions respectively from aqueous solution of low concentration.

The chemical (HNO_3 and K_2CO_3) and thermal activation (873 K for 6 hours) of pine nut shell increases the removal efficiency for toxic metal ions. The results also reveal greater pore diameter and pore volume for significant sorption phenomena. FTIR studies show presence of alcoholic, carboxylic, ether and carbonyl groups in the structure of pine nut shell treated and untreated material and exhibited better performance at pH 4 for the removal of metal ions from aqueous solutions. Further, thermodynamic parameters illustrate exothermic, stable and spontaneous nature of sorption process.

Therefore, PNS and PNSA can be effectively employed for the removal of toxic heavy metals from aqueous solution.

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