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Removal of Cu(II), Zn(II) and Cd(II) ions from aqueous solutions by adsorption on walnut shell-Equilibrium and thermodynamic studies: treatment of effluents from electroplating industry

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ABSTRACT

In this work, the efficiency of walnut shell as a low-cost and natural adsorbent for removing metal ions from aqueous solution and electroplating wastewater has been studied. Batch experiments were conducted to study the effect of some parameters such as contact time, initial concentration, solution pH and temperature on the adsorption of Cu(II), Zn(II) and Cd(II) by walnut shell. Langmuir and Freundlich models were employed for the mechanistic analysis of experimental data and the observation reveals that in our system adsorption follows the Langmuir isotherm. The maximum adsorption capacity of Cu(II), Zn(II) and Cd (II) were found to be 14.53, 7.47 and 7.29 mg/g, respectively. The pseudo-first-order and pseudo-second-order models were employed for kinetic analysis of adsorption process. It was found that adsorption process follows pseudo-second-order kinetics. The adsorption process was subjected to thermodynamic study revealing that adsorption of these metals on the natural adsorbent was spontaneous and endothermic in nature. According to the experimental investigation, walnut shell seems to be an effective, natural, low-cost and alternative adsorbent for the removal of these metal ions from aqueous solutions. The efficacy of walnut shell in the treatment of effluent from electroplating industry has been explored and the results have been found encouraging.

Keywords: Heavy metal ions; Adsorption isotherm; Adsorption kinetics; Langmuir isotherm; Freundlich isotherm

1. Introduction

Heavy metals are frequently released into aquatic system by different industrial wastewaters. The existence of heavy metals in aquatic systems can be detrimental to a variety of living species [1]. They are important contaminants of liquid wastes discharged from a number of industries such as electroplating, dyes and dye intermediates, textiles, tanneries, oil refineries, electroplating, mining, smelters and so forth. Unlike organic wastes, heavy metals are non-biodegradable and they tend to accumulate in living tissues, causing various diseases and disorders; therefore, these must be removed from wastewaters [2]. They pose a significant threat to the environment and public health because of toxicity, incremental

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accumulation in the food chain and persistence in the ecosystem [3]. Due to heavy metal contamination in aquatic environment, several episodes increased the awareness about the heavy metal toxicity. Among these, Minamata tragedy due to mercury poisoning and Itali-Itali disease in Japan due to cadmium toxicity are well known [4]. There are various methods for the removal of heavy metals including: chemical precipitation, reverse osmosis, membrane separation, ion exchange [5]. These methods have significant disadvantages, including high energy requirements, incomplete metal removal, generation of toxic sludge, needs treatment and expensive equipment [6]. Strict environmental protection legislation and public environmental concerns lead the global search for novel and low-cost techniques to remove heavy metals from industrial wastewater [7]. Hence, recent research is directed to developing cost-effective technologies for the removal of metal ions from aqueous solutions.

Biosorption of toxic heavy metals by biomaterials has been suggested as a potential alternative to the conventional methods for recovery of toxic heavy metals from wastewater [8]. Many biomaterials such as walnut hull [9], almond green hull [10], banana skin, green tea waste, oak leaf, walnut shell, peanut shell and rice husk [11], groundnut shell [12], olive stone [13], grape waste [14], hazelnut [15], walnut, hazelnut and almond shell [16], agriculture wastes, carbons [17], rice husk-based active carbon [18], fruit shell of gulmohar [19], coconut husk [20], husk of bengal gram [21], eucalyptus bark [22], agricultural waste biomass [23], pine needles [24], sugar cane bagasse [25], leaf mould [26], chemically modified coir pith [27], groundnut shell [28] and waste pomace of olive factory [29] have been investigated.

The mechanism of sorption on these lignocellulosic substances is complex and includes ion exchange, complexation, chelation, adsorption by physical forces, entrapment in capillaries and spaces of the polysaccharide network and diffusion through cell walls and membranes. Apart from amino and carbonyl groups, the two main functional groups that attract and sequester the metal ions in biosorbents are carboxyl groups in proteins and hydroxyl groups in polysaccharides.

In this study, walnut shell (*Juglans regia*) has been investigated as an adsorbent for the removal of some toxic metal ions from aqueous solution. Walnut belongs to the family *Juglandaceae* and is one of the most important fruits of Kashmir. Therefore, it is worthwhile to investigate the potential of walnut shell as an adsorbent for the removal of some toxic metal ions from aqueous solution as a first step.

2. Materials and methods

2.1. Adsorbent

Walnut fruit was collected from a local fruit field in the southern part of Kashmir and the brown hard shell of the walnut fruit was thoroughly rinsed with distilled water to remove dust and soluble materials. After washing, it was allowed to dry at room temperature. The walnut shell was crushed and sieved through a range of sieves, and only the particles that passed through a 0.2 mm mesh were used.

2.2. Chemicals

The stock solutions of Cu(II), Zn(II) and Cd(II) (1,000 mg/L) were prepared by dissolving their respective nitrates in double-distilled water. All the chemicals were Analytical Grade reagents from E. Merck India Limited and were used as received. The stock solutions were further diluted with double-distilled water to required concentrations before use.

2.3. Adsorption experiments

Batch adsorption experiments were carried out in stoppered Erlenmayer flasks using the batch equilibrium technique. One gram of adsorbent was treated with 100 mL aliquot of the metal ion solution of desired concentration and shaken on a flask shaker for required time interval. After equilibration, the solution was filtered and the filtrate analysed for the metal ion concentration. Metal ion concentration was determined on Atomic Absorption Spectrometer (PerkinElmer Model Analyst-800). In order to obtain the adsorption capacity, the amount of ions adsorbed per mass unit of adsorbent (mg/g) was evaluated using the following expression:

$$q_e = (C_0 - C_e)V/m \tag{1}$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_0 is the initial metal ions concentration (mg/L), C_e is the equilibrium metal ions concentration (mg/L), V is the volume of the aqueous phase (L) and m is the amount of the adsorbent used (g).

2.4. SEM images

The surface morphology of walnut shell was obtained using scanning electron microscope Model Hitachi S3000H (Fig. 1). Scanning electron micrographs of walnut shell were taken before and after adsorption of metal ions.

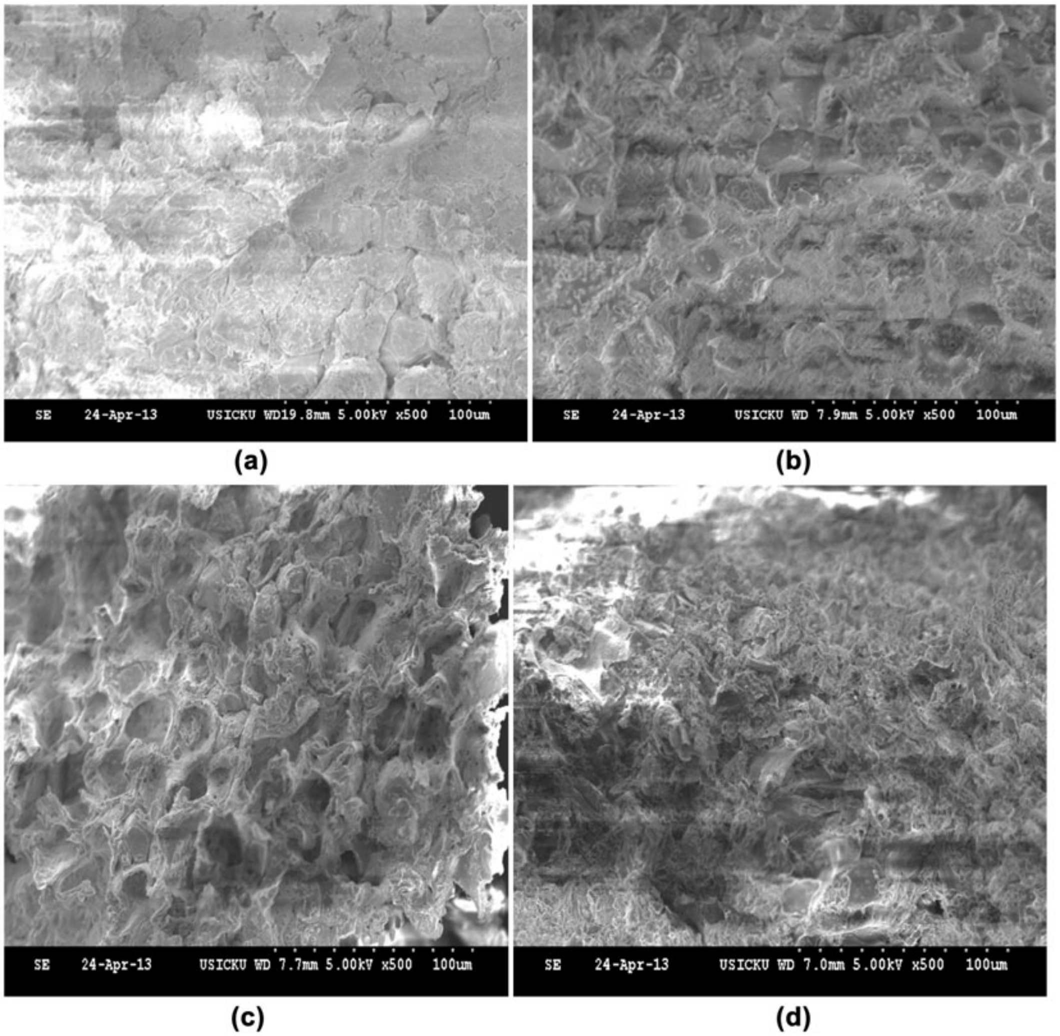

Fig. 1. SEM images of (a) walnut shell powder, (b) Cd(II) loaded walnut shell, (c) Cu(II) loaded walnut shell and (d) Zn (II) loaded walnut shell.

2.5. Effect of contact time

One gram of adsorbent was added to a number of stoppered conical flasks containing 100 mL of metal ion solution (100 mg/L) and were placed on an orbital shaker and agitated at 120 rpm, for different contact times chosen (10, 20, 30, 40 ... 80 min). After the given time interval, the mixture was filtered and the filtered analysed for final metal ion concentration.

2.6. Effect of pH

The effect of pH on the amount of metal ion adsorbed was analysed over the pH range 1–7. The experiments were not conducted above pH 7 to avoid possible hydroxide precipitation as reported by Giraldo and Moreno-Pirajan [30]. The pH of the solutions was adjusted to the required value by the addition of 0.1 M HNO_3 and 0.1 M NaOH solutions.

2.7. Effect of initial metal ion concentration (adsorption equilibrium)

The effect of initial metal ion concentration on the adsorption was studied by shaking 1 g of adsorbent with 100 mL aliquots of metal ion solutions of different initial concentrations (20–200 mg/L) for 70 min. After equilibration for 70 min, the supernatant solutions were filtered and the filtrates analysed for the final metal ion concentration.

2.8. Effect of temperature

The effect of temperature on the adsorption was studied at three different temperatures of 20, 30 and 40˚C by shaking 1 g of adsorbent with 100 mL aliquots of metal ion solutions of a particular concentration (100 mg/L). The mixture was heated to the appropriate temperature and shaken by using temperature controlled flask shaker for 80 min. The supernatant solutions were filtered and filtrates analysed for the final metal ion concentration.

3. Results and discussion

3.1. Surface characteristics

Walnut shell is a lignocellulosic material, mainly composed of 40–60% cellulose, 23–30% lignin and small amounts of nitrogeneous matter and ash [31]. Gondhalekar and Shukla [31] and Farhan et al. [32] have carried out IR analysis of the walnut shell. The authors have reported the presence of a broad peak around 3,400 cm^{-1} characteristic of bonded hydroxyl group, 1,630 cm^{-1} corresponding to C=C stretching that may be attributed to lignin aromatic group, 1,725 cm^{-1} assigned to C–O stretching (Ar–C(O)–O–R) of the acetyl and ester groups in hemicelluloses and cellulose or from ester linkages among lignin and hemicelluloses [33], 1,233 cm^{-1} band unique to C=O stretch vibrations in lignin and hemicellulose [33,34], 2,905 cm^{-1} and C–H stretching at 2,905 cm^{-1}.

The SEM images of the walnut shell reveal an uneven and rough surface with pores and cavities which make it suitable for adsorption of metal ions. Upon adsorption, the surface morphology seems to undergo changes due to interaction of the metal ions with donor functional groups on the walnut shell.

3.2. Effect of contact time

The effect of contact time on the adsorption of Cu(II), Cd(II) and Zn(II) is presented in Fig. 2. The results show that adsorption increases with the increasing contact time and reaches equilibrium after 60 min at 100 mg/L initial concentration of the metal ions. The study revealed that biosorption took place in two steps, a rapid surface adsorption and slow intercellular adsorption. The rapid rate of sorption of the metal ions in the initial period of the process may be due to a higher number of adsorption sites available on the surface of the adsorbent and the higher concentration gradient between the adsorbate in the solution and the adsorbate on the surface of the adsorbent. As the uptake of the metal ion progresses, the concentration gradient between the metal ions in the solution and the metal ions on the adsorbent surface decreases and the number of the vacant adsorption sites on the adsorbent surface also decreases leading to a decrease in the sorption rate with time. As the surface adsorption sites become exhausted, i.e. at equilibrium, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. For all subsequent experiments, contact time of 80 min was set for the sake of simplicity and to ensure that complete equilibrium is achieved.

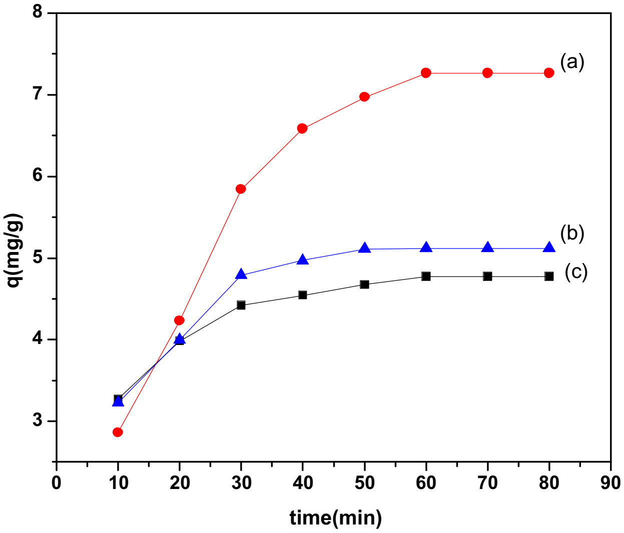

Fig. 2. Effect of time on the adsorption of (a) Cu(II), (b) Zn(II) and (c) Cd(II) on walnut shell.

The order of adsorption of metals on walnut shell under the same conditions is:

Cu(II) > Zn(II) > Cd(II).

The difference in amount adsorbed of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the difference in their chemical affinity and ion-exchange capacity with respect to the chemical functional groups such as carboxylic, hydroxyl, amine and carbonyl on the surface of these adsorbents.

3.3. Adsorption kinetics

In order to investigate the mechanism of adsorption, kinetic models are generally used to test the experimental data. The first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases.

The pseudo-first-order kinetic model known as the Lagergen equation is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

where q_t and q_e are the amounts of ion adsorbed at time t and at equilibrium (mg/g), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The slope and intercept of plots of $\log(q_e - q_t)$ vs. t were used to determine the first-order rate constant k_1 and equilibrium adsorption capacity q_e (see Fig. 3).

The pseudo-second-order kinetic model is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{3}$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The plot of t/q_t vs. t gives a linear relationship, and k_2 and q_e can be calculated from the slope and intercept of the line, respectively. The results are given in Table 1. It can be seen that the correlation coefficients (r^2) for the pseudo-second-order equation is very close to unity and that the calculated q_e values agree well with the experimental ones (see Fig. 4). These results suggest that the pseudo-second-order model describes the sorption kinetics more appropriately than the pseudo-first-order model. The pseudo-second-order model is based on the assumption that the rate limiting step may be a chemical adsorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

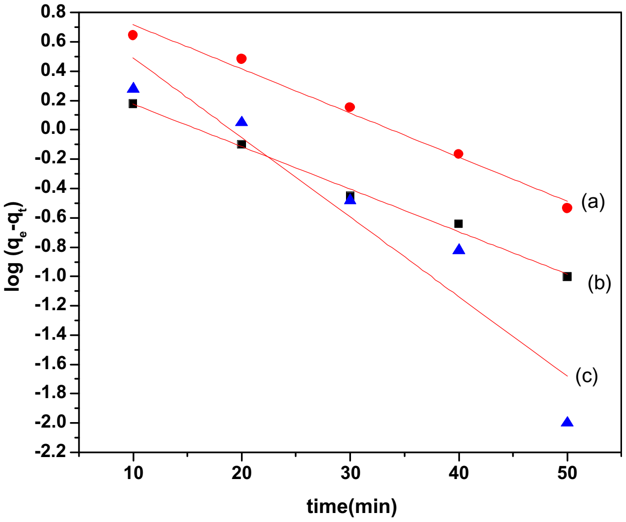

Fig. 3. Plot of $\log(q_e - q_t)$ vs. t (min) for (a) Cu(II), (b) Cd (II) and (c) Zn(II).

3.4. Effect of pH

pH is an important parameter affecting the adsorption of metal ions on biosorbent because it affects metal speciation in solution as well as influences the surface properties of the adsorbents in terms of dissociation of functional groups and surface charge. Fig. 5 depicts the effect of pH on the adsorption of Cd(II), Cu(II) and Zn(II). The results show that adsorption increases with increasing pH and attaining a maximum adsorption at pH 5 for Cu(II) and Zn(II) and pH 6 for Cd(II).

It is widely accepted that the adsorption of the metal ions on the adsorbent is because of the functional groups of lignin, tannin, carbohydrates and proteins present in it. At low pH values, there is excessive protonation of the polar functional groups like aldehyde, ketone, amine, alcohol, phenol and carboxyl resulting in the decrease in adsorption. Therefore, at low pH uptake of metal ions is low. The increase in metal adsorption with increasing pH can be explained on the basis of a decrease in competition between the protons and positively charged metal ions at the surface sites. Therefore, at higher pH, uptake of the metal ions increases. The results conform to the ion-exchange and complexation mechanism of the adsorption of the metal ions on the walnut shell. At more basic pH, however, the metal ions start precipitating, which defeats the very purpose of employing adsorption and precludes further investigation.

3.5. Adsorption isotherms

The effect of initial concentration (20–200 mg/L) of Cd(II), Cu(II) and Zn(II) on their adsorption on walnut shell from aqueous solution was investigated. The results, presented in Fig. 6, show that adsorption starts from a low concentration, and with an increase in the metal ion concentration the amount of metal ion adsorbed increases. At low concentrations, metal ions are adsorbed at specific sites and with increasing metal concentrations the binding sites become more quickly saturated as the amount of adsorbent remained constant. That is, there is some metal concentration that produces the maximum adsorption for a given mass of adsorbent and thereafter, adding more metal cannot increase adsorption because no more sites are available.

Adsorption isotherm describes the equilibrium relationships between adsorbent and adsorbate.

Table 1
Kinetic parameters for the adsorption of some heavy metal ions on walnut shell

		Pseudo-first-order kinetics			Pseudo-second-order kinetics		
Metal	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	K_1 (min^{-1})	r^2	$q_{e,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	r^2
Zn(II)	5.112	10.794	0.125	0.888	5.633	0.02708	0.996
Cu(II)	7.26	10.416	0.069	0.979	9.57	0.0048	0.982
Cd(II)	4.771	2.922	0.0667	0.991	5.15	0.036	0.999

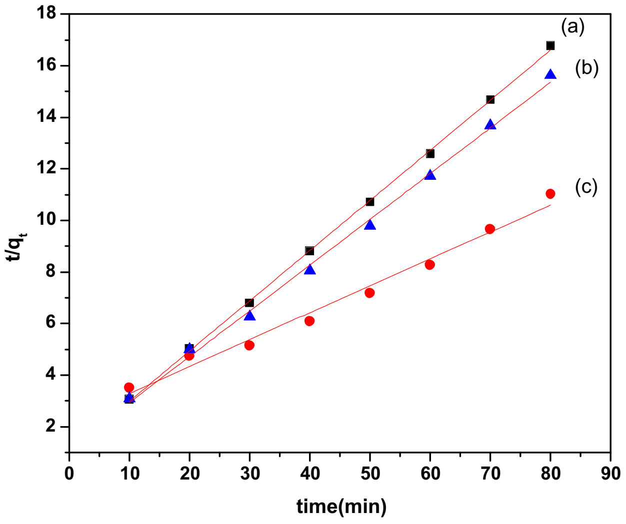

Fig. 4. Plot of t/q_t vs. t (min) for (a) Cd(II), (b) Zn(II) and (c) Cu(II).

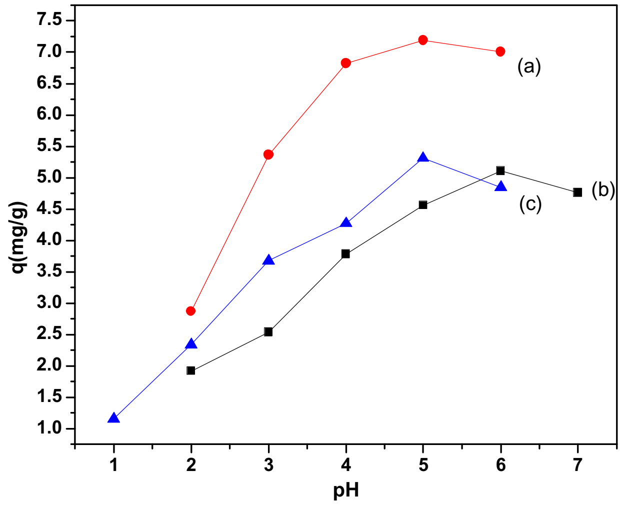

Fig. 5. Effect of pH on the adsorption of (a) Cu(II), (b) Cd (II) and (c) Zn(II) metal ions on walnut shell.

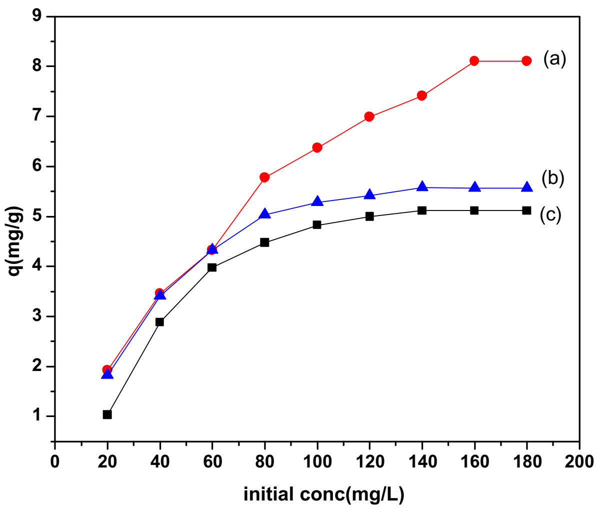

Fig. 6. Effect of initial concentration on the adsorption of (a) Cu(II), (b) Zn(II) and (c) Cd(II) on walnut shell.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with homogeneous adsorption sites. The linearized form of the Langmuir equation can be written as:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_e K_L} \cdot \frac{1}{C_e} \tag{4}$$

where q_0 (mg g^{-1}) and K_L (mg L^{-1}) are Langmuir parameters related to maximum adsorption capacity and free energy of adsorption, respectively. C_e is the equilibrium concentration in the aqueous solution and q_e is the equilibrium adsorption capacity of adsorbent. Fig. 7 represents the Langmuir isotherms of the mentioned metal ions.

The Freundlich model is an empirical equation based on adsorption on heterogeneous surface. The linearized form of the Freundlich isotherm can be written as:

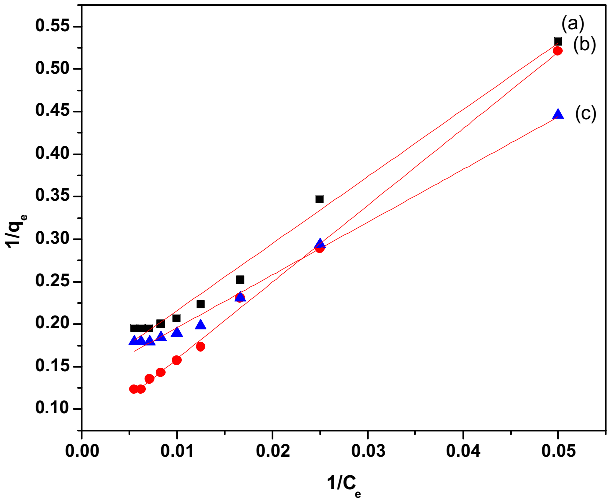

Fig. 7. Langmuir adsorption isotherm for the adsorption of (a) Cd(II), (b) Cu(II) and (c) Zn(II) on walnut shell.

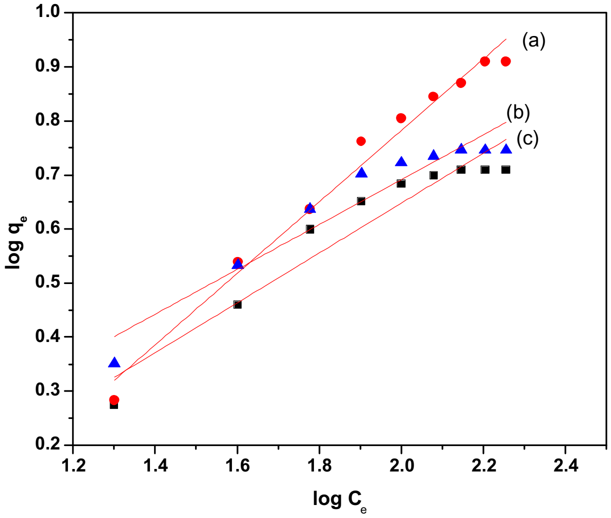

Fig. 8. Freundlich adsorption isotherm for the adsorption of (a) Cu(II), (b) Zn(II) and (c) Cd(II) on walnut shell.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (5)$$

where K_F $(\mathrm{mg\,g^{-1}})(\mathrm{L\,mg^{-1}})^{1/n}$ and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively. The Freundlich constants, K_f and $1/n$, can be determined from the intercept and slope of linear plot of $\ln q_e$ vs. $\ln C_e$, respectively (Fig. 8).

The isotherm constants and correlation coefficients are given in Table 2. From the plots it is clear that the adsorption equilibrium data fitted the Langmuir as well as the Freundlich equations well with good correlation coefficients. However, the adsorption equilibrium data for Cd(II), Cu(II) and Zn(II) fitted the Langmuir isotherm equation with correlation coefficient of 0.989, 0.997, 0.992 as compared to 0.913, 0.979, 0.911 for Freundlich isotherm equation, respectively, and thus indicating the best fit of the adsorption equilibrium data in the Langmuir isotherm than in case of Freundlich isotherm.

A further analysis of the Langmuir and the Freundlich constants supports favourable adsorption of Cd(II), Cu(II) and Zn(II) on the walnut shell. According to some workers [35,36], if the value of the Freundlich constant "n" is such that $0.1 < 1/n < 1$, the adsorption is favourable. It can be seen from Table 2 that the value of $1/n$ for all the metal ions is between 0.1 and 1, thus indicating a favourable adsorption.

3.6. Adsorption thermodynamics

Fig. 9 shows the adsorption of metal ions on walnut shell increases as temperature increases. The increase in adsorption capacity with temperature suggested that the active sites available for adsorption increase with temperature. This could also be attributed to the pore size variation and enhancing rate of intraparticle diffusion of solute since diffusion is an endothermic process.

In order to explain the effect of temperature on the adsorption of metal ions on walnut shell, thermodynamic parameters: Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were obtained by using the following equations:

$$\Delta G = -RT \ln K \qquad (6)$$

where R is the ideal gas constant ($\mathrm{JK^{-1}\,mol^{-1}}$) and T is the temperature (K).

The enthalpy and entropy of adsorption were determined from the Van't Hoff equation:

$$\ln K = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \qquad (7)$$

where ΔH and ΔS were obtained from the slope and intercept of the Van't Hoff's plot of $\ln K$ vs. $1/T$ as shown in Fig. 10.

The results of the thermodynamic calculations are shown in Table 3. The negative value of ΔG indicates the feasibility of the adsorption process and high affinity of the metal ion towards the adsorbent. A positive value of ΔH confirms the endothermic nature of the process. The positive value of ΔS shows the increased

Table 2
Langmuir and Freundlich adsorption isotherm parameters of some heavy metals on walnut shell

Metal	Langmuir constant			Freundlich constant		
	q_0 (mg g^{-1})	K_L (mg L^{-1})	r^2	K (mg g^{-1})(L mg^{-1})$^{1/n}$	$1/n$	r^2
Zn(II)	7.477	0.02155	0.992	0.7254	0.415	0.911
Cu(II)	14.536	0.0076	0.997	0.287	0.66	0.979
Cd(II)	7.292	0.0174	0.989	0.5306	0.4614	0.9134

randomness at solid/solution interface during the adsorption process. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. The enhancement of adsorption at higher temperature may be attributed to the enlargement of pore size and/or activation of adsorbent surface.

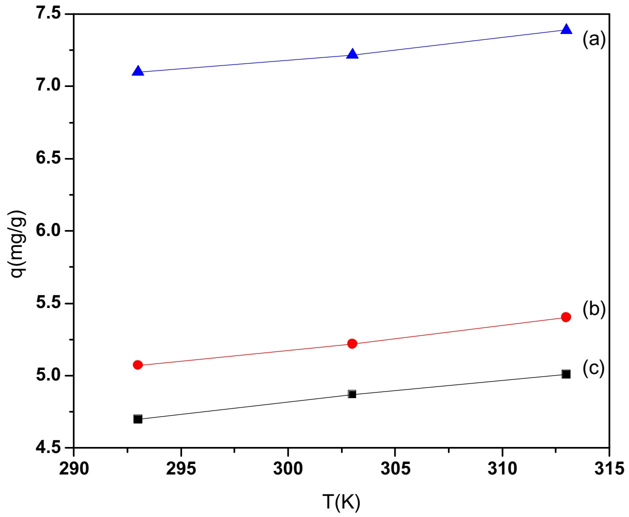

Fig. 9. Effect of temperature on the adsorption of (a) Cu (II), (b) Zn(II) and (c) Cd(II) on walnut shell.

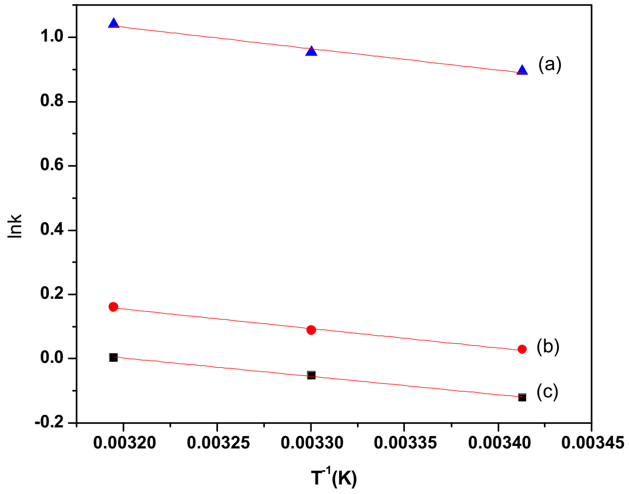

Fig. 10. Plot of ln k vs. T^{-1} (K) for (a) Cu(II), (b) Zn(II) and (c) Cd(II).

3.7. Treatment of electroplating wastewater using glass column

Electroplating wastewater was collected from the nearby electroplating industry. The electroplating effluent was filtered through filter paper and the heavy metals present in the wastewater sample were determined. The initial concentration of the metal ions Cd(II), Cu(II) and Zn(II) present in the wastewater were found 47.2, 115 and 78.91 mg/g, respectively. Different concentrations of the metal ions were prepared from the electroplating effluent by dilution with distilled water for comparison with synthetic metal ion solutions.

Column experiments were carried out using a glass column with internal diameter of 1 cm. The column was packed with 4 g of walnut shell powder. Distilled water was run through the column and equilibrated for an hour. Different concentrations of the above metal ions were prepared from their corresponding nitrates. A volume of 100 mL of each of the synthetic heavy metal ion solution with different metal ion concentrations was passed through the column separately at an optimum pH and at room temperature. The rate of flow of the metal ion solution was kept constant (1 mL/min) using a stopcock. The procedure was repeated for the electroplating wastewater. The difference between the metal uptake from the synthetic metal ion solution and the effluent may be attributed to the presence of other ions and impurities which compete with particular metal for the binding sites (Table 4).

Table 3
Values of thermodynamic parameters for the adsorption of some heavy metal ions on walnut shell at various temperatures

Metal	T (K)	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} k^{-1})
Zn(II)	293	−0.06918	5.0357	0.01739
	303	−0.2196		
	313	−0.418		
Cu(II)	293	−2.178	5.54618	0.02631
	303	−2.400		
	313	−2.707		
Cd(II)	293	0.294	4.733	0.015
	303	0.1310		
	313	−0.00809		

Table 4
Comparison between the metal uptake from synthetic metal solution and the electroplating effluent on walnut shell

Heavy metals	Initial concentration (mg/L)	Final concentration (mg/L)	
		Synthetic solution	Industrial effluent
Cu(II)	20	1.18	1.29
	40	7.18	7.97
	60	18.52	20.3
	80	23.7	27.81
	100	31.6	38.76
Cd(II)	10	0.05	0.13
	20	1.14	1.82
	30	4.79	5.08
	40	12.36	13.27
	45	9.51	10.58
Zn(II)	20	1.87	2.1
	40	8.49	9.08
	60	18.34	19.84
	75	32.56	34.46

In another experiment, 100 mL of the above metal ion solution of concentrations (as shown in Table 5) was passed through the column at an optimum pH and at room temperature and the flow rate was kept constant. The amount of metal ion left in the solution was determined. This solution was again passed through another column and then analysed for final metal ion concentration. The procedure was repeated till the complete removal of metal ions.

Table 5
Removal of Cu(II), Zn(II) and Cd(II) from electroplating effluent on walnut shell by using column

Heavy metal	Initial concentration (mg/L)	Final concentration (mg/L)
Cu(II)	100	38.76
	38.7	6.95
	6.95	0.08
Cd(II)	45	10.58
	10.58	0.4
Zn(II)	75	34.46
	34.46	8.04
	8.04	0.3

3.8. Desorption studies

It is important to desorb metal ions from the adsorbent in order to make the sorption process more economical. Desorption studies were carried out by batch process. Desorption of Cu(II), Zn(II) and Cd(II) were carried out by treating 1 g adsorbent with 100 mL aliquot of the metal ion solution of desired concentration (100 mg/L). The solution was filtered after 24 h and filtrate was analysed for metal ions. The sorbent was then washed several times with double

Table 6
Desorption of Cu(II), Zn(II) and Cd(II) by using 1 N HCl

Metal ion	Amount of metal ion adsorbed (mg/g)	Amount of metal ion recovered (mg)	Recovery (%)
Zn(II)	7.18	5.76	80.2
Cu(II)	13.70	10.74	78.3
Cd(II)	6.92	4.85	70

distilled water to remove any excess of metal ions. It was then treated with 100 mL of 0.1 M HCl solution and filtered after 24 h. The filtrate was analysed for metal ions desorbed (Table 6).

4. Conclusion

(1) Walnut shell *J. regia* was found to adsorb substantially Cd(II), Cu(II) and Zn(II) from aqueous solution.
(2) Various thermodynamic parameters like ΔH, ΔS and ΔG were calculated. These thermodynamic parameters together with Langmuir and Freundlich isotherm constants indicated a favourable adsorption of Cd(II), Cu(II) and Zn (II) on the Walnut shell.
(3) The adsorption of Cd(II), Cu(II) and Zn(II) on the Walnut shell was found to be endothermic and spontaneous in nature.
(4) The adsorption of Cd(II), Cu(II) and Zn(II) on the Walnut shell increased with increasing temperature.
(5) The equilibrium was attained after 60 min.
(6) The maximum adsorption capacity of walnut shell for Cu(II), Zn(II) and Cd(II) were found to be 14.536, 7.477 and 7.292 mg/g, respectively, at optimum conditions.
(7) The efficacy of Walnut shell in the treatment of effluent from electroplating industry has been investigated and the results have been found satisfactory.
(8) On the basis of the above, it can be concluded that walnut shell can be effectively used as a low-cost, sustainable and easily available adsorbent for the removal of toxic metals from aqueous solution.

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