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SYNTHESIS AND CHARACTERIZATION OF CELLULOSE SULPHANILIC ACID [CSA] RESIN AND ITS APPLICATION IN INDUSTRIAL WASTEWATER TREATMENT

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ABSTRACT

Batch shaking adsorption experiments were carried out to evaluate the performance of synthesized cellulose sulphanilic acid (CSA) resins in the adsorption of heavy metal ions from wastewater of Balaji steel industry, Jodhpur, India. The influences of experimental parameters, viz. solution PH, resin dose, agitation speed and contact time were investigated. Optimum adsorption conditions were found to be PH 6.0, 0.1 g resin dosage, 120 rpm agitation speed and 120 min equilibrium time. The maximum adsorption of Pb^{+2}, Cd^{+2}, Zn^{+2}, Cu^{+2} and Fe^{+2} ions on CSA resin was found to be 87.56, 90.96, 93.81, 95.67 and 97.89 % respectively. The adsorption is an exothermic process which runs spontaneously. The adsorption mechanism of CSA resin was explained as an ion-exchange process. However, it was observed that chelating effect is also playing an important role in the adsorption of metal ions into CSA resin

INTRODUCTION

The pollution of the environment with heavy metal ions is a result of many human activities, such as mining and metallurgy which adversely affect the ecosystem. The problem of water pollution is increasing with developing technology. Heavy metal ions not only reach the surface water but also contaminate underground water in trace amounts by leaching from soil after rain. Heavy metals such as, Iron , Copper, Zinc, Lead, etc are detected in waste streams from mining operations, tanneries, electroplating, battery and steel industries. It has a harmful effect on human physiology and other biological systems when they exceed the tolerance levels. These are non biodegradable and accumulate in living organisms [1], causing various types of disorders. Therefore, their presence in water should be controlled. In view of this, there is need of developing technologies that can not only cleanup but also recover valuable components from industrial wastewater. The removal of heavy metal ions from wastewater can be achieved by several processes, such as precipitation [2], solvent extraction [3, 4] , chemical and electrochemical technique [5], advanced oxidation process [6], and resin adsorption [7-14]. Among these technologies, the resin adsorption seems to be the most suitable method for the recovery of heavy metal ions from aqueous solution because of its low cost, ease of handling and high efficiency.

In recent years, polysaccharide based chelating resins have been synthesized for removal of heavy metal ions from wastewater [15-23]. The adsorption of metal ions using chelating ion exchange resins is a green analytical method since it does not involve the use of toxic chlorinated organic solvents, which are very frequently used in conventional liquid-liquid extraction technique or other methods [24]. The interest in this type of chelating resins are due to the rapid adsorption of metal ions, higher selectivity and less swelling, in comparison with the analogous organic polymers [2].

In this work, the synthesis and characterization of CSA resin and its applications for removal and recovery of heavy metal ions from wastewater of Balaji steel industry, Jodhpur, India, is described. The main objective of this research work is preparation of insoluble functionalized polymers which can provide more flexible working conditions together with good stability and high capacity for certain metal ions.

MATERIALS AND METHOD

Chemicals

Analytical grade chemicals supplied by (Loba Chemic, Mumbai and E Merk, Mumbai, India) were used in all experiments. Cellulose powder was supplied by (Ases Chemical Works, Jodhpur, India). All other compounds used in the synthesis were of commercial high purity grade, and used without further purification.

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Apparatus

Atomic absorption spectrometry
The concentrations of studied metal ions were measured by Perkin Elmer 2380 atomic absorption spectrophotometer (AAS). The atomic absorption is a very common technique for detecting metal ions present in a liquid sample. The technique is based on the fact that that ground state metals absorb light at specific wavelengths which quantitatively measures the concentrations of elements present in a sample.

FTIR spectrometer
The structure of CSA resin was characterized by Perkin Elemer model 5000 FTIR spectrometer. The solid samples were tested with KBr pellet method. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure.

P^H - meter
The P^H –measurement of metal ions and buffer solution were carried out by Beckman digital P^H meter model 335.

Shaking machine
The sample was shaken with a DSHZ−300A temperature constant shaking machine.

Sample
The wastewater of Balaji Steel industry has the following characteristic features which are summarized in (Table 1).

Table 1. The characteristics features of wastewater of Balaji Steel Industry, Jodhpur, India

Appearance: Turbid   pH: 4.4   Total hardness: 965

Metal ions (in ppm)	Concentration
Fe^{+2}	1.15
Cu^{+2}	2.02
Zn^{+2}	3.25
Pb^{+2}	0.18
Cd^{+2}	0.82
Cr^{+2}	0.72
Ni^{+2}	0.14
Co^{+2}	0.68
Mg^{+2}	19.20
Ca^{+2}	80.00

Other anions (ppm): Fluoride = 0.27; Sulphate = 840.12; Cyanide = 0.04

Synthesis of Cellulose Sulphanilic Acid [CSA] Resin
The synthesis of cellulose sulphanilic acid [CSA] resin accomplished in the following two steps [A] and [B]
[A] Preparation of Epoxypropyl Ether of Cellulose 32.4 g (0.2 mol) of cellulose powder was taken in round bottom flask and slurred in dioxane. Aqueous solution of sodium hydroxide (50%) was added in the flask to make it alkaline, till P^H reached to 9.5. The solution was stirred for one hour. 9.25 g (0.1mol) epichlorohydrin was added drop wise and stirring was continued for 5 h at 60^0C. The product epoxypropyl ether of cellulose was formed and it was used as such for further reaction.

[B] Preparation of Cellulose Sulphanilic Acid Resin
Epoxy propyl ether of cellulose was allowed to react with 17.3 g (0.1mol) of sulphanilic acid in the alkaline medium and the stirring was continued for another 4 h at 60°C. The product was filtered under vacuum and washed with 90 % methanol, containing few drops of hydrochloric acid to remove inorganic impurities. Finally it was washed with pure methanol. The product cellulose sulphanilic acid resin was free flowing light yellow powder. The yield was 52.03 g.

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Batch Adsorption Experiment

Batch adsorption experiments were conducted using 100 mg of CSA resin with 100 ml of sample solution containing known concentration of heavy metal ions. The P^H of the solution was adjusted with HCl and NaOH and maintained by a suitable buffer at desired values: KCl-HCl buffer for P^H 2, acetate buffer for P^H 3 to 5, phosphate buffer for P^H 6 to 8. Then the contents of the flasks were shaken in a flask-shaker at specific temperature for a 2 h to attain equilibrium with a speed of 120 rpm. The amounts of metal ions in the sample solution before and after equilibration were determined by using atomic absorption spectrometer (AAS). The operating variables studied on the extent of adsorption were pH, contact time, agitation speed, temperature and adsorbent dose.

The removal percentage, (R %) defined as the ratio of decrease in metal concentration after the adsorption (Co-Ce) to the initial concentration in aqueous solution (Co), was calculated according to Eq. (1)

$$R\% = \frac{Co - Ce}{Co} \times 100 \quad\quad (1)$$

Where Co is the initial concentration of metal ions and Ce is the concentration of metal ions after equilibrium with resin.

The distribution coefficient is defined as the ratio of metal ion concentration on the resin to that in the aqueous solution and can be used as a valuable tool to study metal ion mobility. The distribution coefficient (Kd) of metal ions was calculated according to Equation (2)

$$Kd = \frac{\text{Amount of metal ion in resin phase}}{\text{Amount of metal ion in solution phase}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of dry resin}} \quad ml\ g\text{-}1 \quad (2)$$

2.6 Ion Exchange Capacity (IEC) Determination

The ion exchange capacity, which is generally taken as a measure of the hydrogen ion liberated by neutral salt to flow through the composite cation exchanger was determined by standard column process. 1 g (dry mass) of the composite ion exchange material in H^+ form was placed in a glass column with a glass wool support at the bottom. It was washed with demineralized water to remove any excess of acid remained on the particles. The hydrogen ions eluted with 0.1M solution of different alkali and alkaline earth salts. The flow rate was kept 1 ml min−1. The collected wastewater was titrated against a standard solution of sodium hydroxide using phenolphthalein as an indicator. The hydrogen ions released were then calculated according to literature method [26], and it was found to be 35.5 mg/g.

RESULTS AND DISCUSSION

FTIR Characterization

The FTIR spectrum of natural cellulose and cellulose- sulphanilic acid (CSA) resin have recorded and shown in (Fig 1 and 2). The FTIR spectrum of cellulose powder shows broad band in the region 3600 -3100cm^{-1} characteristic - OH stretching. The peak at 2945 cm^{-1} is attributed is to C-H stretching vibration, strong and sharp peak at 1650 cm^{-1} due to O-H banding and variable peak at 1480 - 1350 cm^{-1} is attributed to C-H banding. A strong peak at 1300-1000 cm^{-1} denotes C-O stretching vibration [27].

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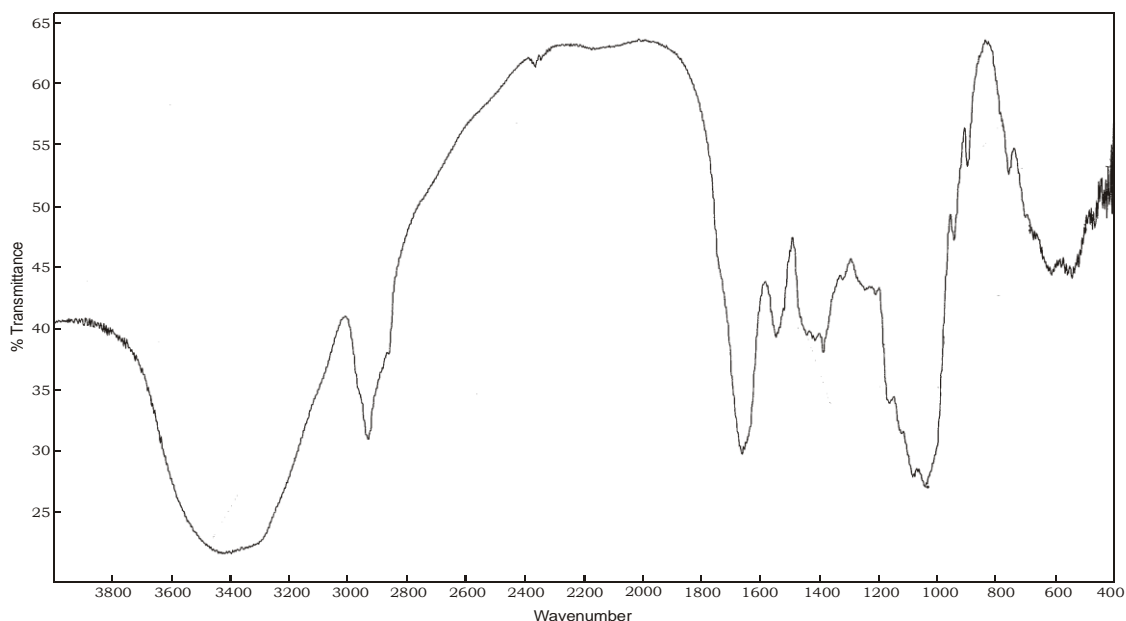
Fig. 1. FTIR spectra of cellulose
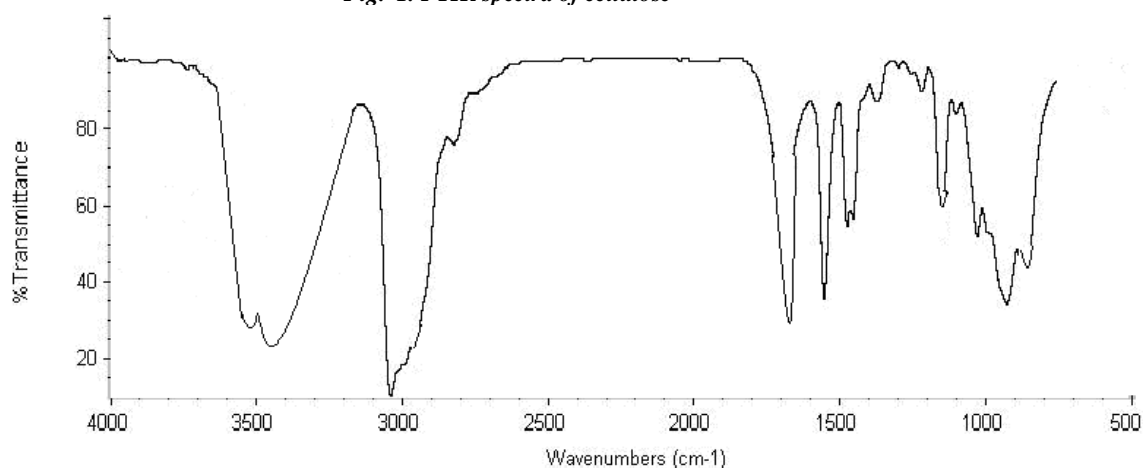
Fig.2. FTIR spectra of cellulose sulphanilic acid (CSA) resin

The CSA resin shows the asymmetric and symmetric S=O stretching frequency in the region 1350 -1342 cm-1 and 1165 – 1150 cm-1 respectively. The band due to the C-N stretching observed at 1200-1020 cm^{-1}, peak in the region 3500-3400 cm^{-1} denotes >NH stretching vibration. Peak in the region 1600-1400 cm^{-1} denotes C=C stretching in aromatic nuclei [28]. The peak at 3050 cm^{-1} is attributed to C-H stretching vibration.

Removal of Metal Ions from Wastewater of Balaji Steel Industry, Jodhpur, India
The results of percentage removal of metal ions from wastewater of Balaji steel industry by CSA resin are given in (Table 2). The adsorption of heavy metal ions increase with increasing pH and maximum adsorption is obtained at pH 6. The pH of the solution is an important factor in the adsorption process, which affects the surface charge of the adsorbent and the degree of ionization and specification of adsorbate [29]. This is due to the surfacecomplexation reactions, which are mostly influenced by the electrostatic force of attraction between metal ions and the surface of the adsorbent. The adsorption of heavy metal ions decreases with the decrease of solution P^H value under $P^H < 6$. This is because that with the decrease of solution P^H value or increase of H+ concentrations, because hydrogen ions in the solution could compete with metals for active sites in the surface of adsorbent [30]. At low P^H values ($P^H < 4$), the low adsorption observation can be explained due to increase in positive charge (protons) density on the surface sites and thus, electrostatic repulsion occurs between the metal ions and the edge group with positive charge (Rs-OH^{2+}) on the surface of resin [31-32] , At higher pH values

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$(4 < P^H < 6)$, the surface of CSA resin becomes negatively charged and thus electrostatic repulsion decreases with an increase in pH value. Reduction of positive charge density on the adsorption site results in an increase in metal adsorption, more increase in P^H values leads to metal precipitation and metal accumulation on resin surface which deteriorates the adsorption mechanism.

Table 2.Percentage removal of metal ions from the industrial wastewater by CSA resin

pH	Pb^{+2}	Cd^{+2}	Zn^{+2}	Cu^{+2}	Fe^{+2}
2.0	47.09	60.24	65.44	68.12	72.18
3.0	51.46	68.57	71.98	74.84	77.69
4.0	61.55	73.81	78.15	81.08	84.67
5.0	71.31	80.65	82.71	86.49	89.54
6.0	**87.56**	**90.96**	**93.81**	**95.67**	**97.89**
7.0	52.38	70.35	73.88	76.84	82.42
8.0	40.32	48.21	52.08	56.74	61.07

Distribution Coefficient (Kd) of Metal Ions.

The P^H has a strong effect on the distribution coefficient (Kd) of metal ions. The results of distribution coefficient (Kd) of metal ions from wastewater of Balaji steel Industry, Jodhpur are given in (Table 3). The perusal of the results have shown that the distribution coefficient value first increases and then decreases with increasing P^H, the optimum results were obtained at P^H 6.0. Metal sorption starts when the P^H rises to the range where most acidic ion exchange sites start to exchange hydronium ion for metal and the capacity reaches the maximum value in the P^H range where all the ion exchange sites take part in the reaction and the functional group is able to form complex with the metal cations [33]. The decrease in Kd values after the maximum in the neutral and alkaline region can be explained by the complex formation of CSA resin with heavy metal ions. High values of distribution coefficient indicate that the metal has been retained by the resin through adsorption process, while low value of kd indicate that a large fraction of the metal remain in solution.

Table 3.Distribution coefficient (Kd) of metal ions (Kd X 10^2)

| pH	Pb^{+2}	Cd^{+2}	Zn^{+2}	Cu^{+2}	Fe^{+2}
2.0	8.88	15.14	18.93	21.36	25.93
3.0	10.59	21.80	25.68	29.74	34.81
4.0	15.97	28.17	35.76	42.85	55.22
5.0	24.81	41.66	47.82	63.99	85.59
6.0	**70.35**	**100.51**	**151.53**	**220.85**	**463.25**
7.0	10.97	23.71	28.28	33.17	46.87
8.0	6.74	930.77	10.86	13.11	15.68

Effect of Treatment Time

The results (Fig. 3) of treatment time indicate that adsorption percentage of metal ions increased with an increase in contact time before equilibrium is reached. It can be seen that adsorption of metal ions on CSA resin increased when contact time was increased from 20 to 120 minutes. Other parameters such as P^H of solution and agitation speed were kept optimum, while temperature was kept at 25^0C. The result indicates that adsorption of

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heavy metals divided into two stages: one in which the rate of adsorption percentage is very high, 56 to 75% of heavy metals adsorbed on CSA resin in a contact time of 60 min. followed by a second stage with a much lower adsorption rate. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.
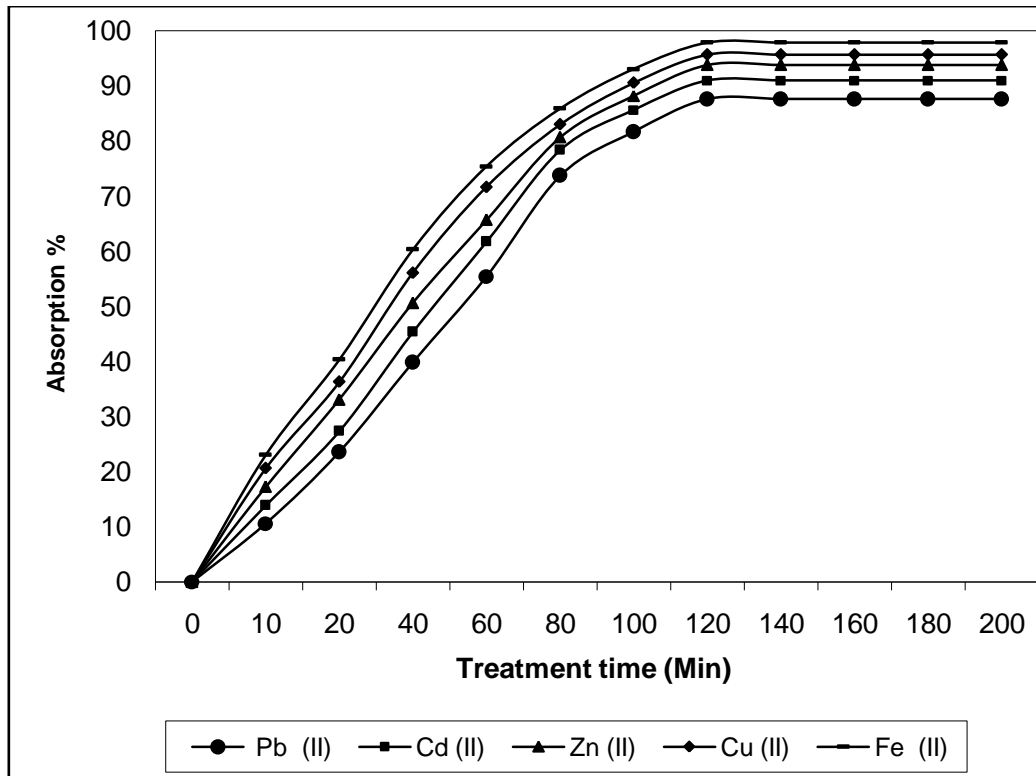
Fig. 3 Effect of changing treatment time on the adsorption of metal ions on CSA resin

Effect of Agitation Speed.
The effect of agitation speed on adsorption of metal ions was studied by varying the speed of agitation from 0 (without shaking) to 200 rpm, while other parameters keeping optimum. As can be seen from (Fig.4), the adsorption of metal ions on CSA resin generally increased with increasing agitation speed. The adsorption of metal ions on CSA resin increased when agitation speed increased from 0 to 120 rpm. These results can be associated to the fact that the increase of the agitation speed, improves the diffusion of metal ions towards the surface of the adsorbents. This also indicates that a shaking rate in the range 100-120 rpm is sufficient to assure that all the surface binding sites are made readily available for metal ions uptake. For convenience, agitation speed of 120 rpm was selected as the optimum speed for CSA resin for removal of metal ions from wastewater of Balaji steel Industry.
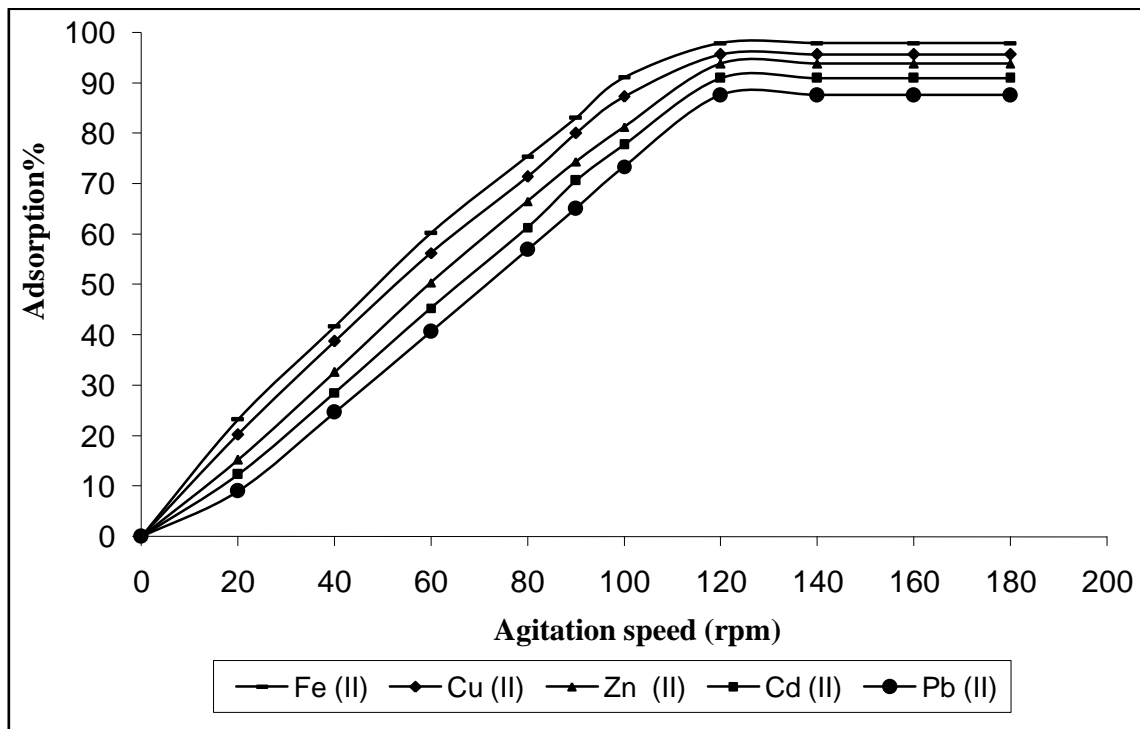
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Fig.4 Effect of agitation speed on adsorption of metal ions on CSA resin.

Adsorption Isotherm

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of an adsorption system. In an adsorption isotherm study, several equilibrium models have been developed to describe adsorption isotherm relationship. The Freundlich equation is the work- widely used model because of their simplicity. The Freundlich equation [34], is an empirical equation based on adsorption on a heterogeneous surface which as follows in Equation 3.

$$\log q_e = \log K_F + 1/n \log C_e \qquad (3)$$

Where q_e (mg/g) is the adsorption amount of adsorbent at equilibrium, C_e (mg/l) is the equilibrium concentration of adsorbate in solution. K_F and n are the Freundlich constants related to the adsorption capacity of the adsorbent and adsorption intensity respectively. Values of K_F and n were calculated from the intercepts and slopes of the Freunclich plots respectively. The results are shows in (fig. 5).
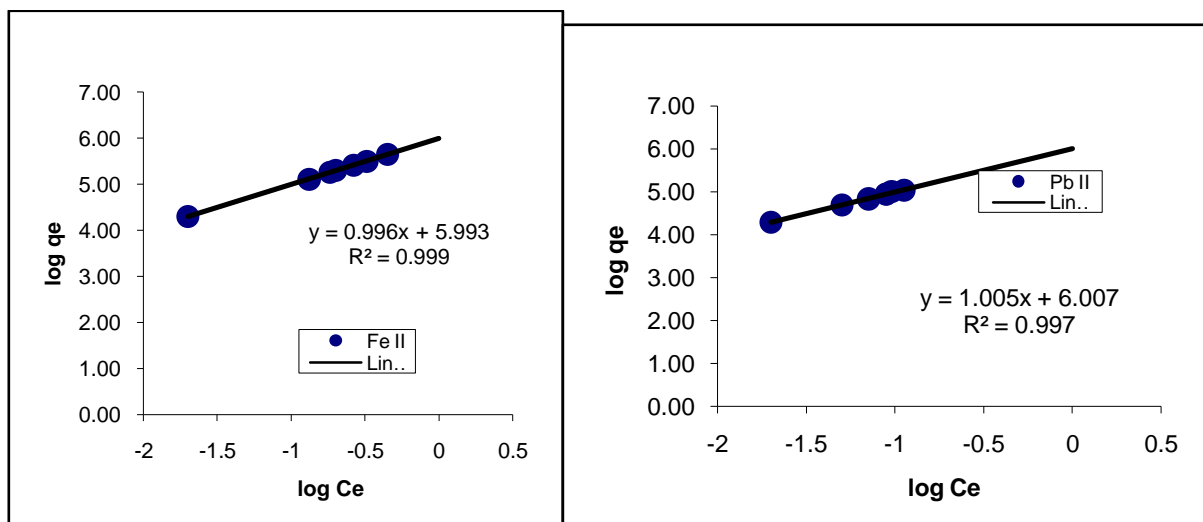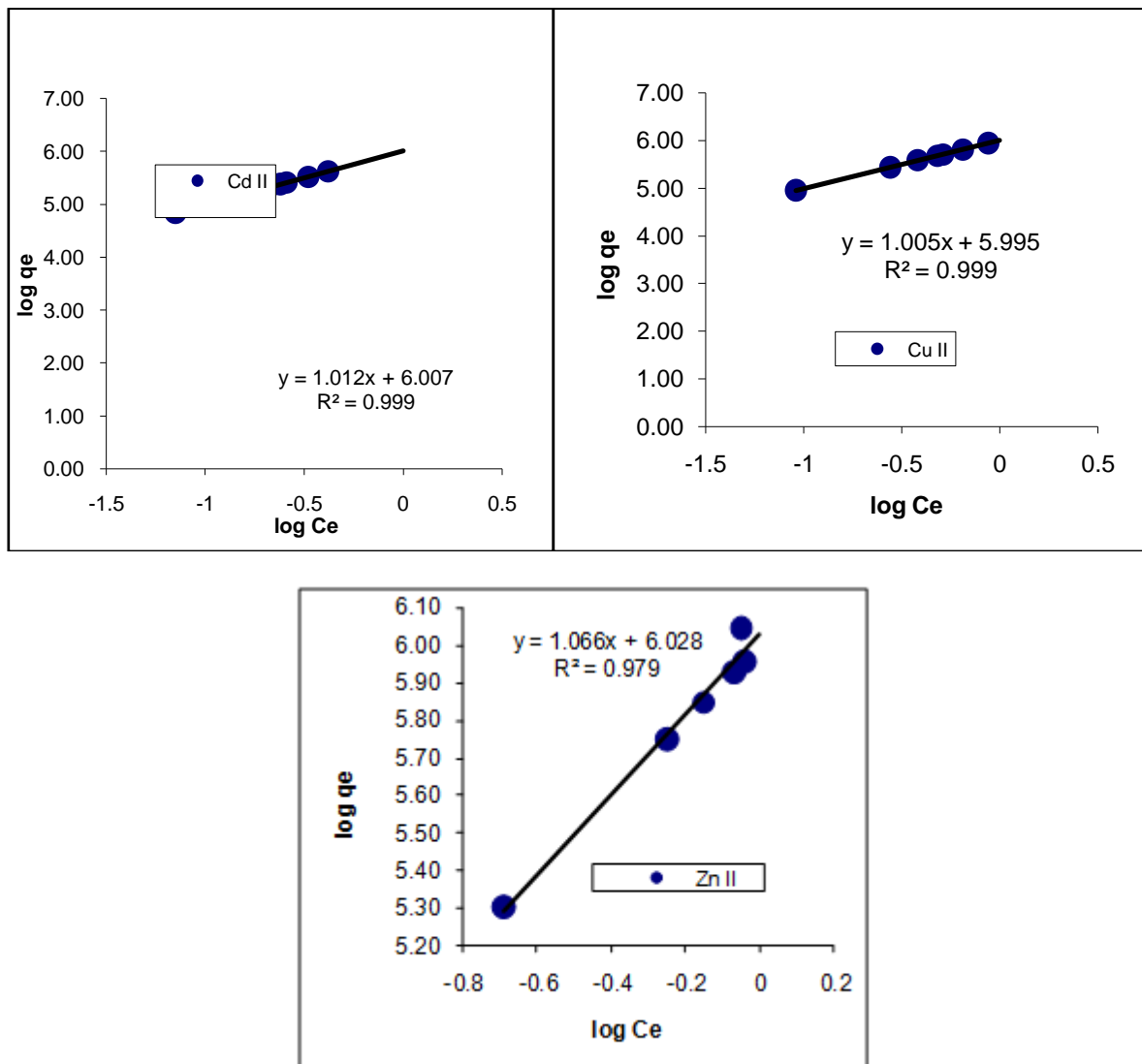
Fig. 5. Freundlich isotherm plots for the adsorption of heavy metal ion

The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentration. This isotherm does not predict only saturation of the adsorbent by the adsorbate ,but also infinite surface coverage is predicted mathematically, indicating multi layer adsorption on the surface.

Adsorption Thermodynamic
The change of enthalpy ΔH and entropy ΔS during the adsorption process could be calculated by the following equation
$$\ln Kd = - \Delta H/ (RT) + 2.303 \Delta S/R \quad (4)$$

Where Kd, known as the distribution coefficient of heavy metal ions. The isosteric enthalpy can be calculated at given adsorption capacity with the equation 5.
$$\ln Ce = \Delta H / (RT) - \ln Ko \quad (5)$$
Where R is gas constant, Ce is the equilibrium concentration under given adsorption capacity, T is the absolute temperature, and Ko is a constant. ΔH is obtained from the slope of line plotted by ln Ce vs 1/T.

Adsorption free energy change ΔG when the adsorption data fit well to Freundlich isotherm equation, ΔG can be obtained by equation 6.

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$$\Delta G = - nRT \qquad (6)$$

Adsorption entropy (ΔS) is obtained by equation 7.

$$\Delta S = \Delta H - \Delta G / T \qquad (7)$$

At 298, 325 and 398 K, the adsorption thermodynamic parameters of heavy metal ions are shown in (Table 4) . It is clear from the Table 4, that ΔH is negative indicating the adsorption progression and the results of adsorption free energy is negative, indicating the adsorption is with better impetus, and the process runs spontaneously. ΔS values are all negative, showing the adsorption process is impelled by enthalpy.

Table 4. Thermodynamics parameters of adsorption

Metal ions	Qe/mg.g^{-1}	$\triangle H$ (kj.mol^{-1})	$\triangle G$ (kj.mol^{-1})			$\triangle S$ (J.mol^{-1}.K^{-1})		
			298K	323K	348K	298K	323K	348K
Fe^{+2}	5.65	-5.99	-1.03	-1.42	-1.79	-10.32	-9.25	-7.45
Cu^{+2}	5.94	-6.46	-1.34	-1.46	-1.82	-12.32	-11.41	10.06
Zn^{+2}	6.05	-7.05	- 1.48	-1.79	- 2.02	-14.14	-13.98	-13.37
Cd^{+2}	5.62	-5.61	-1.01	-1.32	-1.68	-9.32	-8.29	-7.02
Pb^{+2}	5.04	-5.40	-.98	--1.29	-1.62	-8.25	-7.29	-6.58

Effect of CSA Dose on Adsorption of Metal Ions

The adsorption of metal ions is significantly influenced by the amount of the CSA resin added. The amount of CSA resin added into the solution determined the number of binding sites available for the adsorption. The effect of the adsorbent dose on the amount of metal ions adsorbed was studied by the application of varying CSA doses. The maximum adsorption by CSA resin was achieved with an adsorbent dose of 0.1 g. The initial increase adsorption percentage of metal ions was due to the availability of more adsorption sites. On increasing the CSA resin concentration further, the adsorption percentage of metal ions constant. This effect might be attributed to overlapping of adsorption sites of resin resulting constant of total surface area of the adsorbent. The results are shown in (Fig.6).
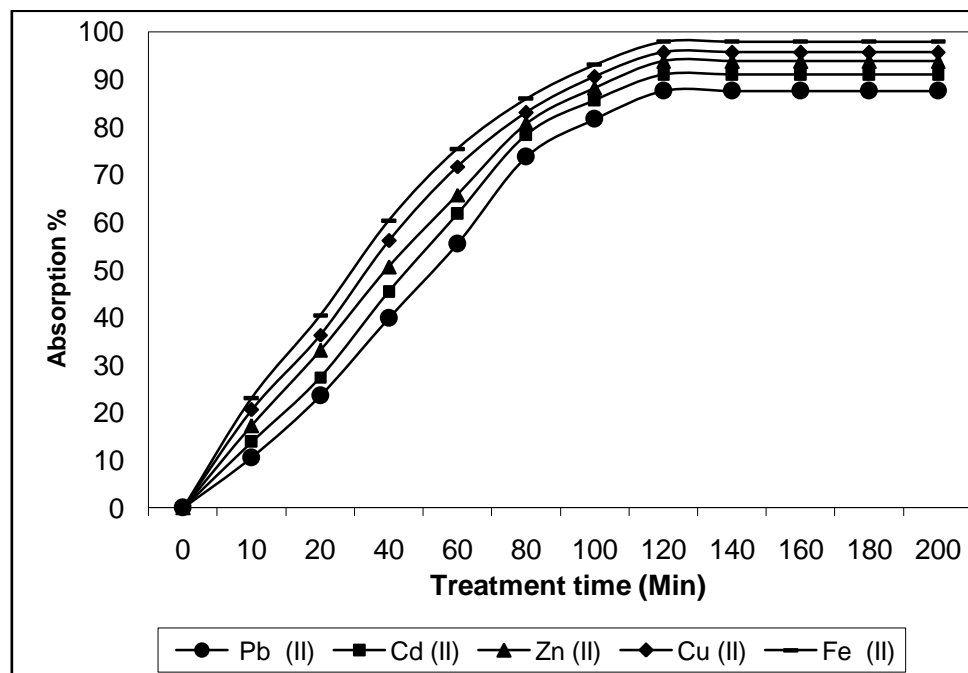
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Fig. 3 Effect of changing treatment time on the adsorption of metal ions on CSA resin

Quantitative Separation of Metal Ions

The superior selectivity of CSA resin towards different metal ions has been demonstrated in column experiments by using Kd values. The values of Kd are shown in (Table 3). The considerable difference in distribution coefficient of the metal ions implies that separation of metal ion from their mixtures would be possible. An ideal situation would be such that one Kd value is greater than the Kd value for other metal ions. The first eluting fractions of hydrochloric acid carry one metal ion which has smaller Kd value. The second metal ion was eluted by changing the hydrochloric acid concentrations. In the case of the separation of Pb^{+2} from other metal [35], chelating Pb complex and other metals were separated by selective adsorption. The Pb^{+2} was eluted with 0.05 N HCl solution, because at the same condition other metal ions shows higher kd values. Therefore, first few fractions contained only Pb^{+2} and other metal ions were eluted quantitatively with different strength of HCl solution. The results are given in (Table 5). The recoveries of metal ions by elution were calculated according to the equation 8.

Table 5.Quantitative separation of metal ions on CSA column

Metal ion	Amount loaded on CSA resin	Amount found in elution medium	% Recovery	Eluent use	Eluent volume
Pb^{+2}	0.15	0.14	93.00	0.05 N HCl	60
Cd^{+2}	0.74	0.72	97.85	0.5 N HCl	50
Zn^{+2}	3.04	3.01	99.08	1.0 N HCl	45
Cu^{+2}	1.93	1.91	98.99	1.5 N HCl	40
Fe^{+2}	1.12	1.12	100.00	2.0 N HCl	30

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$$Recovery \% = \frac{Amount\ of\ metal\ ions\ desorbed\ to\ the\ elution\ medium}{Amount\ of\ metal\ ions\ anions\ adsorbed\ on\ the\ resin} \times 100 \qquad (8)$$

Elution and Regeneration Cycles
After adsorption of metal ions, the resin needs to be regenerated for cycling use. The extra sample solution inside the column was pumped out leaving only solid CSA loaded with metal ions. Desorption was carried out by different concentration of HCl solution through the bed in the downward direction at a flow rate of 3.5 ml/min, slightly less that the adsorption flow rate 4.0 ml/min so that volume of regenerate is less which helps in easy handling and high in concentration so that economical metal recovery is possible. The regenerations were carried in the counter-current mode, that is, in the down flow mode. Counter-current operation generally reduces regeneration costs and regenerate volume and increases wastewater quality The desorbed column was washed with 200 ml distilled water at a flow rate of 20 ml/min followed by reactivation with 0.01 mol/l NaOH with a flow rate of 10 ml/min and finally washed again with 200 ml distilled water at a flow rate of 20 ml/min, all in up flow direction of the column. The reactivated and regenerated column was reused for second cycle of adsorption–desorption of metal ions. It was observed that the absorbance of different metal ion on the CSA resin in 10 cycles for all the five metal ions varied by less than only 6-8%. These results indicate that the resin has good durability as well as good efficiency for repeated use. The results are given in (Table 6).

Table 6. The adsorption percentage of different metal ions onto CSA resin (adsorption and desorption)

Metal Ions	adsorption percentage of different metal ions onto CSA resin				
	1 cycle	2 cycles	4 cycles	8 cycles	10 cycles
Fe^{+2}	97.89	95.87	92.35	91.02	90.83
Cu^{+2}	95.67	91.48	88.16	88.27	88.36
Zn^{+2}	93.81	91.63	89.43	87.92	86.73
Cd^{+2}	90.96	88.45	85.41	82.01	83.41
Pb^{+2}	87.96	85.94	83.06	81.76	80.24

Mechanisms for adsorption of Metal ions on CSA resin.
The heavy metal ions adsorption onto the surface of these CSA resin is assumed to occur through ion-exchange between charged heavy metal ions and ionized sulphonate group, which can be schemed as the following equation.

$$Rs - SO_3H \rightarrow Rs - SO_3^- + H^+$$

$$n\ Rs - SO_3^- + M^{+2} \rightarrow (Rs - SO_3^-)n\ M^{+2}$$
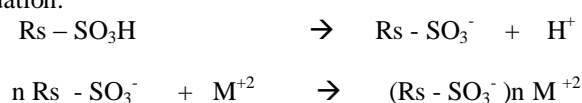
The above adsorption mechanism can be confirmed by the following facts: (i) during the experiment, it was found that the P^H value decreased perfectly from the original 4.4 to even 3.0. As we have known, the CSA resin has lots of $– SO_3H$, which can serve as the adsorption sites for ion – exchange process. In an aqueous solution, these groups within the resin dissociate to yield protons by which the solution P^H will decrease. This has been

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testified by the P^H variation of the suspension before and after the adsorption, as stated above. It can be concluded that ion exchange processes play an important role in adsorption of heavy metals ions on CSA resin. The relative standard deviation values (RSD) of optimum removal percentage of metal ions are shown in (Table 7). All data represent the mean of three independent experiments. The results revealed that the relative standard deviation (R.S.D) of the method was lower than 3.0, which indicated that the method had good precision for the analysis of trace metal ions in solution samples

Table 7. Optimum results for the removal of metal ions from the industrial wastewater by CSA resin at pH 6.0

Metal ions	Amount of metal ions in wastewater.	Amount loaded on CSA Resin	% Removal	RSD %
Pb^{+2}	0.18	0.15	87.56	1.19
Cd^{+2}	0.82	0.74	90.96	1.88
Zn^{+2}	3.25	3.04	93.81	2.77
Cu^{+2}	2.02	1.93	95.67	2.82
Fe^{+2}	1.15	1.12	97.89	2.98

CONCLUSIONS

Under the studied conditions, the adsorption of heavy metal on CSA resin from aqueous solution is an exothermic process which runs spontaneously and the equilibrium adsorption data fit Freundlich isotherm. A cationic strong acid resin (CSA) is employed as a new adsorbent for up taking of heavy metals in aqueous solution. The adsorption characteristics are examined at different P^H values, temperature, shaking speed and adsorbent doses, in the form of batch process. Thermodynamic parameters including enthalpy , entropy and Gibbs free energy indicate that the adsorption of heavy metals on CSA resin is a spontaneous process and is exothermic in nature CSA resin contains sulphanilic acid functional group, which possesses not only protons that can exchange with metal ions, but also have oxygen atoms that can coordinate directly with metal ions. Therefore, the adsorption ability of CSA resin for enriching metal ion may be very strong.

ACKNOWLEDGMENTS

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