



Removal of Hg (II) ions from aqueous solution by Acid Acrylic Resin A Study through Adsorption isotherms Analysis

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Abstract

The feasibility of using Amberlite IRC-86, a weak acid cation- exchange resin as an adsorbent for mercury (II) ions removal was examined. The influences of experimental parameters such as pH, initial mercury concentration, and agitation time and resin dosage were investigated. The data were analyzed on the basis of Lagergren pseudo-first order, Ho pseudo-second order, Langmuir, Freundlich and Redlich- Peterson isotherm models. The ion -exchange process, which is pH dependant, indicated that maximum removal of mercury (II) was obtained at pH 7 ± 0.1 and a resin dosage of 0.1g. Through fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and scanning electron microscopy coupled energy dispersive X-ray (SEM-EDAX) analysis, the ion -exchange mechanism was confirmed. Finally, the resin can be regenerated by treatment of the spent resin with HCl. The experimental results indicate that Amberlite IRC-86, weak acid cation exchange resin is a promising adsorbent, which could be used effectively for the removal of mercury (II) ions from aqueous medium.

Keywords: Amberlite IRC-86 resin, mercury (II), adsorption, isotherm, kinetics, desorption

Introduction

The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. The existence of heavy metals in wastewaters contributes to water toxicity and represents an increasing danger for the environment, human beings and other living organisms¹. Heavy metal pollution of the environment has become a growing ecological crisis and concern and therefore the subject of many researches². Mercury is well known for its extremely high toxicity and the serious threat to human life and natural environment. The drinking water criterion for mercury established by USEPA is, 2 $\mu\text{g/L}$ and the permitted discharge limit of wastewater for total mercury is 10 $\mu\text{g/L}$. Therefore, it is very important to reduce the residual mercury concentration below the safety limit for mercury ions from industrial wastewater, especially from drinking water³.

Several methods such as evaporation, electro-deposition, solvent extraction, reverse osmosis, membrane separation process and activated carbon adsorption are employed for the removal of heavy metal ions from water waste⁴. However, these techniques have certain disadvantages such as higher operational cost, requiring additional chemical, high energy consumption and residual metal sludge disposable. Due to forbidding cost of these processes, the uses of resins have been received with considerable attention. In recent years a number of commercial resins such as Amberlite IR-120, Amberlite IRC-748, Amberlite IRC-718, Lewatit TP-207 and a wide range of anion exchange resins with styrenic structures have been used to remove heavy metals from wastewater^{5,6,7,8}. However, the applicability of cation exchange

resin containing acrylic matrix for the removal of heavy metal ions from wastewater is not well documented.

In the present work, the removal of Hg(II) ions from aqueous solutions using a weak acid cation exchange resin containing acrylic matrix (Amberlite IRC-86) was investigated. The aim of this work was to study the influence of experimental parameters such as pH, contact time, adsorbent dosage on Hg(II) removal and to understand the kinetics of the mechanism, thereby exploring the potential of acrylic acid resin in the removal of Hg(II) ions from the aqueous solutions.

Material and Methods

Ion-exchange resin: Commercial synthetic Amberlite IRC-86, weak acid cation exchange resin in hydrogen form was obtained from Sigma Aldrich Co. The properties of the resin are given in table -1. The resin was washed with double distilled water to remove impurities and dried in an oven at 80°C for 24 h. Dried resin was used for further experimental studies.

Preparation of standard solution: A stock solution of 1000 mg /L of Hg(II) was prepared by dissolving 1.354 g of HgCl_2 in double distilled water acidified with 5ml of conc. HNO_3 to prevent hydrolysis and diluting to 1000ml. The required lower concentrations were prepared by dilution of the stock solution, which was prepared freshly for each experiment.

Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM) analysis: Infrared spectra of the resins before and after ion-exchange experiment were obtained using a Fourier transform infrared spectrometer in the frequency range

of 400-4000cm⁻¹. With the help of scanning electron microscopy (SEM), the images of the resin surface was taken both before and after treatment with Hg(II) ions. The concentration of Hg(II) ions on the resin surface was determined by Scanning Electron Microscopy coupled energy dispersive X-ray Analysis (SEM –EDAX).

Table -1
Physico-chemical properties of weakly acidic Amberlite IRC-86 resin.

| Characteristics | Value |
|--|------------------------------|
| Physical Characteristics | |
| Particle size range | 16-50 mesh |
| Temperature limitations | 120 °C |
| Chemical Characteristics | |
| Structure | Gel |
| Matrix | Acrylic Polymer |
| Functional Group | Carboxylic Acid |
| Ionic form | H ⁺ |
| pH limitations | 4 -14 |
| Total Exchange capacity | 10.7 meq /g by dry weight |
| Matter Soluble in H ₂ O (%) | 4.2 meq/ml wetted bed volume |
| Moisture retention | Ω 50% |

Adsorption experiments: The batch mode experiments were performed in 100ml conical flasks by addition of desired amount of resin to 50ml of Hg(II) solutions. In all experiments, the flasks were shaken at 250 rpm on the orbital shaker for predetermined time intervals at room temperature (30 ±2°C). After agitation, the resin was separated by filtration and some aliquots of filtrate in the supernatant were analyzed using spectronic 20 UV spectrophotometer at 565 nm with Rhodamine 6G⁹. The amount of metal ion adsorbed on the resin was computed by the following equation:

$$q_e = V/W (C_0 - C_e) \quad (1)$$

Where C_e and C₀ (mg/L) are the liquid -phase concentrations of solutes at the initial and equilibrium time t, respectively. V (L) is the volume of solution and W (g) is the mass of dry resin.

The effect of initial pH on the removal of Hg(II) ions from aqueous solution was studied in the range of 2 to 9 pH , which was adjusted using 0.01 N HCl and 0.01 N NaOH solutions. For these experiments 50 ml of (20mg /L and 50 mg/L) Hg(II) solution was agitated with 0.1 g of resin for a period of 60 minutes.

The influence of adsorbent dosage on Hg(II) removal was studied with various resin dosage (0.05 to 0.2 g/L) for 50 mg/L Hg(II) solution.

Various isotherm models such as Langmuir, Freundlich, and Redlich-Peterson were investigated. Reaction-based kinetic models such as Lagergren pseudo- first order and Ho pseudo - second order models were studied. The thermodynamic parameters such as free energy (ΔG⁰), enthalpy (ΔH⁰) and entropy (ΔS⁰) changes for the sorption process were determined.

Desorption Studies: Desorption studies help to elucidate the mechanism of adsorption and recovery of metal ions and adsorbent. 50ml of 20mg/L and 50 mg/L of Hg(II) ion solutions were agitated with 01.g resin for the equilibrium time. After agitation, the spent resin was treated with 50 ml of varying HCl concentration and again agitated for the predetermined time of adsorption. The desorbed Hg (II) ion solution was filtered and estimated as before.

Results and discussion

Effect of agitation time and initial Hg(II) ion concentration on the adsorption of Hg(II) ions from aqueous solution: Figure-1 shows the time dependant behavior of the removal of Hg(II) ions from aqueous solution by the resin. From the plot, it is clear that the removal amount of Hg(II) increased as the contact time elapsed. The equilibrium time was reached within 50 min. The initial adsorption rate was very fast which may be due to the existence of greater number of resin sites available for metal ions adsorption. As the remaining vacant surface sites decreases, the adsorption rate slowed down due to the formation of repulsive forces between the metals on the solid surface and in the liquid phase. Moreover, as the initial concentration of metal ion was increased, the percentage removal of Hg(II) ions from the aqueous solution was decreased. The kinetic curves are single, smooth and continuous, indicating the possible monolayer coverage of metal ions on the surface of the resin¹⁰.

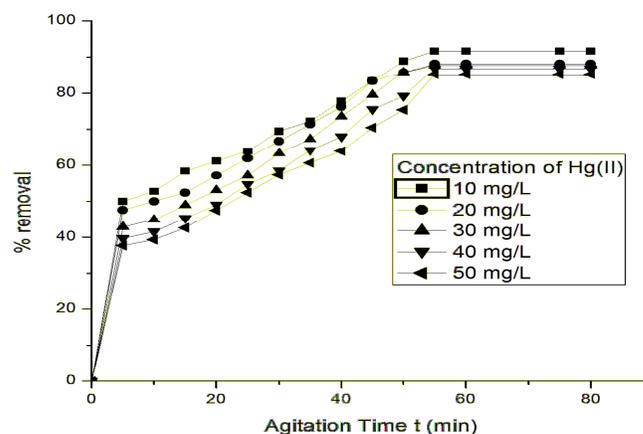


Figure-1
Effect of agitation time and initial Hg(II) ion concentration on the adsorption of Hg(II) ions by: Amberlite IRC86 resin

Adsorption isotherms

Langmuir isotherm: The Langmuir equation assumes that the solid surface presents a finite number of identical sites which are energetically uniform and a monolayer is formed when the solid surface reaches saturation. The linear form of the Langmuir equation is given by¹¹

$$C_e/q_e = 1/Q_0 + C_e/Q_0 \quad (2)$$

Where, C_e is the equilibrium concentration of metal (mg/L), Q₀ and b are Langmuir constants related to adsorption capacity and

adsorption energy respectively. The plot of C_e/q_e against C_e gives a straight line (figure -2) showing the applicability of Langmuir isotherm. The values of Q_0 and b are obtained from slope and intercept of the plot and are presented in table- 2. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called, the equilibrium parameter R_L which perfectly determines the favorability and shape of the isotherm of the adsorption process by applying Equation -3

$$R_L = 1/(1 + bC_0) \quad (3)$$

Where, C_0 is the initial Hg(II) ion concentration (mg/L). As the R_L values obtained lies between 0 and 1, the adsorption process is favorable.

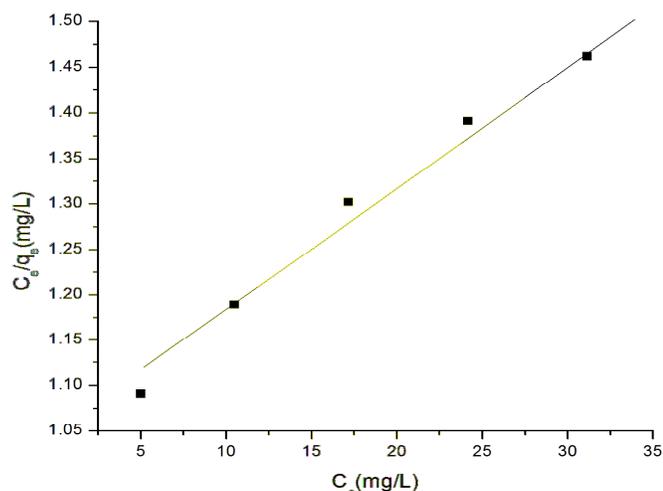


Figure-2
Langmuir plot for Hg(II) adsorption

Freundlich isotherm: The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface suggesting that binding sites are not equivalent. The linear logarithmic form of Freundlich equation is as follows¹²

$$\log q_e = \log K_f + 1/n \log C_e \quad (4)$$

Where, K_f (mg/g) and n are constants related to adsorption capacity and adsorption intensity, respectively. Linear plots of $\log q_e$ versus $\log C_e$ (figure 3) showed that the adsorption obeys Freundlich isotherm. The values of K_f and n are presented in table- 2.

Redlich - Peterson isotherm: This isotherm is a combination of Langmuir and Freundlich models which is defined as follows¹³

$$q_e = K_R C_e / (1 + a_R C_e^\beta) \quad (5)$$

Where, a_R and K_R are the constant of Redlich - Peterson and β is the exponent of equation which lies between 0 and 1. When $\beta=1$, this equation changes to Langmuir isotherm and when $\beta=0$, it changes to Henry equation which is defined as follows:

$$q_e = K_R C_e / (1 + a_R) \quad (6)$$

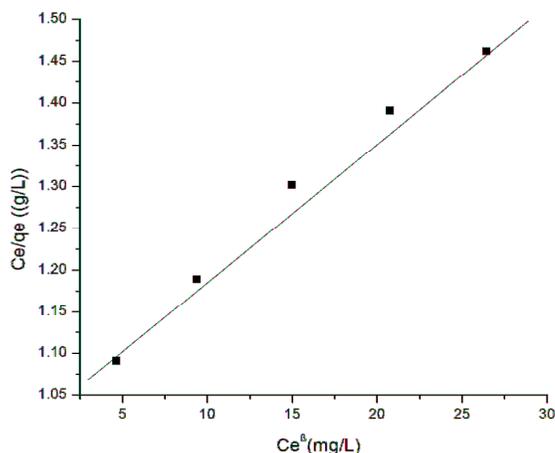


Figure-3
Freundlich plot for Hg(II) adsorption

Redlich - Peterson equation can be expressed in linear form as follows:

$$C_e/q_e = 1/K_R + a_R/K_R C_e^\beta \quad (7)$$

From the plot of C_e/q_e versus C_e^β (figure- 4), the values of a_R and K_R were determined and are presented in table- 2.

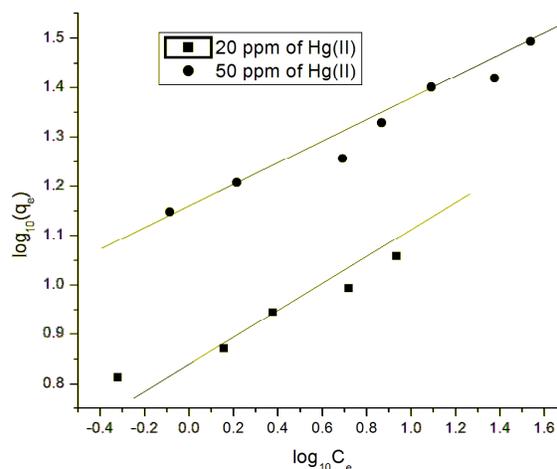


Figure-4
Plot for Redlich-Peterson isotherm

Adsorption Kinetics

Lagergren Pseudo - first order kinetic model: By studying adsorption kinetics, the efficiency of the adsorbent was evaluated. The rate constant of adsorption was determined from Lagergren Pseudo - first order equation which is generally expressed as¹⁴

$$\log(q_e - q_t) = \log q_e - K_1 t / 2.303 \quad (8)$$

Where, q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time t , respectively and K_1 is the rate constant for pseudo - first order adsorption. From the plots of $\log(q_e - q_t)$ against t , the values of K_1 and q_e were determined (figure- 5) and are presented in table- 3.

Table- 2
Isotherm parameters for removal of Hg(II) by Amberlite IRC86 resin (conditions: pH:7±0.1, volume:50 ml, resin mass: 100mg, agitation time: 60 min, temperature:303K)

| Isotherm models | Constants | Value | |
|------------------|--------------|----------------------|-----------|
| Langmuir | Q_0 (mg/g) | 70.422 | |
| | b (L/mg) | 0.0137 | |
| | R^2 | 0.9933 | |
| Freundlich | | Hg(II) concentration | |
| | | 20 (mg/L) | 50 (mg/L) |
| | K_F (mg/g) | 7.201 | 14.252 |
| | n | 3.79 | 4.844 |
| | R^2 | 0.9201 | 0.9825 |
| Redlich-Peterson | K_R (L/g) | 0.9743 | |
| | a_R (L/mg) | 0.0166 | |
| | R^2 | 0.9946 | |

Table- 3
Kinetic parameters for the removal of Hg(II) by Amberlite IRC86 resin (conditions: pH:7±0.1, volume:50 ml, resin mass: 100mg, agitation time: 60 min, temperature:303K)

| Conc of Hg(II) (mg/L) | q_e (mg/g) (Exp) | Pseudo-first-order model | | | Pseudo-second-order model | | |
|-----------------------|--------------------|--------------------------|------------------------------|--------|---------------------------|----------------------------------|--------|
| | | q_e (mg/g) (Cal) | $K_1 \times 10^{-2}$ (1/min) | R^2 | q_e (mg/g) (Cal) | $K_2 \times 10^{-2}$ (g/ mg min) | R^2 |
| 10 | 4.583 | 3.755 | 4.987 | 0.9005 | 4.9043 | 2.092 | 0.9806 |
| 20 | 8.81 | 8.361 | 5.768 | 0.9172 | 9.891 | 0.8873 | 0.9761 |
| 30 | 13.163 | 13.896 | 5.606 | 0.8821 | 14.992 | 0.4783 | 0.9646 |
| 40 | 17.358 | 14.648 | 3.855 | 0.9480 | 18.796 | 0.3754 | 0.9663 |
| 50 | 21.311 | 16.904 | 3.278 | 0.9592 | 22.075 | 0.3316 | 0.9710 |

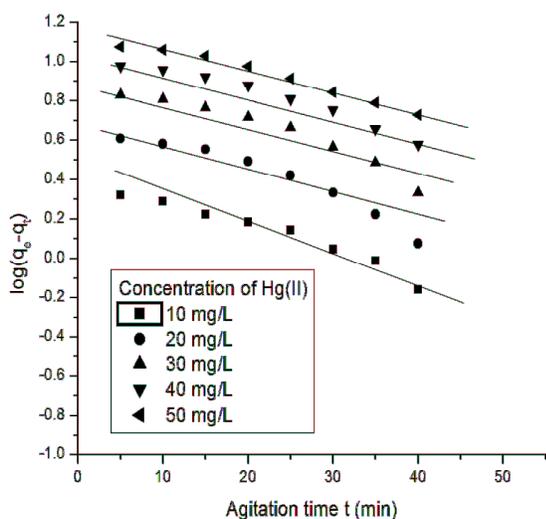


Figure-5
Pseudo-first-order Lagergren plots for Hg(II) adsorption onto Amberlite IRC86

Ho Pseudo - second order kinetic model: The linear form of Ho pseudo - second order kinetic model is expressed as¹⁵
 $t/q_t = 1/K_2 q_e^2 + t/q_e$ (9)

Where, K_2 is the rate constant of second order adsorption (g/mg/min). From the plot of t/q_t against t (Figure-6), K_2 and q_e were determined and are presented in table -3.

The best correlation between predicted and experimental q_e values indicates that the adsorption system studied belongs to pseudo - second order kinetic model.

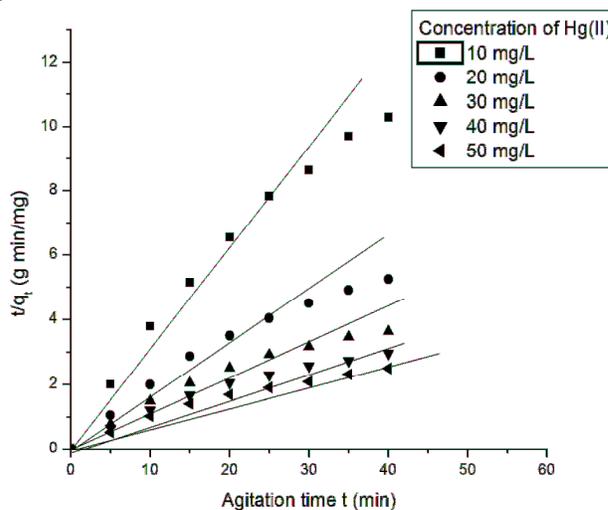


Figure-6
Ho Pseudo-second-order plots for Hg(II) adsorption onto Amberlite IRC86 resin

Effect of pH on Hg(II) adsorption from aqueous solution: The solution pH is an important factor controlling the surface charge of the adsorbent and the degree of ionization of the adsorbate in aqueous solution¹⁶. The effect of pH on the sorption of Hg(II) ions was tested at different pH values (2.0-8.0) using 0.1 g of Amberlite IRC - 86, weak acid cation - exchange resin for Hg(II) concentration of 20mg/L and 50 mg/L. The results indicated that the maximum uptake of Hg(II) ions occurred at initial pH of 7.0. The adsorption capacity of the resin increased with increase in pH of the aqueous solution. This can be explained on the basis of decrease in competition between protons (H⁺ ions) and metal cations (Hg²⁺ ions) for the same functional groups (-COO⁻) and by decrease in the positive surface charge on the resin resulting in a lower electrostatic repulsion between the surface of resin and mercury (II) ions¹⁷. The low level of mercury (II) ions uptake at lower pH may be explained on the basis of the overall surface charge on the resin becoming positive and active sites being protonated, which will inhibit the approach of positively charged metal ions. Sorption at pH above 8.0 was not carried out to avoid any possible interference from metal precipitation in solution. Hence the optimal pH for the removal of Hg(II) from aqueous solution by the resin was found to be 7.0±0.1, which was maintained throughout the experimental studies.

Effect of resin dosage on Hg (II) sorption from aqueous solution: The amount of adsorbent is one of the parameters affecting strongly the sorption capacity. The adsorption of Hg(II) ions from aqueous media on Amberlite IRC-86 resin was studied by varying amount of the ion-exchanger from 0.025 to 0.150 g at pH 7.0±0.1 for Hg(II) concentration of 20 mg/L and 50 mg/L respectively. Optimum resin dosage was fixed as 0.1g. The removal percentage increased with increase in ion - exchanger dose.

Thermodynamic study: The thermodynamic equilibrium constant K_c for the adsorption of Hg(II) onto resin was determined by using the equation,

$$K_c = C_A/C_e \quad (10)$$

Where C_A is the amount of metal ion adsorbed on the adsorbent at equilibrium (mg/L) and C_e is the equilibrium concentration of metal ion in solution. The change in standard free energy ΔG⁰ was

calculated using the following equation and its value is given in table -4.

$$\Delta G^0 = -RT \ln K_c \quad (11)$$

Where R is the gas constant and T is temperature (K)

According to Vant Hoff's equation,

$$\ln K_c = \Delta S^0 / R - \Delta H^0 / RT \quad (12)$$

Where ΔS⁰ and ΔH⁰ are the changes in entropy and enthalpy of adsorption, respectively.

A plot of lnK_c versus 1/T (Figure-7) was found to be linear.

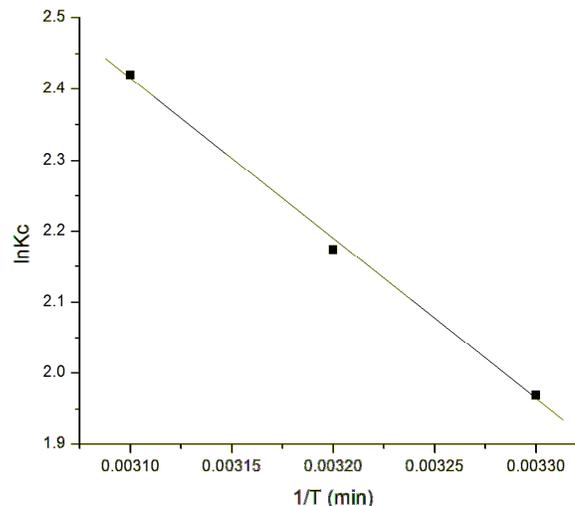


Figure-7

Vant Hoff's plot for Hg(II) removal by Amberlite IRC86 resin

The values of ΔH⁰ and ΔS⁰ were evaluated from the slope and intercept of Vant Hoff's plot and are presented in table-4. The positive value of ΔH⁰ confirms the endothermic nature of adsorption. When the temperature increased from 303K to 323K, the magnitude of free energy change shifted to a high negative value suggesting that adsorption was rapid and spontaneous. The positive value of ΔS⁰ suggested an increase in randomness at the solid-solution interface during the adsorption of Hg(II) on resin¹⁸.

Table -4
Thermodynamic parameters for the adsorption of Hg(II) by Amberlite IRC86
(conditions: pH:7±0.1, volume:50 ml, resin mass: 100mg, agitation time: 60 min)

| Temperature (K) | lnK _c | -ΔG [kJ/mol] | ΔH [kJ/mol] | ΔS [J/mol K] |
|-----------------|------------------|--------------|-------------|--------------|
| 303 | 1.969 | 4.96 | 18.748 | 0.0781 |
| 313 | 2.174 | 5.657 | | |
| 323 | 2.420 | 6.498 | | |

Table- 5
Wave number (cm⁻¹) for dominant peak from FTIR of resin and Hg(II) loaded resin

| Control frequency (cm ⁻¹) of Amberlite resin | Frequency of Amberlite resin after treatment with 50mg/L of Hg(II) solution (cm ⁻¹) | Functional groups |
|--|---|--|
| 2914.47 | 2924.47 | CH stretching |
| 1661.12 | 1654.65 | C=C stretching |
| 1372.16 | 1398.96 | COO ⁻ symmetric stretching |
| 1600.25 | 1637.43 | COO ⁻ asymmetric stretching |

FTIR, SEM and SEM-EDAX analysis: The FTIR spectra of the resin and metal loaded resin (figure- 8a, 8b.) showed a shift in wave number of dominant peaks associated with the loaded metal^{19,20}. This shift in the wavelength indicates the metal binding process taking place at the surface of resin. Table -5 represents the fundamental frequencies of control (resin), Hg(II) treated resin and their respective possible band frequencies in the FTIR spectra. It was stated that symmetric and asymmetric vibrations of - COO⁻ groups appeared at 1372.16 and 1600.25 cm⁻¹, respectively²¹. This observation provides evidence that the functional groups of - COO⁻ are involved in binding the Hg(II) ions onto Amberlite resin.

morphology in the Hg(II) adsorbed resin demonstrated that the sorption of Hg(II) ions has taken place onto the adsorbent.

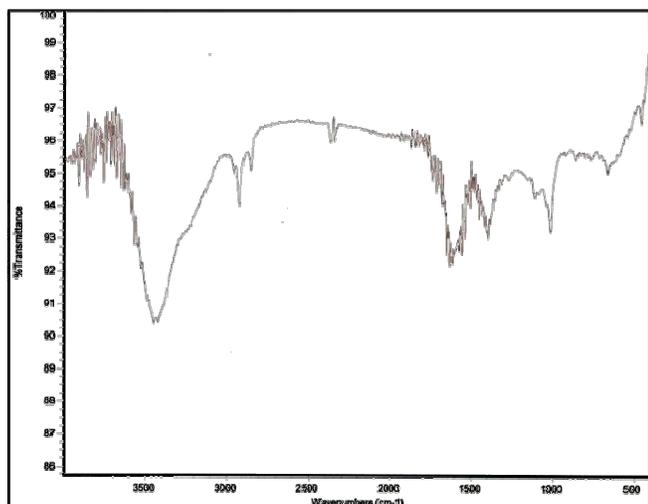


Figure-8a
FTIR spectrum of the resin

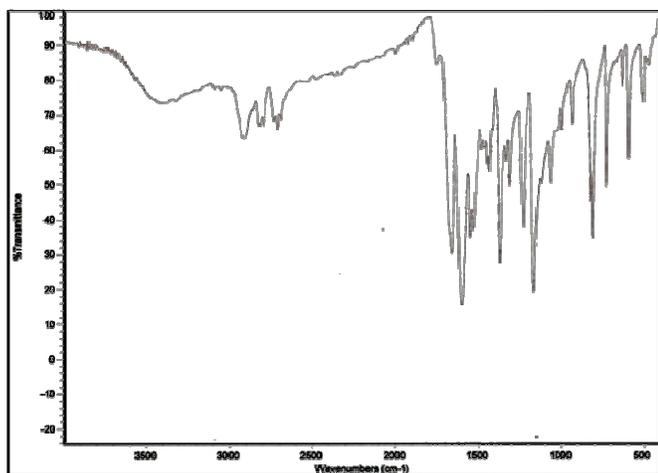


Figure- 8b
FTIR spectrum of Hg(II) loaded resin

SEM images of the cation- exchange resin before and after Hg(II) sorption are shown in figure 9a and 9b, respectively. As could be seen from the figure, a visible change of the surface

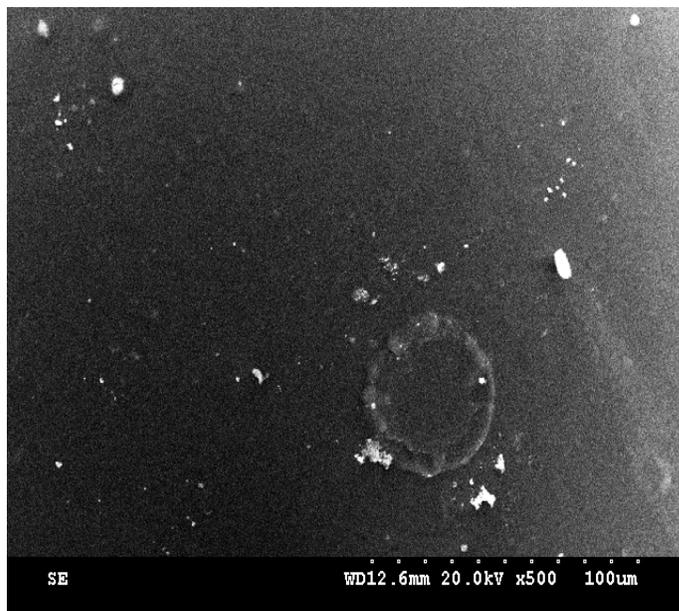


Figure-9a
SEM of Amberlite IRC86 resin before Hg(II) adsorption

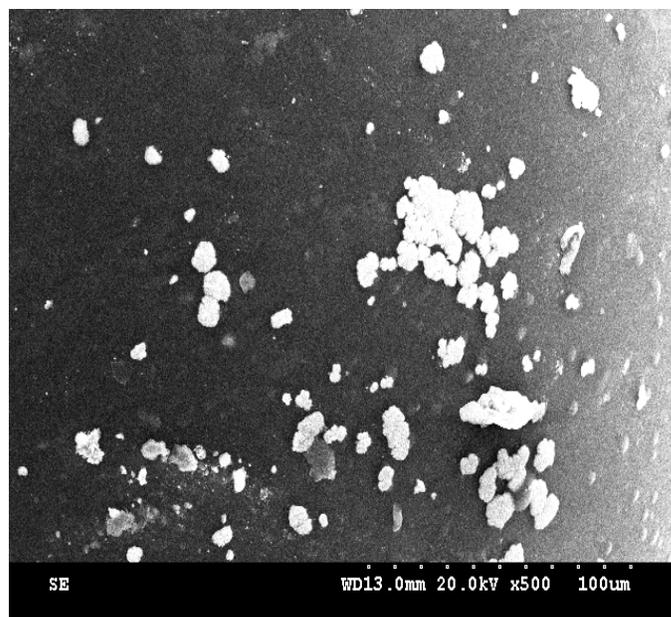


Figure-9b
of Amberlite IRC86 resin after Hg(II) adsorption

The SEM-EDAX spectrum of Hg(II) loaded resin is shown in figure-10. The presence of Hg(II) peak in the spectrum confirms the adsorption of Hg(II) onto Amberlite resin.

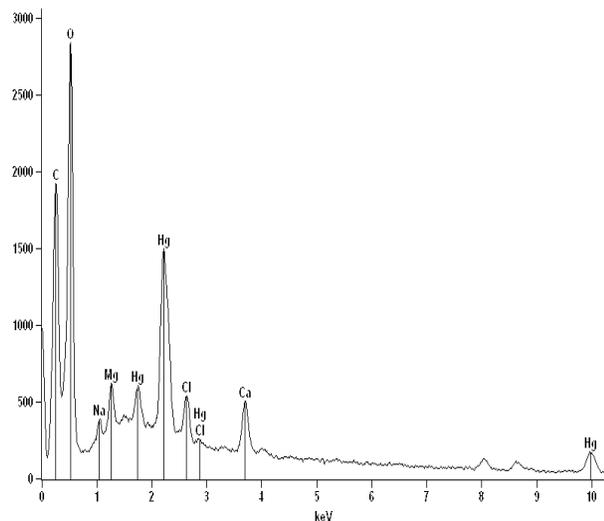


Figure-10
SEM-EDAX spectrum of Hg(II) loaded resin

Desorption studies: Desorption studies were carried out by treating the spent resin with varying concentrations of HCl (0.1 to 0.5N). It was found that 100% recovery was achieved using 0.5N HCl for 20 and 40 mg/L of Hg(II) solution. The results indicate that adsorption is through ion-exchange mechanism

Conclusion

Removal of Hg(II) ions from aqueous solution using weakly acidic cation-exchange resin with acrylic skeleton, namely Amberlite IRC86 was found to be very efficient under optimal conditions. The extent of Hg(II) adsorption increases with contact time and resin dose. The kinetics of adsorption process followed pseudo-second order rate equation indicating chemisorption as the rate-limiting step. Equilibrium adsorption data fitted well into Redlich-Peterson isotherm model. The adsorption capacity was found to be 70.422 mg/g at 303K. Thermodynamic parameters, ΔS , ΔH and ΔG on the adsorption of Hg(II) indicated that the adsorption process was spontaneous and endothermic. Desorption studies showed that the resin can be regenerated and reused. Thus, the weak acid cation-exchange resin with acrylic skeleton, namely Amberlite IRC86 has a very good potential for the removal of Hg(II) from aqueous solution.

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