Available online at http://www.journalijdr.com

IJDR

International Journal of
DEVELOPMENT RESEARCH

ISSN: 2230-9926

International Journal of Development Research
Vol. 3, Issue, 12, pp.001-007, December, 2013

Full Length Research Article

STUDIES ON ADSORPTION OF Pb (II) AND Hg (II) IONS FROM AQUEOUS SOLUTION USING MODIFIED CHITOSAN AS ADSORBENT

Alark, R., Anoop, K. V., Meenakshi, D. S., Supriya Rani, G., Sashikala, M., Vasundhara, K. R., Manish S. Khodwe and *Soundarajan Krishnan

Department of Chemical Engineering, M.V.J. College of Engineering, Channasandra, Bangalore-560 067

ARTICLE INFO

Article History:
Received 05th September, 2013
Received in revised form
11th October, 2013
Accepted 17th November, 2013
Published online 18th December, 2013

Key words:
Adsorption,
Modified chitosan,
Isotherms,
Kinetics,
Toxic heavy metals.

ABSTRACT

Toxic heavy metals are being discharged significantly into the aquatic ecosystems as a result of various industrial operations, causing serious concern, especially in the developing countries over the last few decades. Heavy metals are not biodegradable and hence, accumulate in the living beings, causing diseases and health disorders. It is imperative that these metal ions are removed from the aqueous medium before discharging into the environment. The objective of this project work is to study the adsorption of metal ions like Pb (II) and Hg (II) ions by using modified chitosan as a suitable adsorbent for their removal from the aqueous medium. Experimental data are collected to study the effect of various parameters such as adsorbent dosage, contact time, pH and initial metal-ion concentration, and the optimum conditions for these parameters have been evaluated. Studies on adsorption kinetics and adsorption isotherms have been carried out, and the best fitting models for the rate kinetics and isotherms have been proposed.

INTRODUCTION

The presence of heavy metals in water is causing great concern because of their toxicity to living beings, even in small concentrations. Mercury is a toxic heavy metal found in the effluents of industries such as chloralkali, paint, pharmaceutical, pulp and paper, etc., whereas lead is found in the industrial effluents from storage batteries, lead-smelting and plating industries. The presence of lead in the drinking water above the permissible limit can cause health damage such as delay in physical and mental development of children, and high blood pressure in adults, whereas the presence of mercury above permissible limit will cause chest pain, damages to the central nervous system and chromosomes. Because of increased environmental awareness, the development of cost-effective methods for the removal of lead and mercury ions from aqueous solutions has gained momentum. There are numerous commercially available adsorbents which have been used for metal-ion removal. Chitosan is a biopolymer, which is extracted from crustacean shells or from fungal biomass and it is the universally accepted, non-toxic, fully or partially deacetylated derivative of chitin. Various analytical methods are used to determine the degree of n-deacetylation (Baxter *et al*., 1992; Domard *et al*., 1986; Domard *et al*., 1987; Wei and Hudson, 1993; Sashiwa *et al*., 1991; Tolaimate *et al*., 2000; Niola *et al*., 1983; Pangburn *et al*., 1984; Kasaai *et al*., 2000). Chitosan is a suitable and effective adsorbent for the removal of metal ions. Since the literature relatively lacks information on adsorption of Pb (II) and Hg (II) ions using modified chitosan, the present study aims at investigating the feasibility of Pb (II) and Hg (II) ion removal from aqueous solutions by using economically available and highly effective, modified chitosan as a suitable adsorbent under varied conditions. The effects of different parameters like contact time, adsorbent dosage, pH and initial metal ion concentration have been studied and their optimum values are obtained for which maximum metal- ion removal is possible from the aqueous solution. Studies on adsorption kinetics and adsorption isotherms have been carried out, and the best fitting models for the rate kinetics and isotherms have been proposed.

The objectives of this study are:

- To determine the effectiveness of removing metal ions by using modified chitosan and to study the effects of various experimental parameters such as contact time, pH, initial

---

****Corresponding author: Soundarajan Krishnan***
Department of Chemical Engineering, M.V.J. College of Engineering, Channasandra, Bangalore-560 067

concentration of metal ions and adsorbent dosage on adsorption.

- To investigate the conditions for the performance of chitosan in removing metal ions.
- To carry out adsorption kinetics and isotherms studies on the removal of metal ions using modified chitosan.

MATERIALS AND METHOD

In the present study, the equipments used are electronic balance (Afcoset, FX-300, Max. 310gm, d=0.001gm); UV VIS Spectrophotometer (Elico, SL 159); Digital pH Meter (MK VI) and Orbital Shaker (Scigenics Biotech Private Limited, Chennai, Model: Orbitek). The chemicals used are Modified Chitosan (Otto, Chemika-BioChemika-Reagents, Gujarat); Lead (II) acetate Trihydrate (Merck Specialities Private Limited, Mumbai); Mercuric sulphate (Rankem, Assay NLT 99%, Lab Grade, New Delhi); HCl (Rankem, Assay NLT 35.0%, Lab Grade, New Delhi); NaOH (Fisher Scientific, Assay 97.0%, Lab Grade, Mumbai) and distilled water

Adsorption Kinetics

In order to investigate the controlling mechanisms of the adsorption processes like mass transfer and chemical reactions, pseudo first-order and pseudo second-order kinetic studies are used to test the experimental data. The pseudo first-order kinetic model for the adsorption of solid or fluid system is given by Eq. (1):

$$dq/dt = k_1(qe-qw) \qquad (1)$$

After integrating, Eq. (2) is obtained.

$$\ln(qe-qt) = \ln qe - k_1 t \qquad (2)$$

where, qt is the adsorption capacity at time ‘t’ (mg/g) and k_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption. Ho’s pseudo second-order kinetic model is based on the assumption that the sorption follows second-order chemisorption. Pseudo second-order kinetic model which, after integration, is given by Eq. (3).

$$t/qt = 1/k_2qe^2 + t/qe \qquad (3)$$

where, k_2 (g/mg.min) is the rate constant of the pseudo second-order adsorption and qt is the adsorption capacity at time t (mg/g).

Adsorption Isotherm

Adsorption equilibrium data are typically plotted in the form of an adsorption isotherm. Adsorption isotherms are mathematical models that describe the distribution of adsorbate species among liquid and solid phases, based on a set of assumptions that are related to the heterogeneity/ homogeneity of the solid surface, the type of coverage and the possibility of interaction between the adsorbate species.

Freundlich Isotherm

The Freundlich isotherm describes physical adsorption from the liquids. The empirically derived Freundlich isotherm is defined by Eq. (4):

$$qe = k_F\, Ce^{1/n} \qquad (4)$$

where,

qe: Amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), (mol/g)

Ce: Equilibrium concentration of adsorbate in solution after adsorption (mg/g), (mol/L)

k_F: Empirical Freundlich constant or capacity factor (mg/g), (mol/g)

1/n: Freundlich exponent

The good fit of Freundlich isotherm to an adsorption system means there is almost no limit to the amount adsorbed and there is a multi-layer adsorption. The applicability of the Freundlich equation to a particular case is tested by plotting log qe against log Ce from the logarithmic form of Eq. (5).

$$\log qe = \log k_F + 1/n \log Ce \qquad (5)$$

Such a plot yields a straight line with intercept equal to log k_F and slope equal to 1/n.

Langmuir Isotherm

The Langmuir adsorption isotherm is developed assuming that a fixed number of accessible sites are available on the adsorbent surface, all of which have the same energy; adsorption is reversible; monolayer adsorption occurs and there are no lateral interactions among the adsorbates. The Langmuir adsorption isotherm is defined as

$$qe = qok_LCe/1 + k_LCe \qquad (6)$$

where,

qe: Amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), (mol/g)

Ce: Equilibrium concentration of adsorbate in solution after adsorption (mg/g), (mol/L)

qo: Empirical Langmuir constant which represents maximum adsorption capacity (mg/g), (mol/g)

k : Empirical Langmuir constant (L/mg), (L/mol)

$$Ce/qe = 1/qo\, k_L + Ce/qo \qquad (7)$$

and plotting of Ce/qe vs Ce gives a straight line with a slope 1/qo and intercept 1/qo k_L. The constant k_L, which is commonly referred to as the Langmuir constant, is defined as the equilibrium constant of the adsorption reaction. The Langmuir isotherm is limited in its application to adsorption in monolayer. It applies well to chemisorption and to physical adsorption when saturation is approached.

EXPERIMENTAL

Stock solutions were prepared by adding 0.1 g of Hg and Pb ions in 1 litre standard volumetric flask separately. From this solution, different concentrations were prepared by taking 20 ppm to 100 ppm solutions separately and then, %absorbance was measured by using UV-Spectrophotometer (with wavelength λ_{max} = 656 for Hg and λ_{max} = 630 for Pb) and plotting a calibration plot between % absorbance v/s concentration of Hg ions.

Effect of Adsorbent Dosage for Hg Ions

A standard solution of mercuric sulphate was prepared by dissolving 0.148 g of $HgSO_4$ in one liter of distilled water. Prior to dissolving in water, it was first dissolved in small quantity of HCl. Different concentrations of solutions namely, 20, 40, 60 and 80 ppm were prepared. 20 ppm was prepared by taking 20 ml of $HgSO_4$ solution and 80 ml of water in a 250 ml conical flask. In this way, seven different solutions were prepared in seven different conical flasks. Then, different adsorbent dosage namely, 0.05, 0.1, 0.05, 0.2, 0.25, 0.3 and 0.35 g were added to seven different conical flasks, respectively. Now, these seven flasks were stoppered using rubber stopper and kept for agitation in a shaker for 20 min. Then, their absorbances were measured in a UV-Spectrophotometer with the wavelength of 656nm. The absorbance values were noted. Similarly, the absorbances for 40, 60 and 80 ppm were measured.

Effect of Adsorbent Dosage for Pb Ions

A standard solution of lead (II) acetate trihydrate was prepared by dissolving 0.183 g in one liter of distilled water. Different concentrations of solutions namely, 20, 40, 60 and 80 ppm were prepared. 20 ppm was prepared by taking 20 ml of lead acetate solution and 80 ml of water in a 250 ml conical flask. In this way, seven different solutions were prepared in seven conical flasks. Then, different dosage of adsorbent namely, 0.05, 0.15, 0.2, 0.25, 0.3 and 0.35 g were added to seven different conical flasks, respectively. Then, these flasks were put into a shaker for 20 min. Then, they were taken in a couvette and their absorbance values were measured in a UV-Spectrophotometer at the wavelength of 630nm. The absorbance values were noted for different samples.

Effect of pH for Hg Ions

0.148 g of $HgSO_4$ was dissolved in one liter of distilled water. Then, it was transferred to a one liter volumetric flask and 0.2 g (optimum) of adsorbent (modified chitosan) was added and it was made up to the mark using distilled water. Now, five numbers of 40 ppm solutions were prepared from the above solution. This was done by mixing 40 ml of the above solution and 60 ml distilled water. Then, each of the five conical flasks was adjusted to the desired pH of 4, 5, 6, 7 and 8 using a digital pH meter. The pH was adjusted to the desired pH by using 0.1N HCl and 0.1N NaOH. Then, these flasks were kept for different agitation period for every 15 minutes. Their absorbance values were measured using UV-Spectrophotometer at 656nm range. This procedure was carried out for 60 min.

Effect of pH for Pb Ions

0.183 g of lead acetate trihydrate was dissolved in one liter of distilled water. Then, it was transferred to a one liter volumetric flask and 0.05 g of adsorbent was added, as this was the optimum and it was made up to the mark using distilled water. Now, five numbers of 40 ppm solutions were prepared from the above solution. This was done by mixing 40 ml of the above solution and 60 ml distilled water. Then, each of the five conical flasks were adjusted to the desired pH 4, 5, 6, 7 and 8 using digital pH meter. The pH was adjusted to the desired pH by using 0.1N HCl and 0.1N NaOH. Then, these flasks were kept for agitation for different periods and contact times, and for every 15 min, their absorbance values were measured using UV- Spectrophotometer at 630nm range. This procedure was carried out for 60 min.

Effect of Initial Concentration of Hg Ions

Five different solutions with different concentrations of metal ions were prepared namely, 25, 50, 75, 100 and 125 ppm in a volumetric flask. Also, 0.2 g of chitosan was dissolved and it was made up to the mark. These solutions were mixed to ensure uniform concentrations. 100 ml of each of the above solution were taken in five different 250 ml conical flasks and their pH were adjusted to 5 using 0.1N NaOH and 0.1N HCl. Later, these 5 flasks were stoppered using rubber corks and kept for agitation for different contact times namely, 15, 30, 45, 60, 75 and 90 min. After 90 min, equilibrium was attained. At the end of every 15 minutes, absorbances were measured using UV-Spectrophotometer at a wavelength of 656nm. At the end of 120 min, the absorbance values were almost constant.

Effect of Initial Concentration of Pb Ions

Effect of initial concentration of metal ions was studied by varying its concentrations. Five different solutions with different concentrations of metal ions were studied by taking five different weights of metal ions namely, 25, 50, 75, 100 and 125 mg in one liter of distilled water in a volumetric flask. Also, 0.05 g of Chitosan was dissolved and made up to the mark with distilled water. These solutions were mixed to ensure uniform concentration. 100 ml of each of the above solution was taken in five different 250 ml conical flasks and their pH were adjusted to 6 using 0.1N NaOH and 0.1N HCl. Later, these 5 flasks were stoppered and kept for agitation for different contact time namely, 15, 30, 45, 60, 75 and 90 min. At the end of 90 min, equilibrium was attained. At the end of every 15 min, absorbances were measured using UV-Spectrophotometer at 630nm. At the end of 90 min, the absorbance values were almost constant.

Pseudo-First and Second-Order Adsorption Kinetics

Metal- ion solutions were prepared in two conical flask with metal-ion concentration of 10 mg/L for Pb and Hg and chitosan concentration of 1 mg/ml were added to them. The flasks were put in the incubator shaker (RPM=121, temperature=32.5^{o}C) for two hours. Samples were collected with different time periods and their %absorbance values were determined using UV-Spectrophotometer (λ_{max} = 630 for Pb and λ_{max} = 656 for Hg).

RESULTS AND DISCUSSION

Effect of Adsorbent Dosage for Hg and Pb Ions

Maximum %removal of Hg ion was obtained at a dosage of 0.2 g Hg and 80 ppm concentration, as shown in Fig. 1 and at a dosage of 0.05 g Pb and 80 ppm concentration, as shown in Fig. 2.

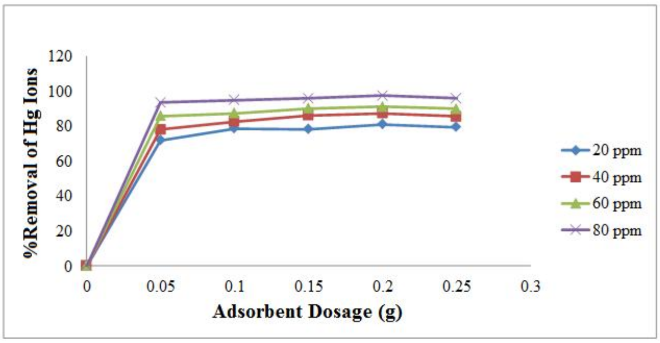

Fig. 1. Effect of Adsorbent Dosage on %Removal of Hg Ions for various Hg Ion Concentrations

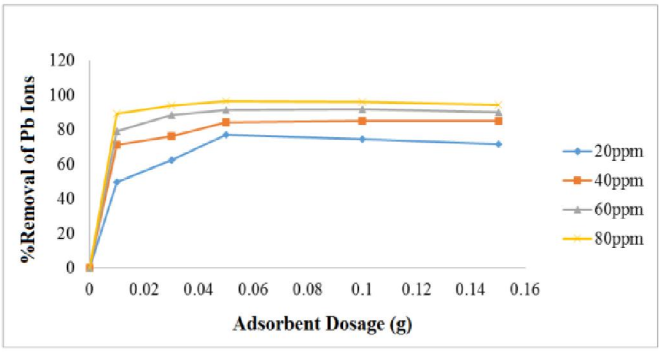

Fig. 2. Effect of Adsorbent Dosage on %Removal of Pb Ions for various Concentrations

Maximum %removal of Hg ions was obtained for a contact time of 45 min at a pH 5, as shown in Fig. 3 whereas, for Pb ions, for a contact time of 45 min at a pH 6, evident in Fig. 4.

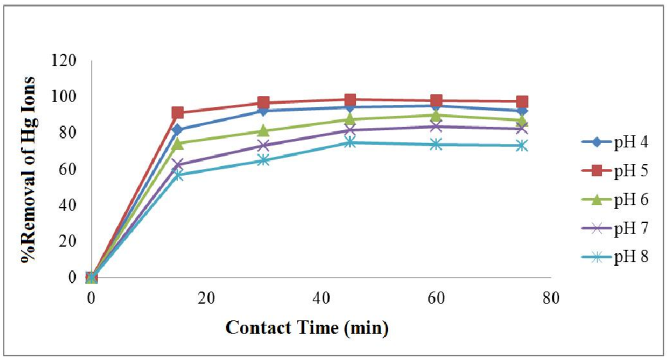

Fig. 3. Effect of Contact Time on % Removal of Hg Ions for various pH

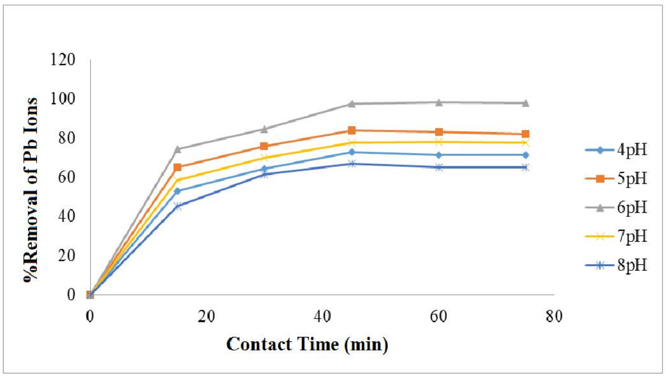

Fig. 4. Effect of Contact Time on %Removal of Pb Ions for various pH

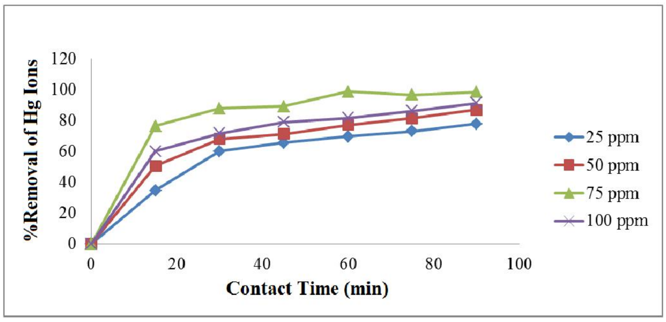

Fig. 5. Effect of Contact Time on % Removal of Hg Ions for various Concentrations

Maximum %removal of Hg ions was obtained for a contact time of 60 min corresponding to initial metal-ion concentration of 125 ppm, as shown in Fig. 6 whereas, for Pb ions, for a contact time of 60 min at initial concentration of 125 ppm, evident in Fig. 4.

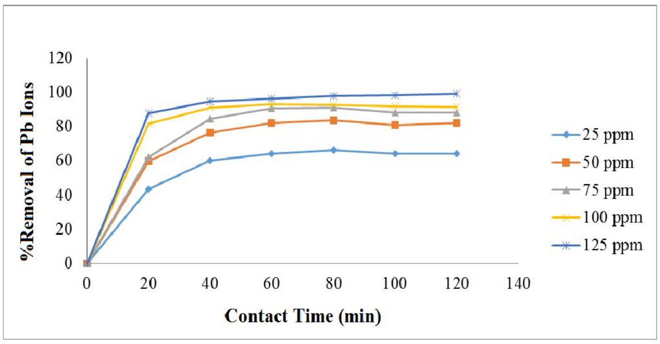

Fig. 6. Effect of Contact Time on %Removal of Pb Ions for various Concentrations

Effect of pH for Hg and Pb Ions

To the optimum concentrations of 80 ppm for Pb and Hg ion solutions, optimum dosage of adsorbent 0.05 g of Pb and 0.2 g of Hg were added separately. Then, pH was varied from 4 to 8 (4, 5, 6, 7 and 8) and after agitation for every 15 minutes, their absorbance values were measured at 630 nm for Pb and 656 nm for Hg. Optimum pH of 5 between 45 and 60 min of agitation for Hg and pH of 6 for Pb were obtained after 60 min of agitation, evident in Figs. 7 and 8, respectively. Adsorption increased with increase in pH. The adsorption of cationic metal ion was mainly influenced by the amount of negative charges in the solution. At pH= 8, there was net positive

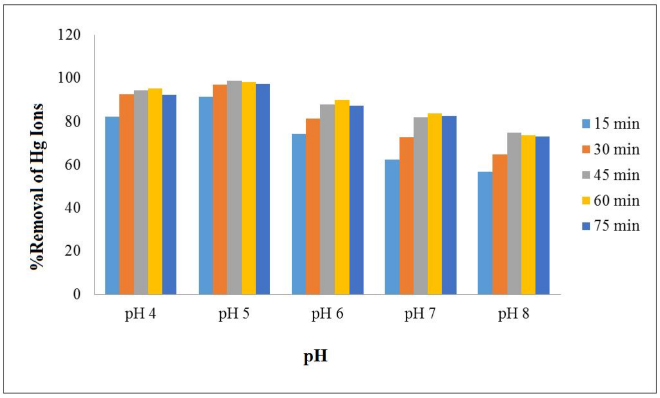

Fig. 7. Effect of pH on %Removal of Hg Ions for various Contact Time

charge in the solution and so, adsorption was less, whereas at pH=5 for Hg ions and pH = 6 for Pb ions, there was increase in negative charges increasing adsorption of metal ions.

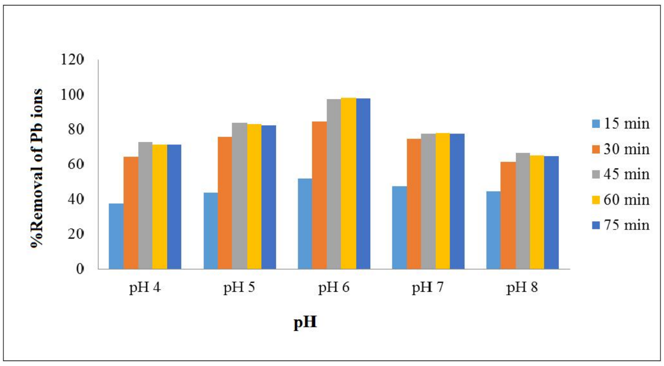

Fig. 8. Effect of pH on %Removal of Pb Ions for various Contact Time

Effect of Initial Concentration of Hg and Pb Ions

Effects of initial concentration of both metal ions have been studied by varying their concentrations from 25 ppm to 100 ppm (25, 50, 75 and 100) for an optimum dosage of 0.2 g for Hg ions and 0.05g for Pb ions, respectively. pH was adjusted to 5 for Hg and 6 for Pb, and absorbance values are measured at 656nm for Hg and 630 nm for Pb. Maximum %removal of metal ions are obtained at initial metal- ion concentration of 75 ppm for Hg ions (Fig. 9) and 125 ppm for Pb ions (Fig. 10).

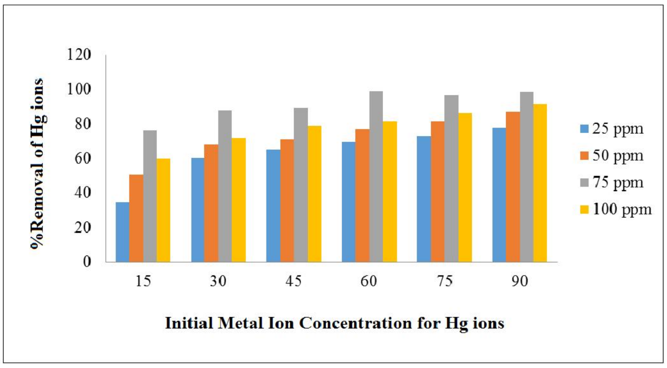

Fig. 9. Effect of Initial Metal Ion Concentration on %Removal of Hg Ions for various Concentrations

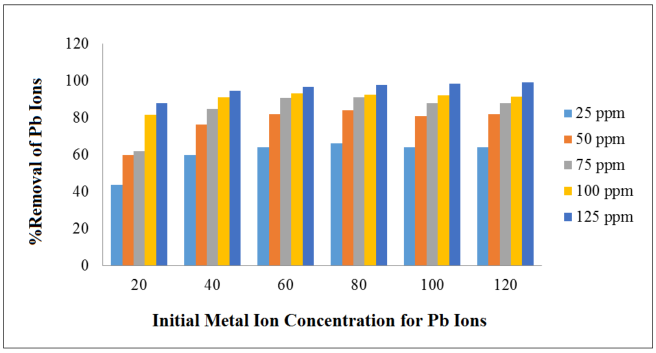

Fig. 10. Effect of Initial Metal Ion Concentration on %Removal of Pb Ions for various Concentrations

Isotherm Models

Tables 1 and 2 give the Freundlich isotherm constants for Hg and Pb ions, respectively whereas, Tables 3 and 4 give the Langmuir isotherm constants for Hg and Pb ions, respectively.

Table 1. Freundlich Isotherm Constants for Hg Ions

Concentration (ppm)	k_F	N	R^2
20	1.304	0.4064	0.985
40	10.267	0.693	0.977
60	3.990	1.141	0.955
80	6.625	1.742	0.969

Table 2. Freundlich Isotherm Constants for Pb Ions

Concentration (ppm)	k_F	N	R^2
20	108.853	0.560	0.959
40	331.040	0.293	0.938
60	501.69	0.873	0.946
80	241.80	0.4199	0.941

Table 3. Langmuir Isotherm Constants for Hg Ions

Concentration (ppm)	k_L	a_L	R^2
20	3.745	0.7	0.996
40	22.727	0.545	0.982
60	142.85	11	0.969
80	111.11	6	0.986

Table 4. Langmuir Isotherm Constants for Pb Ions

Concentration (ppm)	k_L	a_L	R^2
20	22.72	19.2	0.994
40	0.123	0.278	0.967
60	7.692	0.669	0.992
80	1	0.002	0.993

Table 5. Isotherm Constants for Hg Ions

For Hg Ions		20 ppm	40 ppm	60 ppm	80 ppm
Freundlich	k_F	1.304	10.267	3.990	6.625
Isotherm	N	0.4064	0.693	1.141	1.792
	R^2	0.985	0.977	0.955	0.969
Langmuir	k_L	3.745	22.727	142.85	111.11
Isotherm	a_L	0.7	0.545	11	6
	R^2	0.996	0.982	0.969	0.986

Table 6. Isotherm Constants for Pb Ions

For Pb Ions		20 ppm	40 ppm	60 ppm	80 ppm
Freundlich	k_F	108.853	331.04	501.69	241.8
Isotherm	N	0.560	0.293	0.873	0.4199
	R^2	0.959	0.938	0.946	0.941
Langmuir	k_L	22.72	0.123	7.692	1
Isotherm	a_L	19.2	0.278	0.669	0.002
	R^2	0.994	0.967	0.992	0.993

By observing both the isotherms and also comparing correlation coefficient R^2 values in Tables 5 and 6, it can be concluded that Langmuir isotherm is suitable for Hg and Pb ions since R^2 values tend to 1 for Langmuir model.

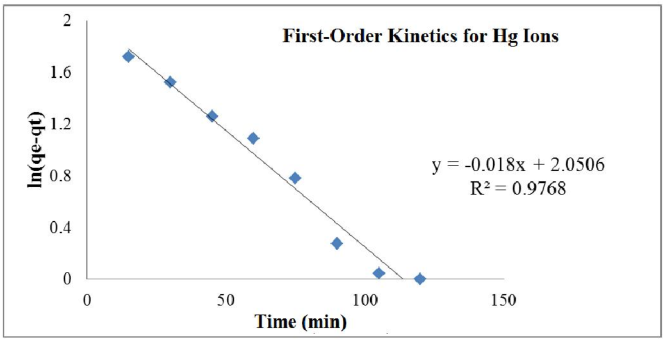

Fig. 11. First-Order Kinetics Plot for Hg Ions

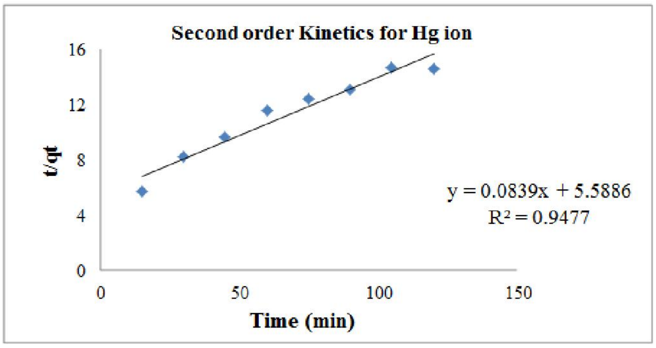

Fig. 12. Second-Order Kinetics Plot for Hg Ions

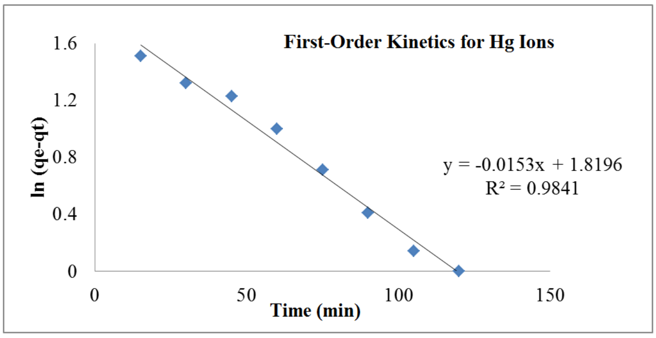

Fig. 13. First-Order Kinetics Plot for Pb Ions

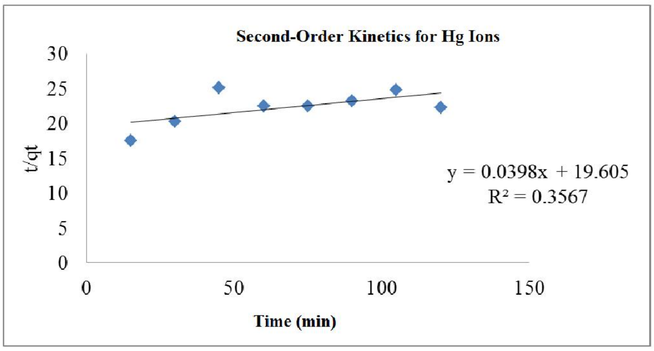

Fig. 14 . Second-Order Kinetics Plot for Pb Ions

Pseudo First-Order and Pseudo Second-Order Adsorption Kinetics

qt for different time intervals and qe at 120 min are calculated. Thus, using the equations for pseudo first-order and pseudo second-order kinetic models, the best fitting kinetic model has been determined for the system.

Table 7. Kinetic Values for Hg Ions

Order of Reaction	Co (mg/L	qe (mg/L)	k1(1/min)	R^2
First-Order	10	8.2	0.018	0.9768
Second-Order	10	8.2	25.41	0.9477

Table 8. Kinetic Values for Pb Ions

Order of Reaction	Co (mg/L)	qe (mg/L)	K1(1/min)	R^2
First-Order	10	5.38	0.0153	0.9841
Second-Order	10	5.38	32.20	0.3567

From Tables 7 and 8, comparing the values of R^2 (correlation coefficient) for pseudo first-order and second-order reactions, pseudo first-order is the best fitting model for the system as R^2 tends to 1.

CONCLUSIONS

Studies on removal of Pb and Hg ions from aqueous solutions by adsorption using modified chitosan have been experimentally determined and following observations are made:

- Effects of different parameters like adsorbent dosage, contact time, pH and initial metal-ion concentration have been studied and their optimum values are obtained for which maximum metal ion removal is possible from the aqueous solution.
- As adsorbate dosage increased, increase in adsorption has been observed. Thus, more the adsorbate concentration, more the adsorption. Maximum adsorbate dosage of 125 mg/L has been achieved.
- Adsorption increased with increase in pH. The adsorption of cationic metal ion is mainly influenced by the amount of negative charges in the solution. At pH = 8, there is net positive charge in the solution and so, adsorption is less, whereas at pH=5 for Hg ions and pH = 6 for Pb ions, there is increase in negative charges, increasing adsorption of metal ions. Maximum adsorption has been observed at a pH of 5 for Hg ions and at a pH of 6 for Pb ions.
- As the concentration increased, adsorption also increased due to the free species of metal ions present in the solution. At maximum concentration of 125 ppm, maximum %removal of metal ions is possible.
- By comparing the correlation coefficient (R^2 value) for pseudo first-order kinetic and pseudo second-order kinetics, experimental qe value favored pseudo first-order and thus, the adsorption is assumed to be pseudo first-order.
- The Langmuir equation assumed that there is no interaction between the adsorbate molecules and that the sorption is localized in a monolayer. It is then assumed that once metal ion molecules occupy a site, no further adsorption can take place at that site. So, Langmuir is the best isotherm for metal-ion removal with a correlation coefficient R^2 of 0.993, almost tending to 1.

REFERENCES

Baxter, A., Dillon, M., Taylor, K.D.A. and Roberts, G.A.F., 1992. “Improved Method for IR Determination of the Degree of *N*-Acetylation of Chitosan”, *International Journal of Biological Macromolecules,* Vol. 14, p. 166.

Domard, A., 1986. “Circular Dichroism Study on *N*-Acetylglucosamine Oligomers”, *International Journal of Biological Macromolecules,* Vol. 8, p. 243.

Domard, A., 1987. “pH and c.d. Measurements on a Fully Deacetylated Chitosan: Application to Cu (II)–Polymer Interactions”, *International Journal of Biological Macromolecules,* Vol. 9, p. 98.

Kasaai, M.R., Arul, J. and Charlet, G., 2000. “Intrinsic Viscosity–Molecular Weight Relationship for Chitosan”, *Journal of Polymer Science and Polymer Physics*, Vol. 38, pp. 2591–2598.

Niola, F., Basora, N., Chornet, E. and Vidal, P.F., 1983. “A Rapid Method for the Determination of the Degree of *N*-Acetylation of Chitin–Chitosan Sample by Acid Hydrolysis and HPLC”, *Journal of Thermal Analysis and Calorimetry,* Vol. 28, p. 189.

Pangburn, S.H., Trescony, P.V. and Heller, H.S., 1984. "*Chitin, Chitosan and Related Enzymes",* edited by Zikakis, J.P., (Harcourt Brace Janovich, New York), p. 3.

Sashiwa, H., Saimoto, H., Shigemasa, Y., Ogawa, R. and Tokura, S. 1991. "Distribution of the Acetamido Group in Partially Deacetylated Chitins", *Carbohydrate Polymers.* Vol. 16, p. 291.

Schwarzenbach, R.P., Gschwend, M.P. and Imboden, D.M., 2003. *Environmental Organic Chemistry*, John Wiley & Sons, Inc. Publication, Canada.

Tolaimate, A., Desbrières, J., Rhazi, M., Alagui, A., Vincendon, M. and Vottero, P., 2000. "On the Influence of Deacetylation Process on the Physico Chemical Characteristics of Chitosan from Squid Chitin", *Polymer*, Vol. 41, pp. 2463-2469.

Wei, Y.C. and Hudson, S.M., 1993. "Binding of Sodium Dodecyl Sulfate to a Polyelectrolyte Based Chitosan", *Macromolecules,* Vol. 26, p. 4151.

****