Synthesis and Characterization of Chitosan-Amidoxime Chelating Resin (CACR) and Application for lead Removal from Aqueous Medium

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ABSTRACT

This study deals with new modified chitosan beads with pendent amidoxime moieties [chitosan amidoxime chelating resin (CACR)] prepared by reaction of cross-linking chitosan beads with acrylonitrile and hydroxylamine. The resulting (CACR) resin was characterized using Fourier transform infrared, energy dispersive X-ray analysis, Scanning Electron Microscopy and BET surface area. To remove lead ions from aqueous solution the study was carried out under several variables include the initial concentration (50-250 mg/L), the amount of CACR (1-5 g/L), contact time (10-300 min) and the pH value (1.5-3.5) to indicate the removal efficiency of the (CACR). Glutaraldehyde. The batch experiment cited that the maximum adsorption efficiency of 55.5 mg/g was recorded at the optimum conditions of pH 3, 200 mg/L of Pb ions concentration and contact time 120min. using 2 g/L of [CACR]. The adsorption of lead ions with [CACR] follows the pseudo-second-order kinetics. The adsorption process was fitted to Langmuir and Freundlich isotherms models with slight advantage for the Langmuir approach.

INTRODUCTION

Wastewater containing heavy metals originated mainly from metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, pigment manufacture, etc (Yadla *et al*. 2012). These industries discharge heavy metals and wastewater directly or indirectly into the environment especially in developing countries. Due to their toxicity and non- biodegradability, they tend to accumulate in living organism. Therefore they cause numerous diseases and disorders. Zinc, copper, nickel, mercury, cadmium, lead and chromium are considered as toxic metals of particular concern in wastewater treatment. Thus, treatment of industrial wastewater containing soluble heavy metals has become essential in order to increase the quality of water (Saha *et al*. 2008). Industrial complexes have now become foci of environmental pollution. The control of these toxic priority pollutants is to be based on the application of the best available technology economically achievable. Metals of particular concern in treatment of industrial wastewaters include Fe^{+2}, Mn^{+2}, Cu^{+2}, Zn^{+2}, Ni^{+2}, Pb^{+2}, and

Cd^{+2} which are toxic to living organisms at fairly low concentrations and tend to either biologically magnify or accumulate in plant and animal systems. Thus, the disposal of heavy metals bearing wastes into water bodies or on land is of great concern due to their adverse effects. In general, to be removed from wastewater, the metals must be precipitated or otherwise attached to an insoluble form through nanoparticles adsorbents (Kurniawan *et al.* 2006; Lakherwal, 2014 and Lalhruaitluanga *et al.* 2010).

Lead is one of the common contaminants of industrial wastewaters. Lead pollution exists in aqueous waste streams of many industries such as manufacture of storage batteries, printing, painting, pigments, dying, leaded glass (Patterson, 1985 and Ramos *et al.* 2002). Lead poisoning causes various health hazards, such as damage to liver, kidney and reduction in hemoglobin formation, mental retardation, infertility and abnormalities in pregnant women (WHO, 2011 and Nadeem *et al.* 2005). Unlike organic compounds, lead is non-biodegradable and accumulates in living organism, therefore, must be removed from water and wastewater. Various methods of lead removal from wastewater have been applied including chemical precipitation, membrane processes, ion-exchange and adsorption. One of the most effective methods for the treatment of heavy metals from aqueous solution has been based on adsorption using low-cost adsorbents (Curkovic *et al.* 1997 and Bailey *et al.* 1999).

Chitosan is a unique basic polysaccharide and partially deacetylated polymer of glucosamine obtained after alkaline deacetylation of the chitin (Karthikeyan *et al.* 2004). It contains reactive amino groups, which selectively binds to all transition metal ions and not binds to alkali and alkaline metal ions and it has been extensively studied for metal ions adsorption (Al-Wakeel, *et al.* 2015). Chitin consists of mainly of β-(1-4-2- acetamido-2-deoxy-D-glucose) units and is the second most abundant biopolymer on earth after cellulose. It is widely distributed in crustacean shells and cell walls of fungus (Pentari *et al.* 2010 and Wana *et al.* 2010). Chitosan is soluble in dilute acids. The solubilization occurs by the protonation of the $-NH_2$ function on the C-2 position of the D-glucosamine repeat unit, where the polysaccharide is converted to a polyelectrolyte in acidic media (Ramya *et al.* 2011a and Ramya *et al.* 2011b). The chelation ability is directly affected by the chelating group and the polymeric matrix. One of the significantproperties of chelating resins is that it's intensive presence in many countries, also their great sorption ability for metal ions enabled them to spread in many applications like [separation of mixtures containing more than one metal] which may be present in low concentration in solution (Khalil, *et al.* 2014). Glutaraldehyde (GLA) is the most frequently used cross-linking agent as it is capable in preventing the dissolution of chitosan in acidic solution. Although the stability of the cross-linked chitosan was improved, this cross-linking process decreases the number of amino groups, resulting in a decrease in the adsorption capacity. Currently, other alternatively modifications have been performed to improve the chemical stability without losing the adsorption capacity of chitosan (Bingjie, *et al.* 2013). Chitosan being a linear polyelectrolyte at acidic pH is capable of forming electrostatic complexes with synthetic or natural polyelectrolyte especially alginate. Alginate is derived from brown algae and it comprises of two repeating carboxylate monosaccharide units. Chitosan and alginate can be blended to form polyelectrolyte complex through ionic interaction between the protonated amines on chitosan and carboxylate moieties found on alginate. This interaction forms a three dimensional matrix, and the beads are known as physically cross-linked. This polyelectrolyte complex has a wide range of usage in the medical and biological field

(Wan Ngah and Hanafiah, 2008). The main objective of this study was to remove lead from aqueous medium using newly developed (CACR). Isotherm and kinetic studies were used to quantify the adsorption process.

MATERIALS AND METHODS

Chemicals and Preparations:

Chitosan (de-acetylation degree 93%) was purchased from Oxford Lab Chem (India), glutaraldehyde (GA), acrylonitrile (AN), acetic acid (AA), liquid paraffin (LP), and hydroxylamine hydrochloride were purchased from Alpha ChemiKa (India) and were used directly. Metal salts were pure grade products of Nice Chemicals Pvt. Ltd., (India) were used as source for Pb^{2+}. De-ionized distilled water was used though the experiment.

Preparation of cross-linked chitosan beads (CLCB):

Cross-linked chitosan beads were prepared according to the method described by Wang *et al*. (2010). In brief, 10.0 g of chitosan was dissolved in 200 ml aqueous solution of acetic acid (3%) for 48h and then added to a 1000 ml beaker flask containing 200 ml of liquid paraffin, continuously stirred for 20 min at 40 ℃. After that, the temperature was increased to 60 ℃, and 10 ml of (10%) glutaraldehyde was added as the cross-linking agent, continuous stirring at 300 rpm for 3h to generate the polymeric beads. The resulted beads were washed several times with petroleum ether, ethanol and de-ionized water in sequence to remove any unreacted fraction and dried at 50 ℃ under vacuum for 24 h.

Preparation of cyanoethylated chitosan beads (CECB):

Cross-linked chitosan beads (CLCB) (5 g) and acrylonitrile (AN) (50 ml) were mixed in 100 ml methanol then acetic acid (0.2 ml, 99.7%) was added to a flask supported with a magnetic stirrer and reflux. The reaction mixture was stirred at 300 rpm for 48h and 75 ℃. After cooling, CECB was filtered, washed several limes with ethanol and water and dried at 50 ℃ under vacuum for 24h.

Synthesis of chitosan-amidoxime chelating resin (CACR):

A suspension of CECB (5 g) and $NH_2OH.HCl$ (4gm) in 70ml methanol-water solution (5:1 v/v) was added to a flask equipped with a magnetic stirrer and reflux condenser. About 15 ml of NaOH aqueous solution (7.5 M) was added to this mixture and the pH was kept at 8. The above mixture was stirred for 48h at 70 C. Finally, the resulted CACR beads was filtered out, washed several times with water and ethanol and dried at 50℃ under vacuum for 24h (Fig. 1).

Preparation of aqueous solution

A stock solutions of Pb ions was prepared by dissolving a known quantities of Pb $(NO_3)_2 \cdot 4H_2O$ in deionized water. The residual metals in solutions were analyzed using GBC atomic absorption reader (Model SavantAA AAS with Flame and GF 5000 Graphite Furnace). The pH adjustments were done using 1.0 M NaOH and 1.0 M HCl (**APHA, 2005**).
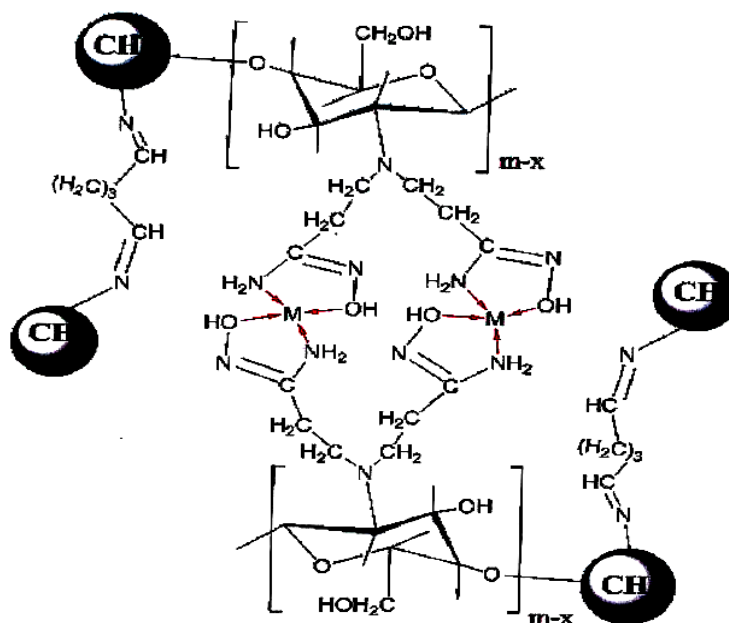
Fig. 1: Chelation of chitosan amidoxime chelating resin for metal ions.

Characterization Technique:

Fourier Transform infrared spectra (FTIR) of the prepared resins were obtained with an FTIR spectrometer (jasco 6100, Japan) in the 400-4000 cm⁻¹ range. Thermal gravimetric analysis (DSC/TG) for prepared resin (CACR) was determined using NETZSCH STA 409 C/CD instrument, Germany. The experiment was carried out in a dynamic atmosphere of helium from room temperature to 70°C at heating rate of 10 °C /min and a helium flow rate 1 ml/min. BET surface area, before examination, the resin was put in vaccum at 300 ℃ for 2h by means of adsorption of ultra-pure nitrogen at 77.35 k. The surface area was measured using the Brunauer-Emmett-Teller (EBT) and BJH method based on adsorption data in the partial pressure (P/P$_0$) range of 0.09-0.29 the total pore volume was determined from the amount of the nitrogen adsorbed at P/P0=0.29729.

Batch adsorption studies

All experiments were performed with 0.1 g resin in 250 ml bottles with 50 ml of single metal ion solution on a temperature controlled shaker 300 rpm, all experiments were carried out at 30 ℃ except the effect of temperature experiments. The desired pH of solution was adjusted using few drops of 0.1 M HCI and 0.1M NaOH solutions. A known volume (50 mL) each was pipette into the series of cultural vial to which (1 – 5 g/l) of the [CACR] as adsorbent was added. Upon completion of the given contact time (10-300 min) between adsorbent and adsorbate, A detailed investigation on the initial concentration (50 – 250 mg/L), the solution pH (1.5-3.5) and temperature (30-70 °C) on Pb metal ions removal from a solution was carried out. The removal percentage (R %) can be calculated using the following equation (1) :

$$R \% = \frac{(C_0 - C_e)}{C_0} X\ 100 \quad (1)$$

Where C_0 and C_e are concentration (mg/l) of metal ions in the initial and equilibrium solutions, respectively. The equilibrium adsorption capacity (q_e) of each sorbent was calculated using equation (2):

$$q_e = \frac{(C_0 - C_e)\, V}{W} \quad (2)$$

Where, q_e is the amount of metal ions adsorbed at equilibrium (mg/g), V is the volume of the initial solution taken at equilibrium (liter) and W is mass of the sorbent (gram) (**Matthew *et al* 2003**).

RESULTS AND DISCUSSION

Characterization:

FT-IR Analysis:
Fourier Transform Infrared absorption spectra of chitosan, CLCB, CECB and CACR were illustrated in Fig. (2-1). In the spectrum of pure chitosan, the -OH and –NH2 (stretching vibration) groups are presented at peak 3491.11cm-1 (broad band). The C-O-C bridge absorption band (asymmetric stretching) was observed at 1421.06 cm^{-1}, while skeletal vibration of C-O stretching corresponds to the bands at 1091.22 and 1189.14 cm^{-1} (De Vasconcelous *et al.* 2006). FT-IR spectrum of CLCB (Fig2-2) illustrates stretching vibration bands of C-H (symmetric & asymmetric) which enlarges at 2992.11 & 2858.95 cm^{-1} and the peak at 1618.11 cm^{-1} is seen due to imine bonds C=N.
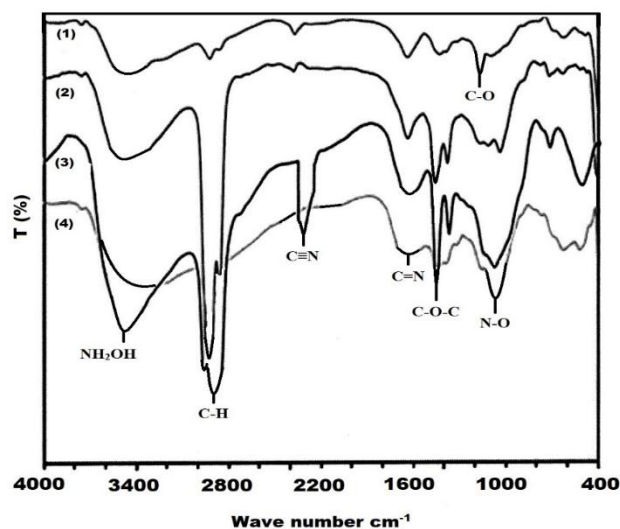

Fig. 2. FT-IR spectra of (1) pure chitosan (2) CLCB, (3) CECB and (4) CACR

After reaction with acrylonitrile, a new absorption band appears at 2742.01 cm^{-1} which is characteristic of the nitrile vibration band as shown in Fig.3c. Finally FTIR spectrum of CACR Fig.(2-3) revealed that the absorption band of the C≡N group at 2360.78 cm^{-1} disappears and a new band at 1032.10 cm^{-1} appears due to vibration adsorption of the N-O bond in the amidoxime group (Bilba *et al.,* 2004).

EDX analysis:

The EDX spectrum (shown in Fig.3) further authenticates the presence of N, oxygen and Cl⁻ in the CACR, which demonstrated that $NH_2OH.HCl$ was adsorbed onto The CECB to produce CACR beads.
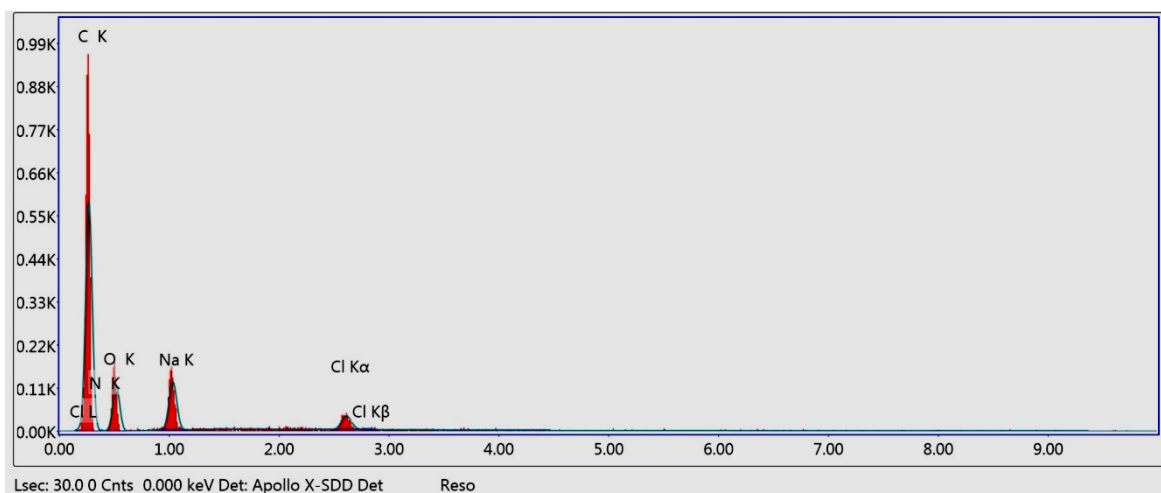

Fig. 3. EDX micrographs of CACR beads adsorption.

Scanning Electron Microscope (SEM) **analysis:**

Figure 4 shows the morphology of CACR before metal ion uptake indicates the clear empty cavities which can help for mass transfer of metal ions to its surface.
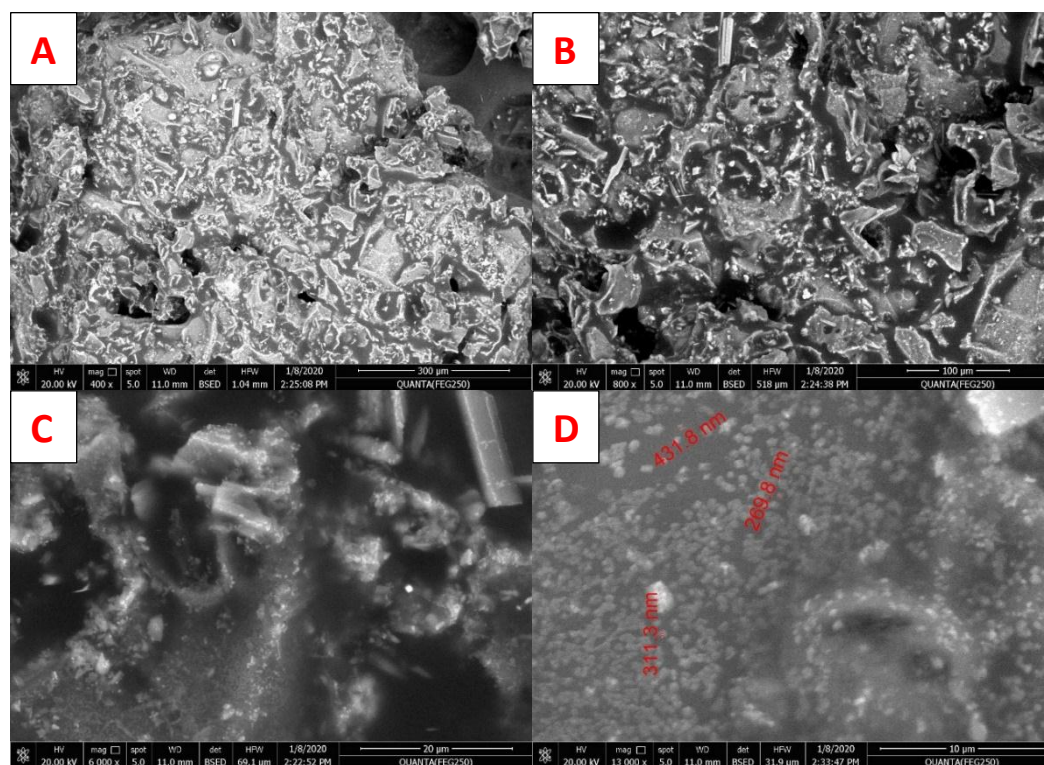

Fig. 4. Photo of CACR beads: (A) SEM image (x400), (B) SEM image (x800), (C) SEM image (x6000) and (D) SEM image (x13000)

BET surface area:
        The BET data show that the resin has a surface area of 39.52 m2/g with a pore diameter of 2.981 nm which to be considered meso-porous structure and leads to the efficient transfer of the metal ions to the internal adsorption sites (Table 1).

Table 1. Porous structure parameters of CACR.

Parameters	Amidoxime
BET surface area (m^2/g)	39.52
BJH desorption average pore diameter (nm)	2.981
BJH desorption cumulative volume of pores (cm^3/g)	0.1254

Batch Sorption Studies:
Effect of contact time on adsorption process:
        In order to determine the influence of contact time between CACR and the aqueous solution of Pb ions adsorption, variations of adsorption capacity (qe) Vs time (10-300 min) were plotted in Fig. (5). It was found that the adsorption of Pb ions is continuously increased with time increase until reaching equilibrium (qe = 50.6 mg/gm) between two phases after 3h. Therefore, this optimum equilibrium time was selected for the next adsorption experiment.
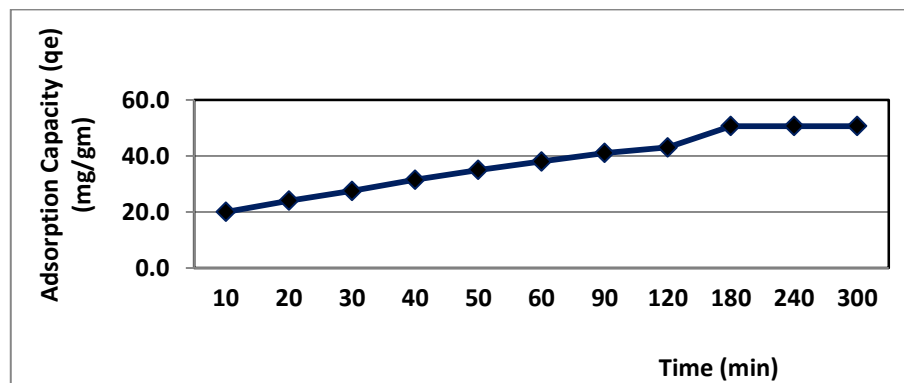

Fig. 5. Effect of contact time on the removal of 150 mg/L of lead using 2gm/L CACR at pH 3

Effect of initial contaminant concentration
        The effect of initial different lead ions concentration (50, 100, 150, 200 & 250 mg/L). At 2 gm/L of [CACR] was used. An influent solution with pH =3 at temp. = $30^oC \pm 1$. Obtained results indicate that the amount of Pb (II) adsorbed onto CACR increased as the initial concentration of metal ions increased before reaching a plateau shape. Fig. (6) showed that the maximum adsorption capacity (qe) of Pb (II) reached 55.50 (mg/gm) at maximum initial concentration of 200 (mg/L). Further increasing of Pb ions to 300 mg/l led to decreasing the adsorption capacity. This may be due to the lack of available adsorbent sites at higher concentrations, and hence, the percentage adsorption of lead decreases, which agrees with those obtained by Srivastava and Sharma (2013).

Mass of adsorbent:
        The effect of CACR mass on the removal lead ions from water has been studied to get the optimum conditions for the removal process. Different masses of Adsorbent (1, 2, 3, 4 and 5g/L) were applied for the removal of lead ions using solutions of 150 mg/L Pb ions a., pH =3 and temp. = $30^oC \pm 1$ (Fig. 7).
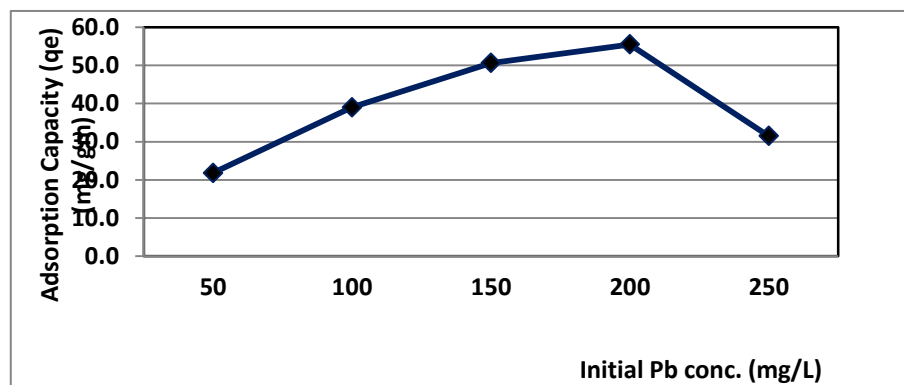
Fig. 6. Effect of initial concentration for removal of lead at using 2 gm/L CACR at pH 3 and contact time 180 m
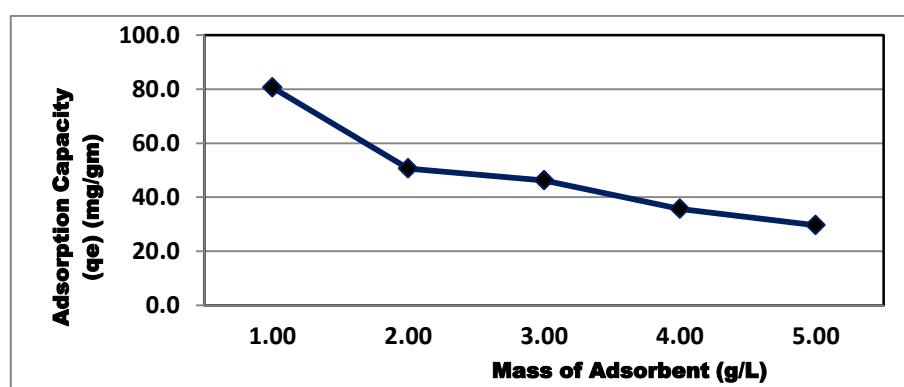

Fig. 7. Effect of Mass of CACR on removal of 150 mg/L of lead ions at pH 3 and contact time 180 m

The observations indicated that the variation in mass of CACR affects the removal of lead ions in such a way that as the mass of the CACR increase. Where the number of adsorption sites increase and consequently the removal of lead ions is improved. The determination of effect of adsorbent dosage gives an idea about the minimum amount of adsorbent need to be used for adsorption process. This value is useful in the viewpoint of cost (Gupta and Babu, 2010).

Effect of solution pH:
The pH of the solution is an important parameter, which controls the adsorption process. It influences the ionization of the adsorptive molecule and hence the surface charge of the adsorbent. The pH effect on the removal process of 150 ppm lead ions. at pH = 1.5, 2, 2.5, 3 and pH=3.5. Using 0.1gm of [CACR] and the contact time was adjusted to be 120min and temp. = $30^{o}C \pm 1$ Fig.(8). The adsorption capacity (qe) values were 17.4, 92.5, 45.2, 47.7, 50.6 and 43.9 mg/gm for pH = 1.5, 2, 2.5, 3 and pH=3.5, respectively.

The variation of pH parameter showed remarkable effect on the removal process. All the consequent experiments were performed at pH 3. Above this optimum pH, metal is precipitated as metal (II) hydroxide and the adsorption of these ions cannot be measured accurately. From the previous observations, we can concluded that the optimum condition to remove Pb from solution using 0.1 gram of [CACR] with adsorption efficiency up to 55.5 mg/g, was recorded at , pH 3 , 200 ppm of Pb ions in solution and contact time 180 min.
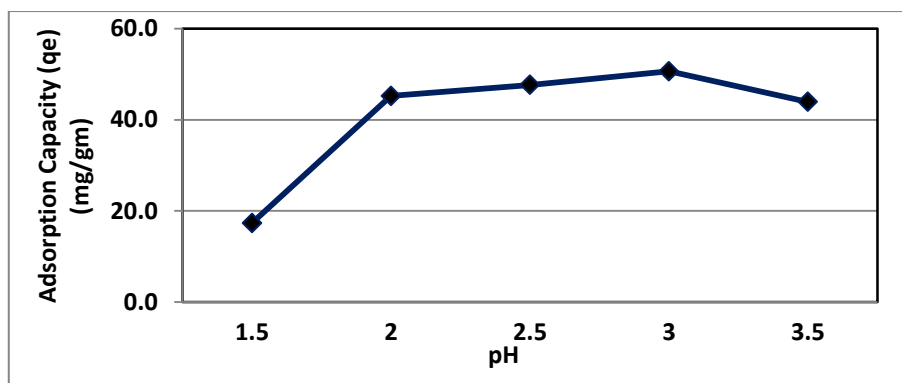
Fig. 8. Effect of pH value for removal of 150 mg/L of lead ions using 2gm/L CACR at 180m contact time

Effect of temperature:

The influence of solution temperature on the adsorption capacity of Pb ions on CACR was examined, while other effective parameters were kept constant (contact time 180 min, 150 ppm concentration, and pH 3) Fig. (9).

The results indicates that the capacity is considerably increased by enhancing the solution temperature from 30 to 70 ^{0}C in steps of to this enhancing of adsorption can be attributed to the fact at higher temperatures, cations move faster. This could be due to the fact that the specific or electrostatic interactions become weaker and the ions become smaller, since salvation is reduced (Abd El-Latif and ElKady, 2010). According to this explanation, it is clear that the adsorption of Pb (II) ions on the amidoxime chelating resin is an endothermic process.
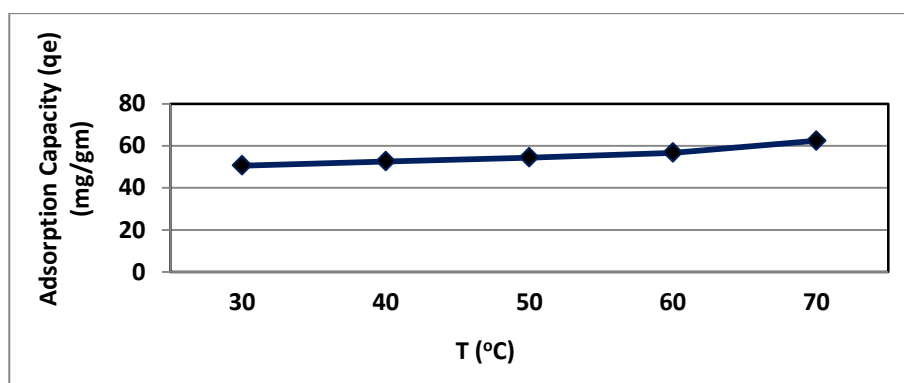
Fig. 9. Effect of temperature on the removal of 150 mg/L of lead ions using 2gm/L CACR at pH 3 and 180 min contact time

Kinetic studies:

Kinetic performance of a given adsorbent is of at most important to get an indication about the solute uptake rate. It determines the residence time required to complete the adsorption reaction (Qiu, 2009). Due to the importance, the kinetic studies have been performed in majority of studies (Srivastava and Sharma, 2013). The pseudo First-order and pseudo second-order models developed by Ho and McKay (1998), connected with the reaction based models, two different kinetic models were applied to determine the mechanism involved in adsorption process. A relatively high R^2 value indicates that the model successfully describes the adsorption kinetics (Fadali *et al.,* 2005).

Pseudo-first-order kinetic model:

The sorption kinetics may also be described by a pseudo first order equation (Özacar, 2003) is represented by the non-linear equation shown in equation (3):

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (3)$$

Where q_e and q_t is the lead concentrations in solid phase at equilibrium and at time t [mg/g], respectively. K_1 is the rate constant for the pseudo-first-order adsorption process [1/min]. It can be simplified and expressed in linearized form as below equation (4):

$$log(q_e - q_t) = log q_e - \frac{K_1}{2.303}t \qquad (4)$$

The equilibrium experimental data are plotted between $\log(q_e - q_t)$ and t as shown in Fig. (10) for the removal of lead. The correlation coefficients (R^2) and the model parameters are evaluated and tabulated in Table (2).
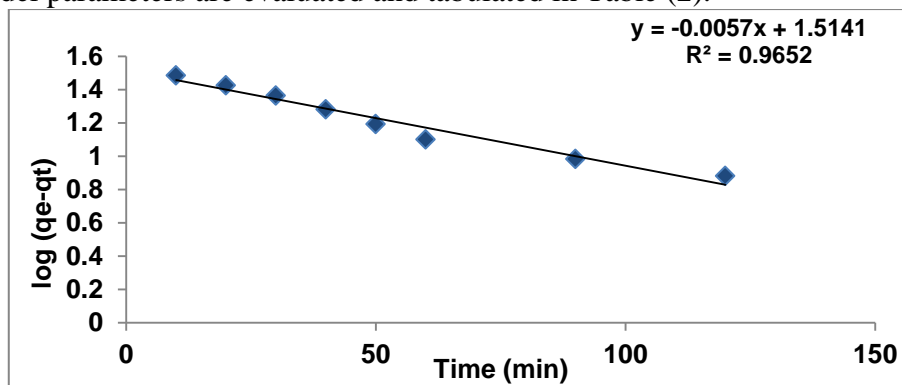

Fig. 10. Pseudo-first-order kinetic model plot for the removal of lead using CACR.

Pseudo-second-order kinetic model

A pseudo-second-order kinetic model is also utilized to explain the kinetic behavior of the operation. The applicability of the second-order kinetics is represented by the equation (5):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (5)$$

Where k_2 is the pseudo-second order rate constant of adsorption in (g/mg. min), qe and qt is the amount of adsorbate adsorbed at equilibrium time and *t* time respectively, in (mg/g) and *t* is the contact time in minutes. It can be simplified and expressed in linearized form as below equation (6):

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \qquad (6)$$

The equilibrium experimental data are plotted between $1/(q_e - q_t)$ and t as shown in Fig. (11) for the removal of Lead. The correlation coefficients (R^2) and the model parameters are evaluated and tabulated in Table (2).
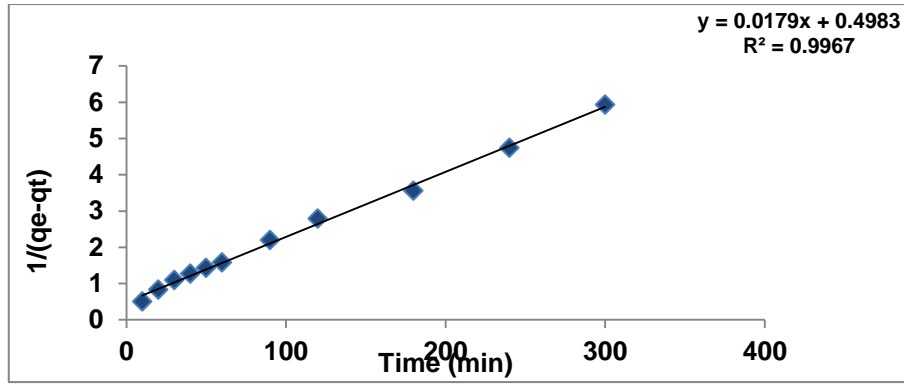
Fig. (11): Pseudo-second-order kinetic model plot for the removal of lead using CACR

Table (2): Kinetic parameters for the removal of lead using CACR

Pseudo-First-Order kinetic model				Pseudo-Second-Order kinetic model			
K_1 (l/min)	R^2	q_e Cal (mg/gm)	qexp	K_2 (g/mg.min)	R^2	q_e Cal (mg/gm)	qexp
0.01313	0.9652	32.67	50.60	0.00064301	0.9967	55.87	50.6

Table (2) shows that the calculated adsorption capacities were 32.67 and 55.87 mg/g and the of correlation coefficients (R^2) were 0.9652 and 0.9967 for pseudo-first order and pseudo-second order models, respectively compared to the experimental one of 50.60. Thus, the validation of the kinetic suggests the applicability of pseudo-second order kinetics for the adsorption of lead onto the CACR. As the surface functional groups become exhausted, the rate of sorption is controlled by the rate of transport from the external to the internal sites (**Gupta and Babu, 2009**).

Adsorption isotherm model:

Adsorption models of Langmuir (Langmuir, 1918) and Freundlich (Kalavathy *et al.* 2005) were applied to determine the relationship of lead adsorption with different induced concentration. The best-fitting isotherm was evaluated by linear regression, and the parameters obtained from the intercept and slope of the linear plots of these models (Lalhruaitluanga *et al.* 2010).

Langmuir isotherm model:

Estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the resin was calculated using the Langmuir isotherm model, since the saturated monolayer isotherm can be explained by the non-linear equation of Langmuir equation (7):

$$q_e = \frac{q_{max} K_a C_e}{1 + K_a C_e} \qquad (7)$$

The linearized Langmuir isotherm model is expressed as given in equation (8):

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max} K_a}\right)\left(\frac{1}{C_e}\right) \qquad (8)$$

Where, qe is the amount of adsorbate at the time of equilibrium in mg/g. Ce is the equilibrium concentration of adsorbate in the solution in mg/L, q_{max} is the maximum adsorption capacity in mg/g (is the maximum quantity of adsorbate required to form a single monolayer on unit mass of adsorbent mg/g) and Ka is the Langmuir isotherm constant in L/mg (adsorption equilibrium constant). As shown in Fig. (12) The equilibrium experimental data are plotted between 1/qe and 1/Ce. The

correlation coefficients and the model parameters are evaluated and tabulated in Table (3).
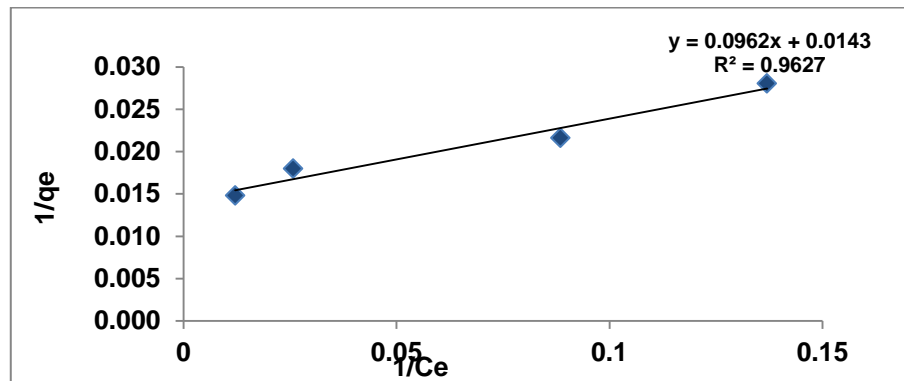

Fig. (12): Langmuir isotherm model plots for the removal of lead using CACR

The degree of suitability of CACR for the sorption of lead was also estimated from the values of the separation factor constant (RL) according to the following equation (9):

$$R_L = (1)/(1 + K_a C_0) \quad (9)$$

The value of RL > 1 indicates unfavorable, RL = 1 linear, 0 < RL <1 favorable or RL = 0 irreversible sorption. The RL value for the adsorption of lead on [CACR] is favorable and presented in Table (3).

Freundlich isotherm model:

The Freundlich model suggests a heterogeneous adsorption of the solute on the adsorbent surface (Gupta and Babu, 2010). The model Non-linear equation is expressed by the following equation (10):

$$q_e = K_f C_e^{\frac{1}{n}} \quad (10)$$

The Freundlich equation can be linearized and expressed as equation (11): (Kalavathy *et al.* 2005).

$$log q_e = log K_f + \frac{1}{n} log C_e \quad (11)$$

Where K_F is representing the Freundlich constant, which is indicating the relative adsorption capacity of the adsorbent related to the bonding energy in mg/g and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. n is the adsorption constant for Freundlich in L/mg, usually greater than one. It can be stated that, if the 1/n value is below unity, this implies that the adsorption process is chemical; if the value is above unity, adsorption is a favorable physical process (Gimbert, 2008). The experimental data are plotted between log qe and log Ce and shown in Fig. (13) for the removal of lead ions. The coefficients for Freundlich isotherm are evaluated and tabulated in Table (3). The sorption data fitted for both Langmuir and Freundlich isotherms with slightly advantage for the Langmuir approach.
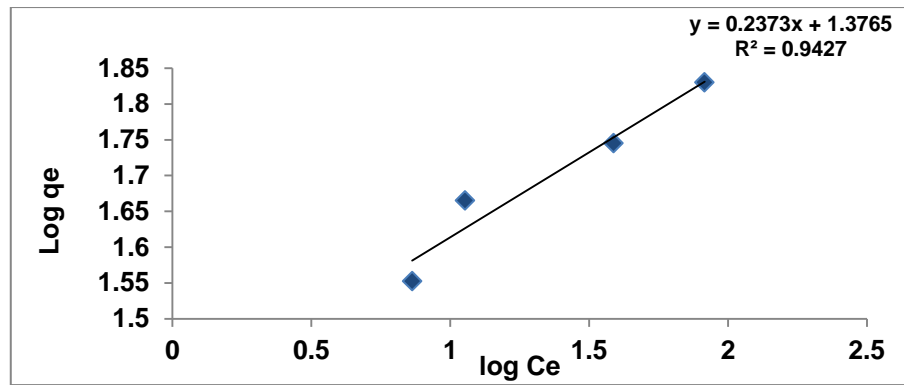
Fig 13. Freundlich isotherm model plots for the removal of lead ions using CACR.

Table 3. Isotherm parameters for the removal of lead using CACR

Langmuir isotherm model				Freundlich isotherm model			
Ka	R^2	R_L	qmax	n	R^2	Kf	1/n
0.149	0.9627	0.043	69.930	4.214	0.9427	23.796	0.237

CONCLUSION

Chitosan amidoxime chelating resin (CACR) was used to remove Pb ions from aqueous solution. The batch experiment cited that the maximum adsorption efficiency of 50.6 mg/g was recorded at the optimum conditions of pH 3, 200 mg/L of Pb ions concentration and contact time 120min. using 2gL gm of [CACR]. The adsorption of lead ions with [CACR] follows the pseudo second-order kinetics. The adsorption process was fitted to Langmuir and Freundlich adsorption isotherm models. The values of adsorption intensities ($0 < R_L < 1$) indicate that the adsorption of lead with [CACR] is favorable and it is good sorbent for lead ions removal.

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