Synthesising Magnetic Chitosan Nanocomposites for the Removal of Cr$_{6+}$ Ions from Aqueous Soution

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Abstract—*Feasibility of magnetic chitosan nanoaparticles (MCN) for the removal of heavy metal ion chromium was investigated from aqueous solutions. Batch-adsorption technique was employed to determine adsorption behavior of magnetic chitosan nanoparticles and their removal efficiency was analyzed by varying pH of the solution, time of contact between the adsorbate and adsorbent and the temperature to determine the optimum conditions at which maximum adsorption of Cr6+ ions takes place. Adsorption isotherms were also determined and appropriately described by the Langmuir model.*

Low dispersed chitosan-bound Fe3O4 nanoparticles were developed as a novel magnetic nanoadsorbent for the removal of heavy metal ion. The study provides potential application of magnetic chitosan nanoparticles for adsorption of toxic metals from industrial wastewater. Another important advantage of using chitosan nanoadsorbents for the removal of environmental pollutants lies in the fact that they are cost-effective and meet the environmental regulation for wastewater treatment. Their production process is simple leading to reduced operating and processing costs.

This paper outlines the synthesis of MCN and study of adsorption performances for Cr6+ ions using 797 VA computrace, Metrohm (Switzerland). Voltammetric instrument provides both qualitative and quantitative analysis of the metal ions present in the given sample by plotting a current-voltage graph

Keywords: *Chitosan, Fe3O4 nanoparticles, VA Computrace, Heavy Metals.*

1. INTRODUCTION

In recent years, much attention has been focused on the contamination of aquatic media by heavy metals; because heavy metals are highly toxic even at low concentrations and can accumulate in living organisms causing various disorders and diseases [1]. Chromium, one of the heavy metals, is highly toxic to humans, plants and animals. The metal is of special concern because it is nondegradable and therefore persistent.

Several attempts employed to remove heavy metals from waste water are chemical precipitation, filtration, membrane separation, electrochemical treatment, ion exchange, and adsorption [2, 3].

Among these the effective technique proved is adsorption. Adsorption basically is binding or attachment of a chemical substance (adsorbate) onto the surface of a solid (adsorbent), the process of mass transfer in which a substance is transferred from the liquid phase to the surface of a solid, and the two surfaces become bound by physical and/or chemical interactions [4].

Chitosan (CS) a well known excellent natural biosorbent of heavy metal ions, dyes and proteins because its amino and hydroxyl groups serves as coordination sites forming complexes with various heavy metal ions such as Cu^{2+}, Ni^{2+}, Pb^{2+}, Cr^{6+} [5]. Chitosan is as alkaline deacetylated product of chitin, derived from the exoskeleton of crustaceans. It is non-toxic, hydrophilic, biocompatible, biodegradable and anti-bacterial. Chitosan and its derivatives have great potential applications in areas of biotechnology, biomedicine, food ingredients, and cosmetics. Note worthily, chitosan is also capable of adsorbing number of metal ions since its amino groups can serve as chelation sites. However, one factor that hampers their application is the fact that because of their extremely small size these nanomaterials cannot be easily separated from the aqueous solution by filtration or centrifugation. This drawback is over come by the application of magnetic nano-adsorbents that can easily be separated from aqueous solutions using external magnetic field [6].

In recent years, the superparamagnetic iron oxide nanoparticles have attracted researchers from various fields such as physics, medicine, biology, and materials science due to their multifunctional properties such as small size, superparamagnetism and low toxicity [7].

In order to improve the stability and biocompatibility, the superparamagnetic iron oxide nanoparticles are often modified with some surfactants or polymers [8]. The superparamagnetic Fe3O4 nanoparticles coated with polymers are usually composed of the magnetic cores to ensure a strong magnetic

response and a polymeric shell to provide favorable functional groups and features. Thus, the binding of chitosan onto Fe3O4 nanoparticles will probably yield another novel magnetic nanoadsorbent for the efficient removal of heavy metal ions. Therefore, the use of magnetite chitosan nanoparticles (MCN) as adsorbents in water treatment provides a convenient and economical approach for separating and removing the contaminants by applying external magnetic fields. Here we present the use of chitosan coated magnetite nanoparticles (Fe3O4 Nps) for the removal of Cr6+ ions from waters.

2. MATERIALS AND METHODS

2.1. Materials

Low molecular weight chitosan, ferrous chloride tetrahydrate, ferric chloride hexahydrate, ammonium hydroxide and potassium chromate were purchased from Sigma Aldrich, New Delhi. All chemicals were of analytic grade and were used without further purification.

2. Synthesis of Magnetic Nanoparticles

The first step involves the synthesis of Magnetite (Fe3O4) core. It was synthesised by chemical coprecipitation technique. 0.5 M of FeSO4 solution is mixed with 1M of FeCl3 along with constant stirring till it forms a transparent solution. Then, NH4OH is added slowly drop by drop to the solution along with stirring till the pH of the solution becomes 10. A dark colored precipitate is formed at the end of this duration and this precipitate is actually the Fe3O4 nanoparticles. The particles are separated using an external magnet and then dried in the oven. The magnetite particles are stored for further use.

3. Synthesis of Magnetic Chitosan Nanoparticles (MCN)

The second step involves coating he magnetic core (Fe3O4) prepared with chitosan polymer.

For that, 5% of chitosan solution was prepared by dissolving 0.25 g of low molecular weight (LMW) chitosan in 50 ml of 2% CH3COOH solution. The solution is thoroughly stirred to form the chitosan solution. To this solution 2g of previously prepared Fe3O4 nanoparticles are added, and the resulting solution is again stirred for about 2 hrs to facilitate maximum coating of the magnetite particles with chitosan. The magnetic chitosan nanoparticles are separated and stored for further use.

4. Characterization of Magnetic Chitosan Nanoparticles

Fourier transform infrared Spectra (FTIR) of MCNs was recorded on a Perkin-Elmer FTIR spectrometer, samples were prepared in KBr disks. The scanning range was 400-4000cm-1. Phase identification and structural analysis of the bare MCNs were studied by Powder X-Ray Diffraction (XRD) using CuKα radiation in the range of 2Θ = 20 to 1000 C

5. Analytical Measurements

The total metal-ion concentration in the aqeous solution was determined by voltametric measurements using a Metrohm, 797 VA Computrace (Switzerland). It consists of a three-electrode system that consists of a hanging mercury dropping electrode (HMDE) as the wording electrode, a platinum plate as the auxillary electrode, and KCl (3 M) as the reference electrode. The metal ion concentration was determined through Differential Pulse Anodic Stripping voltameters (DPASV) which accounts for measuring the oxidation current of metal ions deposited on HMDE, as a function of added standard metal-ions solution. The process involves an initial deposition period after which the potential on Hg- electrode is scanned towards positive, and the current from amalgamated metal is measured by the machine [17]. The voltammograme obtained for Cr6+ ion using 797 VA computrace is depicted in Figure 1.
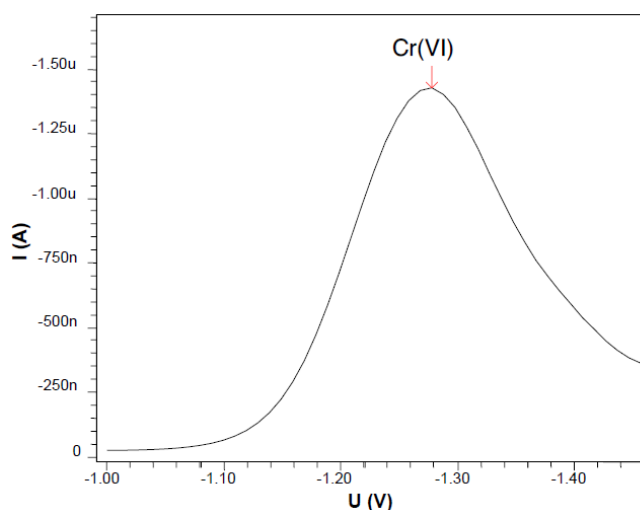

Figure 1: Voltammograme for Cr6+ metal ions

ADSORPTION EXPERIMENT

The adsorption of Cr6+ on chitosan- magnetite nanoparticles was investigated using a batch method.

In order to determine the optimum conditions required to achieve maximum efficiency of MCN for the removal of Cr6+ ions, the effect of the most important parameters, namely pH, temperature and contact time were studied.

In batch adsorption experiments a fixed amount (0.005 g) of MCN was added to the metal ion solution in order to calculate the adsorption constant using different isotherms. 100 ml of metal ion -1.00 -1.10 -1.20 -1.30 -1.40 **U (V)** 0 -250n -500n -750n -1.00u -1.25u -1.50u **I (A)** Cr(VI) solution containing Cr6+ salts was used. Prepared MNC (0.005 g) was added to flasks and agitated at 250 C at 100 rpm for 60 mins. The initial and final concentrations of the solutions were

determined using 797 VA Computrace and the adsorption capacities of the adsorbent were calculated.

The metal uptake capacity for each sample was calculated using equation 1.

$$qe = (Co - Ce)V/m \qquad (1)$$

where,

m (g) is the mass of adsorbent,

V (L) is the volume of the solution,

Co (mgL-1) is the initial concentration of metal,

Ce (mgL-1) is the metal concentration at equilibrium or at time (t) and

qe (mg/g) is the metal quantity adsorbed at equilibrium.

The percent removal of metals from the solution was calculated by the following equation 2.

$$\text{Percentage Removal R (\%)} = (Co - Ct) Co \; X \; 100 \; \% \qquad (2)$$

Where,

Co (mg/L) is the initial metal ion concentration and

Ct (mg/L) is the final metal ion concentration in the solution.

1. Effect of pH

To determine pH that supports maximum removal efficiency of Cr6+ ions by prepared MNC, 100 ml solution containing Cr6+ metal salts had their pH values adjusted in the range from 2 to 7 of all the six solutions and added 0.005 g of MNCs . Each metal ion solution was stirred continuously for 20 min in a thermostatic bath with controlled agitation at a temperature of 25 °C. After the completion of 20 mins, metal ion solutions were examined by 797 VAC, and concentration of Cr6+ metal ions was recorded. The initial pH of the solution was adjusted with either HCl or NaOH .

2. Effect of Temperature

To determine the effect of temperature on the adsorption efficiency of MCN 0.005 g of dry MCN was added in a series of flasks maintained at different temperatures from 200 to 400 C containing 20ml of previously prepared metal ion. All solutions were maintained at pH 5. The individual flasks were stirred well using a shaker at 150 rpm for 20 mins while keeping the temperature at 200, 250, 300, 350 and 400 C. After adsorption, solution was filtered and residual concentration of metal ions were determined.

3. Effect of Contact Time

Estimation of metal uptake capacity of MCN for Cr6+ ions was done by batch method. 0.005 gm of dry MCN was added to a flask containing 100 ml of Cr6+ salt solution. The conical flask was agitated at 150 rpm at 250 C. Samples were taken out at time intervals of 10-10 mins for determination of residual metal concentration in the solution.

2. ADSORPTION ISOTHERM

Study of adsorption Isotherms for a particular adsorption process provides information about the capacity of the adsorbent. An adsorption isotherm was characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of adsorbent for different pollutants. Experimental data can be analyzed using commonly known adsorption systems. Several mathematical models describe experimental data of adsorption isotherms but in this paper Langmuir model is employed to analyse adsorption.

3. RESULTS AND DISCUSSION

3.1. Characterization of Magnetic Chitosan Nanoparticles

3.1.1. X-Ray Diffraction Spectroscopy

XRD patterns of pure Fe3O4 and MCN are shown in Figure 2. The peaks indicate the presence of iron oxide particles (Fe3O4), known to have magnetic properties and thus used for magnetic separation.

The XRD analysis results show that the peaks of pure Fe3O4 and magnetic chitosan nanoparticles mostly coincide. Six characteristic peaks for Fe3O4 (2θ = 30.1, 35.5, 43.5, 53.4, 57.5 and 62.3) were observed in both samples.
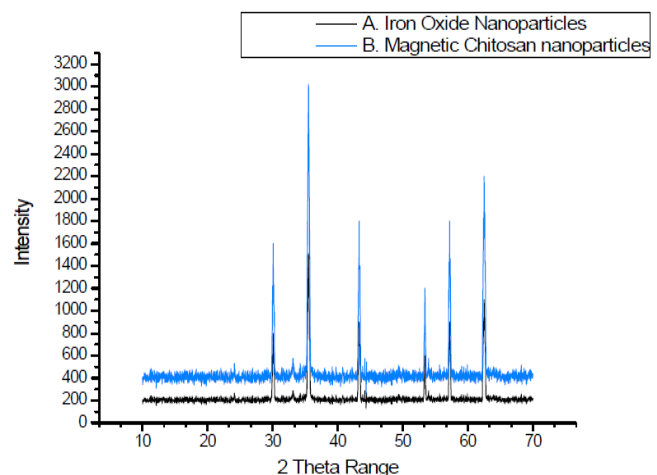

Fig. 2: XRD images of (A) Fe3O4 (B) Magnetic Chitosan Nanoparticles(MCN)

3.1.2. Fourier Transform Spectroscopy (FTIR)

To confirm the existence of surface coating FTIR spectra of magnetic chitosan nanoparticles were examined as shown in Figure 3.The spectra of MCN show a characteristic peak of primary amine (-NH2) that appears at 3145 cm-1 which is related to O-H bond stretching and N-H bond stretching.

Band at 2363 cm-1 appears for C-H stretching. The band around 1127 cm-1 depicts the stretching vibration of C-O bond. Finally the band at 600 cm-1 corresponds to Fe-O group that confirms the presence of Fe3O4 particles. The IR spectra thus confirm that both chitosan and Fe3O4 are present in the magnetic chitosan nanoparticles.
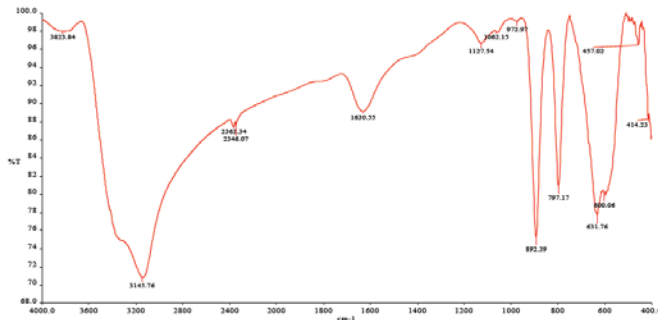

Fig. 3. FTIR Bands of Magnetic Chitosan nanoparticles (MCN)

3.2. EFFECT OF pH

Figure 4 shows the effect of initial pH of metal ion solutions on the efficiency of MCN for the removal of Cr6+ metal ions. The removal efficiency of MCN as a function of pH was calculated according to Eq. (2) and its values were plotted as a graph.
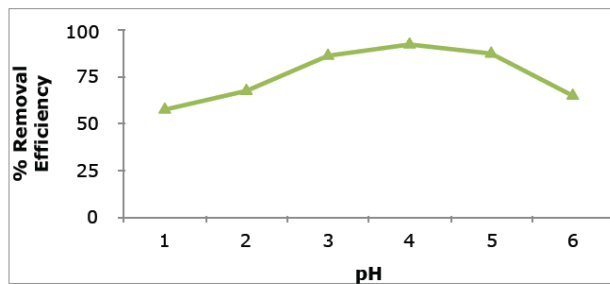

Fig. 4. Effect of pH of the solution on Removal Efficiency of MCN

It is evident from the graph that on increasing the pH from 2 to 7 the metal removal efficiency of MCN also increases. For Cr6+ metal ions, the highest adsorption occurs approximately at pH≥5.

The maximum adsorption capacity of MCN for Cr6+ is observed at pH 5. This trend can be explained on the basis of protonation of active groups on chitosan polymer chain. It is reported that deprotonation on the surface of sorbent is favoured at high pH [18].

Hence, increasing the pH increases the surface deprotonation which, in turn, results in increasing the negatively charged sites on the polymer chain leading to an enhanced attraction between the surface of adsorbent and metal ions, and thus results in an increase in the uptake capacity of the adsorbent.

At lower pH, however, the ratio of positively surface charged sites to negatively charged sites is more.

Positivity on the surface of adsorbent exhibits repulsion for the positively charged metal ions and in turn leads to decrease in adsorption. At pH $\leq$ 2 comparatively lower uptake for Cr6+ ions was reported. The observed lower removal efficiency of MCN in acidic medium may occur because of the partial protonation of the active groups on the chitosan chain and competition of H+ with metal ions for the adsorption sites on the magnetic chitosan nanoparticles.

3.3. Effect of Temperature

As shown in Figure 5, the removal efficiency of MCN for the metal ions decreases with the increase in temperature due to the fact that interaction between metal ions with the active groups of MCN is lower at higher temperature.
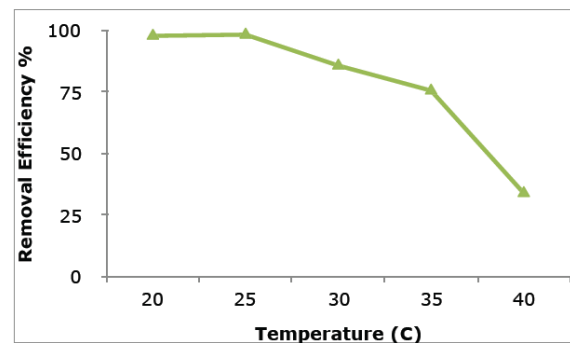

Fig. 5. Effect of Temperature on the Removal efficiency of MCN

When temperature is increased from 20 to250 C, percentage removal of Cr6+ ions also increases from 97.90% to 98.37%. This conclude that MCN exhibits maximum metal ion removal efficiency at 250C.

The subsequent increase in temperature however decreases the magnitude of adsorption for metal ions .With further increase in temperature from 250C to 400C there is a continuous decrease in removal efficiency of MCN. From figure 5 it is clear that low temperatures favours Cr6+ ion removal due to the fact that as temperature increases, mobility of metal ions increases causing desorption or dechelation from the surface of MCN [9]. The result shows that adsorption mechanism related with removal of Cr6+ is exothermic in nature.

3.4. Effect of Contact Time

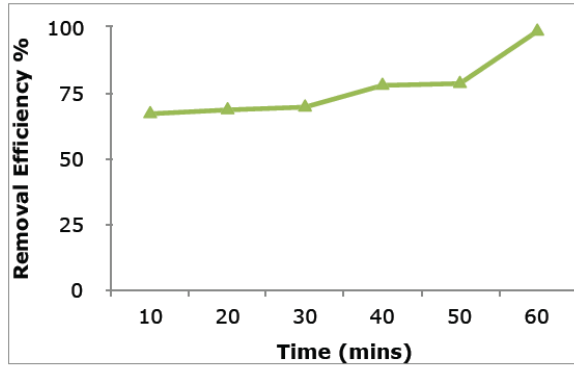Figure 6 indicates that metal ions removal increased with an increase in contact time.

Fig. 6. Effect of Time on the Removal Efficiency of MCN

All parameters such as dose of adsorbent and pH of solution were kept constant. The results indicated an increase in Cr6+ removal with increased time of contact between the adsorbent and the adsorbate.

3.5. Langmuir Adsorption Isotherms

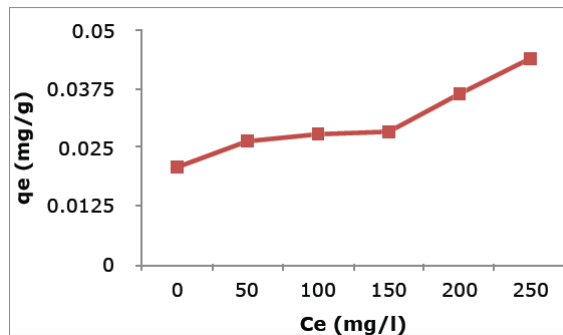Adsorption isotherms for both the metal ions were plotted with the obtained result as shown in figure 7.

Fig. 7: Adsorption Isotherms of Cr6+ ions by MCN

For interpretation of the adsorption data, Langmuir isotherm model was used.

The linear form of Langmuir Isotherm is given by equation 3.

$$Ce/qe = (1/KL\ qm) + (Ce/qm) \tag{3}$$

where,

qe (mg/g) is the amount of adsorbent adsorbed,

Ce (mg/L) is the concentration of adsorbate in the solution,

KL (L/mg) is langmuir constant,

qm (mg/g) is the maximum adsorption capacity for monolayer formation on adsorbent.

The linear plot of specific adsorption (Ce/qe) against the concentration (Ct) at different time shows that adsorption obeys Langmuir model. The constants KL and qm relate to the energy of adsorption and maximum adsorption capacity, their values obtained from slope and interception of the plot are presented in Table 1.

The essential features of langmuir adsorption isotherm parameter can be used to predict the affinity between the sorbate and sorbent using a dimensionless constant called separation factor or equilibrium parameter (RL), expressed by the following equation 4 [21, 22].

$$RL = 1/(1 + KL\ Ci) \tag{4}$$

Where

KL is the Langmuir constant and

Ci is the initial concentration.

The RL values between 0 and 1 indicate favourable adsorption. The RL value in the present investigation was found to be 0.9851 for Cr6+indicating favourable adsorption of metal ion onto MCN.

The results obtained from adsorption isotherms for Cr6+ ions by magnetic chitosan nanoparticles are shown in table 1:

Table 1. Parameters for Cr6+ ions adsorption by MCN according to Langmuir adsorption isotherms.

The maximum adsorption values (qm) was found to be 83.33 mg/g for Cr6+ ions with 0.9327 being its respective R2 value.

4. CONCLUSION

Adsorption equilibrium experiments were carried out as a function of contact time, pH and temperature. The equilibrium time of Cr6+ adsorption was found to be 60 min. The maximum adsorption capacity was found within each optimal pH range and maximum adsorption capacity was Metals Langmuir Isotherm Constants

KL (l/mg) qm (mg/g) R2

Cr6+ 1.2 83.33 0.9327

at pH 6. The percentage removal of Cr6+ decreased with rise in temperature from 250 to 400 C which identified its exothermic nature and binding strength increased as the temperature decreased. The adsorption of Cr6+ fitted with Langmuir isotherm model, suggesting monolayer coverage of adsorbent surface. The maximum adsorption capacity of Cr6+ according to the isotherm study was 83.33 mg/g.

5. ACKNOWLEDGMENT

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