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Research Article

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Cadmium Removal Using Magnetized Chitosan Beads From Wastewater

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Abstract

The deterioration of our water resources due to indiscriminate discharge of untreated industrial effluents containing toxic metals, various dyes, untreated sewage and other anthropogenic activities like urbanization, population growths and land development along river basin have become major concerns throughout the world. There is a need for the appropriate method for removal of heavy toxic metals from the drinking water. In this research work, magnetic chitosan beads have been synthesized for the removal cadmium metal ions from wastewater. The magnetic beads were characterized by using FTIR, TGA and EDAX techniques. Particle and crystal size were determined using scanning electron microscopy, SEM and X-ray diffraction, XRD techniques respectively. The various parameters taken were pH (2- 12), temperatures (40-60^{0}C) and contact time (1-4h) for this research work. The results showed that the optimal adsorbent dosage was 0.04g from the working range of 0.01-0.04g respectively. The R_L values calculated were within the range of $0<R_L<1$ showing the adsorption process is favourable one. Different isotherm constants for Cd (II) at the equilibrium were calculated from the Langmuir, Freundlich and Temkinisotherms. Importance of magnetic beads lies with the removal of cadmium from wastewater due to low cost, environment friendly and its regeneration for further use.

Introduction

Environmental pollution caused by heavy metals is a serious and complex problem because most inorganic and organic contaminants do not undergo degradation even at low concentration. Removal of heavy metals from water is important to protect the public health [1-2]. Heavy metals like iron, manganese, nickel, cobalt, beryllium and copper, if present in permissible limits act as the minerals. However, if these are present at high concentrations as is the case in contaminated environments? Heavy metals may be released into the environment from metal smelting and refining industries, scrap metal, plastic and rubber industries and from burning of waste containing these elements. Due to their non-biodegradability and persistence, can accumulate in the food chain, and thus may pose a significant danger to living beings [3].

Cadmium is among the heavy metal found in industrial effluent including metal processing, electroplating industries, textile, alloy industry and composting. Even at low concentration of cadmium (II) ions in water, is extremely harmful and can cause both acute and chronic intoxication [4]. Different methods have been analyzed in order to remove the heavy metals such as: the reverse osmosis process, electro dialysis and ion exchange etc. Such processes have some special deficits due to their inability to remove of heavy metals fully and also due to the economical aspect. One of the methods in metals removal is sorption by chitosan, obtained from natural biopolymer chitin. The chitosan is an effective substance used in the removal of cadmium.

Chitosan, poly (β-1, 4)-2-amino-2 deoxy-D-glucopyranose, is deacetylated form of chitin, obtained from crustacean shells. It has biocompatible and biodegradable characterstics and can be easily regenerate for further use [5]. Due to presence of amino group (-NH2) in the polymer, which can interact with heavy metals ion in solution by ion exchange and complexation reactions. Several modifications were proposed in order to improve pore size, mechanical strength, chemical stability, hydrophilicity and also biocompatibility [6].

In this paper, magnetic chitosan beads prepared can absorb pollutants from wastewater and can be separated easily [7]. Effects of various experimental condition such as adsorbent dose, contact time, pH and temperature on the adsorption were evaluated through batch equilibrium techniques.

Materials

Chemicals

Chitosan (crab shell) used for the preparation of magnetic chitosan beads (MCSB) was procured from Sigma-Aldrich. $FeSO_4.7H_2O$, $FeCl_3.7H_2O$, CH_3COOH (99.5%), NaOH & $CdCl_2.H_2O$ was supplied by Central drug house (P) Ltd. (CDH). All the chemicals used were AR or GR grade.

Method

Synthesis of magnetic chitosan beads

Magnetic chitosan (CS) beads were prepared by co-precipitation of Fe^{+2}& Fe^{+3} ions in NaOH in the presence of chitosan. Chitosan (0.5gm) in 100ml of 5% CH_3COOH solution was dissolved in $FeSO_4$ & $FeCl_3$ in 1:2molar ratio. Then resulting solution was dropped slowly into 30% NaOH solution to obtain wet magnetic chitosan beads [7, 8]. The suspension was kept at room temperature for 24 h without stirring and separated beads were washed several times in

water to remove alkali. The particles were finally dried in vacuum at 60 ^{0}C for overnight to obtain magnetic chitosan beads.

Finally, the dark brown color beads are taken out and washed again extensively with distilled water, and then dried in vacuum. The dark brown appearance and retention by a bar magnet are the indications of magnetic behavior.

Preparing an aqueous solution of cadmium ion

Stock solution was prepared by dissolving 100mg of cadmium chloride ($CdCl_2.H_2O$) in one litre of double distilled water. It was further diluted to obtain 1ppm solution.

Characterizations of magnetic beads

The degree of deacetylation of chitosan was calculated from the FTIR (Perkin Elmer) analysis. FTIR analysis was also required to know the interaction between polymer and iron oxide. The spectral range of 4000-400 cm^{-1} wave number was used. XRD analysis was performed using a X-ray diffractometer with Cu K _radiation (λ = 1.54060 A). The surface morphology was studied using a field emission Scanning Electron Microscope (JOEL JS 6610Lv instrument). Thermal stability was studied with thermo-gravimetric analyser (Perkin Elmer) at a temperature range of 25-750^{0}C. The elemental composition in the sample is identified by the EDAX technique.

Result and Discussion

Fourier Transform infrared spectra (FTIR) analysis

FTIR spectra of chitosan magnetic beads are recorded on a spectrum XIFTIR (Perkin Elmer) spectrometer in the range 4000–400 cm^{-1}using KBr pellets (Fig 1). This technique was used to understand the nature of the bonds and functional groups of the molecules and how they were altered after the synthesis processes [9]. For magnetic beads, the peaks at 618cm^{-1} corresponds to Fe-O group; the peaks at 3430cm^{-1}is attributed to O-H stretching vibration and C-H stretching vibration of the polymer lying at 2926 and 2850 cm^{-1}. A band at 1385 cm^{-1} arises due to symmetric >CH_2 streching vibration attributed to pyranose ring. The bio-sorption bands of >N-H amine appears at 1627 cm^{-1}. The band around 1095cm^{-1} display the stretch vibration of C-O bond.

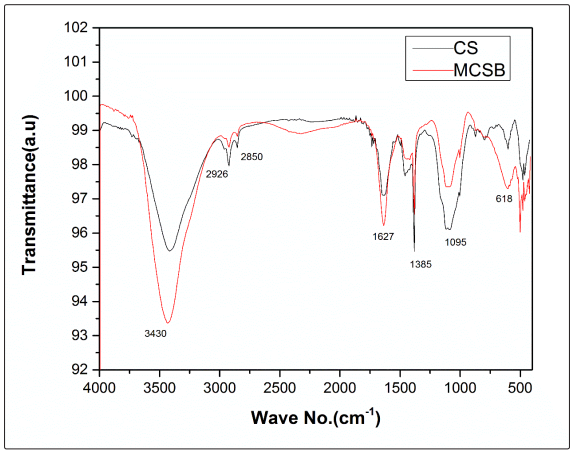

Figure 1: FTIR bands of magnetic chitosan beads

Thermo-gravimetric analysis (TGA)

To evaluate the thermal stability of the magnetic chitosan beads, TGA analysis was carried out under N_2 atmosphere. The thermo grams of materials were recorded on the gravimetric instrument of Perkin Elmer which works within a temperature range of 25^{0}C to 1000^{0}C with Platinum crucible and alpha alumina powder as reference. Three stages of weight loss were observed in the TGA curve for chitosan and its magnetic beads. Thermal degradation studies have been useful for estimating the relative amounts of chitosan (CS) and magnetic chitosan beads (MCSB).

The pure chitosan (CS) show slower weight loss from room temperature to 200 ^{0}C is 7%, due to decomposition of low molecular weight species. Thermal decomposition is more in the region between 250 ^{0}C to 400 ^{0}C is about 42%, relating to the complex dehydration of saccharide rings, depolymerization, and decomposition of the acetylated and deacetylated units of the polymer. In third stage, weight loss in the region between 450 ^{0}C to 650 ^{0}C is about 42%, were caused by a modification of the material occurs when the structure is almost completely reduced causing the production of methane and the consequent formation of graphite like structure via dehydrogenation mechanism. The TGA curve (Fig 2) of magnetic chitosan beads (MCSB) also shows the three stages of weight loss. The first stage weight loss from 25 ^{0}C to 200 ^{0}C is about 7%, as a result of the evaporation of adsorbed water. The other two stages of main weight loss at 200 ^{0}C to 350 ^{0}C and 400 ^{0}C to 700 ^{0}C is about 20%, were caused by the decomposition of chitosan in the magnetic chitosan beads. Over all weight loss of the CS is about 91% and MCSB is about 27%. The decomposition thermo grams for CS and MCSB vary between studies, suggesting that the introduction of magnetic iron oxide particles reduces crystallization [10-11].

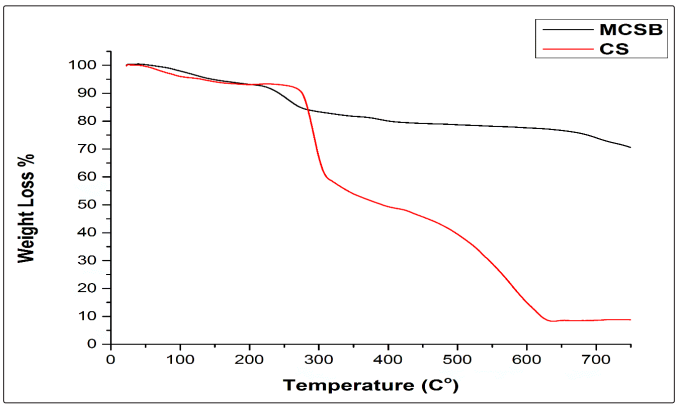

Figure 2: TGA graph of magnetic chitosan beads

Scanning Electron Microscopy

The morphology of magnetic chitosan beads is important to determinate how they interact with target pollutants. Scanning electron microscopy (SEM) is used to visualize the morphology and homogeneity surface structures. The sample powder were completely dried and then coated with gold in vacuum with sputter coater. Magnetic beads showed presence of holes and small opening on the surface which increases the contact area and facilitates the pore diffusion for the metal (Cd^{2+}) during adsorption. SEM at magnification of 30000 and 6000 for chitosan (Fig 3) and magnetic chitosan (Fig 4) beads is illustrated below. Magnetic chitosan beads are semi-spherical and have highly folded surface area for easily adsorption of metal ions.

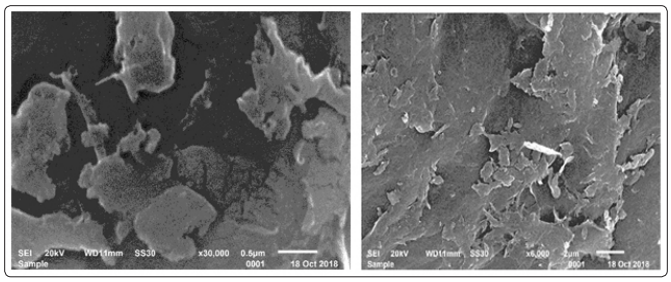

Figure 3: SEM Images of chitosan

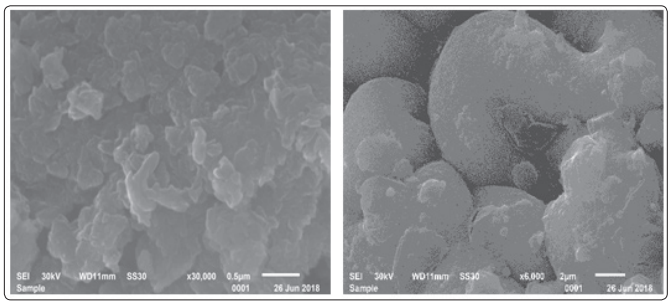

Figure 4: SEM Images of Magnetic chitosan beads

Energy Dispersive X-Ray Spectrometer (EDAX)

EDAX technique is often used to identify elemental composition and is given in Fig5. It gives the information about relative proportions and distribution within sample. The objective of performing EDAX analysis on metal loaded beads was to investigate the presence of metal ions and confirm the adsorption process. The content of iron (Fe) and oxygen (O) within the sample that confers a magnetic property of the beads. Percentage compositions of different element are given in Table 1.

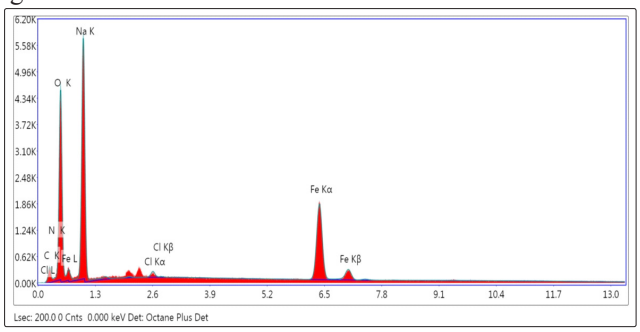

Figure 5: EDAX of magnetic chitosan beads

Table 1: Elemental composition of magnetic chitosan beads by EDAX

Element	Weight %	Atomic weight %
C K	8.18	14.76
N K	1.32	2.05
O K	27.5	37.23
Na K	38.67	36.43
Cl K	0.5	0.31
Fe K	23.82	9.24

E. X- Ray Diffraction analysis (XRD)

XRD studies have shown that MCSB exhibits crystallinity mainly due to the presence of iron oxide particles (Fig 6). Chitosan exhibits a highly amouphous nature with broad signal [12-13]. XRD patterns of the magnetic chitosan beads, the five peaks of magnetic beads are identified by their indices: (111), (220), (311), (400) and (422). The interplanar spacing d_{hkl} are determined by equation, which is obtained from Bragg`s law.

$d_{hkl} = \lambda / 2\sin\theta$

XRD patterns were also used for determining the size of the MCSB: the half width at half maximum is correlated to the particles size using the Debye - Scherrer equation:

$D = (k\lambda/\beta\cos\theta)$

Where D is the average diameter of particles (nm), λ is the wavelength of X- Ray radiation, θ is the angle of diffraction, k is the Debye-scherrer constant (0.9 for Cu Kα radiation) and β is the full width at half maximum of X-Ray diffraction peaks.

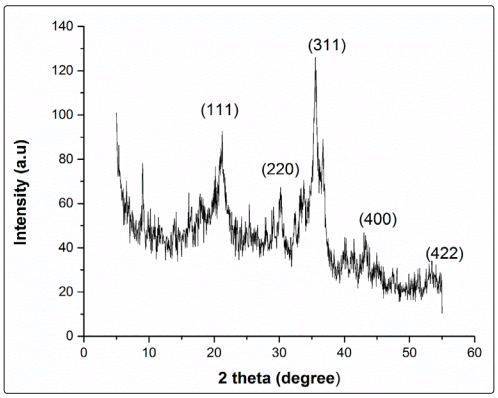

Figure 6: XRD pattern of magnetic chitosan beads

Effect of amount of adsorbent dose

A plot of removal efficiency of Cd (II) metal ions versus adsorbent dosage is shown in figure 7. The dependence of Cd (II) adsorption on dose was studied by varying the amount of adsorbents. The plot clearly shows that removal efficiency increases with the increase in amount of the adsorbent dose. This is due to the fact that the higher the dose of adsorbents in the solution, the greater the availability of active sites for the Cd (II) ions. However, the increase in the dose of adsorbent from 0.04 to 0.06gm did not exhibit considerable improvement in the removal .

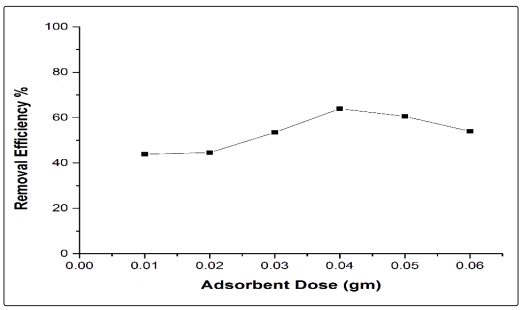

Figure 7: Effect of Adsorbent dose on the removal efficiency of MCSB

Higher uptake value of maximum adsorption at 0.04gm. This suggests that after a certain dose of adsorbent, the adsorption is reached at equilibrium [14].

Effect of pH

A plot of percentage removal efficiency of MCSB versus pH is shown in figure 8. The effect of the pH on the percent removal of

MCSB was studied over the pH range from 2 to 12. It is found that the adsorption rate is rapid during the initial stages of the adsorption process. At low pH value, the competition between hydrogen ion and Cd (II) ion limit the uptake efficiency [15]. With increase of pH value, the coordination and chelating ability of these functional groups towards Cd (II) will be strengthened. Highest uptake value is observed at pH= 6. However, with further increase of the pH value, the adsorption capacities decrease.

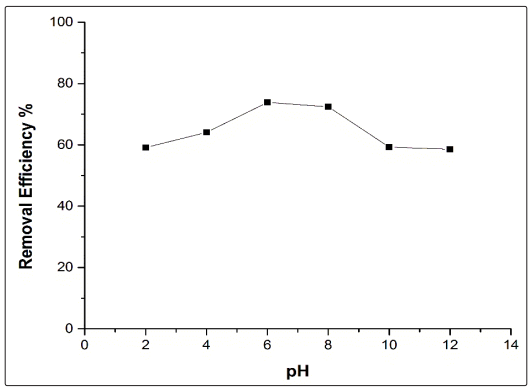

Figure 8: Effect of pH on the removal efficiency of MCSB

Contact Time

The effect of contact time on the removal of Cd (II) ions by the MCSB is shown in figure 9. The contact time curves show rapid adsorption rate of Cd (II) ions is increased. After that, uptake rate slowly declines with lapse of time and tends to be equilibrium at 4 h. It can be explained that there were plenty of available adsorption sites. With the adsorption process proceeding, the adsorption sites were occupied gradually and the percent removal elevated slowly and the adsorption reaches its equilibrium in 4 h.

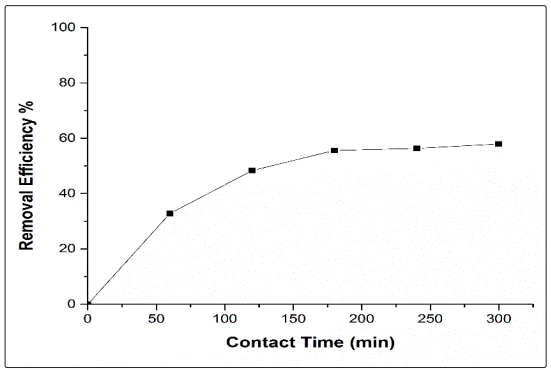

Figure 9: Effect of contact time on the removal efficiency of MCSB

Effect of Temperature

It is important to investigate the effect of temperature on adsorption in the experiment. The adsorption experiment of magnetic chitosan beads for Cd (II) at different temperatures shows, removal efficiency of magnetic beads decreases with increasing temperature (Fig 10). The behavior confirms that the removal efficiency of magnetic chitosan beads is exothermic. This observation can be attributed that physical adsorption occurs. It occurs more readily at lower temperatures and decreases with increase in temperature (Le-Chatelier's Principle). This causes a decrease in the surface energy of the adsorbent.

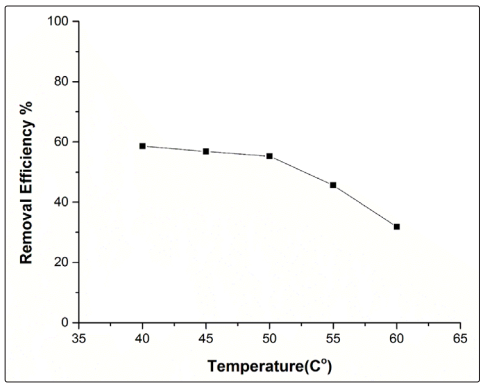

Figure 10: Effect of temperature on the removal efficiency of MCSB

Isotherms study

In order to understand the adsorption behavior of adsorbents, equilibrium data can be analysed using commonly known adsorption systems. In this study, for the interpretation of the adsorption data three isotherms models were used, Langmuir, Freundlich and Temkin isotherms to analysis adsorption occurring in experiment [16].

The Langmuir isotherm model assumes that equilibrium is attained when a monolayer of the adsorbate molecules saturated the adsorbent. The Langmuir model is based on the assumption that solid surface has limited adsorption sites which are energetically and sterically independent of the adsorbent quantity valid only for monolayer sorption. The linear form of Langmuir model is given in equation (1):

$$C_t / q_t = (1 / KL \times q_{max}) + (Ct / q_{max}) \quad \ldots\ldots\ldots\ldots (1)$$

Where C_t (mg/L) is the concentration of adsorbate in the solution at time t, q_t (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, K_L (L/mg) is the Langmuir constant and is related to the affinity between the adsorbate and adsorbent while q_{max} (mg/g) is the maximum adsorption capacity for monolayer formation on adsorbent. The values of qmax and KL could be determined by plotting C_t/q_t vs. C_t. the value of q_t can be calculated by using the following equation (2):

$$qt = \frac{(Co-Ct)V}{m} \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where C_o is the initial concentration of adsorbate (mg/L), V is the volume of solution (L), m is the mass of adsorbent used (g). The essential charactersticsof the Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter (R_L) which can be defined as follows (equation 3):

$$R_L = 1 / (1+ K_L . C_o) \quad \ldots\ldots\ldots\ldots\ldots (3)$$

The value of R_L, indicates the type of isotherm to be either favorable ($0<R_L<1$), unfavorable ($R_L>1$), linear ($R_L=1$) or irreversible ($R_L=0$).

The Freundlich equilibrium isotherm equation was also used to describe experimental adsorption data. This isotherm is an empirical equation which is used for the description of multilayer adsorption with interaction between adsorbed molecules. The Freundlich model for metal sorption is based on the relation between the adsorbed quantity and the solute concentration remained in the liquid phase. The Freundlich equation (4) can be written as:

$qt = K_F C_t^{1/n}$ …… (4)

Where, K_F (mg/g) is the Freundlich isotherm constant, C_t (mg/g) is the concentration of adsorbate at time t and q_t (mg/g) is the amount of metal adsorbed per gram of the adsorbent at time t. A value of 1/n, ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity. A value for n greater than one indicates of favourable adsorption process. If n=1, then the partition between the two phases are independent of the concentration. When 1/n <1, it shows normal adsorption. If 1/n >1, cooperative adsorption is supported.The Freundlich Equation (5) is expressed in linearized form as:

$\log q_t = \log K_F + 1/n \log C$ ……(5)

Temkin Isotherm is usually used for heterogenous surface energy systems (non-uniform distribution of sorption heat). It also takes into account the adsorbent – adsorbate interactions. The model assumes that heat of adsorption of all molecules in the layer would decreases linearly rather than logarithmic with coverage. The linear form of Temkin isotherm (6) is expressed
According to:

$qt = (RT/b) \ln A + (RT/b) \ln Ct$ …… (6)

where(RT/b=B), b is the Temkin isotherm constant, A(L/g) is the Temkin isotherm equilibrium binding constant, R is the universal gas constant($8.314 Jmol^{-1}K^{-1}$), and T is the absolute temperature being 298K.

A plot of quantity adsorbed (q_t) v/s C_t enables the determination of the constants A and B from its slope and intercept respectively.

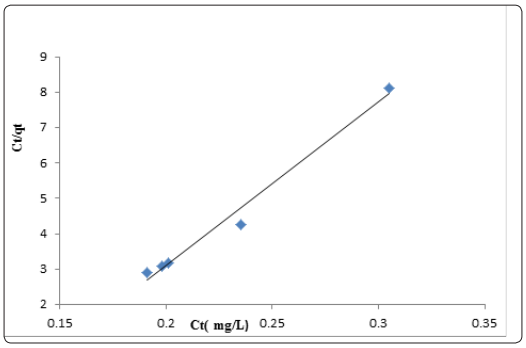

Figure11: Linearized Langmuir Isotherm Plot for the adsorption of Cd^{+2} Ions on MCSB

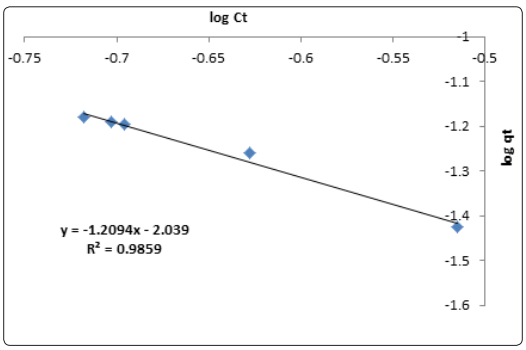

Figure 12: Linearized Freundlich Isotherm Plot for the adsorption of Cd^{+2} Ions on MCSB

Isotherm constants for the adsorption of Cd^{+2} metal ions on MCSB

Metal Ion	Experimental q_{max} (mgg^{-1})	calculated q_{max} (mgg^{-1})	K_L (Lmg^{-1})	R_L	R^2
Cd+2	0.191	0.0216	7.525	0.226	0.9857

Metal ion	K_F (mgg^{-1})	n	R2
Cd+2	109.395	0.826	0.9859

Metal ion	A (Lg-1)	B ($Jmol^{-1}$)	R^2
Cd+2	5.39	1.209	0.9859

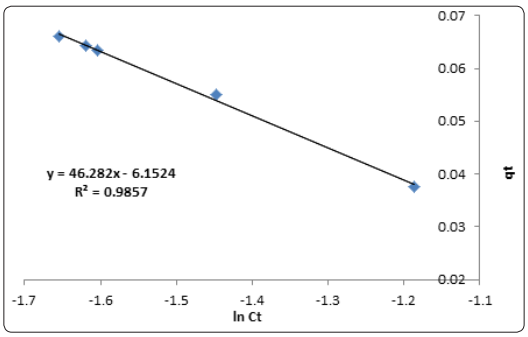

Figure13: Linearized Temkin Isotherm Plot for the Adsorption of Cd^{+2} Ions on MCSB

Thermodynamic study

The thermodynamic parameters for the adsorption process were calculated using the following equations (7):

$\ln K = -(\Delta H/RT) + (\Delta S/R)$ ……(7)

where, R(8.314J/molK) is the universal gas constant, T(K) is the absolute solution temperature and K is the adsorption equilibrium constant (dimensionless), ΔH is the change in enthalpy and ΔS is the change in entropy.

According to the Vant′ Hoff equation, the values of ΔH and ΔS are determined from the slopes and intercept of the $\ln(q_t/C_t)$ v/s (1/T). ΔG was calculated using the relationship
Below (equation 8):

$\Delta G = -RT \ln K$ …… (8)

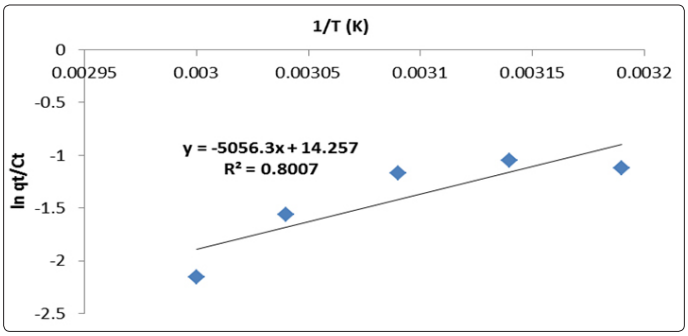

Figure 14: Vant′Hoff Plot for Adsorption of Cd^{+2} Ions on MCSB

The positive value of ΔH value (+42.03KJ mol^{-1}) obtained in the study of Cd^{+2} metal ion confirms the endothermic nature of the adsorption process [17]. The positive values of ΔS (+118.53 Jmol-

$1K^{-1}$) for Cd^{+2} ions are attributed to the increase in randomness at the solid interface.

Conclusion

Magnetic chitosan beads have been synthesized, characterized and efficiently tested for Cd^{+2}ions recovery. The results of this study show that magnetic chitosan beads for removal of cadmium from waste water under optimal conditions (times of 4h, pH=6, adsorbent dosage of 0.04 g and concentration of 1ppm cadmium) has very good efficiency. The Langmuir equation fits well with adsorption isotherm compared to other conventional models. The reaction is endothermic (ΔH^o= +42.03KJ mol^{-1}), increased randomness after metal adsorption (ΔS^o = +118.53 $Jmol^{-1}$ K^{-1})and the value of ΔG^o decreases as the temperatures increases. This indicates the spontaneous nature and feasibility of the process.

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