

Adsorption of Cd(II) by Chitosan: Langmuir Isotherms Studies

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Chitosan is a biopolymer found in the body of the shellfish, crustaceans and some fungi. The free amino groups of this biopolymer shows different properties such as antimicrobial, anti-acid and chelating of metal ions. Chitosan is very efficient at binding through the chelating mechanism involving the interaction of amino group of chitosan with different metal ions such as Cu(II), Pb(II), Cr(VI) and Cd(II) etc. Adsorption isotherm of one adsorbate, Cd(II), at initial concentration of 0.33 ppm at pH 3.5 and also at pH 4 was carried out. Adsorption isotherm data could be well interpreted by using the Langmuir equation. The Ubbelohde viscometer was used to determine the molecular weight of the chitosan employed. The degree of deacetylation 80%, was found from $^1\text{H NMR}$, 300 MHz spectrophotometer. The presence of $-\text{OH}$, $-\text{CNH}_2$ and $-\text{CH}_2\text{OH}$ was established from IR spectra. Solubility of chitosan in acidic medium was observed to be good and with the increase of pH it diminishes and becomes constant. Desorption experiment of Cd (II) conducted at different pH values in EDTA solution, favours the acidic medium, which indicates that adsorption mechanism occurred by electrostatic interaction and covalent bonds.

Key Words: Chitosan; Adsorption Isotherm; Heavy Metals; Langmuir Equation

1. Introduction

Discharge of effluents contaminated with heavy metals like Cd(II), As(III), Hg(II), Pb(II), Cr(VI), Cu(II), and Zn(II) etc are poisonous even at very low concentrations. These metals are naturally occurring components of the earth, crust which cannot be destroyed or degraded by any means. These heavy metals have many industrial applications due to their technological importance. Cadmium is widely used in several industries including metallurgy, surface treatment, dye synthesis, nickel-cadmium batteries, cadmium alloy, cadmium electronic components, pesticides and dyes etc in aqueous solutions [1-2]. The input of cadmium to the soil is from both natural and anthropogenic sources. The cadmium in soil occurs at very low levels, but it is added to the soil by the other products such as fertilizers, phosphogypsum, and certain zinc additives. The study

of literature reveals that the occupational exposure standards which formerly lied between 100 and 200 $\mu\text{g}/\text{m}^3$ have been made stricter and now lie between 2 and 50 $\mu\text{g}/\text{m}^3$ (ILO 1991). Pollution by cadmium usually comes from the waste water from industries and have permanent toxic effects on the environment and human beings [3].

Cadmium affects the environment and is considered to be carcinogenic, is absorbed from industrial effluents by the micro-organism. Eventually, cadmium will be transferred to human body via the food chain and once absorbed by the body is very difficult to expel and causes damage to vital organs even at very low concentration. Cadmium toxicity is linked to renal dysfunction, lung diseases, bone degeneration, increased blood pressure, and several types of cancers. Due to the high toxicity cadmium removal from the industrial effluents and

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wastewater have been considered as a priority since the last decade.

Protection of environment becomes a difficult task while many industries produce waste that causes serious pollution and the removal of heavy metals and dyes etc., from waste water is fundamental to environmental conservation and public health [4]. There are a number of methods used for the removal of pollutants from water by chemicals, precipitation, complexation, reverse-osmosis, adsorption, ion-exchange, electrochemical deposition, filtering and membrane system etc alongwith the cross-linked chitosan membrane for Hg(II) ions [5].

Adsorption is an economical and effective method using the chitosan-coated sand for the removal of Cu(II) and Pb(II) metals from aqueous solution [6]. Adsorption by activated carbon is generally used in conjugation with precipitation, filtration and ion-exchange. These processes are very expensive for some metals and the efficiency is related with the type of carbon used. The use of recyclable magnetic chitosan nanocomposite has been used for the removal of metal ions effectively from wastewater [7]. The Cd(II) from wastewater of electroplating bath was recovered by using a mixture of different chitosans in a specific technique [8]. Using low cost biosorbents such as agricultural wastes, clay materials, biomass and seafood processing wastes may be alternative wastewater technologies because they are inexpensive and capable of removing even the trace levels of heavy metal ions [9].

Biopolymers are potential adsorbents due to their biodegradability, non-toxicity, efficiency and easy availability. These are inexpensive natural polymers and thus are competitive with ion-exchange resins and activated carbon [10, 11]. They contain chemically active functional groups that serve as an efficient sites to bind with metal ions. Notably, chitosan has the highest adsorption capacity among the biopolymers. It is a deacetylated derivative of chitin, the second most abundant organic compound in nature next to the cellulose, and is extracted from the shells of crustaceans, it has several desirable

characteristics such as biocompatibility, biodegradability, bioactivity and non-toxicity [12].

Chitosan is natural cationic polymer formed by the N-deacetylation of chitin, which is present in fungi, insects and exoskeleton of shellfish like shrimp or crab. It is hydrophilic and a basic polymer due to the presences of amino and hydroxyl groups. Chitosan has been known for its metal adsorption properties since 1970s and is described as an excellent metal adsorbent by many investigators [13]. Chitosan has been successfully used for the removal of heavy metal ions like arsenic, gold, cadmium, molybdenum, lead, cobalt, iron, silver, copper, nickel, mercury, zinc and uranium from aqueous solution successfully [14, 15].

2. Experimental

2.1 Materials

Chitosan, a powdery material, with degree of deacetylation approximately $\geq 80\%$, chitosan medium molecular weight, and deuterium oxide (D_2O), 99.9 atom % D were purchased from Sigma-Aldrich. Acetic acid (glacial 99-100%) was from E. Merck Specialities Pvt. Ltd., Worli, Mumbai. Sodium tripolyphosphate anhydrous (STP) and Cadmium chloride AR, were CHD Laboratory Reagents. HCl, NaOH and EDTA (ethylene diamine tetra acetic acid) reagents used were of analytical grade. Double distilled water was used to prepare the solutions.

2.2 Method: Preparation of Chitosan Beads

0.5 g chitosan powder was dissolved in 50 ml of 5%, acetic acid and 20 ml of double distilled water. Solution was stirred for 24 hours. After that the chitosan solution was transferred in a microburette and 20 ml of 1% STP solution was taken in a petri dish. Controlling the flow from the knob of the microburette, the chitosan solution was allowed to fall in STP solution resulting in the formation of tiny spherical uniform chitosan beads [16, 17]. Beads were left in STP solution overnight and after that washed thoroughly (2 or 3 times) with distilled water. The washed chitosan beads are kept in distilled water for 24 hours, then water decanted off and finally dried in oven to remove water. The chitosan beads so

obtained are rigid and crystalline and are totally insoluble in acidic medium. This property makes the chitosan beads a better adsorbent than chitosan gel.

2.3 Swelling Analysis

0.1 g chitosan beads were taken in a non-woven polypropylene bag and suspended in the respective 0.1N CH₃COOH or 0.1N NaOH solution for 24 hours. The weight of the wet swollen beads was determined and the swelling percentage of beads was calculated from the following equation (1):

$$\% \text{ Swelling, } E_{sw} = [(W_s - W) / W] \times 100 \quad (1)$$

where, E_{sw} is the swelling percentage of the beads at equilibrium, W_s denotes the weight of the beads when the swelling equilibrium is reached and W is the initial weight of the unswollen beads.

2.4 Chitosan Solubility at Different pHs

The chitosan solubility was studied at pH ranging from 2-5 using 0.1N HCl and 8-11 with 0.1N NaOH solution. 0.2 g of chitosan powder is taken in an already weighed empty non-woven polypropylene bag, suspended in an Erlenmeyer flask containing 100 ml of acidic or basic solutions at desired pH. The experiments were carried out for 24 hours at 25°C with constant agitation. After this, the bags were removed from the flask and dried in an oven at 60°C for 12 hours. Finally, the remaining chitosan in the bag was weighed and the percentage of dissolved chitosan was calculated (Fig. 1).

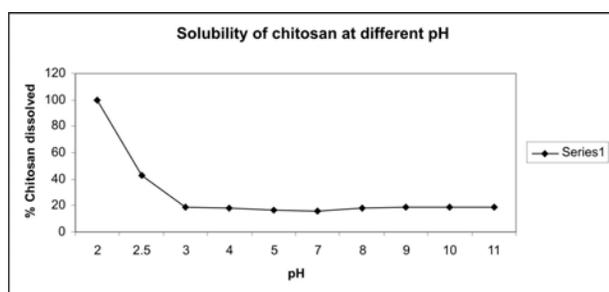


Fig. 1: Solubility of chitosan at different pH values

2.5 Determination of Molecular Weight

The average molecular weight was determined by using Ubbelohde viscometer. A solution of (0.2%) of

polymer was prepared by using 0.1 g middle molecular weight chitosan in 7 ml of acetic acid of 5% and double distilled water was added to make the solution 50 ml in a standard flask and stirring it overnight. 10 ml of 0.2% of chitosan solution was taken in viscometer and time of flow was recorded. The viscometric constants were calculated by using Mark-Houwink's equation [18].

$$[\eta] = K \times [M]^\alpha, \quad (2)$$

where, $\alpha = 0.85$ and $K = 1.38 \times 10^{-5}$ L/g. The molecular weight of middle molecular chitosan powder was 1.89×10^6 g/mol and was determined by the methodology described above.

3. Result and Discussions

3.1 Study of Solubility and Swelling Behaviour

The solubility of chitosan was maximum (99.9%) at pH 2, decreases afterwards and is steady and minimum in basic medium (Table 1). Between the pH 2 and 3, the chitosan acquired a gel-like appearance and therefore the adsorption experiments were carried out at pH between 4 and 7. The swelling behaviour of chitosan beads in 0.1N NaOH, 0.1N CH₃COOH and water are reported in Table 2. The degree of swelling is about nine times higher in acidic

Table 1: Chitosan solubility at different pH values

S.N.	pH		% of Solubility	
	From	To	From	To
1.	2.0	7.0	99.9	12.3
2.	7.0	8.0	12.3	12.5
3.	8.0	11.0	12.5	15.0

Table 2: Swelling Behaviour of Chitosan Beads Adsorbate: Chitosan Beads

S.No.	Solution	% of swelling
1.	Water	265.8
2.	0.1N CH ₃ COOH	3682.8
3.	0.1N NaOH	400.6

medium than that in alkaline medium. This is due to the inherent hydrophobicity of the chitosan beads dominating in alkaline medium and which prevents the swelling [19].

3.2 Adsorption Experiment

The experiment was performed by dissolving 2.65×10^{-4} moles of CdCl_2 salt in 250 ml of double distilled water in a standard flask. The 50 ml of Cd (II) solution and 0.1 g of chitosan beads were taken in a beaker, to this 0.7 ml or 1.0 ml of 0.1N HCl was added to maintain the pH at 3.5 and 4.0 respectively. The samples were taken out at the interval of 20 minutes with continuous stirring. Experimental samples were filtered using Whatman filter paper No. 1 and the filtrates after suitable dilution were analyzed. The solution concentration was analyzed by using Atomic Adsorption Spectrophotometer (model AA7000 Lab India). Absorption was measured at a λ_{max} 228 nm using slit width of 0.2 mm (Table 3).

3.3 Adsorption and Desorption Equilibrium Studies

Adsorption isotherms of the solution containing the metal ion and a weighed amount of chitosan were taken in an Erlenmeyer flask which served as an experimental batch adsorber. The solution of cadmium of 10^{-4} moles L^{-1} and 0.2 g of chitosan were placed inside the Erlenmeyer flask and pH 1 to 5 was adjusted by adding 0.1N of HNO_3 and pH 7 to 8 with 0.1N NaOH solution. The chitosan mass was placed in an unwoven polypropylene bag before introducing into the batch adsorber. The solution and the chitosan

Table 3: Study of adsorption of Cd^{+2} on chitosan at pH 3.5 and 4.0 by atomic absorption spectroscopy at different time intervals

	Time (minutes)	Absorbance		Cd^{+2} (mg L^{-1})	
		pH = 3.5	pH = 4.0	pH = 3.5	pH = 4.0
1.	20	0.2229	0.2367	3.0	2.9
2.	40	0.2109	0.2023	2.8	2.6
3.	60	0.2030	0.1916	2.6	2.4
4.	80	0.1990	0.1559	2.4	1.8

were kept for 48 hours and the experimental samples were taken for analysis after suitable dilutions. The metal concentration was determined by Atomic Absorption Spectrophotometer (AA 7000-Lab India) (Table 4).

Desorption is the reverse of the adsorption process and desorption studies are made once the adsorption equilibrium is attained [20]. For this, the bag containing chitosan was taken out from the solution and rinsed with reactive water set at the same pH as the solution used in the adsorption experiment to remove metal residues that remained in the chitosan. Subsequently, the bag with chitosan was suspended in the reactive water at the desired pH for 48 hours. Finally, the metal concentration was determined as described above (Figs. 2 & 3).

Desorption study of CdCl_2 from chitosan beads was also studied in 0.001M EDTA solution at different pH values. A comparative study reveals that desorption at pH 2 is highest at about 84.9% in 0.001M EDTA solution. Adsorption and desorption data for chitosan beads are given in Table 4.

3.4 Degree of Deacetylation of Chitosan

$^1\text{HNMR}$ spectrum of deacetylated chitosan recorded on 300 MHz instrument is shown in Fig. 4. The

Table 4: Adsorption and desorption studies of cadmium at different pH values

S.No.	pH	Adsorption of CdCl_2 on chitosan (ppm)	Desorption of CdCl_2 from chitosan (ppm)	Desorption CdCl_2 from chitosan in EDTA solution of 0.001M (ppm)
1.	1.0	2.10	0.07	1.78
2.	2.0	2.45	0.03	2.08
3.	3.0	2.15	0.18	1.81
4.	3.5	1.74	0.22	1.48
5.	4.0	1.40	0.12	1.20
6.	5.0	1.07	0.02	0.91
7.	7.0	1.09	0.03	0.89
8.	8.0	1.10	0.03	0.92

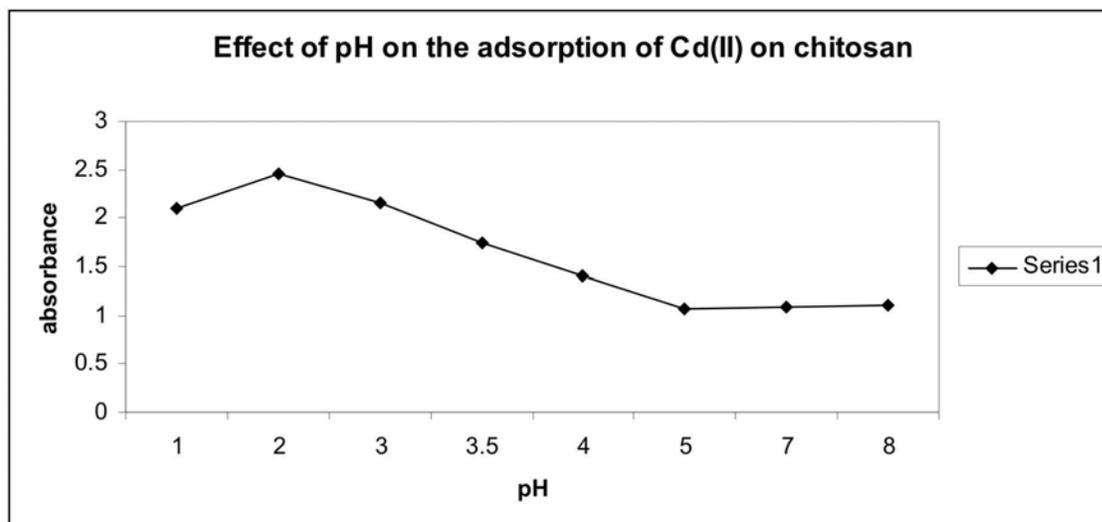


Fig. 2: Effect of pH on the adsorption of Cd(II) on chitosan

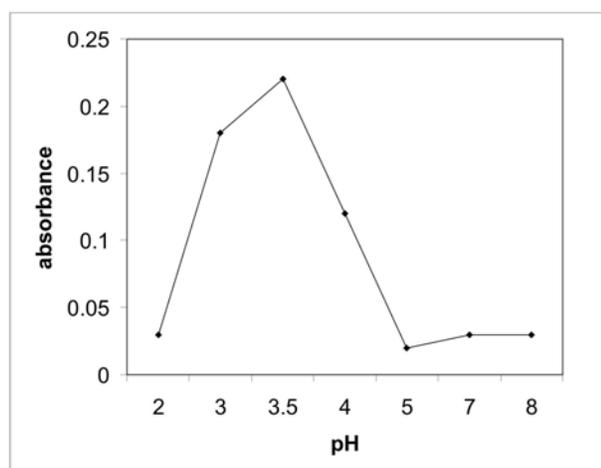


Fig. 3: A plot of absorbance with pH for the desorption of Cd(II) in reactive water

chemical shifts of chitosan protons and intensity values in D₂O at 70°C are mentioned in Table 5. The degree of deacetylation was calculated by equation (3) using integral intensities of I_{CH₃} of this CH₃ residue and the sum of integral intensities I_{H₂-H₆'} of H₂, H₃, H₄, H₅ H₆ and H₆' protons²¹.

$$\text{DDA}\% = [1 - (1/3 I_{\text{CH}_3} / 1/6 I_{\text{H}_2\text{-H}_6'})] \times 100 \quad (3)$$

In this treatment base line was given by a straight line connecting the intensities at 1 ppm to 5 ppm. For calculation of D_{deac}, the total integral

Table 5: ¹H spin-lattice relaxation times (T₁) for chitosan in D₂O measured at 300 MHz at 70°C

Protons	Chemical Shift (ppm)	Intensity (T ₁) S
H1	4.930, 4.768	0.99
H2	2.911	1.00
H3,4,5,6,6'	4.66, 4.610, 4.577, 3.644	1.33, 0.34
N-acetyl	1.952, 1.820	0.34

intensity of all the 7 protons included in a pyranose ring is divided by 7, but in this work, 6 protons were used to avoid possible error in estimating 1' integral intensity. If we use the integral intensity shown in figure, somewhat (2-3%) lower D_{deac} value may be obtained as calculated, because the overlap portions due to HOD cannot be evaluated [22].

3.5 Characterization by Infrared Spectroscopy

IR studies were made on chitosan beads before and after being in contact with Cd²⁺ solutions. The IR spectra recorded for chitosan beads (Fig. 5) and chitosan beads in contact with Cd²⁺ solutions (Fig. 6) at pH 2.0 show that there is remarkable difference between the two. Similar results were obtained, with pure chitosan powder and chitosan powder in Cd²⁺ solution at pH 3.0.

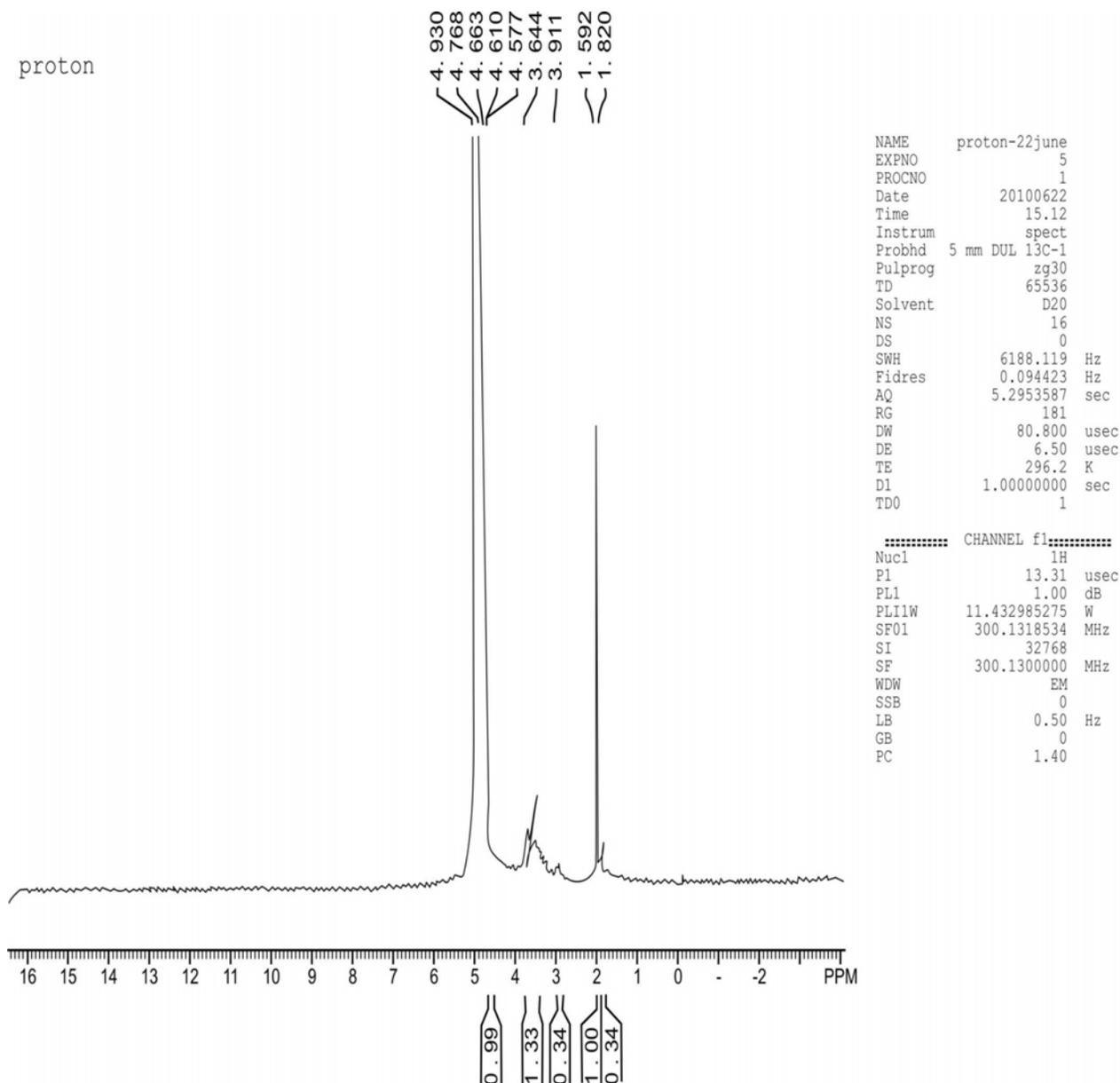


Fig. 4: 300 MHz ^1H NMR spectrum of chitosan beads with degree of deacetylation 75% in D_2O at 70°C

Infrared spectrum analysis reveals that the band at 3433 cm^{-1} is due to the elongation of N-H and O-H bonds, therefore it can be assigned to several functional groups present in the sample as $-\text{NH}_2$ primary amines, R_2NH secondary amines and alcoholic group [23]. The band at 2925 cm^{-1} is due to C-H ($-\text{CH}_3 > \text{CH}_2$) bond elongation, this band is characteristic of materials with saturated carbons or sp^3 type hybridisation. The band at 1660 cm^{-1} is characteristic of the $>\text{C}=\text{O}$ bond of an amide which

was expected, since the chitosan was prepared from chitin by partial deacetylation. The band at 1654 cm^{-1} is due to the flexion of amine and amide N-H bond plus the band observed at 1419 cm^{-1} is caused by the bond flexion of methyl (or groups of $-\text{CH}_2$). Also the band around 1500 cm^{-1} is due to the N-H bond flexion.

The difference between the IR spectra of chitosan before and after the cadmium was adsorbed

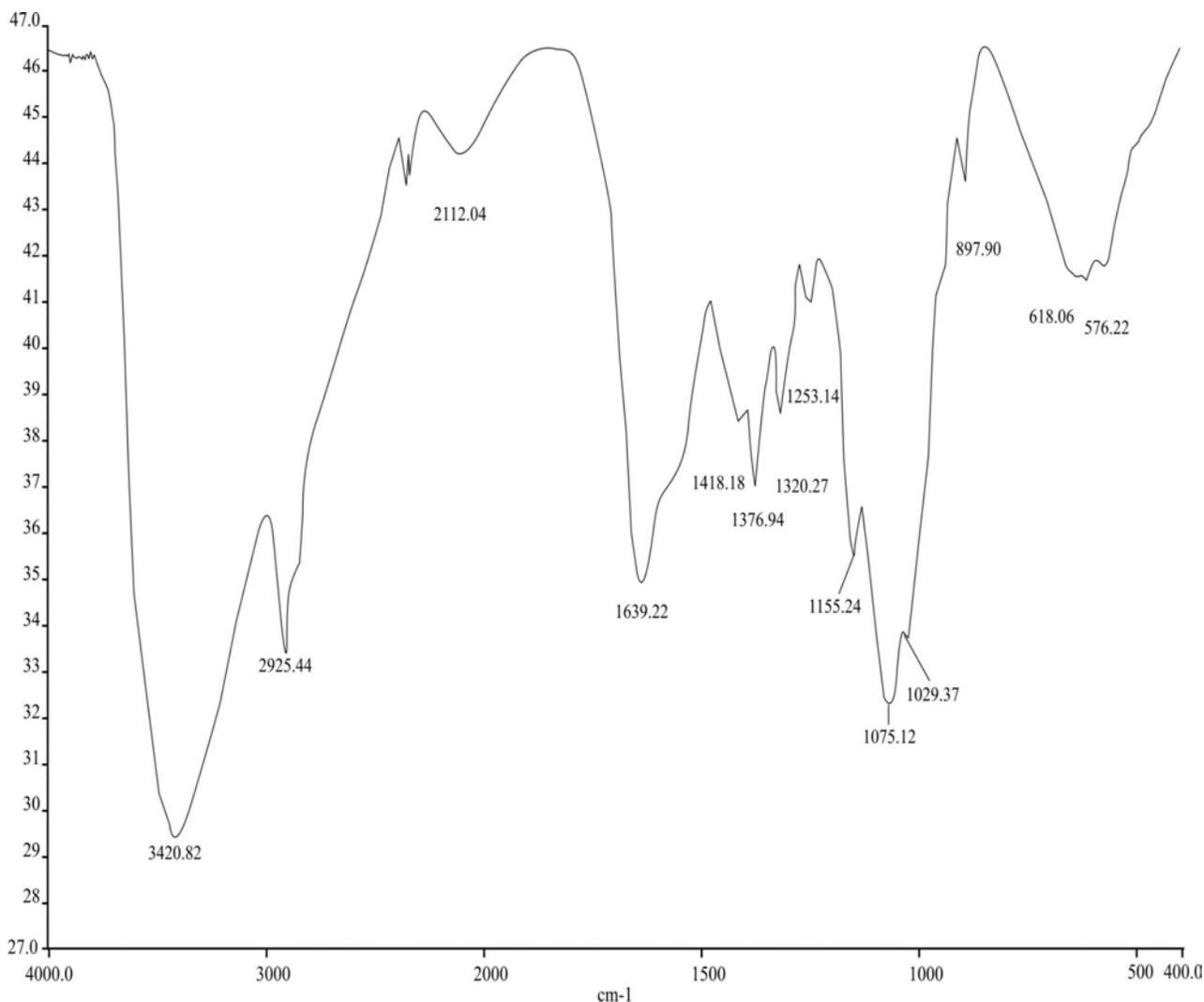


Fig. 5: IR spectrum of pure chitosan beads

is a wide band at 3433 cm^{-1} , which is assigned to amines that changed very much in intensity due to vibration of the N-H bond and is modified while forming a bond between the nitrogen (by its free pair of electrons) and the metal. The band at 1654 cm^{-1} is also assigned to N-H bond that is decreased considerably in intensity and was displaced to 1639 cm^{-1} .

There are several bands in the IR spectrum that neither present a reduction in their intensity nor change position, this indicates that the metal does not associate with the functional groups that generate these bands. Results from IR spectrograph suggest that a coordination complex is formed between the

chitosan and the metal with the participation of the amino and secondary alcohol functional group. It suggests that the metal predominantly associates with $-\text{NH}_2$ and $-\text{OH}$ of secondary alcohols. No participation of $-\text{CH}_2\text{OH}$ is observed.

3.6 Adsorption Isotherm: Langmuir Equilibrium

Adsorption experiment involving Cd(II) metal was carried out to determine the chitosan adsorption capacity and its selectivity. Experiment was performed at pH 3.5 and 4. The bioadsorbent was stirred with fixed volume of metal ion solution varying the initial concentration in the equilibrium time. The experimental equilibrium isotherm for

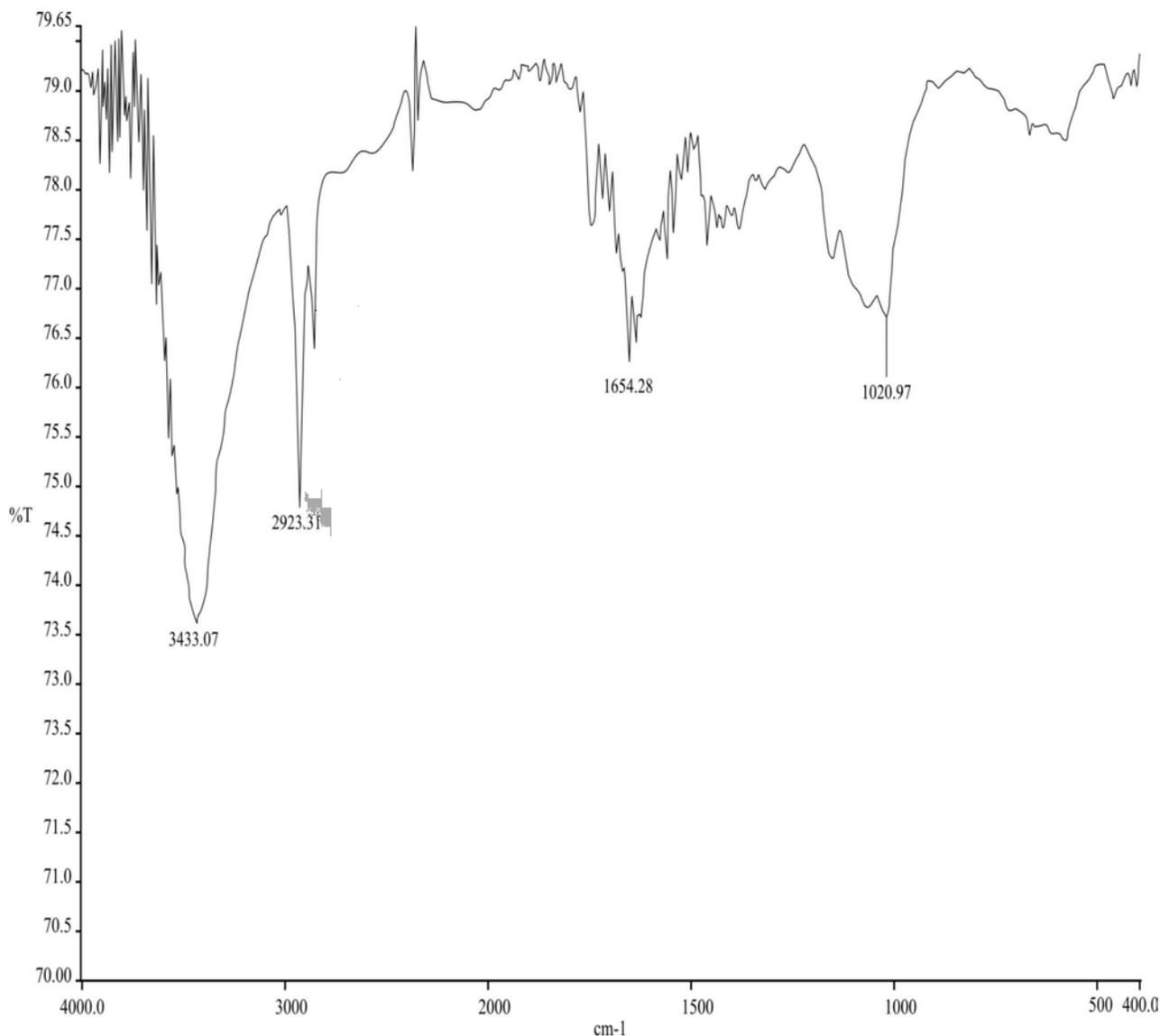


Fig. 6: IR spectrum of chitosan beads after being in contact with cadmium chloride solution

adsorption of Cd (II) on chitosan can be described with the Langmuir adsorption [24] equation (4):

$$C_e/X = [C_e/X_{max}] + [(1/X_{max})b] \quad (4)$$

where, C_e is the equilibrium or final concentration of Cd(II) in ppm, X is the amount of Cd(II) adsorbed per unit weight of chitosan beads at maximum adsorption at monolayer coverage (mg g^{-1}) and b is the Langmuir adsorption equilibrium constant (ml mg^{-1}). Cadmium with positive charge can easily occupy surface binding sites at nitrogen of chitosan whereas the water molecule cannot due to the

presence of lone pair of electrons.

A linearized plot of C_e/X versus C_e (Fig. 7), was used to calculate the adsorption constants X_{max} , 86.9 mg g^{-1} and b , 4.5 ml mg^{-1} . The beads under the concentration range were studied (correlation coefficient, $r > 0.99$).

It has been reported that the isotherm shape can be used to predicting if an adsorption system is favourable or unfavourable. The essential feature of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or

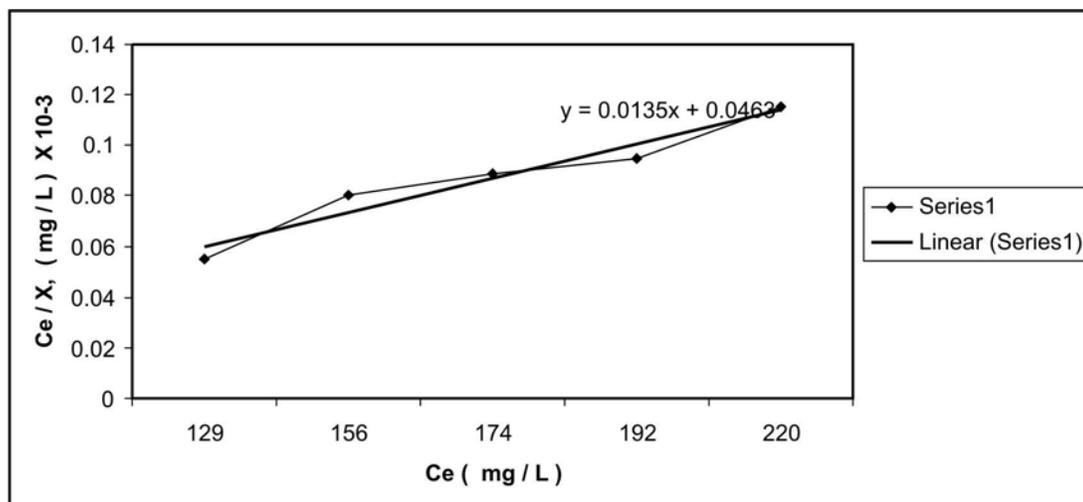


Fig. 7: A linear plot of C_e / X versus C_e to calculate X_{max} and b values

equilibrium parameter, R_L which is calculated from equation (5) : $4.74 \times 10^{-4} = 0.0869 / 183.32$

$$R_L = [1 / (1 + b \cdot C_0)] \quad (5)$$

where, C_0 is the initial Cd (II) concentration, mg L^{-1} and b is Langmuir adsorption equilibrium constant (ml mg^{-1}). The parameter values, R_L indicate the isotherm shape according to the Table 6.

Table 6: Effect of separation factor on isotherm shape

S.No.	R_L	Type of isotherm
1.	$R_L > 1$	Unfavorable
2.	$R_L = 1$	Linear
3.	$0 < R_L < 1$	Favorable
4.	$R_L = 0$	Irreversible

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Conclusion

This study shows that chitosan, particularly of medium molecular weight, absorbs heavy metals in particular cadmium ions, and hence can be used to remove not only cadmium but also other heavy metals from aqueous effluents. Chitosan used in this study is more soluble at $3 > \text{pH} > 7$. Swelling behaviour of chitosan beads in acidic medium is much higher in comparison with alkaline medium. Moreover, desorption studies illustrated that adsorbed metal ions can be recovered under acidic condition; the amount of cadmium desorbed is a function of H^+ concentration.

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