

Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater

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Abstract

Chitosan was chemically modified by introducing xanthate group onto its backbone using carbondisulfide under alkaline conditions. The chemically modified chitosan flakes (CMC) was used as an adsorbent for the removal of cadmium ions from electroplating waste effluent under laboratory conditions. CMC was found to be far more efficient than the conventionally used adsorbent activated carbon. The maximum uptake of cadmium by CMC in batch studies was found to be 357.14 mg/g at an optimum pH of 8.0 whereas for plain chitosan flakes it was 85.47 mg/g. Since electroplating wastewater contains cyanide in appreciable concentrations, interference of cyanide ions in cadmium adsorption was found to be very significant. This problem could be easily overcome by using higher doses of CMC, however, activated carbon was not found to be effective even at higher doses. Due to the high formation constant of cadmium with xanthate and adsorption was carried out at pH 8, cations like Pb(II), Cu(II), Ni(II) and Zn(II) did not interfere in the adsorption. Dynamics of the sorption process were studied and the values of rate constant of adsorption were calculated. Desorption of the bound cadmium from CMC was accomplished with 0.01N H₂SO₄. The data from regeneration efficiencies for 10 cycles evidenced the reusability of CMC in the treatment of cadmium-laden wastewater.

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Keywords: Cadmium; Electroplating wastewater; Biosorption; Chitosan

1. Introduction

The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems [1]. These contaminants must be removed from wastewaters before discharge, as they are considered persistent, bioaccumulative and toxic [2]. Of special technical and economic importance is the selective removal of metals derived from the discharge from electrochemical activities into industrial wastewater. In comparison with other industries, the electrochemical industries uses less water, hence, the volume of wastewater produced is smaller, and the wastewater is highly toxic in nature because of the presence of high concentrations of metals such as copper, nickel, zinc, cadmium and cyanides. The use of cadmium cyanide baths in the electroplating industry generates a strong concern related to environmental impacts due to high cadmium and cyanide toxicity [3]. Adverse health

effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans [3]. To minimize these environmental impacts, wastewater treatment processes using biosorbents have attracted wide attention in recent years [4–6].

The use of chitosan as biosorbent for heavy metals offers a potential alternative to conventional methods such as chemical precipitation, ion exchange, electrochemical treatments, etc. Chitosan is a hydrophilic, natural cationic polymer and an effective ion-exchanger, with a large number of amino groups which are responsible for the high adsorption property of chitosan. The oxygen atom in the hydroxyl group of the chitosan can be classified as a hard ligand group having less affinity for heavy metals according to the HSAB (hard and soft acids and bases) classification system [7]. If soft ligand groups such as sulfur can be introduced on to the chitosan backbone, it will increase the uptake capacity for many heavy metals because cadmium can be classified as soft acids, which have a strong affinity to soft ligands. Since sulfur has a very strong affinity for most heavy metals, the metal–sulfur complex is very stable in basic

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conditions [8]. The use of materials with surface functional groups, such as xanthate group, shows improved selectivity for the removal of heavy metals in wastewater [9].

For this purpose, we have developed [10] an effective, simple and low cost alternative employing chelating agent with xanthate groups incorporated on chemically modified chitosan flakes (CMC). This modified chitosan can further enhance the metal binding capacities of chitosan. Comparative evaluation of CMC with plain flakes (PF) and activated carbon (AC) was investigated. Influence of the presence of different ions such as: sulfate, chloride, carbonate, cyanide and other cations at various initial concentrations on cadmium sorption by CMC, in batch conditions were studied. The present study also explores the possibilities of recycling the electroplating wastewaters free of cadmium ions. The economic and environmental advantages of recycling and reusing waste make CMC adsorbent an attractive treatment option.

2. Materials and methods

2.1. Materials

Chitosan flakes was purchased from Sigma Chemicals and used in the present study without any further purification. The degree of deacetylation was reported to be 85% by the manufacturer. Glutaraldehyde and carbondisulfide were purchased from Sigma–Aldrich and used without further purification. Stock

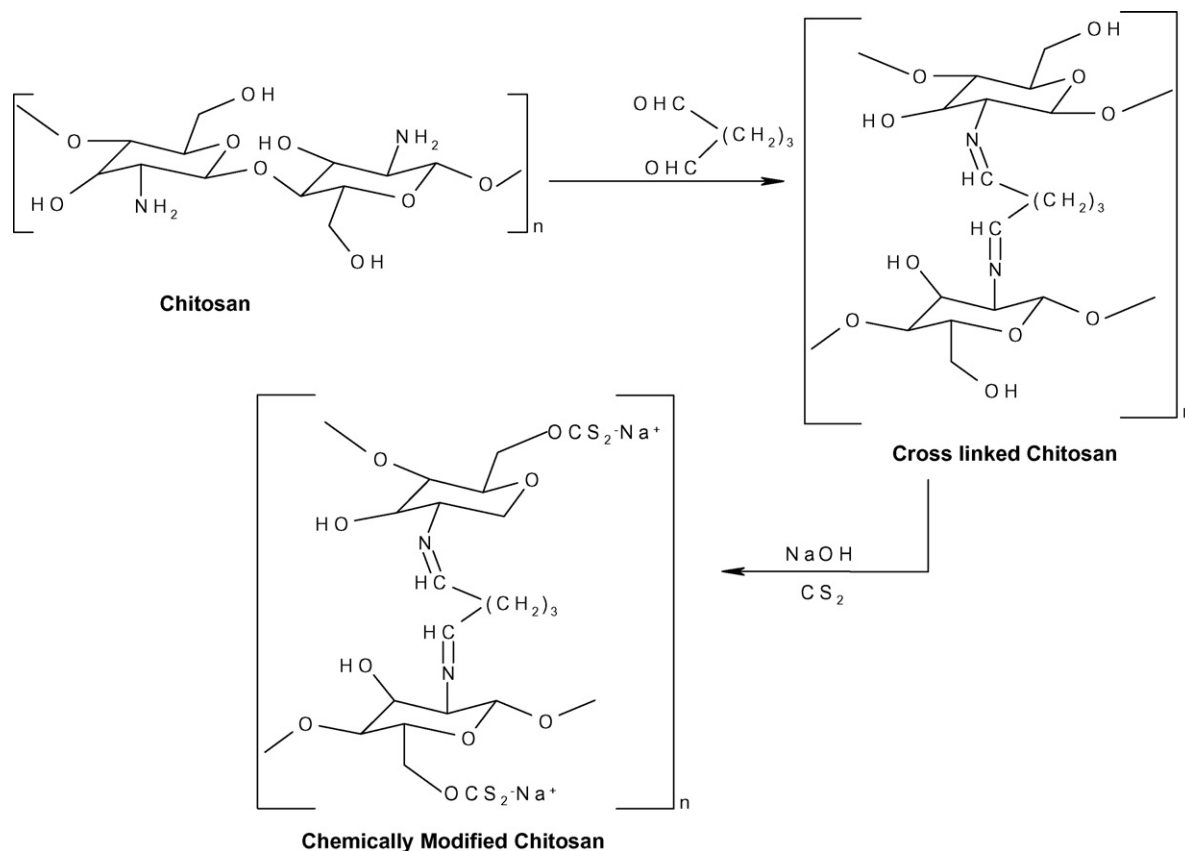
solution of Cd(II) was prepared using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (BDH chemicals). All the inorganic chemicals used were analar grade and all reagents were prepared in Millipore milli-Q deionised water.

2.2. Chemical modification of the chitosan flakes (CMC)

Chitosan flakes were cross-linked with glutaraldehyde and chemically modified (Scheme 1) and characterized as described earlier [10]. To obtain 20% cross-linking [11], chitosan flakes (ca. 0.5 g) were suspended in methanol (100 ml), and a 25% aqueous glutaraldehyde solution (0.046 ml, 0.12 mmol) was added. After stirring at room temperature for 6 h, the product was filtered. Cross-linked chitosan flakes (0.5 g) were treated with 25 ml of 14% NaOH and 1 ml of CS_2 . The mixture was stirred at room temperature for 24 h. The obtained orange product, cross-linked chemically modified chitosan flakes were washed thoroughly with water, air-dried and used for further experiments.

2.3. Metal concentration analysis

Dissolved cadmium was determined by Analyst 400 Perkin-Elmer Atomic Absorption Spectrophotometer using an air–acetylene burner. The measurements were done at wavelength 228.8 nm using a slit width of 0.7 nm. Experimental samples were filtered using Whatman 0.45 mm filter paper and



Scheme 1. Chemical modification of plain chitosan flakes.

the filtrates after suitable dilutions, were analyzed. Control experiments showed that no sorption occurred on either glassware or filtration systems. All assays were carried out in triplicate and only mean values are presented.

2.4. Wastewater samples

The samples were acquired from a local electroplating industry located in Kanpur City, U.P., India, during September 2005. The wastewater samples were analyzed promptly after collection using standard analytical methods [12]. The characteristics of electroplating wastewater were: color, colorless; pH 11.1; TDS, 55,292 mg/l; TSS, 5397 mg/l; cadmium, 1570 mg/l; cyanide, 3322 mg/l; sulfate, 1784 mg/l; carbonate, 50,312 mg/l.

2.5. Cadmium adsorption batch experiments

Batch experiments were carried out with synthetic solutions of cadmium in 100 ml flasks with stopper at 100 rpm of orbital stirring in an incubator shaker, at room temperature and 16 h of contact time with the adsorbent. Samples were then filtered with Whatman No. 42 filter paper, diluted and analyzed for Cd(II). Unless otherwise stated, the parameters with synthetic water were: sample volume, 20 ml; sorbent dose, 5 g/l; initial metal ion concentration, 100 mg/l; pH 8; equilibration time, 16 h. For pH studies, the pH was varied from 2 to 10 keeping the other conditions the same. For the effect of initial adsorbent dose, the doses were varied from 0.25 to 9 g/l. For kinetic studies, the sample volume was maintained at 50 ml and at every 1 h sample was withdrawn for analysis. For equilibrium studies, the adsorbent dose was minimized to 0.5 g/l varying the initial Cd concentration from 10 to 100 ppm. The adsorbents used were all sieved through a sieve of 0.4–0.6 mm particle size range.

2.6. Studies with real electroplating wastewater

The effect of sorbent dose and sorption–desorption studies were carried out with real electroplating wastewater whereby the sorbent dose was varied from 1 to 50 g/l keeping the other conditions same as with synthetic wastewater. Since the electroplating wastewater had very high concentrations of cadmium, it was diluted before use to the working range.

Sorption–desorption studies were carried out for 10 cycles whereby the adsorption conditions were same as for synthetic wastewater and the stripping solutions used for desorption studies were distilled water, 0.01N HCl, 0.01N EDTA and 0.01N H₂SO₄ with shaking time 2 h.

2.7. Effect of other ions

The effect of anions were studied using sulfate, chloride, carbonate and cyanide with varying concentrations from 0.1 to 5 g/l keeping other conditions same as that with synthetic wastewater. The effect of cations were studied using 100 mg/l solution of Cu²⁺ (CuSO₄·5H₂O), Pb²⁺ (Pb(NO₃)₂), Zn²⁺ (ZnSO₄·7H₂O) and Ni²⁺ (NiSO₄·7H₂O) either alone or in combination as given in Table 6.

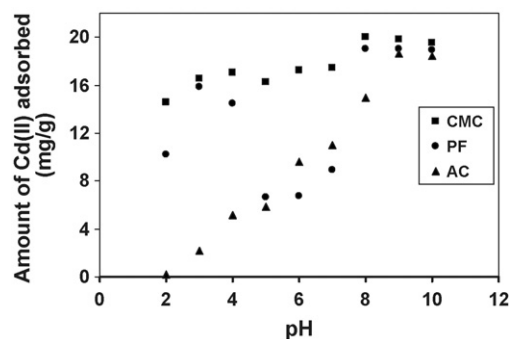


Fig. 1. Effect of initial pH on cadmium adsorption: sample volume, 20 ml; sorbent dose, 5 g/l; initial pH 2–10; Cd²⁺ conc., 100 mg/l; equilibration time, 16 h.

3. Results and discussion

3.1. Effect of pH

A pH effect test is performed to determine the pH of adsorption at which maximum uptake of metal occurs. The pH from 2 to 10 was adjusted initially with either hydrochloric acid or sodium hydroxide (0.1 M). No efforts were made to maintain the pH throughout the adsorption procedure. The removal increased from 81.5 to 99.9% with increase of pH from 6.0 to 8.0 and thereafter a slight decline in removal was observed with increase in pH (Fig. 1). The optimum pH for the removal of Cd(II) by chitosan flakes as well as by CMC was found to be 8.0. In the case of AC, maximum removal was found to be pH 9. Hence, further experiments were conducted at pH 8 for CMC and PF and pH 9 for AC. Uptake of cadmium even at lower pH values could be attributed to the change in initial pH (Fig. 2). At lower pH values, due to inherent alkalinity present in CMC, within 10 min of equilibration time the initial pH increased sharply and attained equilibrium after 30 min (Fig. 2). A similar trend was observed with plain flakes (results not shown). The results obtained for the plain flakes was in agreement with an earlier report where around 80% removal was observed at pH 4 [13]. When the experiments were conducted at pH 3 using citrate buffer, adsorption of cadmium by CMC reduced from 80 to 50%. This could be attributed to two factors. First, protonation of amine groups and the unavailability of amine groups for complexation with cadmium and second, H⁺ ions compete with cadmium ions to same

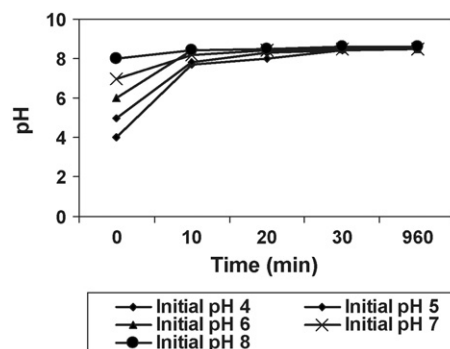


Fig. 2. Change in pH with time: sample volume, 20 ml; sorbent dose, 5 g/l; initial pH 4–8; Cd²⁺ conc., 100 mg/l; equilibration time, 16 h.

Table 1
Cadmium speciation with pH

pH	Cadmium species
<7	Cd ²⁺
7–8.6	Cd(OH) ⁺
>8.6	Cd(OH) ₂

binding sites on the adsorbent. From Table 1, it is evident that at pH 8 cadmium predominantly exists as Cd(OH)⁺ species. Hydroxy metal complexes are known to adsorb with a higher affinity than the completely hydrated metals because the formation of an OH group on the metal reduced the free energy requirement for adsorption [14]. Therefore, it seems that the adsorption of cadmium ions can be related to the change in the availability of Cd(OH)⁺. The pK_a of xanthate–xanthic acid dissociation constant is reported to be 1.70. Thus, in the pH range used in the present study, the characteristics of surface group of the adsorbent are unlikely to change.

3.2. Effect of initial adsorbent dose

It is evident from Fig. 3 that for lower adsorbent doses, CMC is adsorbent of choice and shows complete removal of Cd(II) at around 4 g/l. The efficiency of PF and AC were comparable and could achieve complete removal at a higher dose of around 7 g/l.

3.3. Sorption kinetics

The kinetics of cadmium removal by PF and CMC indicated rapid binding of cadmium by the sorbent during the first few minutes followed by a slow increase until a state of equilibrium is reached. The necessary time to reach this equilibrium was 16 h and further increase in equilibration time up to 24 h showed no change in the uptake capacity. Hence, the equilibrium time was maintained at 16 h in subsequent analysis. These observations were in agreement with the work reported earlier with the other metal ion–biomaterial systems [15].

Kinetics of heavy metals adsorption was modeled by the pseudo second-order equation [16]:

$$\frac{t}{q_t} = \frac{1}{k'q_e^2} + \frac{t}{q_e} \quad (1)$$

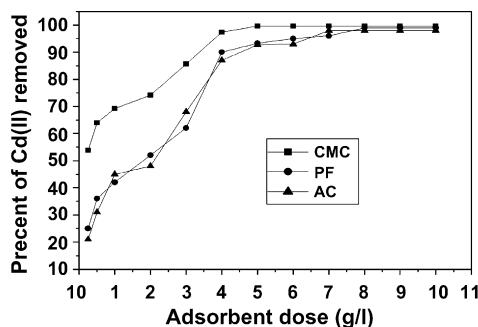


Fig. 3. Effect of adsorption dose on cadmium adsorption: sample volume, 20 ml, sorbent dose, 0.25–9 g/l; initial pH 8; Cd²⁺ conc., 100 mg/l; equilibration time, 16 h.

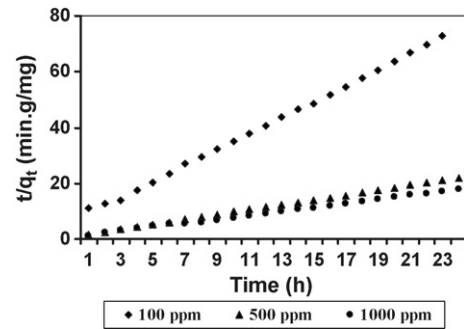


Fig. 4. Pseudo second-order plot of CMC with cadmium(II): sample volume, 50 ml; sorbent dose, 0.5 g/l; initial pH 8; Cd²⁺ conc., 100, 500 and 1000 mg/l; equilibration time, 1–24 h.

Table 2
Pseudo second-order sorption kinetics of Cd(II) by CMC

Conc. (mg/l)	R ²	k' (g/mg/min)
100	0.9991	0.622
500	0.9996	0.442
1000	0.9974	0.280

where k' is the pseudo second-order rate constant of adsorption (g/mg/min) and q_e and q_t are the amounts of metal ion sorbed (mg/g) at equilibrium and at time t , respectively. Linear plots of t/q_t versus t for CMCF for 100, 500 and 1000 mg/l of cadmium are shown in Fig. 4. The results obtained for the model are also furnished in Table 2. It is evident from the table that the prepared adsorbent followed pseudo second-order kinetics for the concentration range studied.

3.4. Sorption equilibrium

Sorption isotherms are modeled using Langmuir model represented by Eq. (2) and shown in Fig. 5.

$$q_{eq} = q_{max} \left(\frac{bC_{eq}}{1 + bC_{eq}} \right) \quad (2)$$

where q_{eq} is the equilibrium adsorbate loading on the adsorbent, C_{eq} the equilibrium concentration of the adsorbate, q_{max} the ultimate capacity and b is the relative energy (intensity)

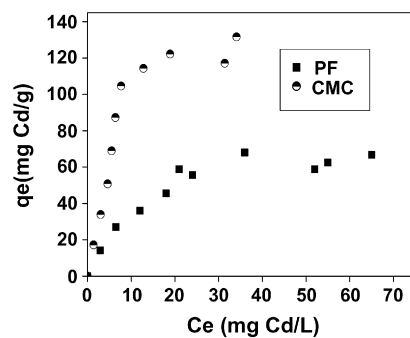


Fig. 5. Sorption isotherms of plain and chemically modified chitosan flakes: sample volume, 20 ml; sorbent dose, 0.5 g/l; initial pH 8; Cd²⁺ conc., 0–100 mg/l; equilibration time, 16 h.

Table 3
Adsorption capacities of cadmium by various biosorbents

Source of the material	Adsorption capacity (mg/g)	Reference
Xanthated chitosan	357.1	Present work
Chitosan flakes	5.93	[12]
Chitosan beads	250.0	[17]
<i>Cystoseira baccata</i>	77.0	[18]
<i>Gelidium</i> algae	18.0	[19]
<i>Streptomyces clavuligerus</i>	28.0	[20]
<i>Saccharomyces cerevisiae</i>	<5	[4]
<i>Aspergillus oryzae</i>	30	[4]
<i>Bacillus lentus</i>	30	[4]
<i>Phomopsis</i> sp.	26	[5]
Ceiba pentandra hulls	19.5	[6]
Loofa sponge	89	[22]

of adsorption, also known as binding constant. CMC exhibit approximately four times the capacity for uptake compared to the plain flakes. Maximum adsorption capacities were 357.1 and 85.5 mg Cd/g for modified and plain flakes, respectively. These values are considerably higher than those obtained on activated carbon, natural materials and loofa sponge [6,19,22]: sorption capacities in these cases are less than 75 mg Cd/g of the sorbent (Table 3). According to HSAB theory, soft bases tend to form stable complexes with metals such as Cd^{2+} , Pb^{2+} and Cu^{2+} [7]. Since xanthate groups can be classified, as soft bases xanthated chitosan will have a much higher affinity and sorption capacity when compared to that of plain chitosan. The strong affinity between sulfur and cadmium may result in high affinity constant and hence high uptake capacity. The results of the various Langmuir constants including the q_{max} , b and R^2 values are presented in Table 4.

3.5. Effect of cations and anions

In wastewater streams, the metal of interest is usually found in a matrix containing several metal ions [21]. These ions can interact with heavy metals and thus modify their behavior towards the sorbent material used. The sorption performance of adsorbent towards a given ion in solution could therefore vary. Some anions can have an affinity towards the metal, so that they form an insoluble or soluble complex, displaced with difficulty in the presence of the sorbent material [21]. So, the role of anions (Cl^- , SO_4^{2-} , CN^-) possibly present in electroplating wastewater in cadmium adsorption by CMC was investigated. Cadmium sorption can be inhibited only by anions forming sufficiently stable complexes. Stability constants ($\log k$) of cadmium with Cl^- , SO_4^{2-} , CO_3^{2-} , CN^- and xanthate are 1.98, 2.4, 4.02, 18.78 and 14.55, respectively [18,23–25]. As expected from the low stability constant values of chloride, sulfate and carbonate they

Table 4
Isotherm constants and correlation coefficients for biosorption of Cd(VI) ions from aqueous solutions

Sorbent	Langmuir constant			Freundlich constant		
	q_{max} (mg/g)	b (ml/mg)	R^2	n	k_f	R^2
Plain flakes	85.47	0.036	0.9958	14.47	27.70	0.7505
CMC	357.14	0.066	0.9774	11.46	29.83	0.8255

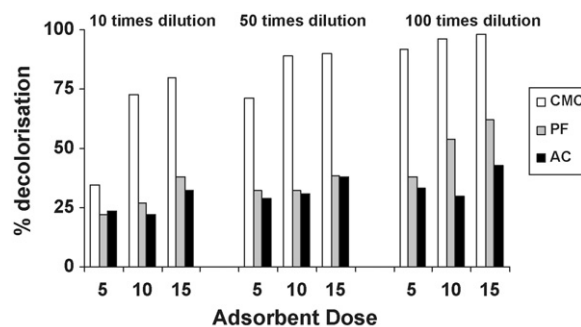


Fig. 6. Effect of adsorbent dose and dilutions on cadmium removal from electroplating wastewater: sample volume, 20 ml; sorbent dose, 5, 10 and 15 g/l; initial pH 8; equilibration time, 16 h.

did not have much effect on the adsorption behavior of cadmium (Table 5). However, the influence of cyanide ions on the sorption kinetics of cadmium is significantly marked. Even the presence of low concentration of cyanide in the range of 0.1 g/100 ml was found to substantially decrease the adsorption capacity of CMC to one-half whereas at higher concentrations, no amount of cadmium could be adsorbed by CMC.

To study the applicability of cadmium in real wastewater samples effect of other cations on the adsorption behavior of cadmium were also studied. The results obtained are given in Table 6. For a mixed-metal solutions, the hierarchy of xanthate precipitation is in the following order: $\text{Cu}^{2+}-\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+}-\text{Mg}^{2+}-\text{Mn}^{2+} \gg \text{Na}^+$ [26]. Under alkaline conditions (pH 8), the metal ions Pb^{2+} , Hg^{2+} and Cu^{2+} which have higher formation constant than cadmium precipitate as hydroxides and does not interfere in the adsorption.

3.6. Effect of adsorbent dose and adsorption in electroplating wastewater

Interference of cyanide ions in cadmium adsorption was found to be significant (Table 5) and since electroplating wastewater contains cyanide in appreciable concentration (cadmium: 1570 mg/l; cyanide: 3322 mg/l), studies were conducted with the wastewater by increasing the adsorbent dose. Experiments were also conducted with PF and AC to compare the removal efficiency with the prepared adsorbent (Fig. 6). When electroplating wastewater was used without dilution, cadmium removal was not observed in all the three adsorbents (AC, PF and CMC). So, the wastewater was diluted to a working range. From Fig. 6, it is evident that at 10 times dilution CMC could remove 76% Cd(II) only at a high adsorbent dose of 15 g/l whereas PF and AC could not go beyond 28% (with synthetic solutions of 100 ppm and

Table 5
Effect of anions on Cd(II) adsorption

Conc. of anions (g/100 ml)	Amount of cadmium adsorbed/gram of adsorbent (mg/g)			
	Sulfate	Chloride	Carbonate	Cyanide
0.1	19.98	19.99	19.99	10.10
0.2	19.96	19.98	19.89	2.20
0.5	19.84	19.78	19.99	0.00
0.8	19.56	18.88	18.98	0.00
1.0	18.86	18.79	18.89	0.00
2.0	18.46	18.68	19.79	0.00
3.0	17.88	17.69	19.79	0.00
4.0	17.89	17.77	19.79	0.00
5.0	17.99	17.89	19.88	0.00

Sample volume, 20 ml; sorbent dose, 5 g/l; initial pH 8; equilibration time, 16 h.

adsorbent dose of 5 g/l: 100% removal for CMC and around 93% for PF and AC was achieved). With further increase in dilutions, CMC could attain almost complete removal but at a higher adsorbent dose. The interference of cyanide ions is well marked by the fact that even 100 times dilutions could not enhance the performance of AC at higher adsorbent dose. However, PF did show some improvement at increased dilution and increased adsorbent dose.

The study revealed that influence of cyanide ions could be overcome by CMC but only at a higher adsorbent dose. The prepared adsorbent was found to be very efficient compared to the commercially available AC.

3.7. Desorption studies

Desorption studies were carried out with various solutions namely distilled water, 0.01N HCl, 0.01N EDTA and 0.01N H₂SO₄. Among these stripping solutions, it was observed only 30% of the loaded Cd(II) stripped in 0.01N EDTA and 0.01N HCl and 80% stripped with 0.01N H₂SO₄. Hence, further experiments were carried out only with 0.01N H₂SO₄ solutions. The study also revealed that 2 h of equilibration time was sufficient for the quantitative stripping. After the optimization of the stripping conditions, the adsorbent/desorption cycles were repeated for 10 cycles using 0.1 g of the adsorbent and 20 ml of electroplating wastewater for adsorption and desorption was carried out with 20 ml of 0.01N H₂SO₄. The results obtained are furnished in Fig. 7. Cadmium adsorption remained unaltered up to

Table 6
Effect of cations on Cd(II) adsorption

S. no.	Cations ^a	Amount of Cd(II) adsorbed/gram of adsorbent (mg/g)
1	Cd ²⁺	19.85
2	Cd ²⁺ and Zn ²⁺	18.80
3	Cd ²⁺ and Ni ²⁺	19.70
4	Cd ²⁺ and Pb ²⁺	19.40
5	Cd ²⁺ and Cu ²⁺	19.70
6	Cd ²⁺ , Pb ²⁺ and Zn ²⁺	19.80
7	Cd ²⁺ , Pb ²⁺ and Zn ²⁺	18.95
8	Cd ²⁺ , Cu ²⁺ , Pb ²⁺ , Zn ²⁺ and Ni ²⁺	19.85

Sample volume, 20 ml; sorbent dose, 5 g/l; initial pH 8; equilibration time, 16 h.

^a Concentration of cations added in these studies were 100 mg/l each.

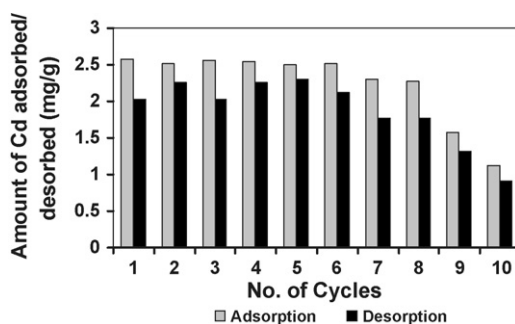


Fig. 7. Adsorption and desorption cycles: Adsorption—sample volume, 20 ml; sorbent dose, 5 g/l; initial pH 8; equilibration time, 16 h; Desorption—sample volume, 20 ml of 0.01N H₂SO₄; equilibration time, 2 h.

six cycles and thereafter there was a steady decline in adsorption. But by the end of the 10th cycle, the adsorption capacity reduced to almost one-half.

4. Conclusions

Chemical modification of the chitosan flakes with xanthate group increased the adsorption capacity to more than four times compared to the plain flakes. Adsorption followed Langmuir isotherm model. Adsorbent–adsorbate kinetics exhibited pseudo second-order. Due to the high stability constant of cadmium with xanthate group, interference from common cations and other electrolytes like sulfate, chloride and carbonate were not found. Cyanide ions were found to interfere even at low concentrations and this problem was conveniently overcome by using an increased adsorbent dose of CMC. However, by increasing the dose, appreciable enhancement was not observed in the performance of PF and AC. Applicability of the adsorbent in real electroplating effluent was successfully demonstrated for 10 adsorption and desorption cycles. The prepared adsorbent was found to be much more efficient than the commercially available activated carbon. The xanthated chitosan could be an excellent adsorbent for the removal and recovery of cadmium ions from electroplating wastewater where cyanide ions are the main interfering ions. This method is very promising compared to other conventional and generally more expensive processes.

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