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Removal of Chromium(VI) by Natural Polymer Chitin and Deacetylated Chitin from Aqueous Media

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Chitin and its deacetylated form has been used as adsorbent for the removal of Cr(VI) in aqueous media. The effect of various parameters influencing the Cr(VI) adsorption such as pH, initial metal ion concentration and adsorbent dose has been studied. The optimum pH for adsorption of Cr(VI) on chitin and deacetylated chitin was found to be 2.0 and 3.0 respectively. It has been found that metal removal percentage increases with adsorbent dose. Increase in initial metal ion concentration decreases the per cent removal, but the amount of Cr(VI) adsorbed per unit weight of adsorbent increases. It has been also found that deacetylated chitin shows greater potential for removal of Cr(VI) as compared to chitin. The data obtained from batch process was used to fit in Freundlich and Langmuir adsorption model.

Key Words: Natural polymer, Chromium(VI), Batch adsorption process, Polymer chitin, Deacetylated chitin.

INTRODUCTION

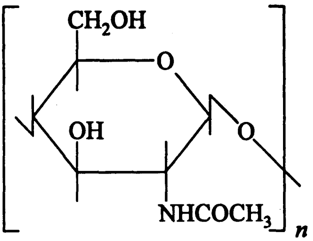
Chromium has been found at 1036 of 1591 National Priority List sites identified by the Environmental Protection Agency (EPA)[1]. It is introduced on to natural water or on to land through industrial discharge from chrome plating, aluminium anodizing, leather tanning, ink and pigment unit, lithography, photography and ceramic industries. The wastewater generated by these industries contains appreciable amount of chromium[2]. Chromium(VI) has received attention probably due to its toxicological potential which is well documented. However, in trace amount Cr(III) is an essential trace element in mammalian metabolism and together with insulin is responsible for the clearance of glucose from blood stream[3]. Due to the corrosive nature of Chromium(VI), it causes skin and mucous membrane ulceration usually observed among chrome plating workers[4]. Ingestion of large amount of Cr(VI) can cause stomach upsets, ulcers, convulsions, kidney and liver damage and even death. Cr(VI) compounds can increase the risk of lung cancer. The World Health Organisation (WHO) has determined that Cr(VI) is a human carcinogen[1]. In view of potential toxicity, efficient and economical methods for removal of Cr(VI) from wastewater are of vital significance. Various methods have been suggested for the treatment of Cr(VI) bearing wastewater include chemical reduction followed by precipitation[5], electrolytic separation[6], ion exchange[7], bacterial reduction[8] and bioaccumulation[9].

Adsorption is one of the widely used techniques for wastewater treatment. In most of the industries activated carbon has been used as adsorbent but it is expensive. Various low cost adsorbents such as tree bark[10], leaves[11], sawdust[12], onion skin[13], coalchar[14], coconut fibre pith based pseudo activated carbon[15], rice husk[16], sphagnum moss peat[17] and fly ash[18] has been reported for Cr(VI) removal. One of the most widely studied techniques for metal removal is chelation ion exchange. Some of the best chelating ion exchange materials are natural polymers such as cellulose, alginates, carrangeenan, lignins, proteins, chitin and chitin derivatives[19]. These substances are industrially attractive because they have excellent metal binding ability, wide availability and are environmentally safe. The natural polymer possesses a number of different functional groups containing oxygen and nitrogen atom to which metal ions can bind either by chemical or physical adsorption[20].

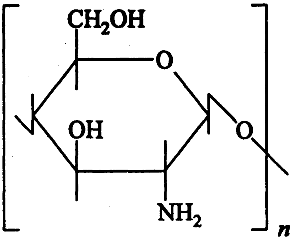
In the present communication an attempt has been made to assess the efficiency of chitin and deacetylated chitin for Cr(VI) removal from aqueous media.

EXPERIMENTAL

Chitin was procured from Loba Chem., Mumbai. Deacetylation of chitin was carried out by refluxing it with 40% NaOH for 3 h[21]. The product resulting from filtration of the reaction mixture was washed extensively with distilled water and air dried at room temperature prior to use. The product was characterized by IR spectrum which exhibits a strong band appearing as coupled doublet at 3424 cm^{-1} due to ν(—N—H) stretching of primary amine. The band at 2931 cm^{-1} is due to ν(C—H) stretching. The presence of band at 1640 cm^{-1} and 1155 cm^{-1} is due to the ν(N—H) bending vibration of primary amine and ν(C—O—C) or ν(C—N) stretching respectively.



Chitin



Deacetylated chitin

The stock solution of Cr(VI) was prepared by dissolving 0.282 g $K_2Cr_2O_7$ in 1000 mL distilled water. Batch adsorption experiments were carried out at room temperature. Different amounts of adsorbents (1, 2, 3 g/L) were agitated with 50 mL Cr(VI) solution of desired concentration. The initial pH of Cr(VI) solution was adjusted by digital pH-meter (model Equiptronics EQ 610) using either 0.1 N HCl or 0.1 N NaOH. Samples were withdrawn at appropriate interval of time and concentration of Cr(VI) remaining in solution was determined spectrophotometrically (model Systronics 118) after developing colour with 1,5-diphenylcarbazide.

RESULTS AND DISCUSSION

Effect of pH: The variation in the adsorption of Cr(VI) as a function of pH was studied over pH range 2–7 using 50 mL 5 mg/L Cr(VI) solution with adsorbent concentration 1 g/L. The removal of metal ion by adsorption is highly dependent upon pH of the solution, which affects surface charges of adsorbent, degree of ionization and speciation of adsorbate species. Cr(VI) forms stable complexes such as $Cr_2O_7^{2-}$, $HCr_2O_7^-$, CrO^-, $HCrO^-$; the fraction of any particular species is dependent upon concentration and pH of solution[22]. It is evident from Fig. 1 that maximum removal of Cr(VI) was obtained at pH 2 and 3 for chitin and deacetylated chitin respectively. At lower pH values nitrogen atom of N-acetyl (chitin) and amino (deacetylated chitin) functional groups present on adsorbent will be protonated and thus the adsorbents behave as an anion exchanger. At higher pH values a decrease in adsorption of Cr(VI) was observed, which may be due to the ionic repulsion between anionic sites of adsorbent surface and chromate ions. Mcafee *et al.*[23] reported maximum adsorption 39 mg/g of Cr(VI) at initial concentration of 50 mg/L with 1 g/L of chitosan at pH 3.

Effect of contact time of initial Cr(VI) concentration: Batch adsorption studies were conducted to determine variation in adsorption of Cr(VI) with initial concentration (5, 10, 20 mg/L). The equilibrium Cr(VI) concentration was determined at regular time interval (20 min) for both adsorbents at their respective optimized pH values. It was observed from Fig. 2(a & b) that the amount of Cr(VI) adsorbed increases rapidly initially; then the system approaches equilibrium within 120 min. At lower adsorbent dose (1 g/L) the amount of Cr(VI) adsorbed per unit weight of adsorbent increases from 0.726 to 2.250 mg/g and 4.585 to 16.5 mg/g on increasing the metal ion concentration from 5 to 20 mg/L for chitin and deacetylated chitin respectively. The colour of adsorbent changes from pale white to yellowish brown on adsorption of Cr(VI). The amount of Cr(VI) adsorbed increases (% removal decreases) at higher concentration, may be due to the fact that the total adsorption cited is limited for fixed adsorbent dose.

Effect of adsorbent dose: Effect of adsorbent (chitin and deacetylated chitin) dose on adsorption of Cr(VI) is shown in Fig. 3(a & b). The amount of chromium adsorbend per unit weight of adsorbent decreases with increase in adsorbent dose. This may be due to the fact that at lower adsorbent dose the adsorbate is more easily accessible. However, percentage removal increases with adsorbent dose because of increased surface area owing to the increase in the total number of adsorption sites resulting in higher Cr(VI) removal at fixed adsorbate concentration and contact time.

Adsorption isotherm: Freundlich and Langmuir model was used to find the pattern of adsorption by both adsorbents for Cr(VI) removal. The systems were equilibriated with adsorbent concentration of 1, 2 and 3 g/L for 120 min with different Cr(VI) concentration at room temperature. The logarithmic form of Freundlich equation is

$$\log \frac{X}{m} = \frac{1}{n} \log C_e + \log K$$

where X/m is the amount of Cr(VI) adsorbed per unit weight of adsorbent, C_e is the equilibrium concentration of Cr(VI). Freundlich constants K and 1/n represent the adsorption capacity and adsorption intensity respectively obtained from the plot. A linear plot (Fig. 4a & b) are obtained which indicate the applicability of Freundlich model for the present system. The value of n > 1 (Table-1) represents favourable adsorption of Cr(VI) on to chitin and deacetylated chitin. The adsorption intensity (1/n) for deacetylated chitin was found to be higher as compared to chitin. The value of adsorption capacity (K) decreases with increase in adsorbent dose while adsorption intensity increases (1/n). Similar trends of observations were reported by Baisakh and Patnaik[14] for Cr(VI) removal by coalchar.

The Freundlich equation can be used for calculating the amount of adsorbent required to reduce any initial concentration (C_0) to predetermined final concentration (C_e)

$$\log \frac{C_0 - C_e}{m} = \frac{1}{n} \log C + \log K$$

The linear form of Langmuir model is

$$\frac{C_e}{X/m} = \frac{1}{bV_m} + \frac{C_e}{V_m}$$

where C_e, X/m have the same meaning as described in Freundlich equation. Langmuir constants b and V_m represent adsorption bond energy and maximum adsorption density corresponding to a monolayer covering the surface of the adsorbent. The plot of $C_e/(X/m)$ with C_e yields straight line (Fig. 5a and b) indicating the applicability of Langmuir model. The Langmuir constants b and V_m were calculated from slope and intercept respectively and are given in Table-1. The maximum adsorption density V_m for deacetylated chitin was found to be higher than chitin. The value of V_m decreases with increase in adsorbent dose for both the adsorbents. The adsorption bond energy (b) was found to be in the ranges 0.0267–0.05003 and 0.5098–0.5527 for chitin and deacetylated chitin respectively.

TABLE-1
VALUES OF FREUNDLICH AND LANGMUIR CONSTANTS FOR ADSORPTION OF Cr(VI)

Absorbents	Absorbent dose (g/L)	Freundlich constants		Langmuir constants	
		K	n	V_m	b
Chitin	1	0.2398	1.2369	6.7159	0.0321
	2	0.2113	1.2212	3.8066	0.0503
	3	0.1905	1.2038	5.7570	0.0267
Deacetylated chitin	1	8.1283	1.6113	24.783	0.5401
	2	5.6234	1.4359	16.863	0.5527
	3	4.4668	1.3345	13.793	0.5098

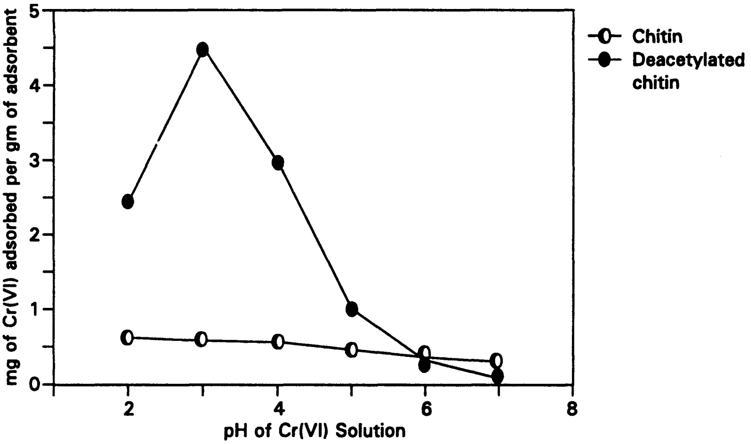


Fig. 1. Effect of pH on removed of Cr(VI)

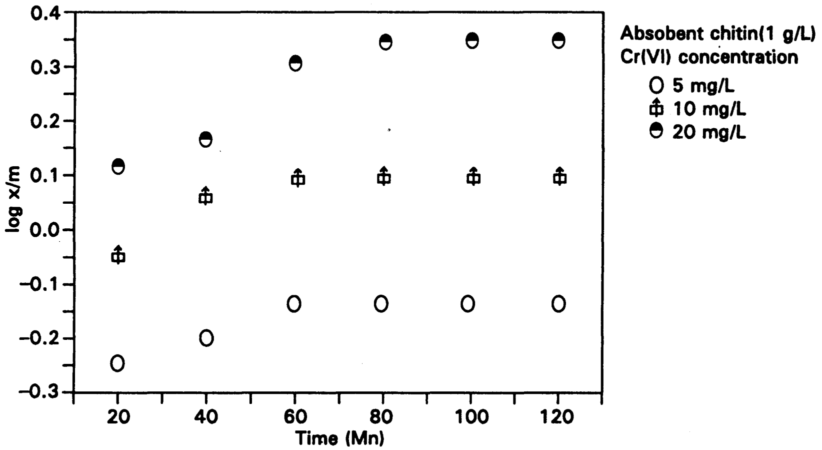


Fig. 2a. Effect of contact time and initial Cr(VI) concentration

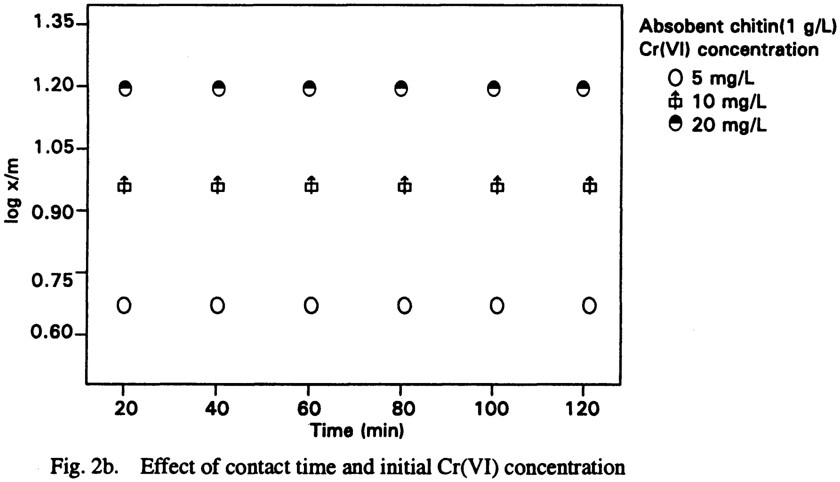


Fig. 2b. Effect of contact time and initial Cr(VI) concentration

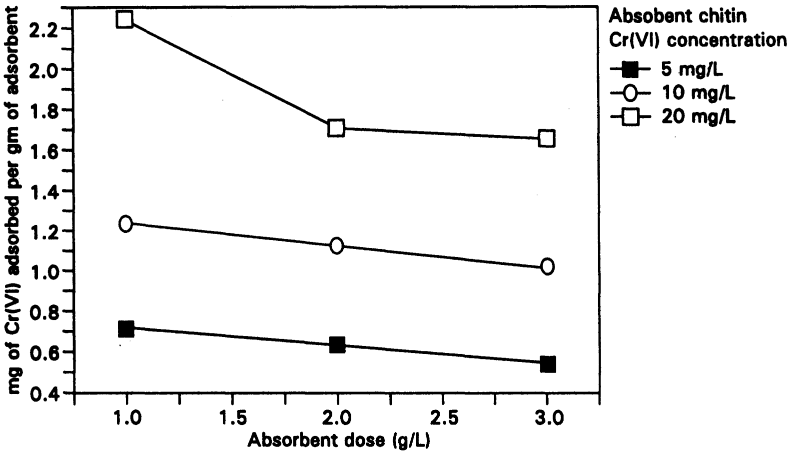


Fig. 3a. Effect of adsorbent dose on Cr(VI) removal

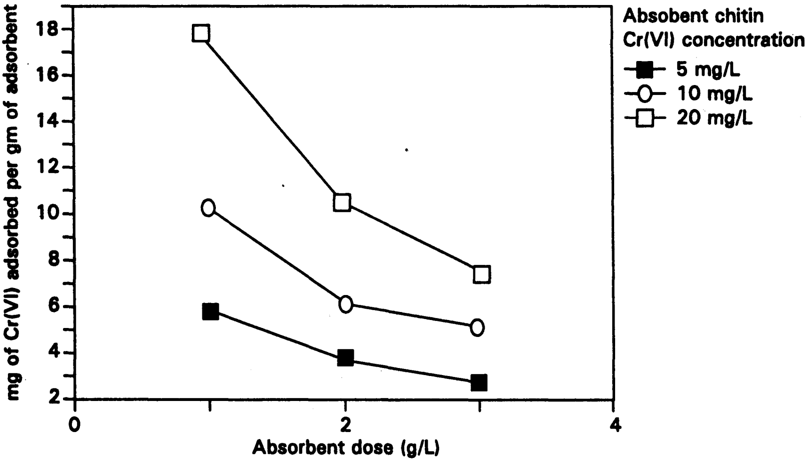


Fig. 3b. Effect of adsorbent dose on Cr(VI) removal

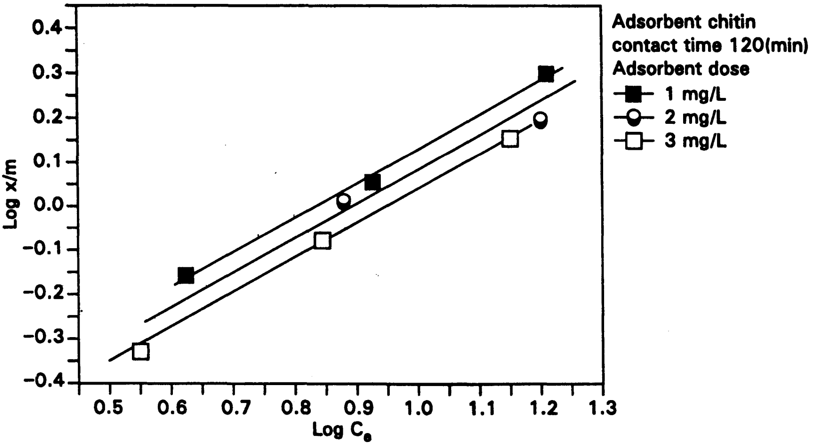


Fig. 4a. Freundlich plots for adsorption of Cr(VI)

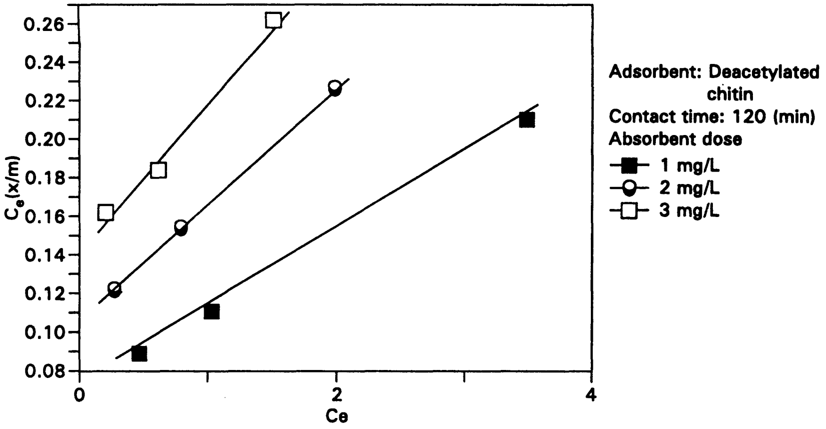


Fig. 4b. Freundich plots for adsorption of Cr(VI)

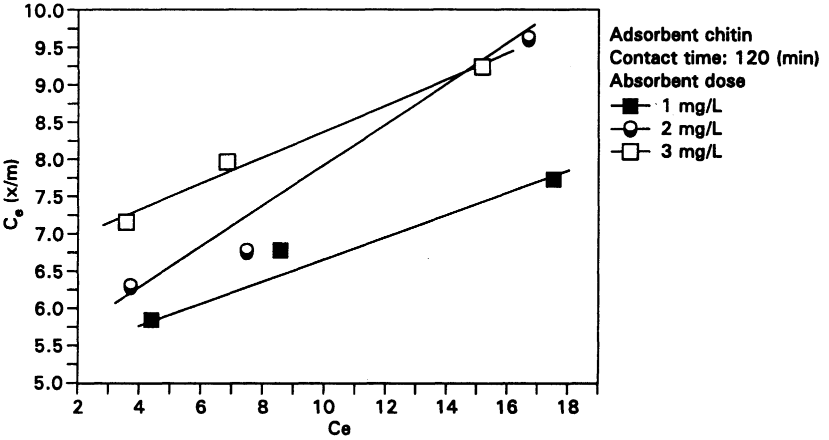


Fig. 5a. Langmuir plots for adsorption of Cr(VI)

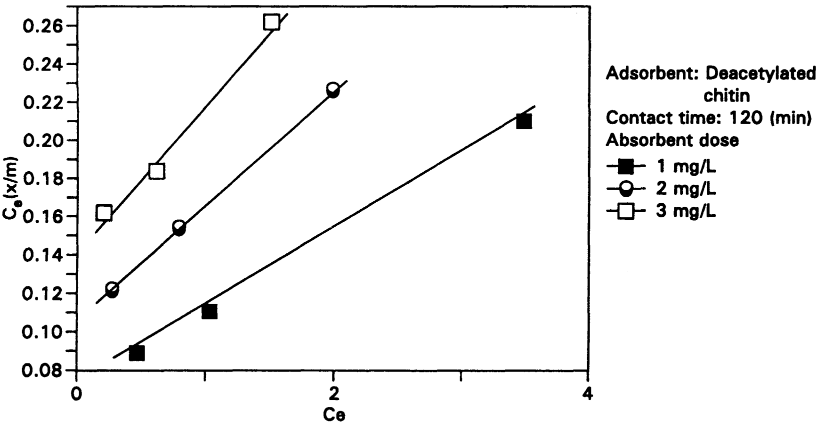


Fig. 5b. Langmuri plots for adsorption of Cr(VI)

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