

Hexavalent chromium removal from wastewater using aniline formaldehyde condensate coated silica gel

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Abstract

A resinous polymer, aniline formaldehyde condensate (AFC) coated on silica gel was used as an adsorbent in batch system for removal of hexavalent chromium from aqueous solution by considering the effects of various parameters like reaction pH, dose of AFC coated silica gel, initial Cr(VI) concentration and aniline to formaldehyde ratio in AFC synthesis. The optimum pH for total chromium [Cr(VI) and Cr(III)] adsorption was observed as 3. Total chromium adsorption was second order and equilibrium was achieved within 90–120 min. Aniline to formaldehyde ratio of 1.6:1 during AFC synthesis was ideal for chromium removal. Total chromium adsorption followed Freundlich's isotherm with adsorption capacity of 65 mg/g at initial Cr(VI) 200 mg/L. Total chromium removal was explained as combinations of electrostatic attraction of acid chromate ion by protonated AFC, reduction of Cr(VI) to Cr(III) and bond formation of Cr(III) with nitrogen atom of AFC. Almost 40–84% of adsorbed chromium was recovered during desorption by NaOH, EDTA and mineral acids. AFC coated silica gel can be effectively used for treatment of chromium containing wastewaters as an alternative.

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1. Introduction

Chromium is generated from various industrial processes like electroplating, leather tanning, wood preservations, manufacturing of dye, paint and paper [1]. Chromium exists in environment both as trivalent [Cr(III)] and hexavalent [Cr(VI)] forms. However, hexavalent form is five hundred times more toxic than the trivalent one and human toxicity of Cr(VI) includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage [2]. Adsorption is an effective and versatile method for removal of heavy metals when combined with appropriate desorption step solving the problem of sludge disposal [3]. During recent years, various low-cost and naturally available adsorbents like wool, saw dust, used tyres, seaweed, dead fungal biomass were used for removal of chromium [4–7]. However, many of these naturally available adsorbents have low chromium adsorption capacity and slow process kinetics. Thus, there is

the need to develop innovative low cost adsorbents with affinity towards metal ions for removal of chromium from aqueous solution in a relatively short period of time. Removal of heavy metal ions by functionalized polymer has become an important option in the integrated approach to wastewater treatment. Polyethyleneimine, polyvinylpyridine, composites of polyaniline and polystyrene, polyacrylonitrile fibers were used for removals of metal ions from aqueous solution [8–12]. Present laboratory-scale study aims at investigating the feasibility of using a polymer, named aniline formaldehyde condensate (AFC) for removal of hexavalent chromium from wastewater. Aniline formaldehyde condensate (AFC) is a resinous polymer with amine ($-NH_2$) groups, which can be easily synthesized by polymerization of aniline in presence of formaldehyde in acidic medium [13]. However, metal removal by AFC polymer is relatively few reported in literatures. Since, AFC polymer is in resinous form, effort was made in present work to synthesize a granular adsorbent by coating the polymer on silica gel for easier separation of chromium ions from aqueous solution after chromium–AFC interaction. Reaction pH, dose of adsorbent, initial concentration of Cr(VI) and aniline to formaldehyde ratio

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Table 1
Experimental design during present study

Experimental set	Variable parameter	Controlled parameter
1 ^a	Uncontrolled pH: initial pH 2.1	Initial Cr(VI): 100 mg/L; adsorbent dose: 8 g/L
2 ^a	Controlled pH: 2, 3, 4, 5, 6	Initial Cr(VI): 40 and 100 mg/L; adsorbent dose: 8 g/L; reaction time: 3 h
3 ^a	Initial Cr(VI) (mg/L): 10, 40, 60, 100 and 200	Reaction pH controlled at 3; adsorbent dose: 8 g/L
4 ^a	Adsorbent dose (g/L): 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 6.0, 8.0	Reaction pH controlled at 3; initial Cr(VI): 50, 100, 150, 200 mg/L; reaction time: 3 h
5	Aniline to formaldehyde ratio: 0.5:1 ^b , 1.6:1 and 2:1.	Reaction pH controlled at 3; initial Cr(VI): 50 mg/L; reaction time: 3 h; adsorbent dose: 1, 2, 4 and 8 g/L

^a Set 1–4 were conducted at aniline to formaldehyde ratio of 1.6:1 as reported by Liu and Freud [13].

^b In set 5 at aniline to formaldehyde ratio of 0.5:1, polymer was not formed.

during synthesis of AFC were selected as variable parameters for this study. Attention was also given to evaluate the kinetic constants and mechanism of chromium removal.

2. Materials and methods

2.1. Materials

Commercial grade aniline [C₆H₅NH₂] was purified by distilling over NaOH pellets at 180 °C. Column chromatographic grade silica gel (60–120 mesh size), methanol (CH₃OH) and formaldehyde (37% HCHO) were used as received. Potassium dichromate solution was used as the source of hexavalent chromium.

2.2. Synthesis of aniline formaldehyde condensate (AFC)

Aniline formaldehyde condensate (AFC) was synthesized by reacting formaldehyde (HCHO) with aniline (C₆H₅NH₂) as per Liu and Freund [13] and the reaction scheme is shown in Fig. 1. In a 100 mL beaker, 10 mL of 37% formaldehyde (123 mmol) was added slowly to a mixture of 18.6 g of aniline (200 mmol) and 6 mL of concentrated HCl and kept in the water bath at 80 °C for 2 h with intermittent stirring. Then it was neutralized with 8 mL of 30% NaOH and kept in the water bath for another one hour at 60 °C temperature. Thereafter, it was removed from the water bath and kept at room temperature for 12 h, then washed for three to four times with warm water to remove unreacted aniline and formaldehyde and dried by applying vacuum in a vacuum desiccator. AFC synthesized was of yellow color resinous material.

2.3. Coating of AFC on silica gel

Resinous AFC polymer was dissolved in 25 mL methanol (CH₃OH) solution at 40–45 °C with stirring. Experimentally it

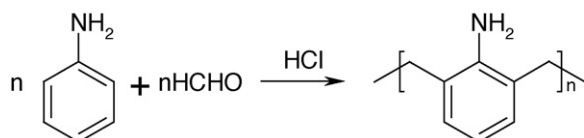


Fig. 1. Synthesis scheme of aniline formaldehyde condensate (AFC).

was observed that maximum 25 g of silica could be added in methanol–AFC solution to completely soak the silica gel and permit mixing. After addition of 25 g silica gel in methanol–AFC mixture, manual stirring was applied for 5 min. Then excess liquid was removed by filtering and AFC coated on silica gel was air dried for 6 h. This AFC coated silica gel was used as the adsorbent in the present work.

2.4. Experimental design

2.4.1. Adsorption experiments

Adsorption experiments were carried out in batch mode at room temperature (23–25 °C). Reaction pH, dose of AFC coated silica gel, initial concentration of Cr(VI) ion and aniline to formaldehyde ratio during AFC synthesis were four variables modified during the study. Total five sets of experiments (set 1–5) were carried out and details of experimental sets are presented in Table 1. All adsorption studies were carried out in a 2 L beaker with 1 L of Cr(VI) solution. Predetermined quantities of adsorbent (AFC coated silica gel) were added in the beaker and mixing was achieved by a magnetic stirrer at 100 rpm. In set 1 experiment initial pH was adjusted at 2.1 by adding 1N H₂SO₄ and solution pH was uncontrolled. In set 2–5 experiments, solution pH was maintained constant during the reaction by adding 0.1/1N H₂SO₄ and 0.1N NaOH. Samples were withdrawn at predetermined time intervals and centrifuged for 10 min at 1000 rpm. The volumes of total withdrawn from the beaker were less than 5% of the initial liquid volume. All experimental runs were performed in duplicates and the average value was considered for data analysis.

2.4.2. Desorption experiments

Desorption studies were conducted by batch experiments. A 1000 mL sample containing 100 mg/L of Cr(VI) was treated with 8 g/L of AFC coated silica gel. Adsorption experiment was conducted for 3 h at a constant solution pH of 3. The mixture was then centrifuged and the filtrate was analyzed for total chromium and Cr(VI). Chromium containing adsorbent was transferred to another beaker and stirred with 1 L of different desorbents for another 3 h. Then it was again centrifuged and desorbed concentration of total chromium and Cr(VI) were determined in the filtrate.

2.5. Analytical procedure

Total chromium [Cr(VI) and Cr(III)] concentration was estimated by an atomic absorption spectrophotometer (Spectra AA Varian, model 55B) using air–acetylene flame at wavelength of 429 nm and slit width of 0.5 nm. Concentration of Cr(VI) was measured by diphenyl carbazide colorimetric method at 540 nm wavelength using UV Spectrophotometer (Varian, model Cary 50) according to APHA [14]. Trivalent chromium concentration was calculated as the difference of total chromium and Cr(VI) of the same sample. Surface morphology of AFC was estimated by scanning electron microscopy (scanning electron microscope, model: LEO, 1430 VP, Carl Zeiss, Germany). NMR spectra of AFC polymer were taken by a 400 MHz FT NMR spectrometer system (BG-M4, BNML-01, Varian, Switzerland).

3. Results and discussion

3.1. Effect of reaction pH

Experiments in set 1 and 2 were conducted to study the effects of pH on chromium removal. In set 1 experiment profiles of chromium concentrations and pH were investigated without pH control (Fig. 2(a)). Cr(VI) concentration decreased

rapidly from 100 to 20 mg/L within 30 min. Cr(VI) removal was associated with increase in solution pH from 2.17 to 3.5 in 30 min (Fig. 2(a)). Proton disappearance was proportional (with R^2 0.99) to Cr(VI) removal with 4.26 mol of protons consumption for each mole of Cr(VI) removal. Consumptions of 3.99 and 2.7 mol of protons for each mole of Cr(VI) removal were observed by dead biomass *Aspergillus niger* and *Rhizopus oryzae*, respectively [7,15]. Total chromium [Cr(VI) and Cr(III)] concentration with time is also presented in Fig. 2(a). After 30 min of reaction time concentration of total chromium in solution was 69 mg/L and corresponding concentration of residual Cr(VI) in solution was 21 mg/L. Hence concentration of Cr(III) in solution was difference of concentration of total chromium and Cr(VI) i.e. 48 mg/L.

In set 2 experiments, study was conducted at constant reaction pH of 2, 3, 4, 5 and 6 at two initial concentrations of Cr(VI): 40 and 100 mg/L. Concentrations of Cr(VI) and total chromium [$\sum\{\text{Cr(VI)} + \text{Cr(III)}\}$] were measured and removals (%) of Cr(VI) and total chromium and amount of initial Cr(VI) present in solution as Cr(III) (%) were calculated as shown below:

$$\begin{aligned} \text{Cr(VI) removal (\%)} &= \frac{\text{initial Cr(VI) (mg/L)} - \text{final Cr(VI) (mg/L)}}{\text{initial Cr(VI) (mg/L)}} \times 100 \quad (1) \end{aligned}$$

$$\begin{aligned} \text{Total chromium removal (\%)} &= \frac{\text{initial Cr(VI) (mg/L)} - \text{final total chromium (mg/L)}}{\text{initial Cr(VI) (mg/L)}} \\ &\times 100 \quad (2) \end{aligned}$$

$$\begin{aligned} \text{Cr(III) in solution (\%)} &= \frac{\text{final total chromium (mg/L)} - \text{final Cr(VI) (mg/L)}}{\text{initial Cr(VI) (mg/L)}} \\ &\times 100 \quad (3a) \end{aligned}$$

In Eq. (3a), substituting values of final Cr(VI) and final total chromium from Eqs. (1) and (2), respectively, it can be written as:

$$\begin{aligned} \text{Cr(III) in solution (\%)} &= \text{Cr(VI) removal (\%)} - \text{total chromium removal (\%)} \quad (3b) \end{aligned}$$

Fig. 2(b) shows that removal of Cr(VI) decreased with increase in solution pH. At reaction pH of 2, 92% and 96% removals of Cr(VI) were achieved (from 40 and 100 mg/L, respectively), which decreased to 13% and 15% when solution pH was maintained at 5. Fig. 2(b) shows that at reaction pH of 2, total chromium removals were 12% and 38% (initial Cr(VI) 40 and 100 mg/L), which increased significantly to 58% and 61% at reaction pH of 3. However, when reaction pH was further increased to 4 and 5, total chromium removal decreased drastically to 36% and 15%, respectively. Above pH 5, change in total chromium removal was negligible. The optimum solution pH for removal of total chromium by AFC coated silica gel was

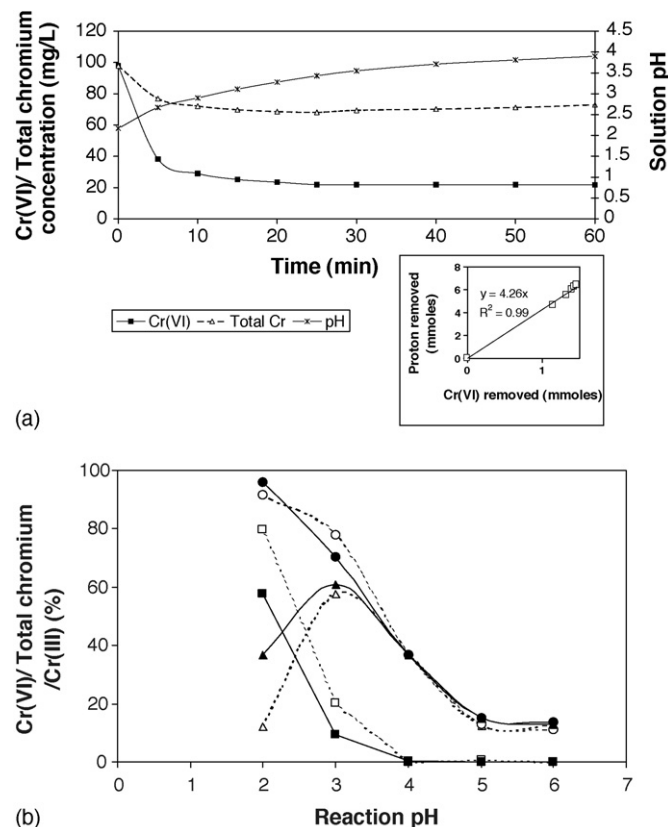
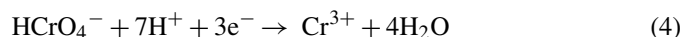


Fig. 2. (a) Profiles of Cr(VI), total chromium and solution pH during uncontrolled reaction pH condition. (b) Effect of controlled reaction pH on chromium removal by AFC coated silica gel (Hollow symbols and filled up symbols for initial Cr(VI) 40 and 100 mg/L respectively; triangles for total chromium removal (%), circles for Cr(VI) removal (%) and squares for Cr(III) in solution (%)).

at 3. Cr(III) (%) present in solution was calculated using Eq. (3b). Fig. 2(b) shows that 58% and 80% of initial Cr(VI) (40 and 100 mg/L, respectively) were present in solution as Cr(III) at controlled reaction pH 2. With increase in reaction pH, Cr(III) fraction in solution decreased steadily and became negligible at pH of 4 and above.

Within the studied pH range (2–6) used in the present work, the predominating form of Cr(VI) in solution is acid chromate ion (HCrO_4^-) [16]. In acidic medium amine group ($-\text{NH}_2$) of AFC exists as protonated ammonium ($-\text{NH}_3^+$) form and electrostatic attraction between protonated ammonium ion and negatively charged HCrO_4^- ion is expected for removal of Cr(VI) from solution. With increase in pH, this electrostatic attraction is less due to decrease in the positive charge of the amine group. Literatures reported that under acidic environment, Cr(VI) spontaneously reduces to Cr(III) ion due to high redox potential (1.3 V at standard state) as shown below [17,12,18].



Eq. (4) suggests that lower the solution pH, reaction will be favoured to right side with higher reduction of Cr(VI) to Cr(III). Within pH range of 2–6, Cr(III) ion released in solution largely exists in the form of $\text{Cr}^{3+}/\text{Cr}(\text{OH})^{2+}$ ion and precipitation of Cr(III) ion can be ruled out since Cr(III) precipitation as $\text{Cr}(\text{OH})_3$ is reported to take place from solution pH above 6 [19]. Nitrogen atom in AFC can form tridentate and bidentate coordination bonds, respectively, with positively charged Cr^{3+} and $\text{Cr}(\text{OH})^{2+}$ ions by sharing electron. With increase in solution pH, amine group is less protonated and bond formation is favoured due to decrease in charge repulsion between positively charge Cr(III) ion and protonated amine group [12].

In the present work when solution pH was controlled at 2, chemical reduction of Cr(VI) to Cr(III) ion was the predominating step and very few HCrO_4^- ion was available in solution for electrostatic bond formation with the protonated amine group. Further, charge repulsion between Cr(III) ion and highly protonated AFC was very high and maximum fraction of Cr(III) remained in solution at pH 2 and total chromium removal was low. When reaction pH was increased by one unit, reduction of Cr(VI) was less and more HCrO_4^- ion was available for electrostatic interaction with AFC. Again, at pH 3, as the number of protonated amines in AFC was less than pH 2, bond formation between Cr(III) ions and adsorbent was more, thus increasing total chromium uptake. Similar observations were also reported during removal of Cr(III) by aminated polyacrylonitrile fibers, where removal of Cr(III) was negligible at pH 2 and started only from solution pH of 3 due to charge repulsion of amine group and Cr(III) ion [12]. In the present work when solution pH was increased above 3, chances of coordination bond formation between Cr(III) ion and less positively charged amine group increased. However, chemical reduction of Cr(VI) ion decreased at higher solution pH and less Cr(III) was available for bond formation. Also electrostatic attraction between HCrO_4^- ion and less protonated amine group decreased above pH 3. Hence, total chromium adsorption by AFC coated silica gel at pH above 3 decreased significantly. Present study indi-

Table 2

Desorption of chromium from AFC coated silica gel by various desorption agents

Desorption agents	Desorption time (h)	Desorption efficiency (%)	
		Cr(VI)	Cr(III)
0.5N NaOH	3	56.62	0
0.5N NH_4OH	3	32.82	0
0.2N EDTA	3	0	37.14
0.2N H_2SO_4	3	0	83.91
0.2N HNO_3	3	0	81.05
0.2N HCl	3	0	76.18

cates that total chromium adsorption by AFC coated silica gel is a combinations of three reactions: electrostatic attraction of acid chromate ion, chemical reduction of Cr(VI) to Cr(III) ion and bond formation of Cr(III) with AFC.

Desorption results also support previously stated mechanism of chromium removal by AFC coated silica gel. Desorption study was conducted using five types of desorption agents and results are given in Table 2. When alkalis like NaOH and NH_4OH were used for desorption, HCrO_4^- ion attached to protonated amine group by electrostatic attraction, were released from AFC as Cr(VI). When 0.2N EDTA was used for desorption, almost 40% of adsorbed total chromium was released in the form of Cr(III) ion. EDTA is known to make polydentate coordination bonds with various metal ions and was able to recover Cr(III) ions attached with nitrogen atom of AFC by bidentate/tridentate coordination bond. Using mineral acids of 0.2N strength, 84%, 81% and 76% of adsorbed chromium were released in solution as Cr(III) ion by H_2SO_4 , HNO_3 and HCl, respectively. Probably HCrO_4^- adsorbed by AFC, was reduced to Cr(III) ion during desorption by mineral acids and this Cr(III) ions were released into solution due to repulsion by protonated nitrogen atom. Similar phenomenon were observed during desorption of chromium from *A. niger* fungi and seaweed by mineral acids [6,7]. Efforts were also made to reuse of AFC coated silica gel for removal of Cr(VI) after desorption of chromium ion. However, after desorption experiment, AFC coated silica gel changed appearance from granular to amorphous form. This amorphous adsorbent was not effective in removing chromium ion. Probably during desorption experiment, properties of AFC coated silica gel changed and further studies are recommended on regeneration and reuse of AFC.

In acidic condition, Cr(VI) reduction to Cr(III) suggests partial oxidation of AFC since no other external reducing agent was added in the solution. In order to study the degradation of AFC in acidic condition, ^1H NMR spectra were taken before interaction with Cr(VI) ion and after reacting with Cr(VI) ion at solution pH of 3 (Fig. 3(a) and (b)). Silica gel does not interfere in ^1H NMR spectrum. The ^1H NMR spectrum of AFC coated silica gel before metal binding show multiple peaks in the aromatic region 6–7 ppm and at 3.5 ppm which is consistent with aromatic ring and methylene ($-\text{CH}_2-$ group connecting between aromatic rings of AFC) groups present in the AFC. The position or shape of the peaks remained unchanged after chromium binding, which clearly indicates very insignificant degradation of AFC during interaction with Cr(VI) ion.

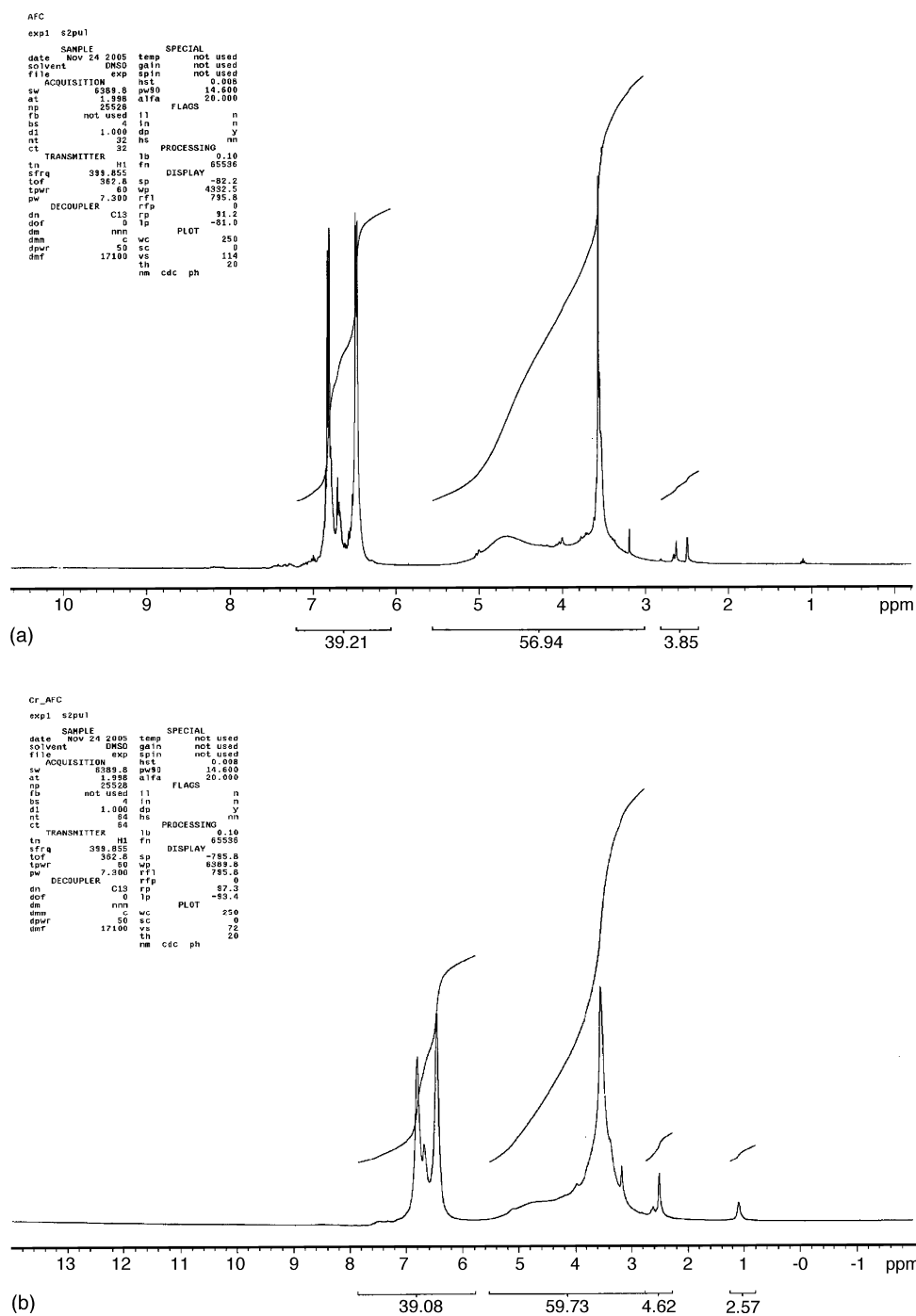


Fig. 3. (a) NMR spectra of AFC coated silica gel before chromium adsorption. (b) NMR spectra of AFC coated silica gel after chromium adsorption.

3.2. Adsorption kinetics

In set 3 experiments, chromium removal kinetics was studied with varying initial Cr(VI) concentrations (10–200 mg/L). Total chromium removals (%) with time is presented in Fig. 4. Almost 30–65% removal of total chromium was adsorbed within initial 20 min and equilibrium was achieved within 90–120 min. Total chromium adsorption by AFC coated gel increased from 43% to 70% with increase in initial Cr(VI) concentration from 10 to 200 mg/L. Similar phenomenon was observed during chromium removal by polyvinylpyridine coated silica gel [10]. Reaction

time of 50–350 h was observed for removal of chromium at pH 2 from initial Cr(VI) 25–200 mg/L by fungal biomass *A. niger* dose of 10 g/L [7]. Another HNO₃ pre-treated seaweed biomass *Ecklonia* required 9 h for complete removal of total chromium from initial concentration of 200 mg/L [20]. Equilibrium times of 2 and 5 h were reported for total chromium removal (initial concentrations 3 and 10 mg/L) by iron hydroxide loaded sugar beet pulp and PVP coated silica gel, respectively [18,10]. In terms of total chromium removal kinetics AFC coated silica gel showed fairly good results. The kinetics of total chromium adsorption by AFC coated silica gel (data of Fig. 4) was tested

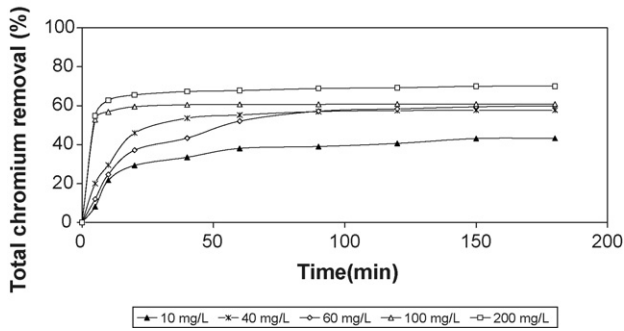


Fig. 4. Total chromium removal with time by AFC coated silica gel at varying initial Cr(VI) concentrations.

with respect to first order model of Lagergren (Eqs. (5a) and (5b)) and second order kinetic model (Eqs. (6a) and (6b)) [21]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{5a}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{5b}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{6a}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6b}$$

where q_t and q_e (mg/g) are total chromium adsorption capacity at time t and at equilibrium, respectively, k_1 and k_2 are the first order and second order rate constants, respectively. Table 3 shows total chromium adsorption rate constants (k_1 and k_2) and correlation coefficients calculated using linearized plots of Eqs. (5b) and (6b), respectively (plot not shown). Lagergren first order model showed correlation coefficient (R^2) of 0.38–0.98 (Table 3). In contrast, the second order kinetic model showed much higher R^2 values (more than 0.99). In order to select the appropriate kinetic model, Chi-square test was also done by the following equation [22]:

$$\chi^2 = \sum \frac{(q_t - q_{tm})^2}{q_{tm}} \tag{7}$$

where q_t and q_{tm} (mg/g) are total chromium adsorption capacity at time t using experimental data and using kinetic model, respectively. It can be seen from Table 3 that errors between calculated and experimental q_t values were much less for second order model (with much less χ^2 value), suggesting chromium adsorption followed second order kinetics. Second order chromium

Table 3
Comparison of first and second order kinetic model for total chromium adsorption

Initial Cr(VI) (mg/L)	First order kinetic model			Second order kinetic model		
	k_1 (L/min)	R^2	χ^2	k_2 (g mg ⁻¹ min ⁻¹)	R^2	χ^2
10	0.034	0.92	0.19	0.09	0.99	0.029
40	0.029	0.98	20.78	0.07	0.99	0.076
60	0.041	0.90	1.58	0.06	0.99	0.06
100	0.054	0.86	456.14	0.04	1.00	0.009
200	0.004	0.38	2365.00	0.03	0.99	0.18

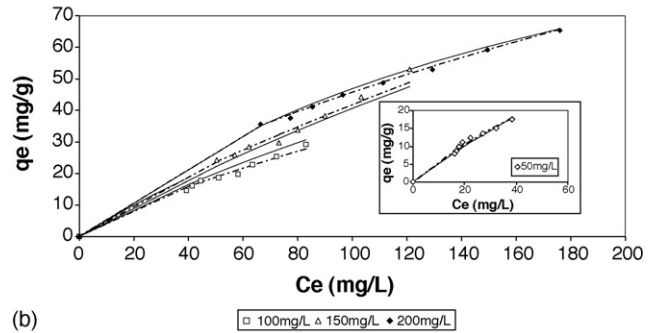
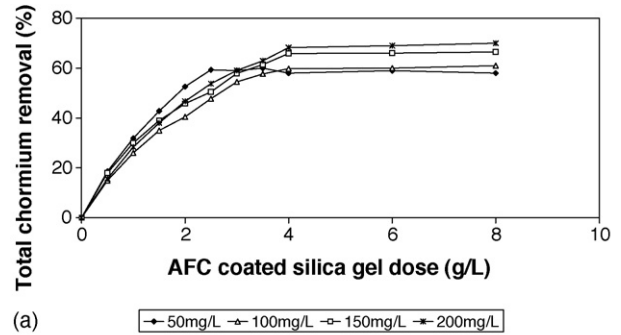


Fig. 5. (a) Effect of adsorbent dose on total chromium removal. (b) Adsorption isotherms for total chromium removal (solid line fitted Langmuir model and dashed line fitted Freundlich model).

removal kinetics were also reported by previous researchers with various adsorbents like used tyres, saw dust, activated carbon prepared from rubber wood saw dust, KOH activated wood carbon, etc. [1,5,23].

3.3. Effect of adsorbent dose and adsorption isotherm

In set 4 experiments, adsorbent dose was varied from 0.5 to 8 g/L with four initial Cr(VI) concentrations: 50, 100, 150 and 200 mg/L. Initially with increase in adsorbent dose up to 4 g/L, total chromium removal increased and remained constant beyond that (Fig. 5(a)). At adsorbent dose of 4 g/L, total chromium removal varied from 60% to 70% depending on initial Cr(VI) concentration with corresponding total chromium adsorption capacity of 7.5–35 mg/g. Only 30% removal of total chromium from initial concentration of 100 mg/L using pyrite as adsorbent at dose of 4 g/L was reported [19]. For 70% removal of total chromium (initial 10 mg/L) adsorbent dose of 10 g/L was

Table 4
Isotherm constants for total chromium adsorption by AFC coated silica gel

Initial Cr(VI) (mg/L)	Freundlich isotherm				Langmuir isotherm				
	K_f (mg/g)	n	R^2	χ^2	Q_m (mg/g)	b (L/mg)	R^2	R_L	χ^2
50	0.89	1.21	0.94	0.34	135.1	0.004	0.92	0.83	0.57
100	0.92	1.30	0.96	0.26	153.8	0.003	0.95	0.77	1.14
150	1.56	1.20	0.97	0.62	243.9	0.002	0.96	0.77	1.17
200	2.39	1.56	0.99	0.07	140.8	0.005	0.98	0.50	0.30
Average	1.44	1.31	–	–	168.4	0.003	–	0.72	–

observed to be necessary by iron hydroxide loaded sugar beet pulp at pH 4.4 [18].

Langmuir and Freundlich isotherm models were used to determine appropriate isotherm for total chromium adsorption by AFC coated silica gel. Langmuir's monolayer isotherm is expressed as [24]:

$$q_e = \frac{Q_m b C_e}{1 + b C_e} \quad (8a)$$

and the linearized form is:

$$\frac{1}{q_e} = \frac{1}{Q_m b C_e} + \frac{1}{Q_m} \quad (8b)$$

where C_e (mg/L) is the equilibrium liquid phase concentration of total chromium, q_e (mg/g) is the total chromium adsorption capacity at equilibrium, Q_m the monolayer adsorbent capacity and b is the energy constant of adsorption. Another dimensionless parameter named separation factor (R_L) is introduced in Langmuir's model to indicate the favourability of the adsorption and is determined by:

$$R_L = \frac{1}{1 + b C_0} \quad (8c)$$

where b is the Langmuir coefficient, C_0 is the initial liquid phase concentration of chromium in equilibrium with the adsorbent and for favourable adsorption, $0 < R_L < 1$. Freundlich's isotherm has the general form $q_e = K_f C_e^{1/n}$, where K_f is Freundlich capacity factor and n is the Freundlich's intensity factor [24].

The value of ' n ' in the range of 1–10 denotes favourable adsorption. The linear form of Freundlich's equation is given by:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (9)$$

Langmuir's and Freundlich's isotherms constants calculated using linearized forms of the models (Eqs. (8b) and (9)) are shown in Table 4. In Fig. 5(b) isotherms plots (as q_e and C_e) using experimental data and Freundlich's and Langmuir's models are shown. Correlation coefficients (R^2) in the linear equations were slightly higher for Freundlich's model. In order to select the best fit isotherm model, Chi-square test was done by the following equation [22]:

$$\chi^2 = \sum \frac{(q_e - q_{em})^2}{q_{em}} \quad (10)$$

where q_e and q_{em} (mg/g) are total chromium adsorption capacity at equilibrium calculated using experimental data and isotherm models, respectively. χ^2 values in Table 4 suggest that total chromium adsorption by AFC coated silica gel can be best described by Freundlich's isotherm. Freundlich's constant n value of 1.31 > 1 clearly indicates total chromium adsorption by AFC coated silica gel as favourable.

A comparison of the chromium adsorption capacity of AFC coated silica gel with various adsorbents in Table 5 shows that chromium adsorption capacity varied in wide range.

However, in many of the reported studies chromium adsorption was estimated only on the removal of Cr(VI) from solution instead of removal of total chromium [Cr(VI) and Cr(III)].

Table 5
Comparison of adsorption capacity of chromium with other adsorbents

Adsorbent	Adsorption capacity (mg/g)	Initial Cr(VI) (mg/L)	pH	Reference
KOH treated AC prepared from wood ^a	160.0	5–200	3.0	[1]
Zinc chloride AC from <i>Terminalia arjuna</i> nuts ^a	28.4	10–30	1.0	[25]
Activated carbon from <i>Hevea brasiliensis</i> saw dust ^a	44.1	200	2.0	[23]
Nanocrystalline akaganeite ^a	80.0	10–50	5.5	[26]
Polyacrylamide grafted sawdust ^a	45.0	100	3.0	[27]
PVP coated silica gel ^b	3.0	10	5.0	[10]
Polyacrylonitrile fibers ^b	35.0	50	5.0	[12]
Hazelnut shell ^b	3.9	–	3.0	[17]
Iron hydroxide loaded sugar beet pulp ^b	4.9	5–200	4.4	[18]
Soya cake ^b	0.3	48	1.0	[28]
Tamarind hull ^b	95.0	50–150	2.0	[29]
AFC ^b	17.0–65.0	50–200	3.0	Present study

^a Chromium removal based on only estimation of Cr(VI) concentration.

^b Chromium removal based on estimation of total chromium (Cr(VI) + Cr(III)) concentration.

Adsorption capacity observed with AFC coated silica gel (17–65 mg/g) compared well with most of the adsorbents, except few materials like tamarind hull and nanocrystalline akaganeite, which exhibited very high adsorption capacity of 95 and 80 mg/g, probably due to basic morphology of the raw material and very high surface area of nanosized particles. AFC coated silica gel can be considered a viable adsorbent for removal of chromium from aqueous solution.

3.4. Effect of aniline to formaldehyde ratio

The molar ratio of aniline to formaldehyde ratio was set at 1.6:1 by Liu and Freund [13] and further possibility of changing the molar ratios of formaldehyde to aniline was suggested to control the molecular weight of AFC polymer [30]. In the present work, aniline to formaldehyde ratio was varied at 0.5:1, 1.6:1 and 2:1 during AFC synthesis. At aniline formaldehyde ratio of 0.5:1, a very rigid and hard material was formed instead of a polymeric material and it was discarded. It was suggested that formaldehyde when used in excess as compared to aniline was responsible for more cross-linking [30]. Probably this cross-linking hindered polymer formation at aniline formaldehyde ratio of 0.5:1. AFC synthesized using aniline and formaldehyde ratio of 1.6:1 and 2:1 were used for Cr(VI) removal and results are shown in Fig. 6. Aniline to formaldehyde ratio of 1.6:1 had total chromium adsorption capability of 10–29% times

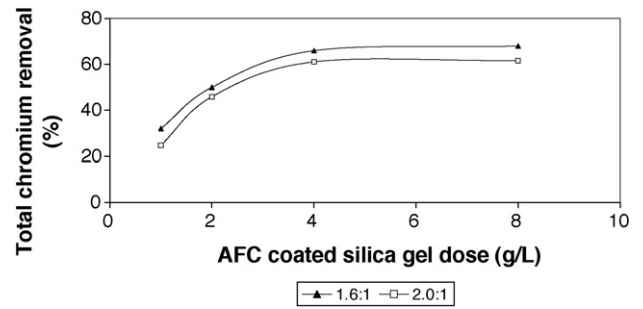


Fig. 6. Effect of aniline and formaldehyde ratio in AFC synthesis on total chromium removal.

higher than that of ratio of 2:1. This result shows that aniline to formaldehyde ratio of 1.6:1 was the optimum in terms of total chromium removal from aqueous solution. Probably at aniline to formaldehyde ratio of 2:1, more diamines were formed, which increased solubility of the AFC polymer [30]. During washing and coating on silica gel some of the polymer was washed away from silica gel surface and this was responsible for small reduction in chromium adsorption capacity of the adsorbent.

3.5. Surface characteristics of AFC coated silica gel

To analyze the surface morphology of AFC polymer SEM images were investigated (Fig. 7(a) and (b)). EDX analysis was

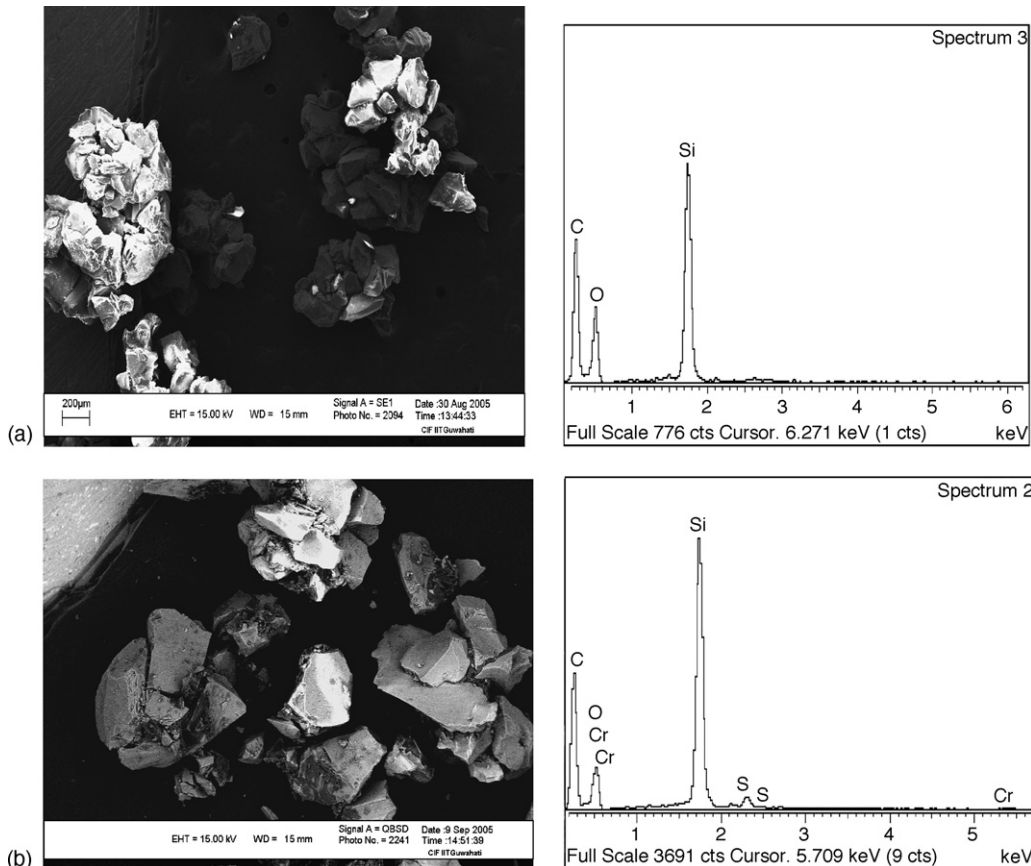


Fig. 7. (a) SEM photograph and EDX spectra of AFC coated silica gel before chromium adsorption. (b) SEM photograph and EDX spectra of AFC coated silica gel after chromium adsorption.

employed to further confirm the adsorption of chromium ions. Before interaction with Cr(VI) ion, only silicon, carbon and oxygen atoms were observed on AFC coated silica gel, whereas chromium peak was present after adsorption. Sulphur peak was present due to addition of sulfuric acid for pH adjustment during adsorption experiment.

4. Summary and conclusions

Aniline formaldehyde condensate (AFC), a polymer with amine group was coated on silica gel to prepare an adsorbent for removal of Cr(VI) from wastewater. Electrostatic attraction of acid chromate ion by protonated amine group of AFC, reduction of Cr(VI) to Cr(III) ion and bond formation between Cr(III) ion with nitrogen atom of AFC were possible mechanisms of total chromium [Cr(VI) and Cr(III)] removal by AFC coated silica gel. The optimum pH for total chromium adsorption was observed to be 3 with 85% and 70% removals of Cr(VI) and total chromium, respectively, from initial Cr(VI) of 100 mg/L. Total chromium adsorption followed second order kinetics and equilibrium was achieved within 90–120 min. Equilibrium data of adsorption was in good agreement with Freundlich's isotherm. Recovery of chromium from AFC coated silica gel was 56% and 76–84% in presence of NaOH and mineral acid. Aniline to formaldehyde ratio of 1.6:1 during AFC synthesis was optimum for chromium removal. Total chromium adsorption capacity varied from 17 to 65 mg/g at initial Cr(VI) concentration 50–200 mg/L. Easy synthesis procedure of AFC polymer, suitability of preparation of granular adsorbent using this polymer, high chromium adsorption and good recovery make it one of the potential alternative for removal of toxic chromium ion from wastewater.

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