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Adsorption behaviour of trivalent chromium on amine-based polymer aniline formaldehyde condensate

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ABSTRACT

An amine-based polymer, aniline formaldehyde condensate (AFC) was coated on silica gel and used as an adsorbent for removal of trivalent chromium [Cr(III)] in aqueous environment. A comparative study with mixed metal solutions containing Cu(II), Cd(II), Pb(II), Cr(III) and Ni(II) showed that adsorption was in the order of Cu(II) > Ni(II) > Cr(III) > Pb(II) > Cd(II). Comparative adsorption of mixed metal ions by AFC was according to preferences dictated by the hard–soft theory of acids and bases and ligand exchange rate of metal ions. It was observed that in mixed metal solution Cr(III) adsorption by AFC though thermodynamically favoured with high binding constant, however, limited kinetically. Cr(III) adsorption by AFC increased with pH achieving maximum removal of 80% at pH 6. Formation of multidentate coordinate bond between $[CrOH]^{2+}$ and $[Cr(OH)_2]^{1+}$ and deprotonated amine group ($-NH_2$) of AFC was probable mechanism for removal of Cr(III) in aqueous environment. Adsorption of Cr(III) on AFC followed Lagergren's second order kinetic model and Langmuir–Freundlich's isotherm model with maximum monolayer coverage of 30.77 mg/g (0.57 mmol/g). Electromagnetic paramagnetic resonance and energy dispersive X-ray spectra confirmed the presence of trivalent chromium ion on surface of AFC coated silica gel.

1. Introduction

Chromium is a well known toxic heavy metal and exists in environment both as trivalent [Cr(III)] and hexavalent [Cr(VI)] forms of which hexavalent form is five hundred times more toxic than the trivalent one [1]. Trivalent and hexavalent chromium are widely used as tanning agent in the leather tanning industry, paints and pigments industry, fungicides industry and ceramic or glass manufacturing [2,3]. Cr(III) though less toxic than Cr(VI), can be oxidized if exposed in the right environment of oxidation. Oxidation of Cr(III) to Cr(VI) was observed in natural lake water and field soils in the presence of oxidized manganese [MnOOH(s)], which served as the electron acceptor in the reaction [4,5]. Over the pH range from 3.0 to 10.1, Cr(III) was found readily oxidized to Cr(VI) by β-MnO_2 (s) [6]. Therefore, removal of both hexavalent and trivalent chromium from industrial wastewater is of great challenge.

Recent investigation reported the removal of Cr(III) by adsorption using biomass [7], ion exchange using zeolite [8] and electrocoagulation process [9]. Low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth were reported to remove Cr(III) but observed to reach the equilibrium in 48 h for initial Cr(III) of 25–100 mg/L [10]. Therefore exploration of techniques with high removal capability of Cr(III) ions in lesser time along with less sludge production is a major challenge in industrial wastewater treatment.

In this article, we have studied removal of Cr(III) by an amine-based polymer, aniline formalydehyde condensate (AFC) coated on silica gel. AFC polymer was synthesized by cross-linking of aniline and formaldehyde in acidic medium and silica gel was coated with this resinous polymer to make a granular adsorbent [11]. This AFC coated silica gel was used separately for removal of hexavalent chromium and divalent copper ions in our previous works [11,12]. Removals of both metals were achieved in relatively shorter time (120–150 min). However, removal mechanisms of these two metals by AFC polymer were observed to be different. Optimum pH for removal of hexavalent chromium was observed as 3 and at this acidic pH, amine group ($-NH_2$) of AFC polymer was in protonated form ($-NH_3^+$) and it removed negatively charged hexavalent chromium [acid chromate ion ($HCrO_4^-$)] by electrostatic attraction. For divalent copper ion, maximum removal was observed at pH of 6. Coordination bond formation between amine group and Cu^{2+} ion was the main mechanism for removal of copper ion by AFC. It seems that removal of heavy metal ion by AFC polymer is complex and involve ion-exchange and complex formation depending on the metal ion and solution pH. This study provides the insight into the behaviour of amine-based AFC polymer for a trivalent metal ion [Cr(III)]. Trivalent chromium is a 3d transition metal like cop-

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per, however, kinetically more immobile. In this work, removal capacity of Cr(III) by AFC coated silica gel with respect to various adsorption dependent factors like reaction pH, initial concentration of Cr(III), effect of co-metal ions and desorption of adsorbed Cr(III) were investigated. Emphasis was also given to identify the nature of kinetics of adsorption and valuate the kinetic constants, rate limiting step of adsorption and mechanism of Cr(III) removal.

2. Materials and methods

2.1. Materials

Commercial grade aniline [$C_6H_5NH_2$] for synthesizing polymers was purified by distilling over KOH pellets at 180 °C (boiling point of aniline). Column chromatographic grade silica gel (60–120 mesh size), methanol (CH_3OH) and formaldehyde (37% HCHO) were used as received. Chromic chloride [$CrCl_3 \cdot 6H_2O$] procured from Central drug house, India, was used as the source of trivalent chromium. Chromium standards procured from Merck, Darmstadt, Germany, were used for calibration of standard concentrations. Synthesis scheme of AFC polymer is shown in Fig. 1. 10 mL of 37% formaldehyde (123 mmol) was mixed with 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. This was neutralized with 8 mL of 30% NaOH and kept at room temperature for 12 h, then washed for three to four times with warm water. This was coated on silica gel by dissolving AFC polymer in methanol. Detail procedure is given in our previous works [11,12].

2.2. Adsorption and desorption experiments

Adsorption experiments were carried out in batch mode at room temperature (20 °C). In order to investigate the nature of Cr(III)–AFC interaction at various conditions, batch experiments were conducted with adsorbent dose, solution pH, initial concentration of Cr(III) ion, effects of co-metal ions as variable parameters. Only one parameter was changed at a time while others were maintained constant.

In the first set of experiment, adsorption capacity of plain silica gel was studied at varying pH of (1–11) at silica dose of 4 g/L and initial Cr(III) of 50 mg/L. Next second set of experiments were conducted varying solution pH (from 1 to 11) at an adsorbent (AFC coated on silica gel) dose of 4 g/L and initial Cr(III) of 50 mg/L. In the third set of experiment AFC coated silica gel dose was varied (1–10 g/L) at initial Cr(III) 50 mg/L and solution pH of 6.

In the fourth set of experiments the initial Cr(III) was varied at three levels (15, 30 and 45 mg/L) at constant adsorbent dose of 4 g/L and solution pH of 5 and 6 to determine Cr(III) removal kinetics by AFC coated silica gel. Adsorption isotherm was studied at a constant adsorbent dose of 4 g/L and varying Cr(III) concentrations (15–500 mg/L) at solution pH of 6 as fifth experiment. The sixth set of experiments were conducted in the presence of co-metal ions: Cu(II), Ni(II), Cd(II), Cr(III) and Pb(II) each of 0.5 mmol at adsorbent dose of 2 g/L at pH of 6.

All adsorption studies were carried out with 1000 mL of metal solution in 2-L of beaker to prevent the spill off of the solution. Predetermined quantities of adsorbent (AFC coated silica gel) were added in the beaker and to achieve the degree of mixing and equilibrium, a paddle stirrer was employed with speed adjusted at 1000 rpm. Solution pH ranges of 3–7 were well adjusted by 0.1 M NaOH and 0.1N H_2SO_4 whereas pHs at extreme acidic and alkaline conditions were adjusted using 1N H_2SO_4 and 1 M NaOH respectively. Addition of acid/base solution to adjust the pH never exceeded 1% of the total volume of the reactor. However for experiment with higher dose of AFC exhibiting high fluctuation in pHs, buffer prepared from potassium hydrogen orthophosphate was used to minimize the fluctuation. Samples were withdrawn at predetermined time intervals, centrifuged for 10 min at 1000 rpm and concentration of Cr(III) was analyzed. The amount of Cr(III) adsorbed by AFC coated silica gel was calculated based on the difference of Cr(III) concentration in aqueous solution before and after adsorption according to the following equation:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where q_t is the amount of Cr(III) ion adsorbed per unit weight of AFC (mg/g) at time t, C_0 and C_t are the concentrations of Cr(III) ions (mg/L) at initial time and at time t respectively, V is the initial volume of Cr(III) sample (L) and m is mass of AFC (g). When t is equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, then the amount of Cr(III) adsorbed at equilibrium, q_e was calculated using Eq. (1).

Desorption experiments were performed after adsorption experiment with Cr(III) loaded AFC-silica gel. Desorption experiments were carried out using four types of desorbents: HCl, H_2SO_4, HNO_3, EDTA each of strength 0.5 moles/L using desorbent volume of 10 mL. All experimental runs were performed in duplicates and the average value was considered for data analysis.

2.3. Analytical procedure

Concentration of Cr(III) in solution was determined 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. In order to confirm the presence of Cr(VI) [due to oxidation of sample Cr(III) to Cr(VI)] concentration of Cr(VI) in the sample was also checked by diphenyl carbazide colorimetric method at 540 nm wavelength using U.V. Spectrophotometer (Varian, model Cary 50) according to APHA [13]. Concentration of Cu(II), Cd(II), Ni(II) and Pb(II) were also estimated using atomic absorption spectrophotometer using air–acetylene flame at wavelength of 218.2, 326.1, 341.5 and 283.3 nm respectively, slit width of 0.2 nm for Cu(II) and Ni(II) and 0.5 nm for Cd(II) and Pb(II). FTIR spectra were recorded on PerkinElmer spectrum one spectrophotometer. Surface morphology of AFC was estimated by scanning electron microscopy and the presence of chromium on AFC was investigated by electron diffraction (EDX) (Scanning electron microscope, Model: LEO, 1430 VP, Carl Zeiss, Germany). The presence of adsorbed Cr(III) on AFC was also examined and confirmed by employing Electromagnetic Paramagnetic Resonance Spectrophotometer (Model: JES-FA 200 ESR System, JEOL, Ltd., Japan).

3. Results and discussion

3.1. Removal of Cr(III) by plain silica gel

AFC polymer is of resinous form. In order to improve the rigidity of the polymer and to facilitate separation of metal ion after metal–polymer interaction, addition of support material such as silica gel in polymer matrix was necessary. However if the inner silica gel of the adsorbent also uptake Cr(III) along with AFC polymer from the solution, then it wont be possible to estimate the full adsorption capacity of lone AFC polymer. Therefore removal efficiency of Cr(III) by silica gel was investigated firstly and results are

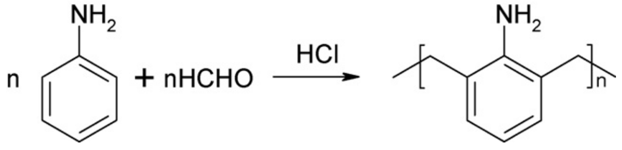

Fig. 1. Synthesis scheme of aniline formaldehyde condensate (AFC) [11,12].

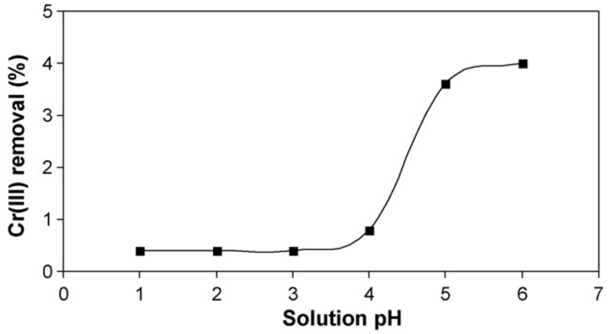

Fig. 2. Removal of Cr(III) by silica gel at different initial pH (initial Cr(III) 50 mg/L; silica gel dose 4 g/L; agitation time 4 h).

shown in Fig. 2. Silica gel exhibits a maximum Cr(III) removal of only 4% at pH 6 and precipitated above pH 6. Since silica gel showed poor adsorbent property, coating AFC on silica gel is justified to reveal the amount of Cr(III) removed by lone AFC polymer.

3.2. Characterization of AFC coated silica gel

Surface morphologies of adsorbent (AFC coated on silica gel) are shown in supplementary files (Supplementary files: S1, S2). The surface of AFC was smooth with resinous layer. EDX analysis was employed to further confirm the presence of chromium ions on AFC coated silica gel. EDX spectra show that before interaction with Cr(III) ion, only silicon, carbon and oxygen atoms were observed on AFC coated silica gel (Supplementary files: S1 and S2), whereas chromium peak was present after adsorption. The presence of potassium (K) and phosphorous (P) peak after adsorption experiment was contributed from buffering agent potassium hydrogen orthophosphate. Confirmation of the presence of Cr(III) on surface of AFC was also investigated by employing ESR (electronic paramagnetic resonance). The ESR spectrum is shown in Fig. 3(a). The resonance signal appears at a magnetic field position corresponding to g value of 1.975, confirming the presence of Cr(III) whose standard signal g value is 1.98 [14].

Here, $g = h\nu/\beta Hr$, where h is the Planck constant (6.626×10^{-27} erg/s); β is the universal constant (9.274×10^{-21} erg/G); ν is the frequency (9.707×10^{9} Hz) and H_r is the resonance of magnetic field (G).

In order to understand the change in functional group after adsorption of Cr(III) FTIR spectra of AFC coated silica gel were obtained with and without Cr(III) and shown in Fig. 3(b). The IR spectrum of AFC coated silica gel before and after Cr(III) binding does not pinpoint much appreciable change. In IR figure the peaks at 1078 cm^{-1} is due to silica gel. Both the spectrum shows very broad absorption 3100–3400 cm^{-1} for NH (amine of AFC) and OH (moisture present in the sample) vibrations, sharp absorption at 1514 and 1622 cm^{-1} for aromatic ring [15].

3.3. Effect of solution pH

Effect of pH on adsorption of Cr(III) by AFC was studied at various pH levels. In Fig. 4(a), removal of Cr(III) increased with increase in pH obtaining maximum removal of 80% at pH 6. Within pH range of 1–4, removal of Cr(III) was almost negligible with removal of only 0.2–7% and increased to 20% and 80% at pH of 5 and 6 respectively. In order to know the reason for lesser removal at acidic pH and maximum removal at 6, and also to understand the mechanism of Cr(III) removal by AFC, it is important to know the different species of Cr(III) at different pH. The distribution of different species of Cr(III) at different pH was studied using equations of complexation between Cr(III) and OH$^-$ ligand using logarithmic constant k_1, k_2, k_3 and k_4 value were 10, 8.3, 5.7 and 4.6 respectively with solubility product k_{sp} of 6×10^{-31} [16]. Species distribution diagram of Cr(III) is shown in Fig. 4(b). In acidic pH 1–4, trivalent Cr^{3+} is the dominant species followed by divalent CrOH^{2+} from pH 4 to almost pH 5.5. In acidic pH range, surface of AFC gets highly protonated as NH$_3{}^+$ form (figure in supplementary file) and this repulsed Cr^{3+} and Cr(OH)$^{2+}$ ions thus yielding very less removal of Cr(III).

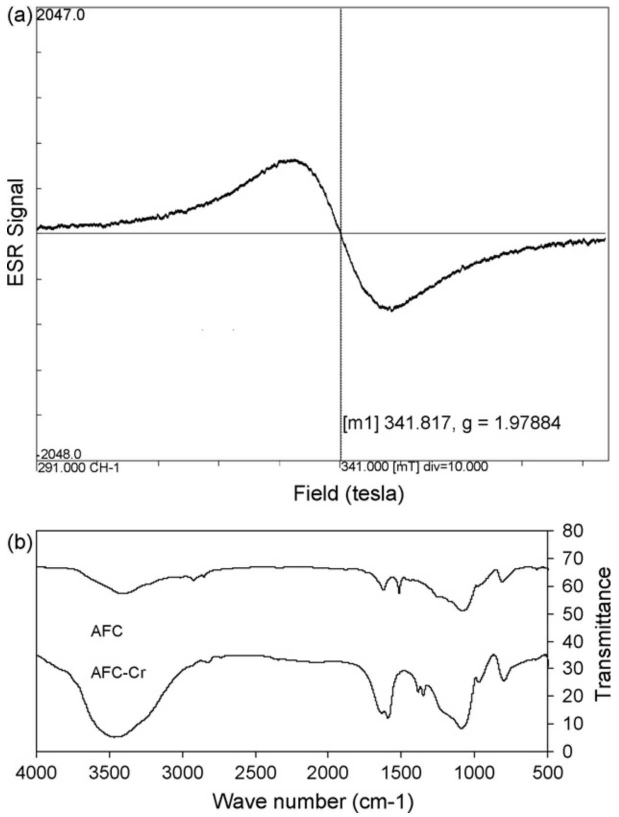

Fig. 3. (a) EPR spectrum of AFC coated silica gel after Cr(III) adsorption. (b) FT-IR spectra of AFC before and after Cr(III) adsorption.

At neutral pH range (pH 5.5 and above), the dominant species of Cr(III) are monovalent Cr(OH)$_2{}^+$ and divalent Cr(OH)$^{2+}$ (Fig. 4b). Cr(III) prefers octahedral geometry (six-coordinate) [17]. [CrOH]$^{2+}$ and [Cr(OH)$_2$]$^{1+}$ species are octahedral ions with one or two hydroxide ligand. In neutral pH range amine group of AFC is deprotonated and Cr(OH)$_2{}^+$ and Cr(OH)$^{2+}$ are bound to the polymer through at least two or three amine group of the polymer with rest of the coordination sites filled up with chloride (starting material is CrCl$_3$) and water molecules (Fig. 4(c)). The binding of amines occurred presumably due to the multidentate (multiple point binding) nature of the polymer compared to monodentate (single point binding) water or halide ion (Type I in Fig. 4(c)). With increase in pH, the bound water molecules will get deprotonated generating more and more [CrOH]$^{2+}$ and [Cr(OH)$_2$]$^{1+}$ species and formed bond with amine group of AFC (Type II in Fig. 4(c)), thus Cr(III) removal by AFC increased with increase in pH from 5.5 to 7.

However, at very high pH (above 10), the hydroxides are known to act as bridging ligands forming multinuclear species in the basic medium (e.g. [(H$_2$O)$_4$Cr(OH)$_2$Cr(H$_2$O)$_4$]$^{4+}$ shown as type (III) in Fig. 4(c)). Thus above pH of 10, large amount of Cr(III) ions formed this bridge structure and adsorption by AFC decreased.

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

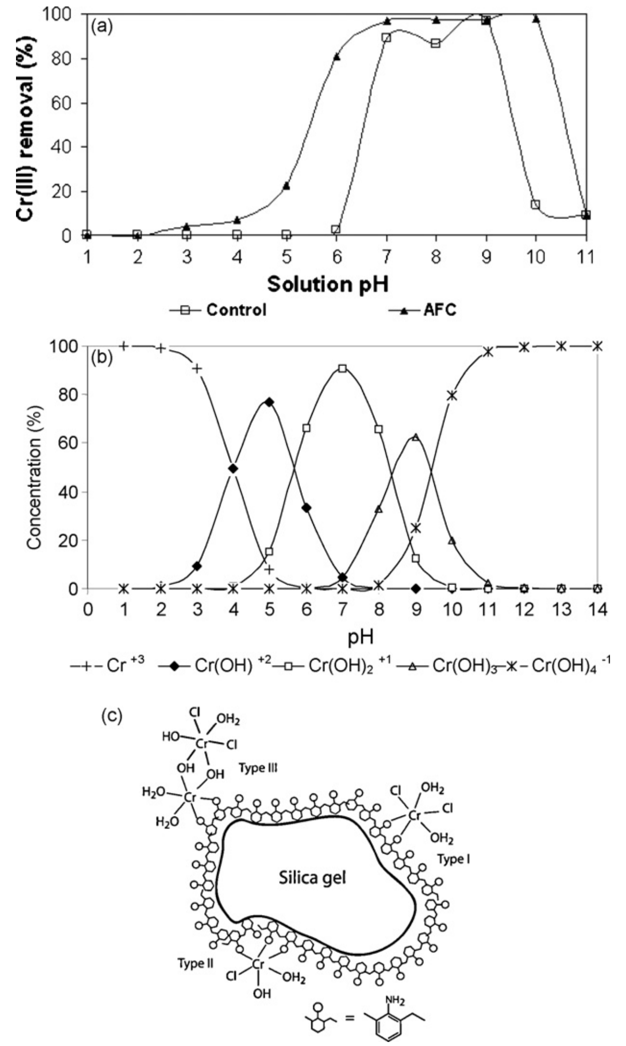

Fig. 4. (a) Removal of Cr(III) at varying solution pH by AFC COATED silica gel (initial Cr(III) 50 mg/L; AFC dose 4 g/L; agitation time 4 h). (b) Concentration distribution diagram of Cr(III) at different pH. (c) Proposed mechanism of Cr(III) adsorption by AFC coated silica gel.

charge repulsion of amine group and Cr(III) ion [18]. At reaction pH above 6, Cr(III) removal increased to 97%. It is reported that Cr(III) starts precipitating at pH above 6 as $Cr(OH)_3$ [19], a control experiment was also conducted in parallel and results are shown in Fig. 4(a). It is very clear that more than 80% removal of Cr(III) at pH of 6 was due to adsorption whereas, from pH 7, removal of Cr(III) was attributed due to precipitation.

3.4. *Effect of adsorbent dose*

Effect of adsorbent dose on Cr(III) removal is shown in Fig. 5. Cr(III) removal increased from 46% to 95% with increased in adsorbent dose from 1 to 10 g/L. With increase in AFC dose more active surface area were available for Cr(III) bindings thus achieving an increase in removal (%). However reverse trend was observed with adsorbed Cr(III) by unit amount of AFC (q_e) which decreased from 23 mg/g at AFC dose of 1 g/L to 4.75 mg/g at AFC dose of 10 g/L. Once the interaction of Cr(III)–AFC reached equilibrium, the addition of extra adsorbent was probably left unutilised or unsaturated. These unutilised mass of AFC were accounted however during the calculation of removal capacity, leading to decrease in value of q_e.

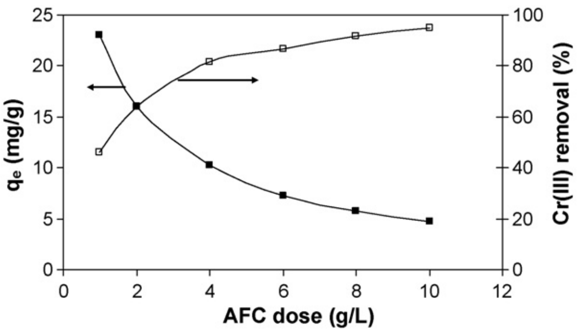

Fig. 5. Effect of adsorbent dose on Cr(III) removal by AFC coated silica gel (initial Cr(III) 50 mg/L; solution pH 6).

3.5. *Initial concentration effect and adsorption kinetics*

The effect of initial concentration of Cr(III) on adsorption is illustrated in Fig. 6(a). Almost 30–70% removal of Cr(III) was adsorbed within initial 20 min and equilibrium was achieved within 90–120 min. Such rapid adsorption was probably due to chemisorptions and also indicates high adsorption rate of Cr(III) ion by AFC. In our previous work with hexavalent chromium and copper equilibrium was achieved within 120–150 min [11,12]. With increase in initial Cr(III) concentration from 15 to 45 mg/L, adsorption increased from 32% to 37% and 78% to 90% at pH 5 and 6 respectively. This finding clearly suggests the dependence of initial concentration of adsorbate on adsorption.

The kinetics of Cr(III) adsorption by AFC coated silica gel was tested with Lagergren first order (Eq. (2)), second order kinetic model (Eq. (3)) [20] and Elovich equation (Eq. (4a))

$$q_t = q_e(1 - \mathrm{e}^{-k_1 t}) \tag{2}$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{3}$$

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = \alpha \exp^{(-\beta q_t)} \tag{4a}$$

where q_t and q_e (mg/g) are Cr(III) adsorption capacity at any instant of time t and at equilibrium time respectively; k_1 and k_2 are the first order and second order rate constants respectively, α is the initial adsorption rate constant ($\mathrm{mg\,g^{-1}\,min^{-1}}$) and β ($\mathrm{g\,mg^{-1}}$) is the desorption rate constant during any one experiment. When the adsorption is based on energetically heterogeneous surface, the parameter β is related to the distribution of activation energies. By assuming that $\alpha\beta t \gg 1$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ [21], Elovich equation becomes

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \tag{4b}$$

Elovich equation described adsorption on highly heterogeneous adsorbents and confirms the chemisorptions even though do not predict any definite mechanism [19].

Degrees of error between experimental and model predicted values were analyzed by employing chi-square test [22] (Eq. (5))

$$\chi^2 = \sum \frac{(q_t - q_m)^2}{q_m} \tag{5}$$

where q_t and q_m (mg/g) are total chromium adsorption capacity at time t using experimental data and predicted model data respectively. Lagergren's first order model showed correlation coefficient (R^2) of 0.95–0.98 (Table 1) whereas that of second order kinetic model is 0.99. It can be seen (Table 1) that χ^2 value for second order is much lesser than first order kinetic model suggesting Cr(III) adsorption on AFC followed second order kinetic model (Fig. 6(b)). Correlation coefficients of above 0.93 at pH 5 and 0.96 at pH 6 for

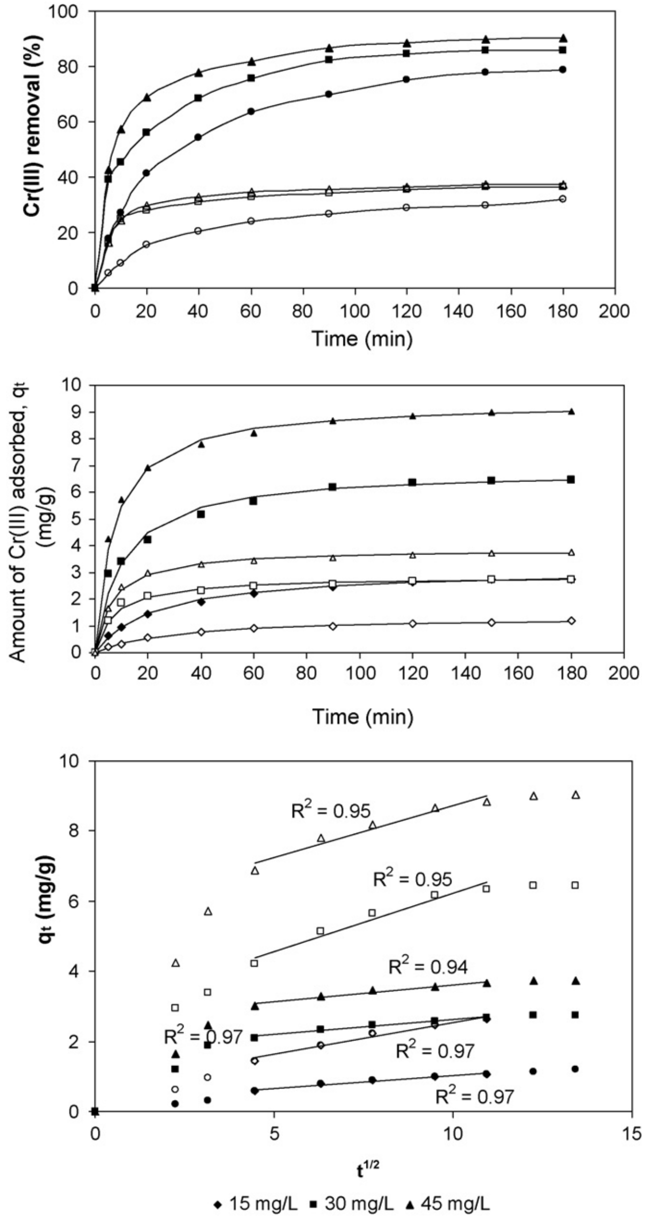

Fig. 6. (a) Cr(III) removal kinetics by AFC coated on silica gel (circle, square and triangle denotes initial Cr(III) of 15, 30 and 45 mg/L respectively. Hollow symbols signify reaction pH 5 and solid symbols show reaction pH 6). (b) Cr(III) adsorption kinetics by AFC coated silica gel (diamond, square and triangle denotes initial Cr(III) of 15, 30 and 45 mg/L respectively. Hollow symbols signify reaction pH 5 and filled signifies reaction pH 6, lines represent predicted second order). (c) Diffusion of Cr(III) on AFC coated silica gel (solid symbols for pH 5 and open symbols for pH 6; R^2 is correlation coefficient).

all different initial Cr(III) also confirm the applicability of Elovich equation suggesting the predominant chemical nature of Cr(III) adsorption on AFC [21].

To identify the diffusion mechanisms, the intraparticle diffusion model was also tested [23]

$$q_t = k_p t^{(1/2)} \tag{6}$$

where k_p is rate parameters for intraparticle diffusion q_t is the amount of Cr(III) adsorbed on AFC at different instance of time t (h). According to this model, it can be assumed that the mechanism involves the diffusion of the species if a straight line is obtained passing through the origin from the plot of Eq. (6), and the slope of the linear curve is the rate constant of intraparticle transport (k_p). As can be seen in Fig. 6(c) (q_t vs. $t^{1/2}$) for both the pH's, the first sharper portion may be considered as an external surface adsorption or faster adsorption stage. The second portion is the gradual adsorption stage where intraparticle diffusion is rate-controlled. The third portion is attributed to the final equilibrium stage where intraparticle diffusion starts to slow down due to the extremely low adsorbate concentrations in solution. In the intermediate stage where the adsorption is gradual, the process may be controlled by intraparticle diffusion. The rate of uptake might be limited by the size of the adsorbate molecule, the concentration of the adsorbate and its affinity to the adsorbent, the diffusion coefficient of the adsorbate in the bulk phase, the pore-size distribution of the adsorbent, and the degree of mixing [24]. From the slope of the linear plot obtained in the intermediate stage for pH 5 and pH 6, the values of k_p were estimated as 0.0762–0.096 and 0.1804–0.2951 h$^{-1/2}$ g/g AFC, respectively.

3.6. *Adsorption isotherm*

Adsorption isotherm was studied by conducting experiment with varying initial concentration of Cr(III) from 15 to 500 mg/L at pH of 6 and AFC dose of 4 g/L. The isothermal data were treated with Langmuir–Freundlich equation [25]:

$$q_e = \frac{Q_m (bC_e)^{1/n}}{1 + (bC_e)^{1/n}} \tag{7}$$

where C_e (mg/L) is the equilibrium Cr(III) concentration, q_e (mg/g) the Cr(III) adsorption capacity at equilibrium, Q_m the monolayer adsorption capacity, b is the equilibrium constant related to energy constant of adsorption and n is the Freundlich's intensity factor. On addition to it chi-square test was done further to confirm the fixing of model by equation [22]:

$$\chi^2 = \sum \frac{(q_e - q_{em})^2}{q_{em}} \tag{8}$$

where q_e and q_{em} (mg/g) are Cr(III) adsorbed at equilibrium calculated using experimental data and isotherm models, respectively.

Isotherm plots (q_e vs. C_e) using experimental and predicted data using Langmuir–Freundlich equation is shown in Fig. 7 and

Table 1
Comparison of first and second order kinetic model and Elovich model for Cr(III) adsorption.

pH	Initial Cr(III) (mg/L)	First order kinetic model			Second order kinetic model			Elovich model parameters		
		k_1	R^2	χ^2	k_2	R^2	χ^2	R^2	α	β
5	15	0.018	0.98	0.58	0.024	0.99	0.01	0.99	1.29	0.28
	30	0.027	0.96	6.51	0.047	0.99	0.04	0.94	20.26	0.39
	45	0.027	0.95	9.83	0.034	0.99	0.01	0.93	14.81	0.53
6	15	0.028	0.98	0.33	0.014	0.99	0.11	0.99	0.81	0.62
	30	0.034	0.98	5.33	0.014	0.99	0.22	0.99	2.59	1.07
	45	0.033	0.96	15.89	0.015	0.99	0.05	0.97	5.79	1.30

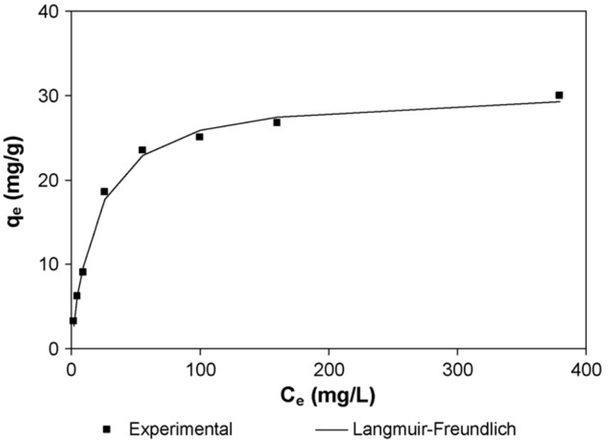

Fig. 7. Adsorption isotherm of Cr(III) by AFC coated silica gel.

isotherm constants were shown in Table 2. Regressions coefficient (R^2) of 0.99 with χ^2 value of 0.297 suggest that the adsorption of Cr(III) on AFC coated silica gel can be well explained by Langmuir–Freundlich's isotherm. Monolayer Cr(III) adsorption capacity (Q_m) was observed as 30.77 mg/g, i.e. 0.57 mmol/g. In our previous studies with divalent copper and hexavalent chromium adsorption by AFC coated silica gel followed Langmuir and Freundlich's models respectively with maximum adsorption capacities of 76 mg/g (1.2 mmol/g) for Cu(II) and 65 mg/g (1.25 mmol/g) for Cr(VI) respectively. It seems that both the transition metals adsorption was dominated by monolayer process, whereas for hexavalent chromium adsorption was heterogeneous in nature. Equilibrium constants for Cr(III) and Cu(II) were observed as 0.080 L/mg (4.160 L/mmol) and 0.022 L/mg (1.386 L/mmol), suggesting binding constant of Cr(III) higher than Cu(II).

Maximum Cr(III) adsorption capacity of 6.24 mg/g and 1.41 mg/g was reported by raw and acid treated palm flower (*Borassus aethiopum*) adsorbents respectively [26]. Lignin was observed to achieved maximum q_e of 17.97 mg Cr(III)/g [27]. A wine processing waste sludge obtained only 26.79 mg/g of Cr(III) when contacted an initial Cr(III) 100 mg/L with 10 g/L adsorbent [28]. Another waste (agricultural) coir pith achieved a maximum removal of 11.52 mg/g of Cr(III) from initial Cr(III) 50 mg/L [29]. Using chelating ion-exchange resins, it was observed that the maximum adsorption capacity of 0.288 mmol of Cr(III)/g for Chelex-100 and 0.341 mmol of Cr(III)/g for Lewatit TP 207 was achieved at pH of 4.5 [30]. Maximum removal of Cr(III) by *Agave lechuguilla* biomass was reported as much as 14.2 mg/g [31]. Very recently Guru et al. [32] had studied Cr(III) removal using low cost natural diatomite. Maximum removal at 318 K was observed as 21.8 mg/g Cr(III) with maximum of 28.1 mg/g at 288 K. Arslan and Pehlivan [33] observed monolayer Cr(III) adsorption capacity by lignite-based humic acid 15.08 mg/g. Comparing with recent adsorbents for removing Cr(III), AFC coated silica gel proved better adsorbent. Only composite alginate–goethite beads showed little higher removal capacity of Cr(III) then AFC with 30.37 mg/g [34].

Table 2
Isotherm constants for Cr(III) adsorption by AFC coated silica gel.

Langmuir–Freundlich isotherm				
Q_m (mg/g)	b (L/mg)	n	R^2	χ^2
30.77	0.052	1.005	0.995	0.297

Solution pH 5.4–5.7, temperature 22–25 °C, adsorbent dose 2 g/L, and initial Cr(III) 15–300 mg/L.

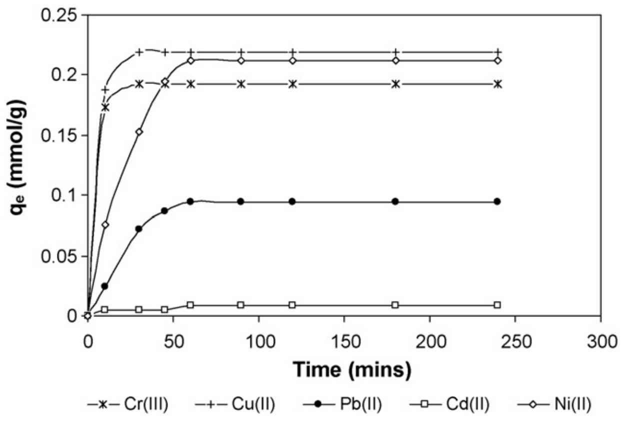

Fig. 8. Effect of other metal ions on removal of Cr(III) by AFC coated silica gel.

3.7. Competitive adsorption of Cr(III) ion

Actual wastewater always contains mixture of metal ions. In order to investigate the affinity of metal ions towards the active sites of AFC coated silica gel, experiment was carried out with simulating wastewater containing mixture of Cu(II), Ni(II), Cr(III), Pb(II), and Cd(II) each of 0.5 mmol with adsorbent dose of 2 g/L at pH of 6. The result of the study is presented in Fig. 8. With q_e value of 0.218 mmol/g, Cu(II) showed the maximum adsorption followed by Ni(II) of slight less q_e value of 0.211 mmol/g. Cr(III) achieved q_e value of 0.192 mmol/g of AFC. Adsorption capacity decreased significantly for Pb(II) (q_e of 0.09 mmol/g) and adsorption was almost negligible for Cd(II). Adsorption behaviour of mixed metals with AFC is governed by thermodynamic and kinetic aspects. According to thermodynamic aspect metals bind to donor ligands according to preferences decided by hard–soft theory of acids and bases as suggested by Pearson [35] and Lippard and Berg [36]. In this classification the term "soft" refers to species that are large and fairly polarizable, whereas "hard" species are small and less easily polarized. The general rule is that hard acids bind preferentially to hard bases and soft acids to soft bases. According to the classification of metal ions (hard or soft acids), Cr(III) is hard acid, Cd(II) and Pb(II) soft acids, whereas Cu(II) and Ni(II) "borderline" acids. Hence hard base amine ($-NH_2$) of AFC formed strong and stable complex with hard and borderline acids Cr(III), Cu(II) and Ni(II) as compared to soft acids Pb(II) and Cd(II). However, Pearson's theory is not able to justify higher removal of "borderline" acids Cu(II) and Ni(II) as compared to hard acid Cr(III).

It is reported that ligand exchange rates are faster for the divalent metal ions as compared to trivalent metals [36]. Exchange rates for water molecules from the first coordination sphere of Cu(II) and Ni(II) and Cr(III) at 25 °C are reported as: Cu(II): $1 \times 10^9\ s^{-1}$; Ni(II): $4 \times 10^4\ s^{-1}$ and Cr(III): $2 \times 10^{-6}\ s^{-1}$ [36], suggesting Cu(II) having higher exchange rate compared to Ni(II) and Cr(III) is kinetically almost immobile compared to Cu(II) and Ni(II). Due to higher ligand exchange rate Cu(II) adsorption was higher than Ni(II), whereas kinetically inert Cr(III) was slow and sluggish to react with AFC. Even though Cr(III)–AFC bond was thermodynamically favoured, but due to kinetic limitation of Cr(III), removal was less compared to Cu(II) and Ni(II) ions. Higher binding constant ("*b*" of Langmuir's model) was observed for Cr(III) as compared to Cu(II) in single metal–AFC studies in our previous study (4.160 L/mmol for Cr(III) and 1.386 L/mmol for Cu(II)), suggesting that Cr(III) adsorption by AFC was thermodynamically favoured than Cu(II). This study was conducted for 250 min at room temperature (22–25 °C). If experiments with mixed metal solution could be conducted at higher temperature for very long time, it would be probably possible to achieve higher q_e value for Cr(III) than Cu(II) and Ni(II) by overcom-

Table 3
Desorption of Cr(III) by different desorbents.

Type of desorbent	HCl	H_2SO_4	HNO_3	EDTA
Desorption efficiency (%)	26.6	30.0	31.66	5.83

Strength of desorbents 0.5 M.

ing the kinetic limitation of Cr(III) adsorption. However, such a long reaction time and higher temperature would not be practical and economical in terms of wastewater treatment.

The effect of ionic interactions on sorption may be represented and explain by the concept of comparing ratio of the sorption capacity for one metal ion in the presence of the other metal ions, Q_{mix}, to the sorption capacity for the same metal when it is present alone in the solution, Q_0 [37]. When $(Q_{mix}/Q_0) > 1$ sorption is promoted by the presence of other metal ions; $(Q_{mix}/Q_0) = 1$ there is no net interaction; when $(Q_{mix}/Q_0) < 1$ sorption is suppressed by other metal ions. From mixed solution of metals, AFC was able to removed 0.192 mmol/g of Cr(III) as against 0.47 mmol/g in mono system thus obtaining $Q_{mix}/Q_0 < 1$ (0.408) suggesting adsorption of Cr(III) decreased by the presence of other metal ions.

3.8. Desorption

From solid waste management point of view, recoveries of adsorbed metal by desorption and concentrating the metal in minimum volume is vital. Study of desorption was carried out by employing three mineral acids and chelating agent EDTA as desorbents and the findings are shown in Table 3. Amount of desorption was estimated using Eq. (9) as

$$\text{Desorption}\,(\%) = \frac{M_d}{M_r} \times 100 \tag{9}$$

where M_d and M_r are the amount of Cr(III) desorbed and adsorbed (mg). Maximum desorption obtained was 33.3%, 41.7% and 41.7% by 0.5 M HCl, H_2SO_4 and HNO_3 respectively whereas EDTA recovers only 5.8%. Irrespective of desorbents type, all desorption process was however observed to complete in 10 min and amount of Cr(III) desorption remained same for AFC even after 48 h. Our previous study reveals a complete desorption of adsorbed Cu(II) from AFC loaded silica gel by 1N mineral acids and 0.2N EDTA [15]. Such less desorption for Cr(III) may be probably due to the formation of both bidentate and tridentate co-ordinate bond between the Cr(III) and AFC which will be more difficult to break as compared to only bidentate co-ordinate bond with Cu(II) ion with AFC. Also, higher kinetic immobility and slower ligand exchange rate of Cr(III) as compared to Cu(II) were responsible for poor desorption performance of Cr(III) ion as compared to Cu(II). This result also suggest that AFC–silica gel can be used as an efficient adsorbent for removal of trace amount of Cr(III) ion from solution.

4. Conclusions

An amine-based polymer, aniline formaldehyde condensate (AFC) was prepared by polymerization of aniline cross-linked with formaldehyde and coated on silica gel and used as an adsorbent for removal of trivalent chromium [Cr(III)] from aqueous solution. With the increase in reaction pH, adsorption of Cr(III) on AFC increased achieving maximum removal of 80% at pH 6. Formation of multidentate coordination bonds between $[CrOH]^{2+}$ and $[Cr(OH)_2]^{1+}$ and deprotonated amine group ($-NH_2$) of AFC was possible mechanisms for removal of Cr(III) by AFC. Adsorption equilibrium for Cr(III) was achieved within 3 h with almost 80% adsorbed within 60 min. Adsorption of Cr(III) by AFC coated silica gel followed Langmuir–Freundlich's isotherm model with maximum monolayer coverage of 30.77 mg/g (0.57 mmol/g). In mixed metal solution "hard acid" Cr(III) showed less adsorption with "hard base" amine due to higher kinetic immobility as compared to "hard and borderline acids" Cu(II) and Ni(II) but Cr(III) adsorption was higher than "soft acids" Pb(II) and Cd(II). Desorption of Cr(III) was observed as low due to lower ligand exchange rate of Cr(III).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2008.11.030.

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