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Chemical Engineering Journal 141 (2008) 130–140

Chemical Engineering Journal

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Removal and recovery of chromium from wastewater using short chain polyaniline synthesized on jute fiber

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Received 7 June 2007; received in revised form 4 October 2007; accepted 4 November 2007

Abstract

In the present study, short chain polyaniline (PANI), a polymer was synthesized on the surface of jute fiber and was used as an adsorbent to remove hexavalent chromium (Cr(VI)). Experiments were conducted in batch mode with the variables such as amount of jute fiber on PANI, chain length of PANI, solution pH, initial concentration of Cr(VI), dose of PANI-jute and temperature. The PANI formed was found to be short chain polyaniline (oligoaniline). Optimum amount of jute fiber and chain terminating agent 1,4-phenylenediamine were observed as 5 g and 3.05 mmol, respectively, for 21.5 mmol of aniline. Maximum adsorption of total chromium (Cr(VI), Cr(III) and its other forms) was observed at reaction pH of 3 by electrostatic attraction of acid chromate ion with protonated PANI-jute. Adsorption equilibrium was achieved within 40–120 min for initial Cr(VI) of 50–500 mg/L. Maximum monolayer capacity of PANI-jute was observed as 62.9 mg/g at pH 3 and temperature 20 °C. Total chromium adsorption decreased with rise in temperature suggesting an exothermic adsorption of chromium. During desorption almost 83% efficiency was achieved within 10 min by 2 M NaOH. By ignition of chromium bounded PANI-jute, 94% Cr(VI) were able to recover as Cr(III) along with reduction in weight by 95%. PANI-jute can be used effectively to remove chromium from wastewater.
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Keywords: Short chain polyaniline; PANI-jute; Total chromium adsorption; Chromium recovery; Amine group; Coordination bond

1. Introduction

Chromium, a priority metal pollutant is widely used by various modern industries like electroplating, tanning, textile, etc. resulting in discharge and accumulation in large quantities into the environment [1]. Chromium exists in environment both as trivalent (Cr(III)) and hexavalent (Cr(VI)) forms of which hexavalent form is 500 times more toxic than the trivalent one [2]. Human toxicity of Cr(VI) includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage [3]. WHO (World Health Organization, 1993) and BIS (Bureau of Indian Standards, 1991) recommended guideline value for chromium (as total chromium) in drinking water as 0.05 mg/L (desirable) with no relaxation on permissible limit [4,5].

Adsorption is an effective and versatile method for removal of heavy metals when combined with appropriate desorption and metal recovery step solving the problem of sludge disposal [6]. It is well known that nitrogen atom in compounds of amine derivative makes co-ordinate bond with positive charge of metals due to the presence of electron in *sp3* orbital of nitrogen. An amine based polymer, aniline formaldehyde condensate (AFC) was coated on silica gel and used recently for removal of hexavalent chromium from wastewater [7]. This AFC polymer though showed high chromium adsorption capacity of 65 mg/g, had several disadvantages like instability for long time storage (above 6 months) and corresponding degradation in metal removal capacity. Also the coating of AFC on silica gel being a physical one was soluble in mild organic solvents like methanol and chloroform and during interaction of chromium–AFC, brown color effluent was generated probably due to degradation of AFC in strong acidic environment. In order to overcome these, the present laboratory-scale study aims at investigating the feasibility of polyaniline (PANI), another polymer with terminal amine (–NH_2) group for removal of Cr(VI) form wastewater. In literatures, some studies on use of polyaniline for metal removal have been published. Removal of mercury by a combination of polyaniline and polystyrene is reported [8]. Olad and Nabavi [9]

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doi:10.1016/j.cej.2007.11.004

used polyaniline in the forms of powder, film on electrodes and free standing film for removal of hexavalent chromium. However, synthesized polyaniline in two different oxidation states of leucoemeraldine and emeraldine showed only good reducing capability of Cr(VI) to Cr(III) [9]. Also, nowadays there is growing concern over disposal of metal contaminated solid waste after adsorption [10]. Recovery of adsorbed metals by igniting the adsorbent and obtaining the adsorbed metals as their oxides is a viable alternative. Therefore selection of combustible adsorbent is a better and obvious choice. In the present work, silica gel as support material was replaced by jute fiber due to its light weight, combustibility and also of lower cost. In order to improve the stability of the coating, polyaniline was directly synthesized on the jute fiber instead of coating the polymer on the support.

Present work was conducted in batch mode on removal of hexavalent chromium and study parameters include amount of jute fiber for PANI to be synthesized, chain length of PANI, reaction pH, initial concentration of Cr(VI), dose of adsorbent and temperature. Emphasis was also given on evaluation of chromium adsorption kinetics, isotherm, desorption and recovery of the adsorbed chromium from PANI-jute.

2. Materials and methods

Commercial grade aniline ($C_6H_5NH_2$) was purified by distilling over KOH pellets at boiling point temperature of aniline (180 °C). Ammonium peroxydisulfate [$(NH_4)_2S_2O_8$] and 1,4-phenylenediamine were used as received. Solution of potassium dichromate [$K_2Cr_2O_7$] salt purchased from Merck, India, was used as the source of hexavalent chromium and that of chromic chloride [$CrCl_3.6H_2O$] procured from Central drug house, India, as trivalent chromium. All chemicals and reagents used were of analytical grade purity and ultra pure water was used for all dilutions and reagents preparations. Jute bags were purchased from local market and washed with detergents to remove dirts. Then these were dried and chopped into fibers of 0.5–1.0 cm length and used in the present work.

2.1. Synthesis of polyaniline polymer on surface of jute fibers

Polyaniline was synthesized by oxidation of aniline ($C_6H_5NH_2$) in presence of 1,4-phenylenediamine, a chain terminator in acidic aqueous medium in presence of an oxidant, ammonium peroxydisulfate [$(NH_4)_2S_2O_8$]. The synthesis scheme of PANI is shown in Fig. 1 [11]. Aniline (2.00 g, 21.5 mmol) and 1,4-phenylenediamine (0.330 g, 3.05 mmol) were dissolved in 66 mL of 1 M HCl (aq.). The mixture was cooled in iced bath to 0–5 °C followed by addition of 5 g jute fibers and stirred for 5 min. The polymerization started by introduction of pre-cooled (5 °C) solution of ammonium peroxydisulfate (1.62 g, 7.10 mmol) in 16 mL of 1 M HCl (aq.). The reaction mixture was kept at 5 °C for 65 min and then kept for overnight at room temperature. Then the liquid was decanted from PANI-jute fiber. To ensure complete deprotonation of PANI-jute, alkali treatment was given by soaking PANI-jute in 1 M NH_4OH for 5 min. The products were then washed with distilled water to adjust the solution to neutral pH. Finally, the blue black colored PANI-jute fiber was dried at 40 °C in the oven.

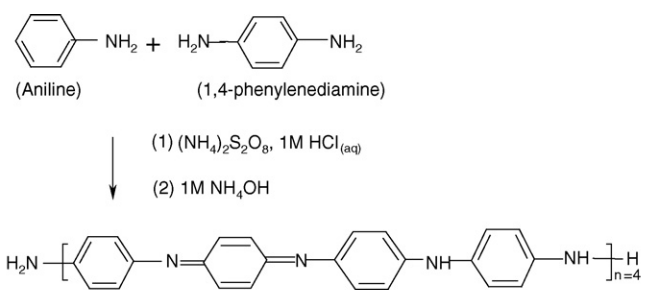

Fig. 1. Synthesis scheme of PANI [11].

2.2. Adsorption experiment

Hexavalent chromium (Cr(VI)) removal by PANI-jute was studied in batch mode. For complete investigation of chromium adsorption on PANI-jute, nine sets of experiments were carried out and details are given in Table 1. Batch experiments were carried out by contacting 1000 mL of hexavalent chromium (Cr(VI)) contaminated solution with predetermined quantities of PANI-jute added into it. To achieve the degree of mixing and equilibrium, a magnetic stirrer was employed with speed adjusted at 100 rpm. Solution pH range of 3–7 were well adjusted by 0.1 M NaOH and 0.1 N H_2SO_4 whereas pHs at extreme acidic and alkaline conditions were adjusted using 1 N 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. Aliquots were drawn at predetermined time intervals and were filtered through Whatman filter paper No. 42 and filtrate was used for estimation of total chromium (Cr(VI), Cr(III) and its other forms) and hexavalent chromium [Cr(VI)] concentrations. The total drawn aliquot volumes were less than 2.5% of total sample volume. A blank solution experiment was run in each set and confirmed the inability of specimen tube and plastic beakers to adsorb both forms of chromium [Cr(VI) and Cr(III)]. All experiments were carried out in two sets and average value was considered for data analysis.

The total chromium adsorbed on PANI-jute was calculated according to

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

where q_t is the amount of total chromium ion adsorbed per unit weight of PANI-jute (mg/g) at time t, C_0 and C_t the concentrations of total chromium ions (mg/L) at initial time and at time t, respectively, V the initial volume of chromium sample (L) and m is the mass of PANI-jute (g). Possibility of error on estimation of amount of chromium adsorbed on PANI-jute cannot be ruled out since estimation was based on analyzing the solution phase rather than the solid adsorbent phase. Estimation was therefore crosschecked on the solid-phase adsorbent also by digesting PANI-jute loaded chromium in a microwave digester

Table 1
Experimental design for adsorption study

Set no.	Control parameters	Variable parameters
1[a]	Initial Cr(VI): 50 mg/L; initial Cr(III): 50 mg/L; jute fiber dose: 2 g/L; agitation time: 3 h	Solution pH: 1, 2, 3, 4, 5, 6
2	Initial Cr(VI): 50 mg/L; PANI-jute: 2 g/L; pH: 3; agitation time: 24 h	Jute fiber (g): 1, 2, 3, 4, 5, 6, 7, 8, 9, 10
3	Aniline: 21.5 mmol; PANI-jute: 2 g/L; pH: 3; agitation time: 24 h; initial Cr(VI): 50 and 120 mg/L	1,4-Phenylenediamine: 2.00, 2.50, 3.05, 3.50, 4.00 mmol
4	Initial Cr(VI): 10 and 50 mg/L; PANI-jute: 2 g/L; agitation time: 24 h	Solution pH: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10
5	Initial Cr(III): 50 mg/L; PANI-jute: 2 g/L; agitation time: 24 h	Solution pH: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11
6	PANI-jute: 2 g/L; agitation time: 24 h; solution pH: 3, 4	Initial Cr(VI) (mg/L): 5, 10, 20, 50, 100, 300, 500
7	PANI-jute: 2 g/L; pH: 3	Initial Cr(VI) (mg/L): 5, 10, 20, 50, 100, 300, 500
8	Initial Cr(VI): 20, 50, 100; pH: 3; agitation time: 3 h	PANI-jute (g/L): 0, 0.2, 0.5, 0.8, 1, 1.5, 2, 3, 4, 5, 6, 8, 10, 12, 16, 18, 20, 25, 30
9	Initial Cr(VI): 50 mg/L, pH: 3; PANI-jute: 2 g/L; agitation time: 3 h	Temperature: 298, 308, 313, 325 K

[a] Set 1 experiment was conducted to investigate chromium adsorption capacity of plain jute fiber in absence of any polymer.

at pressure of 40 psi in presence of nitric acid (0.2 N) and then chromium concentration was measured in digested solution.

2.3. Desorption and recovery of chromium ion from PANI-jute

Desorption studies were conducted by batch experiments. Initially adsorption experiment was conducted with 1000 mL sample containing 50 mg/L of Cr(VI) treated with 4 g/L of PANI-jute 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 10 min. The mixture was again centrifuged and desorbed concentration of total chromium and Cr(VI) were determined in the filtrate.

The adsorbed chromate ions in PANI-jute were recovered back by igniting the chromium bounded PANI-jute at 550 °C for 2 h in muffle furnace. A greenish tint color of obtained chromium oxides were dissolved in 1 N HNO_3 solutions and the chromium concentration was estimated in acid solution.

2.4. Analytical procedure

PANI-jute was characterized using UV Spectrophotometer (Varian Model, Cary 50). Total chromium was estimated by Atomic Absorption Spectrophotometer (Spectra AA, Varian Model) using air–acetylene flame at 429 nm wavelength and slit width of 0.5 nm. Cr(VI) concentration was estimated using UV spectrophotometer at 540 nm wavelength by 1,5-diphenyl carbazide method [12]. Cr(III) concentration of a sample was calculated as difference of total chromium and Cr(VI) for the same sample solution. Chromium bounded PANI-jute were digested at 40 psi with acid using microwave digester (Microwave digestion system, Model: 7295, OI Analytical, Texas). Change in surface morphology of PANI-jute after adsorption of chromium and confirmation of presence of chromate ions on surface of PANI-jute by analyzing EDX was investigated using scanning electron microscopy (Scanning electron microscope, Model: LEO, 1430 VP, Carl Zeiss, Germany). Presence of adsorbed Cr(III) on PANI-jute was examined by employing electromagnetic spin resonance spectrophotometer (ESR) (Model: JES-FA 200 ESR System, JEOL Ltd., Japan).

3. Results and discussions

3.1. Optimization of base support (jute fiber)

Polyaniline is a dark blue colored material of powder form. In order to obtain a solid adsorbent to facilitate the separation of metal ion after adsorption, a support material was required to introduce in polymer matrix. Support materials that adsorb less or no chromium but exhibits high chromium adsorption after synthesizing PANI on it are the obvious choice to understand the total chromium adsorption capabilities by PANI at different physical–chemical conditions. Firstly, raw jute was examined for removal of Cr(III) and Cr(VI) by conducting set 1 experiment and results are shown in Fig. 2(a). At reaction pH range of 1–6, jute adsorbed a maximum of 10% Cr(VI) and 0.5% Cr(III) at pH 3 from initial concentration of 50 mg/L each.

Since jute exhibited very low chromium removal, set 2 experiments were conducted to optimize the amount of jute fiber on PANI during synthesis of the polymer. From Fig. 2(b), it can be seen that PANI-jute exhibited a maximum removal of almost 40% when amount of jute fiber support base was 1 to 5 g. With increase in the amount of jute more than 5 g, removal of total chromium decreased. Probably excess amount of jute resulted less and non-uniform amount of PANI on the surface of jute fiber. Considering the economical point of view, 5 g of jute was fixed for PANI to be synthesized on its surface for the further investigations.

3.2. Optimization of PANI chain length

The molar ratio of amine source (aniline) to chain inhibitor (1,4-phenylenediamine) to control the chain length was varied in set 3 experiment at pH 3 with 2 g/L PANI-jute dose. Results are shown in Table 2. When 1,4-phenylenediamine of 2 mmol was used for synthesis of PANI, amount of total chromium adsorbed were 7.5 and 20 mg/g for initial Cr(VI) concentration of 50 and 120 mg/L, respectively. With increase in 1,4-phenylenediamine

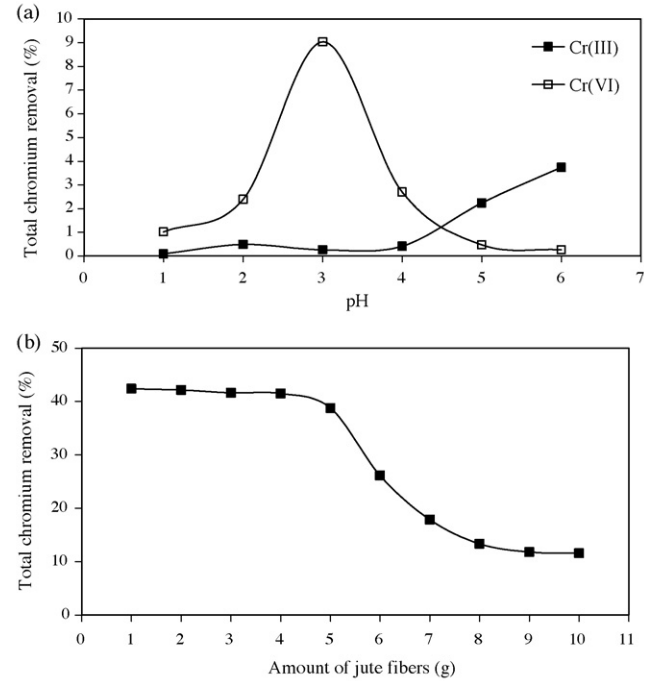

Fig. 2. (a) Removals of Cr(III) and Cr(VI) by jute fiber at different solution pH [50 mg/L of initial Cr(III) or Cr(VI); pH 3; 2 g/L of jute fiber; 3 h of agitation time] and (b) optimisation of support materials (jute) for coating PANI [initial Cr(VI) 50 mg/L; pH 3; adsorbent dose 2 g/L].

amount to 3.05 mmol, amount of total chromium adsorbed increased to 12 and 29.5 mg/g, respectively. However, these decreased to 10.5 and 22 mg/g with further increase in amount of 1,4-phenylenediamine to 4 mmol.

When amount of chain length inhibitor (1,4-phenylenediamine) was increased, chain length of PANI decreased yielding an increase in number of terminal NH_2 groups per gram of polymer due to reduction in formula weight of chain of PANI (Fig. 1), and this was responsible for increase in amount of total chromium adsorbed. With further increase of quantity of chain inhibitor, the solubility of PANI also increased and washed out from jute fiber surface and chromium adsorption decreased due to availability of fewer polymers. Therefore optimum 1,4-phenylenediamine of 3.05 mmol was fixed and used for preparation of PANI-jute for further investigation on removal of Cr(VI).

Table 2
Optimization of chain length of PANI synthesized on jute fiber

Amount of 1,4-phenylenediamine during PANI synthesis (mmol)	Amount of total chromium adsorbed (mg/g) by PANI-jute	
	Initial Cr(VI) 50 (mg/L)	Initial Cr(VI) 120 (mg/L)
2.00	7.5	20
2.50	10	27.5
3.05	12	29.5
3.50	11	24
4.00	10.5	22

3.3. Characteristics of adsorbent (PANI)

PANI synthesized on jute fibers was dissolved in *N*,*N*′-dimethylformamide (DMF) solvent and UV spectra is shown in Fig. 3(a). With λ_{max} of 561 nm, the most predominant form of PANI is the short chain polyaniline (oligoaniline) which have a λ_{max} of 572 nm in DMF solvent [13]. PANI with higher chain length absorbs at 635 nm [14]. The SEM images of PANI-jute before and after chromium adsorption are shown in Figs. 3(b) and (c), respectively. It can be seen from the figures that the surface of PANI-jute before adsorption was smooth and even.

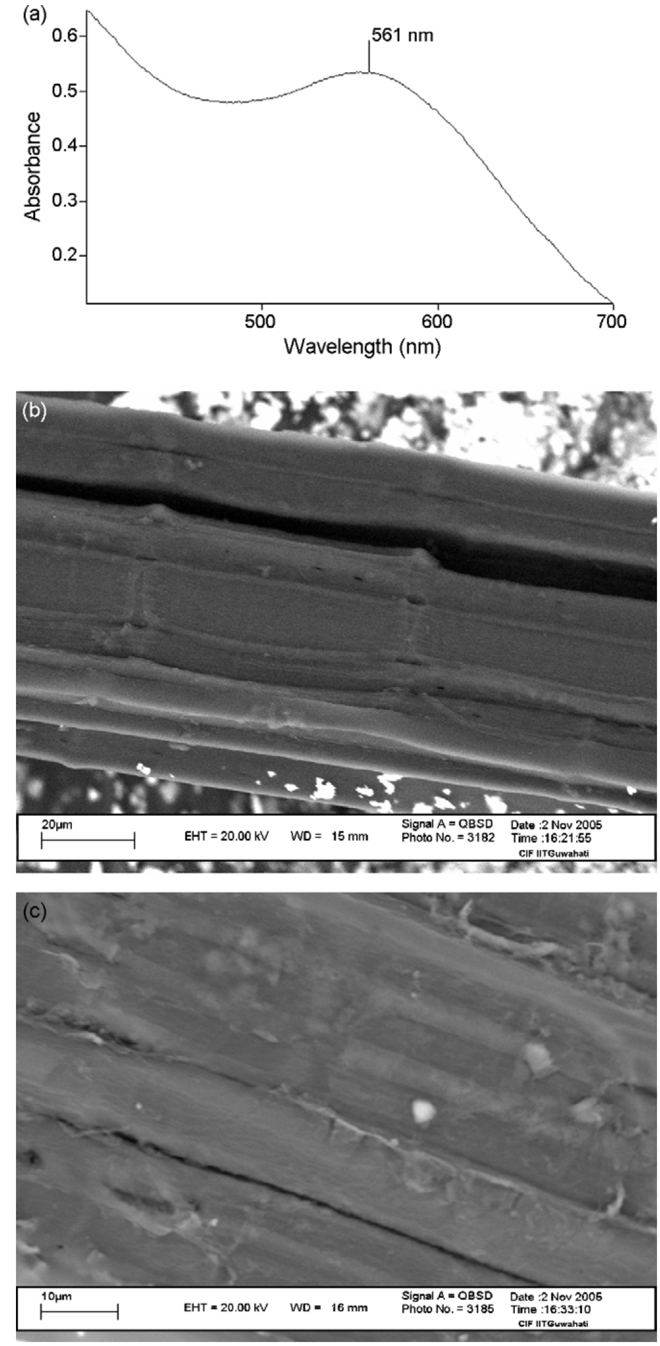

Fig. 3. (a) UV spectra of PANI, (b) SEM of PANI-jute before chromium adsorption and (c) SEM of PANI-jute after chromium adsorption.

The energy dispersive X-ray (EDX) analysis for both the PANI-jute samples was also conducted along with SEM to confirm the presence of chromium ion on the surface of PANI-jute (Supplementary files). Chromium peaks are visible on the surface of PANI-jute after adsorption experiment, which was absent on the adsorbent surface before interaction with chromium ion.

3.4. *Effect of pH*

Solution pH is one of the most important factors during adsorption since it reflects the nature of the physico-chemical interaction of the species in solution and the adsorptive sites of adsorbent [15]. Set 4 experiment was carried out to study the effect of pH (1–10) on removal of Cr(VI) by PANI-jute fibers and results are shown in Fig. 4. It can be seen that, with the increase in solution pH from 1 to 3, total chromium removal increased from 47 to 72% and 35 to 48% for initial Cr(VI) concentrations of 10 and 50 mg/L, respectively, approaching a plateau at pH 3. However with further increase in pH above 3, removal of total chromium decreased significantly with sharp drop at pH 5 and negligible removal at pH 8 and above. In order to check the solubility behavior of Cr(VI) with change in solution pH, parallel experiments of Cr(VI) solution were also conducted without any adsorbents as a control. In control experiment, within studied pH range (1–10), it was observed that the Cr(VI) remained soluble with initial concentration of Cr(VI) remained constant even after 24 h of agitation. Our previous study on removal of chromium by another amine based polymer, aniline formaldehyde condensate (AFC) also showed maximum adsorption of total chromium at pH of 3 [7]. Similar pH trend with plateau formation on removal of chromium were also observed by various adsorbents like wool, olive cake, sawdust, pine needles, almond, coal and cactus with optimum pH 2 as well as by modified PVP-coated silica gel at pH 5.5 [16,17].

Such plateau formation with chromium adsorption decreasing on both sides of optimum pH 3 suggests different mechanisms of interaction of Cr(VI) and PANI-jute. Perusals of literature had observed that at acidic pH, Cr(VI) was easily reduced to Cr(III) as shown in the following equation [7,18,19]:

$$\mathrm{HCrO_4}^- + 7\mathrm{H}^+ + 3\mathrm{e}^- \rightarrow \mathrm{Cr(III)} + 4\mathrm{H_2O} \quad E_\mathrm{o} = 1.33\,\mathrm{V} \tag{2}$$

From Eq. (2), it can be understood that, acid dichromate ion ($\mathrm{HCrO_4}^-$) which is the form of Cr(VI) at pH 1–4, are strong oxidants with redox potential of 1.33 V. Distributions of Cr(VI) (%) and Cr(III) (%) in solution at various pH levels were estimated using Eqs. (3a) and (3b), respectively, and values are given in Table 3 in columns E and F, respectively, for both initial Cr(VI) of 10 and 50 mg/L:

$$\mathrm{Cr(VI)\,(\%)\ in\ solution} = \frac{\{\mathrm{Final\ \ Cr(VI)\ \ in\ \ solution\,(mg/L)}\} \times 100}{\mathrm{Final\ total\ chromium\ in\ solution\,(mg/L)}} \tag{3a}$$

$$\mathrm{Cr(III)\,(\%)in\ \ solution} = \frac{\{\mathrm{Final\ \ total\ \ chromium\ \ in\ \ solution\,(mg/L) - Final\,Cr(VI)\ \ in\ \ solution\,(mg/L)}\} \times 100}{\mathrm{Final\,total\,chromium\ \ in\ \ solution\,(mg/L)}} \tag{3b}$$

In the acidic pH range of 1 and 2, almost 66–73% of total chromium in the treated solution was in the form of reduced Cr(III) for both initial Cr(VI) concentration of 10 and 50 mg/L (column F, Table 3). However the corresponding Cr(III) amount in solution at pH 3 were only 3.9 and 6.6% of treated effluent with 72 and 48% of initial Cr(VI) adsorbed (Fig. 4). At pH above 3, amount of Cr(III) in solution was almost negligible (column D, Table 3). Such insignificant amounts of Cr(III) in the treated solution at pH 3 and above indicates the possibility of either less reduction of Cr(VI) to Cr(III) or adsorption of reduced Cr(III) by PANI-jute.

Therefore, the possibility of Cr(III)-PANI-jute interaction was further investigated by conducting set 5 experiments. From Fig. 5(a), it was very much clear that there was almost no removal of Cr(III) in acidic range of pH 1–4. One of the most possible reason may be that at acidic pH, –$\mathrm{NH_2}$ sites of PANI-jute was highly protonated and this was responsible for repulsion of Cr(III) ions. At pH of 6–9, almost 70% removal of Cr(III) was achieved by PANI-jute. In Fig. 5(a), results of control experiments suggest that removal of Cr(III) at pH between 7 and 9 was attributed due to precipitation of Cr(III). Control experiments showed that with further increasing in pH above 9, Cr(III) became soluble again due to its ampotheric nature. However, removal of Cr(III) in this strong basic region was almost negligible. At pH values above 7, neutral $\mathrm{Cr(OH)_3}$ and anionic $\mathrm{Cr(OH)_4}^-$ species begin to appear, reducing the adsorption capacity of these species with deprotonated amine group of PANI-jute [20].

However, even though adsorption of whatever reduced Cr(III) by PANI-jute can be ruled out, Cr(VI) after adsorption may reduce to Cr(III) on the surface of PANI-jute itself. ESR (Electro spin resonance) technique was used to verify the presence of Cr(III) on PANI-jute surface. After adsorption experiment with Cr(VI) at pH of 2–4, effluent solution and PANI-jute adsorbent were examined by ESR technique. The resonance signal of the effluent solution after adsorption experiment at pH 2 appears at a magnetic field position corresponding to *g* value of 1.975

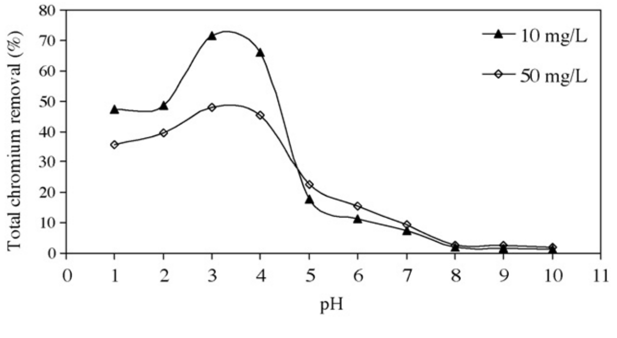

Fig. 4. Effect of pH on total chromium removal (PANI-jute dose 2 g/L; initial Cr(VI) 10 and 50 mg/L; agitation time 24 h).

Table 3
Distribution of Cr(VI) and reduced Cr(III) in treated solution

pH	Initial Cr(VI) 10 mg/L						Initial Cr(VI) 50 mg/L					
	A	B	C	D	E	F	A	B	C	D	E	F
1	5.8	6.0	1.6	4.2	27.58	72.41	31.26	32.00	8.3	22.9	26.55	73.45
2	5.55	5.7	1.73	3.82	31.17	68.82	28.6	29.24	9.62	18.9	33.63	66.36
3	2.81	2.7	2.7	0.11	96.08	3.91	23.9	24.32	22.32	1.58	93.38	6.61
4	3.36	3.40	3.31	0.05	98.51	1.48	25.05	24.67	24.39	0.66	97.36	2.63
5	8.42	8.38	8.4	0.02	99.76	0.23	37.5	38.02	36.97	0.53	98.58	1.41
6	9.04	9.22	9.04	0	100	0	41.52	41.88	41.5	0.02	99.95	0.05
7	9.24	9.42	9.24	0	100	0	46.34	46.24	46.34	0	100	0

A: effluent total Cr (mg/L) after adsorption (estimation based on filtrate solution); B: effluent total Cr (mg/L) after adsorption (estimation based on digestion of PANI-jute); C: Cr(VI) concentration (mg/L) in solution after adsorption; D: Cr(III) concentration (mg/L) in solution after adsorption (subtracting values of column C from column A); E: Cr(VI) in solution (%) with respect to effluent total chromium after adsorption [using values of columns A and C in Eq. (3a)]; F: Cr(III) in solution (%) with respect to effluent total chromium after adsorption [using values of columns A and D in Eq. (3b)].

[Fig. 5(b)], confirming the presence of Cr(III) whose standard signal *g* value is 1.98 [21]. When ESR was employed on effluent solution after adsorption experiment at pH 3 and 4, no spectra was observed indicating insignificant amount of Cr(III) in solution after adsorption experiment at pH 3 and 4. After ESR examination of PANI-jute adsorbent (after adsorption experiment at pH 2–4), no spectrum was observed indicating absence of Cr(III) on solid PANI-jute surface after adsorption. This confirms that total chromium bounded on PANI-jute was predominantly Cr(VI) form with negligible or insignificant amount of Cr(III). However, Cr(VI) may coexist with other oxidation species of chromium on surface of PANI-jute even though quantifying exact amount of Cr(VI) is not easy.

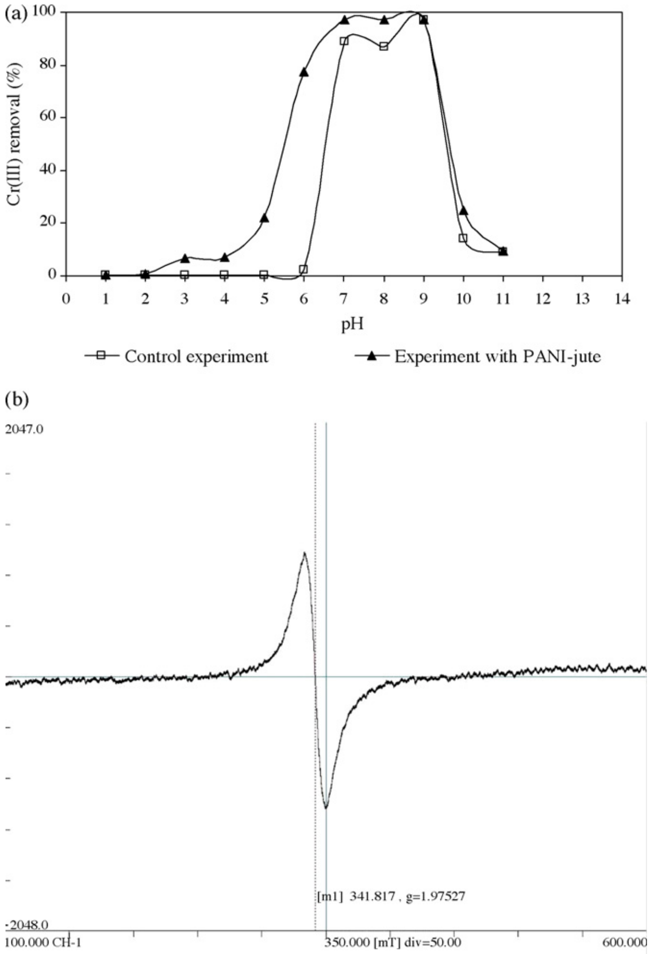

Fig. 5. (a) Effect of pH on removal of Cr(III) [initial Cr(III) 50 mg/L; dose 2 g/L; agitation time 24 h; control experiments without adsorbent] and (b) ESR spectrum of effluent after adsorption experiment at pH 2.

Eq. (2) also suggests the consumption of protons during the reduction of Cr(VI). To cross check the consumption of proton, adsorption of Cr(VI) experiment were further carried out without controlling the reaction pH and it was observed that solution pH increased from initial value of 2.2 to 2.5 on removal of 40 mg/L of Cr(VI) suggesting the consumption of 4 mmol of proton for removal of 1 mmol of Cr(VI). However, no shifting of pH was observed when experiment was conducted at pH 3 and above suggesting negligible reduction. In our previous investigation, consumptions of 4.26 mmol of protons for each mmol of Cr(VI) removal by aniline formaldehyde condensate was observed, while consumption of 3.99 and 2.7 mmol of protons for each mmol of Cr(VI) removal by dead biomass *Aspergillus niger* and *Rhizopus oryzae* were reported [7,19,22].

Based on the results of set 4 and set 5 experiments [effect of pH on removals of Cr(VI) and Cr(III)] and ESR study with PANI-jute, it can be hereby concluded that, adsorption of total chromium on polyaniline-jute was only in the form of Cr(VI). At pH 1–4, Cr(VI) exists in solution as $HCrO_4^-$ (acid chromate) ions. In this acidic pH, $-NH_2$ of polyaniline exists in protonated form ($-NH_3^+$) and can form bond with acid chromate ion by electrostatic attraction. Therefore besides 38–47% and 34–39% of Cr(VI) reductions at pH 1 and 2, respectively, 35–47% and 39–48% of total chromium removals for initial Cr(VI) of 10 and 50 mg/L as well as maximum total chromium removals of 72% at pH 3 attributed due to this electrostatic attraction. With pH increase from 4 to 6, amount of protonation on PANI-jute surface decreased yielding a decrease in total chromium adsorbed from 66 to 7% and 45 to 9% at initial Cr(VI) of 10 and 50 mg/L, respectively. A fate of Cr(VI) when interacted with PANI-jute at pH range of 1–7 is shown in Fig. 6. The optimum pH of 3–4 were also reported during removal of Cr(VI) by biomaterials like *Ecklonia* biomass [23,24]. The main mechanism was reported as reduction coupled adsorption, where Cr(VI) was first completely

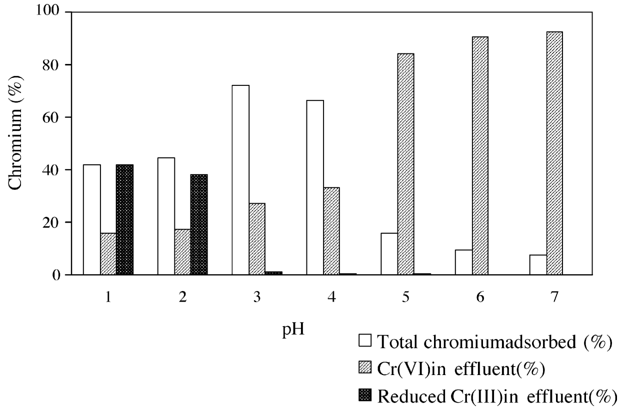

Fig. 6. Fate of Cr(VI) after interaction with PANI at different pH range [initial Cr(VI) 10 mg/L; effluent Cr(VI) and Cr(III) (%) shown are evaluated with respect to initial Cr(VI)].

reduced to Cr(III) at pH 3–4 and reduced Cr(III) formed complex with biomaterials [25,26], whereas in the present work the main mechanism of Cr(VI) removal by polymer at optimum pH 3 was anionic adsorption.

Besides, estimating amount of Cr(VI) in effluent after adsorption (column A, Table 3), chromium bounded PANI-jute was also digested in 0.2 nitric acid and total chromium was estimated in digested solution (column B, Table 3) to cross check the estimation. A difference of 0.47–3.9% indicate a minimum error between the two different types of analysis.

3.5. Adsorption isotherm

To identify the functional relationship between the amount of Cr(VI) in the bulk solution and adsorbed on PANI-jute, set 6 experiments was carried out. The isotherm data were treated with linearized form of Langmuir and Freundlich adsorption isotherm models (Eqs. (4a) and (4b), respectively) [27,28]:

$$\frac{C_\mathrm{e}}{q_\mathrm{e}} = \frac{1}{bq_\mathrm{max}} + \frac{C_\mathrm{e}}{q_\mathrm{max}} \tag{4a}$$

$$\log q_\mathrm{e} = \log K_\mathrm{f} + \frac{1}{n}\log C_\mathrm{e} \tag{4b}$$

where C_e (mg/L) is the equilibrium liquid phase concentration of total chromium, q_e (mg/g) the total chromium adsorption capacity at equilibrium, q_max the monolayer adsorbent capacity, b the energy constant of adsorption, K_f the Freundlich capacity factor and n is the Freundlich's intensity factor. The value of 'n' in the range of 1–10 denotes favorable adsorption. For the case of Langmuir, a dimensionless parameter named separation factor (R_L) is introduced to indicate the favorability of the adsorption and is determined by the following equation [29]:

$$R_\mathrm{L} = \frac{1}{1 + bC_0} \tag{4c}$$

The regression data of Langmuir's and Freundlich's linear isotherm model are shown in Table 4. The regressions coefficient (R^2) for both the isotherms at reaction pH of 3 and 4 were much above 0.98 suggesting the data well fitted on both the isotherms. However, to select the best bit isotherm model, Chi square test was done by the following equation [30]:

$$\chi^2 = \sum \frac{(q_\mathrm{e} - q_\mathrm{em})^2}{q_\mathrm{em}} \tag{4d}$$

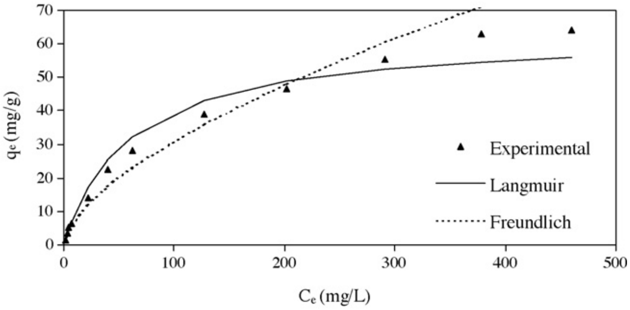

Fig. 7. Adsorption isotherm of total chromium by PANI-jute at pH 3.

where q_e and q_em (mg/g) are total chromium adsorbed at equilibrium calculated using experimental data and isotherm models, respectively. Compared χ^2 values of both the isotherm (Table 4) indicate a better Langmuir's isotherm model for adsorption of chromium by PANI-jute. However, less value χ^2 for Freundlich's isotherm suggest the adsorption of chromium by PANI-jute can be described by both the isotherm models. Isotherm plots (q_e vs. C_e) using experimental and predicted data for both Langmuir and Freundlich at pH 3 is shown in Fig. 7. Freundlich's intensity factor n of 1.60 and 1.50 at pH 3 and pH 4, respectively, along with Langmuir's R_L value 0.90 (less than 1) further suggests the favorability of adsorption of total chromium on PANI-jute. A polymer polyacrylamide grafted sawdust exhibited an adsorption capacity of 45 mg/g from initial chromium concentration of 100 mg/L at pH 3 [31] as compared to 62.9 mg/g of PANI-jute in the present study. Another amine based adsorbent polyacrylonitrile fibers was reported to remove a maximum of 35 mg/g from initial chromium of 50 mg/L at pH 5 [32]. Also, PVP coated on silica gel showed a maximum removal of 3 mg/g from initial chromium of 10 mg/L at pH 5 [17]. Based on total chromium removal capacity, PANI-jute showed a better option.

Table 4
Regression data of Freundlich and Langmuir isotherm models

Solution pH	Frendlich isotherm				Langmuir isotherm				
	K_f (mg/g)	n	R^2	χ^2	q_max (mg/g)	b (L/mg)	R^2	R_L	χ^2
3	1.74	1.60	0.98	8.89	62.89	0.02	0.99	0.90	4.82
4	1.10	1.50	0.98	6.75	62.5	0.01	0.99	0.95	2.62

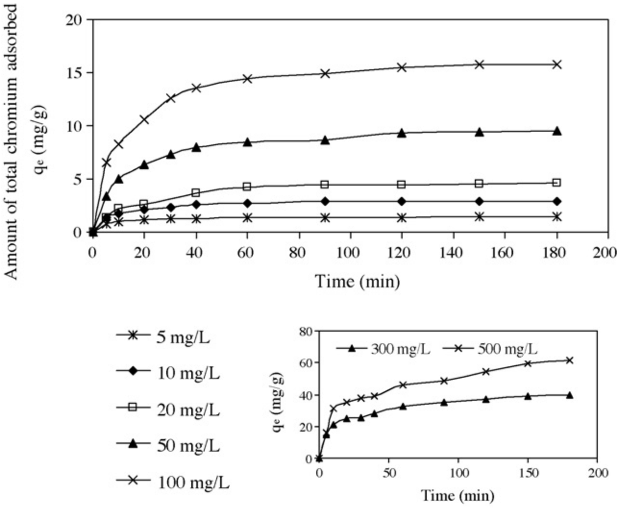

Fig. 8. Effect of initial concentration of Cr(VI) on total chromium adsorption (PANI-jute dose 2 g/L; pH 3).

3.6. Adsorption kinetics

Adsorption kinetics of chromium removal was studied by conducting set 7 experiments and the removal trend is shown in Fig. 8. Adsorption of total chromium increased from 1.43 to 61.65 mg/g with increase in initial Cr(VI) concentrations from 5 to 500 mg/L. With the increase in Cr(VI) concentrations, chances of interaction between chromate ions and PANI-jute increased and fractional removal of total chromium increased. However, equilibrium was almost achieved within 40 min of agitation time for Cr(VI) of 50 mg/L and 2 h for initial Cr(VI) concentration of 500 mg/L. Such a rapid adsorption suggests a readily available, large surface area and smaller diffusion path of PANI-jute for chromium ions adsorption. As compared to 2 h equilibrium time of PANI-jute, seaweed biomass *Ecklonia* pre-treated with HNO_3 required 9 h for complete removal of total chromium from initial concentration of 200 mg/L [33]. To remove Cr(VI) from an initial concentration of 800 mg/L, activated carbon was reported to required 200 h [34]. Another fungal biomass *A. niger* was reported to achieve equilibrium in 50–350 h on removing chromium from initial Cr(VI) 25–200 mg/L by fungal biomass dose of 10 g/L [19]. In terms of total chromium removal kinetics, PANI-jute showed fairly good results.

In order to analyze nature of kinetics and the rate of adsorption of total chromium by PANI-jute, data were further treated with Lagergren's pseudo-first order model (Eqs. (5a) and (5b)) and second-order kinetics models (Eqs. (6a) and (6b)) [35]:

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

or,

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

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

or,

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

where q_e (mg/g) and q_t (mg/g) denotes the total chromium ions adsorbed on PANI-jute at equilibrium time and at time t respectively, while k_1 and k_2 are first-order and second-order rate constant, respectively. Compared values of reaction rates and correlation coefficient of first- and second-order model for varying initial concentration of Cr(VI) is shown in Table 5. In order to identify the appropriate kinetic model, data were further analyze with Chi-square test [30]:

$$\chi^2 = \sum \frac{(q_t - q_{tm})^2}{q_{tm}} \tag{6c}$$

where q_t and q_{tm} (mg/g) are experimental and kinetic model predicted total chromium adsorption capacity at time t, respectively. Correlation coefficient of well above 0.99 (Table 5) along with less error between calculated and experimental q_t values for second-order model (with much less χ^2 value) suggest chromium adsorption following second order kinetics. Fixing of data on second order further confirms that chemisorptions was the rate controlling steps in chromium adsorption by PANI-jute [35]. Several authors also reported second order chromium removal kinetics with various adsorbents like used tyres, sawdust, activated carbon prepared from rubber wood saw dust, KOH activated wood carbon, etc. [36,37]. Confirming the chromium adsorption on PANI-jute followed second order further leads to treat the data and analyzed using the Elovich equation (Eq. (7a)). Elovich equation described adsorption on highly heterogeneous adsorbents [38] like PANI-jute and confirms the chemisorptions even though do not predict any definite mechanism.

$$\frac{dq_t}{dt} = \alpha \exp^{(-\beta q_t)} \tag{7a}$$

where α is the initial adsorption rate constant (mg g^{-1} min^{-1}), β (g mg^{-1}) the desorption rate constant during any one experiment and q_t is the total chromium adsorbed on PANI-jute at any time t. When the adsorption is based on energetically heterogeneous surface, the parameter β is related to the distribution of activation energies. In the diffusion control model, β is a function of both the particle structural-chemical characteristics and solute diffusion coefficient [39]. 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 $t = t$ [40], Eq. (7a) becomes

$$q_t = \beta \ln(\alpha\beta) + \beta \ln(t) \tag{7b}$$

Plotting q_t versus ln (t) of different initial Cr(VI) of 5–500 mg/L yields straight lines and constants were evaluated from the slope and intercepts (Table 5). Correlation coefficients of above 0.96 for all different initial Cr(VI) confirm the applicability of Elovich equation suggesting the predominant chemical nature of chromium adsorption on PANI-jute [40]. From Table 5, it can be seen that with ratio between initial concentration of adsorbate and adsorbent decrease, values of α, the initial rate of adsorption increased with subsequent decrease in β values. This suggests

Table 5
Comparison of kinetic model for total chromium adsorption

Initial Cr(VI) (mg/L)	First-order kinetic model			Second-order kinetic model			Coefficient of Elovich equation		
	k_1 (min^{-1})	R^2	χ^2	k_2 (g mg^{-1} min^{-1})	R^2	χ^2	α (mg g^{-1} min^{-1})	β (g mg^{-1})	R^2
5	0.03	0.92	4.75	0.11	0.99	0.02	136.25	0.18	0.96
10	0.04	0.99	4.44	0.04	0.99	0.03	12.81	0.45	0.96
20	0.03	0.96	4.51	0.02	0.99	0.06	1.02	0.94	0.96
50	0.03	0.97	16.28	0.01	0.99	0.05	1.20	1.69	0.97
100	0.04	0.96	17.22	0.01	0.99	0.19	0.99	2.69	0.96
300	0.02	0.97	68.57	0.01	0.99	2.54	0.25	6.91	0.99
500	0.02	0.93	63.71	0.01	0.99	6.69	0.07	11.53	0.97

that the initial rate of adsorption can be enhanced by increasing the amount of adsorbent dose (decreasing ratio between initial concentration of adsorbate and adsorbent). Similar findings were observed during adsorption of Pb^{2+} by *Azadirachta indica* (Neem) leaf powder [41].

3.7. Dose effects on adsorption

Set 8 experiments were conducted to evaluate the effect of dose of PANI-jute on Cr(VI) and total chromium removal. Fig. 9 shows that concentration of Cr(VI) decreased abruptly with increase in PANI-jute dose from 0 to 10 g/L for all the initial Cr(VI) of 20, 50 and 100 mg/L. The rate of removal of Cr(VI) increased with increase in initial Cr(VI) concentration. Probably higher concentration of Cr(VI) allowed quicker and more bindings than lower initial Cr(VI) concentration at same dose of adsorbent. The trend of adsorption of total chromium at varying doses of PANI-jute is also shown in Fig. 9. Almost 5–98% removals of total chromium were achieved for all initial Cr(VI) concentration of 20, 50 and 100 mg/L with increase in PANI-jute dose from 0.2 to 30 g/L. The trend was as expected since more active sites of adsorbent were exposed when dose of PANI-jute increased. However, after rapid increase of adsorption of chromate ions with increase in PANI-jute dose up to 10 g/L, total chromium removal attained an asymptotic value for larger dose of PANI-jute. Such slow increase in removal beyond an optimum dose may attributed to the attainment of equilibrium between adsorbate and adsorbent at the operating conditions. This effect had been termed as "solid concentration effect", i.e. overcrowding of particles, by Mehrotra et al. [42]. From the economical point of view, 10 g/L would be suggested for the adsorption of total chromium for initial concentration of Cr(VI) of 20–100 mg/L.

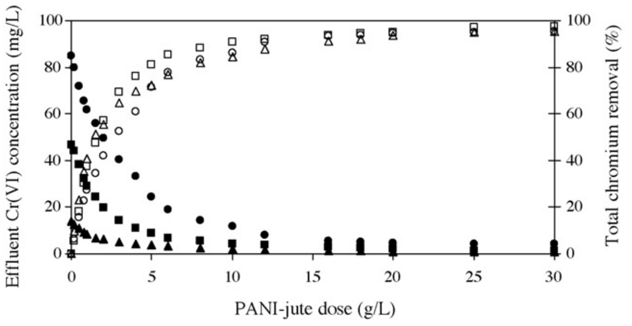

Fig. 9. Effect of PANI-jute dose on total chromium adsorption (pH 3; agitation time 3 h) [hollow symbols for q_e (mg/g) and filled up symbols for total chromium removal (%); triangle, square and circles for initial Cr(VI) of 20, 50 and 100 mg/L].

3.8. Effect of temperature on adsorption

Effect of temperature on adsorption of total chromium was investigated by conducting set 9 experiments. It was observed (Fig. 10) that at 298 K, total chromium removal was 43% with corresponding Cr(VI) effluent of 26 mg/L whereas at 325 K, 17% total chromium was removed with effluent Cr(VI) of almost 40 mg/L. Decrease in total chromium removal with the rise in temperature suggests an exothermic reaction nature of total chromium adsorption by PANI-jute. Similar nature of decrease in chromium adsorption with increase in temperature was also observed with adsorption by heat-activated bauxite [43].

3.9. Desorption and recovery of adsorbed chromate ions

To understand the nature of bonding of Cr(VI) on PANI-jute, desorption experiment was conducted. As Cr(VI) was attached as $HCrO_4^-$ on $-NH_3^+$ site, hydroxides with higher affinity may replace $HCrO_4^-$ from PANI-jute sites. Hence different strength of NaOH and NH_3OH were employed as desorbents. During desorption, 17, 63 and 83% of Cr(VI) were released in solution by 0.5, 1 and 2 M NaOH, respectively, whereas

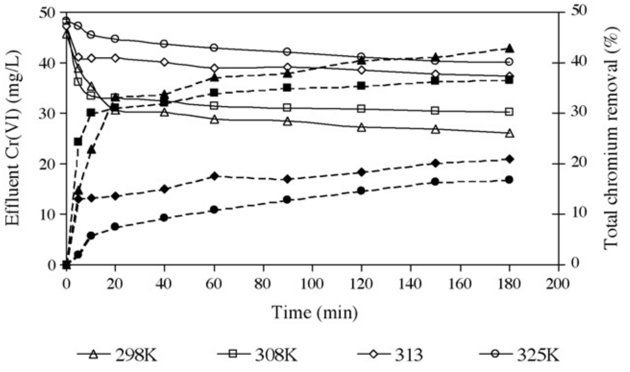

Fig. 10. Effect of temparature on effluent Cr(VI) and removal of total chromium by PANI-jute [pH 3; initial Cr(VI) 50 mg/L; dose 2 g/L; filled symbols for total chromium removal (%) and open symbols for effluent Cr(VI)].

11, 21 and 38% were released by 0.5, 1 and 2 M NH_4OH, respectively. NaOH being the stronger base was responsible for more desorption of chromate ions than NH_4OH. However, even with the strong base like 2 M NaOH, desorption of chromate ions was incomplete. During adsorption, along with the binding of $HCrO_4^-$ with $–NH_3^+$, there is a possibility of formation of chemical bond between the Cr(VI) species and the nitrogen atoms of polyaniline as observed by Deng and Bai [32]. This factor may be responsible for incomplete desorption of Cr(VI). However, maximum desorption occurs in equilibrium time of 10 min indicating adsorption of Cr(VI) mostly on surface of PANI-jute and less of internal diffusion in nature.

To investigate the degree of recovery of chromate ions bound on PANI-jute fibers after adsorption, 4 g of PANI-jute was employed for adsorption of chromium ion [Cr(VI) concentrations 46 and 120 mg/L]. It was observed that weight of PANI-jute increased from 4 to 4.2 g after adsorption experiment probably due to chromate ions binding. After ignition in muffle furnace the weight of PANI-jute-chromium decreased to only 0.2 g thus reducing the weight by 95%. This PANI-jute-chromium after dissolving in nitric acid, almost 94% of the Cr(VI) adsorbed were recovered back in solution in the form of non toxic Cr(III) ion. This study shows that PANI-jute is a better choice for removal and recovery of Cr(VI).

4. Conclusion

Polyaniline (PANI) a polymer was synthesized on the surface of jute fiber and was used as an adsorbent to remove hexavalent chromium from wastewater. 5 g of jute fiber and 3.05 mmol of chain terminating reagent 1,4-phenylenediamine were found to be optimum for aniline concentration of 21.5 mmol yielding short chain polyaniline (oligoaniline). Maximum adsorption of total chromium (Cr(VI) and Cr(III)) of 72 and 48% for initial Cr(VI) of 10 and 50 mg/L, respectively, were observed at reaction pH of 3 by electrostatic attraction of acid chromate ion ($HCrO_4^-$) with protonated amine group of PANI-jute. Total chromium adsorption followed Lagergren's pseudo-second order model and also Elovich model indicating chemical nature of chromium adsorption by PANI-jute. The equilibrium adsorption data fitted both Freundlich's and Langmuir's isotherms with maximum monolayer coverage of 62.9 and 62.5 mg/g at reaction pH 3 and 4, respectively. With the rise in reaction temperature, total chromium adsorption decreased indicating an exothermic nature of adsorption of chromium binding on $–NH_2$ sites of PANI-jute. Maximum desorption efficiency achieved was 83%, however upon ignition of PANI-jute-chromium, almost 94% recovery was achieved as Cr(III) ion. PANI-jute can be used effectively to remove and recover the chromium from wastewaters.

Acknowledgements

Dr. Saswati Chakraborty would like to thank Council of Scientific and Industrial Research (CSIR), Govt. of India (No. 22 (0418)/06/EMR-II) for financial support to this work.

The authors would also like to thank Head, Central Instruments Facility (CIF), Indian Institute of Technology Guwahati, India, for allowing to use SEM and ESR facilities.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2007.11.004.

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