Scientific Paper

# Application of Polyaniline and its Composites for Adsorption/Recovery of Chromium (VI) from Aqueous Solutions

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# Abstract

This paper deals with adsorption of Cr(VI) from aqueous solutions using sawdust coated by polyaniline (SD/PAn) and polyaniline composites with nylon 66 and polyurethane. Nylon and polyurethane are available common polymers that can be easily dissolved in the solvents of PAn (formic acid and NMP). So, the PAn composites with these polymers can be readily prepared via solvent cast method. Polyaniline (PAn) was synthesized chemically and coated on the surface of sawdust (SD) from formic acid via cast method. It was found that polyaniline in the acid doped form (e.g. HCl), can be used for Cr(VI) ion removal in acidic aqueous solutions (pH  $\leq$  2). Adsorption occurs only under acidic conditions and it decreases with increasing the pH of solution significantly. The proposed mechanism for adsorption of Cr(VI) with our currently developed adsorbent seems to be mostly occurring via an anion exchange process. Adsorption of Cr(VI) from water using SD/PAn column is both a simple and efficient method compared to the other adsorbents reported by previous investigators.

Key words: Polyaniline, composite, sawdust, chromium (VI), pH, adsorption and desorption.

# INTRODUCTION

Environmental contamination by heavy metals is a widespread problem, with sources of pollution arising from industrial activities. One of the most important of them in aqueous solutions is chromium. Cr(VI) poses a serious risk to the environment and endangers public health as well as the environment.

Chromium with electron configuration [Ar]4S<sup>1</sup> 3d<sup>5</sup> and atomic weight of 52 g. mol<sup>-1</sup>, is a highly reactive metal and exists in different oxidation states in aqueous solutions (II, III, VI). Chromium is used to harden steel, manufacture stainless steel, and form many useful alloys. It is mostly used in plating to produce a hard, beautiful surface and to prevent corrosion. All of its compounds are colored. The most important are sodium and potassium chromate and dichromate. It is most commonly found in liquid wastes in two oxidation states, Cr(III) and Cr(VI). There is a great difference in the toxicity and bioavailability of these two forms. Of these two valences, Cr (VI) is highly poisonous, extremely mobile in groundwater at wide ranges of pH and has been identified as a potent carcinogenic.<sup>1</sup> Chromium (VI) is a common waste product generated from industrial processes such as electroplating, wood preservation, metal finishing, as mordants in textile industry, pigment, chrome plating and leather tanning. It is also more toxic than Cr(III) to biological activities.<sup>1,2</sup> The threshold value for Cr(VI) has been reported 1ppm. In drinking water the level of chromium is usually low, but contaminated well water may contain the dangerous Cr(VI).

According to National Toxicology Program (NTP, US), there is sufficient evidence for carcinogenicity of Cr(VI) compounds<sup>1</sup>. Research on the toxicological effect of Cr(VI) on water bodies concluded that high concentration of Cr(VI) in water were also lethal to various fish. The maximum Cr(VI) concentration admitted in effluent is  $1 \text{mg L}^{-1}$  before discharge into the sea. For Cr(III), it is a practice to keep the concentration below 4 mg L<sup>-1</sup>. Cr(VI) has been reported to be responsible for lung cancer, chrome ulcer, perforation of nasal septum, brain and kidney damage. Peoples who work in the steel and textile industries or smoke tobacco have higher chance of exposure to chromium toxicity.

Chromium (VI) normally exists in the anionic forms  $(Cr_2O_7^{2-}, HCrO_4^{-} \text{ or } CrO_4^{2-})$  in water depending on pH and concentration. In highly acidic media

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(pH <1) the Cr(VI) ion exists mostly as  $H_2CrO_4$ (pK<sub>1</sub> = 6.51 and pK<sub>2</sub> = 5.65). At pH between 2 and 6 there is equilibrium between  $Cr_2O_7^{-2}$  and  $HCrO_4^{-1}$ ions. Under alkaline conditions (pH>8) it exists predominantly as chromate anion. The equilibrium between chromate and dichromate ions in water can be shown as the following equation:

$$\operatorname{Cr}_2\operatorname{O}_7^{2-}$$
 +  $\operatorname{H}_2\operatorname{O}$   $\rightleftharpoons$   $2\operatorname{Cr}_4^{2-}$  +  $2\operatorname{H}^+$ 

Cr(VI) in the form of dichromate (pH<6) is a relatively strong chemical oxidant. Its oxidative nature is a reason for its toxic and carcinogenic properties. Since it is readily diffused through the skin, it then reacts with the enzymes of the body or biological systems. After the oxidation reaction, it is reduced to Cr(III). The accumulation of Cr(III) in cells results in changing the structure of DNA molecule and disordering the metabolism activities.

Cr(III) is poisonous only at high concentration. Cr(III) occurs naturally in many vegetables, fruits, meats, yeasts and grains. Cr(III) is a more stable, makes less soluble salts (so less mobile in environment), less toxic, and listed as an essential element (in trace concentration) to provide good health. Cr(III) is an important microelement for plant and animal nutrition and essential for the maintenance of glucose as well as for the lipid and protein metabolism.<sup>3</sup> Various treatment techniques have been suggested by investigators for the removal of Cr(VI) from wastewaters.4-12 Contaminated waters containing low concentrations of Cr(VI) are typically treated with ion exchange resins, but this method is also costly due to the high price of the resin. Adsorption on low cost activated carbon (prepared from low cost raw materials), reduction-precipitation and ion exchange methods are the most acceptable ones in terms of capital and waste disposal costs.

The traditional treatment is reduction to trivalent chromium followed by precipitation. The Cr(III) is precipitated as hydroxide at alkaline conditions using either caustic soda or lime. However, this method is only effective at high chromium concentration. The major shortcoming of the conventional treatments involves a lengthy process, significant sludge production, high disposal (sludge) and chemical costs and low efficiency at low concentrations, however the method requires high capital investment.

In this paper a new sorbent system based on the application of polyaniline a polyaromatic amine has been used as an effective adsorbent for removing Cr(VI) from aqueous solutions. Polyaniline is a well-known conducting/electroactive polymer. PAn is one of the most potentially useful conducting polymers and has received considerable attention in recent years by many investigators.<sup>13-21</sup> Polyaniline can be easily synthesised

either chemically or electrochemically from acidic aqueous solutions.<sup>17,19</sup> Chemical structure of PAn can be simply shown in Fig. 1.

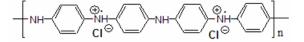


Figure 1. Chemical structure of acid doped as synthesized polyaniline (PAn)

Polyaniline can exist in various oxidation states characterized by the ratio of imine to amine nitrogen.<sup>16</sup> Upon simple treatment of polymer with dilute alkaline solutions (e.g. NH<sub>3</sub> or NaOH) or it changes into a material called emeraldine base (EB), which consists of equal numbers of reduced and oxidized repeated units or y = 0.5 (Figure 2).

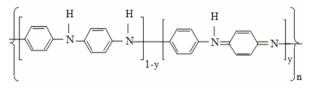


Figure 2. General structure of polyaniline (PAn)

The value of y can be varied between 0 (fully reduced state) to 1 (fully oxidized state). Emeraldine base (EB) is insoluble in water and common organic solvents. It is soluble in few solvents such as formic acid (88%), and 1-methyl 2-pyrrolidinone (NMP). This permits it to be solution processed to produce, flexible, free standing films or coating solid supports through casting and preparation composites with conventional polymers. Emeraldine base (EB, insulator state of PAn) can then be protonated (doped) with a non-oxidising protonic acid such as HCl, H<sub>2</sub>SO<sub>4</sub> or organic acids (e.g. p-toluene sulfonic acid). All of the previously reported of polyaniline conducting polymers are based on its interesting and unique electrical conductivity (metallic) and electroactivity. This paper deals with the new potential application of polyaniline as an anion exchanger material useable for environmental protection in water and wastewater treatment.

## **Experimental**

#### Reagents

All chemicals used were analytical reagents (AR grade). A stock Cr (VI) solution (1000 mg L<sup>-1</sup>) was prepared in distilled water using  $K_2Cr_2O_7$ . Aniline (Merck) was purified by vacuum distillation before polymerization. Poly[(hexamethylene adipamide)] or nylon 66 (as a woven material) and polyurethane (commercial foam) were used for the preparation of polyaniline composites. Formic acid (88%) and

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N-methyl pyrrolidone (NMP) were used as solvents for solution processing (casting) of polyaniline.

## Chemical synthesis of polyaniline (PAn)

Polyaniline powder was synthesized according to a procedure reported in literature after some modifications.<sup>20-22</sup> In this procedure, 5.0 g (0.054 moles) freshly distilled aniline dissolved in 250 mL of HCl 1M (0.215 M). The mixture cooled to below 5 °C by using an ice bath. 250 mL of a pre-cooled 0.3 M NH<sub>4</sub>S<sub>2</sub>O<sub>6</sub> solution in HCl 1M was slowly added under vigorous stirring to monomer solution over a period of 30 minutes. Since the reaction is highly exothermic ( $\Delta H = 372 \text{ KJ mol}^{-1}$ ), the reaction vessel was placed in an ice bath cooling system during addition oxidant. After complete addition of oxidant, the reaction mixture was left stirring for about two hours at low temperature (0-5 °C) and left unstirred overnight at room temperature. The precipitated polymer (dark blue powder) was filtered and washed with copious distilled water and dilute HCl solution until the washing liquid was colorless. In order to remove oligomers and other non-polymeric impurities the precipitate was washed thoroughly with methanol and distilled water. The polymer was dried at 50-60 <sup>o</sup> C in an oven, powdered in a mortar and stored for processing. Based on the weight of the monomer used and the product polymer produced, the polymerization yield was found about 90%.

# Preparation of polyaniline (EB form) and its composites and adsorption experiments

In order to make polyaniline soluble in formic acid for coating and composite formation, the polymer was treated with 0.5 M NaOH solution for 2 hours. Then it was washed with distilled water and dried in an oven at 60 °C. 0.50g of base treated PAn, emeraldine base (EB) was dissolved in 50 mL of formic acid. The polymer solution was filtered in order to remove any non-dissolvable solids. For preparation of polyaniline coated sawdust (SD/PAn), 5 g sawdust were mixed with 50 mL of EB in formic acid (1% w/v) in a beaker (100 cm<sup>3</sup>) and stirred for two hours at room temperature and left for another 2 hours without stirring. The excess of the solvent was evaporated by heating the SD/PAn at ~60 °C in an oven.

SD/PAn can also be prepared via direct synthesis of polymer on the surface of sawdust. However, coating by the cast method was found to give more uniform and homogeneous coating. For adsorption studies 1.0 g of sieved sawdust coated by polyaniline (SD/PAn, 5% coating) was packed as a fixed bed in a glass column (1cm diameter  $\times$  15cm length) with glass wool support at the bottom. In order to remove any dissolvable colored materials in SD or SD/PAn columns, they were washed with acetone and sodium hydroxide (0.2 M) until the washing liquid was colorless. Then the columns were

washed with distilled water and conditioned with HCl or NaOH solutions to obtain desired pH, controlled by a pH meter before each adsorption experiments. Flow rate of the test solutions through the column was selected 5 mL min<sup>-1</sup>.

For preparation of sawdust coated by polyaniline composites with nylon 66 (SD/PAn/Ny) and polyurethane (SD/PAn/Pu), four 25 mL aliquots solutions of polyaniline (EB form, in formic acid and NMP), nylons 66 (in formic acid) and polyurethane (in NMP) were prepared separately with concentration of 1% (w/v). Then solutions of polyaniline in formic acid (1%)and NMP were mixed with nylon and polyurethane solutions (1%), and stirred completely to produce homogeneous mixtures. 5.0 g of previously dried and sieved sawdust was added to each of these solutions and mixed well. The excess of solvent was removed by heating the mixtures in an oven at approx. 50 ° C. Higher temperature should be avoided because of structural changes in polyaniline (such as cross linking) which occur during thermal treatment.<sup>22</sup> Sawdust coated by polyaniline/nylon composites (SD/PAn/Ny) and polyaniline /polyurethane composite (SD/PAn/ Pu) after complete drying were sieved and packed in the same column used for SD/PAn sorbent. The same experiments of Cr(VI) adsorption was carried out for sawdust coated by PAn composites. In order to have a better comparison, adsorption experiments were carried out using sawdust (uncoated) and a commercial grade activated carbon (granulated form, Merck 2186).

### Cr(VI) Determination

Measurement of unadsorbed Cr (VI) ion was carried out spectrophotometrically at pH≥12 using NaOH 0.2 M solution ( $\lambda_{max} = 375 \text{ nm}, \epsilon = 4900 \text{ cm}^{-1} \text{ M}^{-1}$ ) using a calibration or standard curve. Determination of Cr(VI) as chromate ion (yellow color) is more sensitive than its determination as dichromate form(orange) in aqueous solution. For further confirmation, 1, 5-Diphenylcarbazide was also used as the reagent for detection of trace amount of Cr(VI) (LOD = 0.1 ppm). This reagent makes a highly colored violet complex with Cr(VI) in 0.1 to 0.2 M  $H_2SO_4(\epsilon = 41700 \text{ cm}^{-1}\text{M}^{-1}$ at  $\lambda_{max}$ =546 nm). A single beam spectrophotometer (Perkin-Elmer, model 35) was employed for Cr(VI) analysis. Sorption percent of Cr(VI) was calculated from the equation of  $(\mathbf{C}_{o} - \mathbf{C}) / \mathbf{C}_{o} \times 100$ . **C** and  $\mathbf{C}_{o}$  are the unadsorbed and initial concentration of Cr(VI) respectively. The percentage of desorption was calculated using  $\mathbf{C} / \mathbf{C}_{0} \times 100$  equation.

# **Results and discusion**

Sawdust (SD) was found as a suitable substrate for coating polyaniline because of its high polarity

(leading to good adhesion of polymer), hydrophilic nature and adequate chemical and physical stabilities in aqueous solutions. Our preliminary investigations in this research also showed that the sorption capacity of SD is much higher than with other agricultural low cost wastes such as rice husk. This was attributed to the fact that in water Cr(VI) exists in an anionic form and agricultural wastes such as rice husk, wheat and rice bran are excellent sorbents for heavy metal cations. Adsorption of Cr(VI), like for other sorption processes, can be affected by important factors such as contact time, initial chromium concentration, sorbent dosage, flow rate (column operations), temperature and pH (the most important factor).

#### Effect of pH on Cr(VI) sorption by SD/PAn

In order to study the effect of pH, 50 mL of Cr(VI) with an initial concentration of 50 ppm in distilled water was treated with 1.0 g of SD/PAn packed in column at different pH values (unbuffered). The effluent was then analysed for Cr(VI). The maximum percentages of Cr(VI) obtained at different pHs of treated test solutions are summarized in Table 1. In order to have a better comparison, uncoated SD was also used under the same conditions as used for SD/PAn for Cr(VI) adsorption. Adsorption of Cr(VI) by our recently developed adsorbent (SD/PAn) was found to be a strongly pH dependent process. Efficient removal of Cr(VI) occurred at relatively low pH values only. The rate of Cr(VI) sorption by both SD and SD/PAn sorbents decreased substantially with increasing of pH  $(pH \ge 5)$ . Polyaniline in the doped state (possessing releasable dopants such as Cl<sup>-</sup>) can be easily exchanged with anions like Cr(VI) which exists as anionic form in aqueous solutions. At pH values higher than 4, de-doping process occurred in polymer (PAn), and then desorption of Cr(VI) will be the predominant process.

Table 1. The Effect of pH on Cr(VI) sorption by SD/PAn and SD

pH of Cr(VI) solution	Percentage of adsorption (SD/PAn)	Percentage of adsorption (SD)
0	100	-
1-2	100	80
3-4	90	45
5-6	20	30
> 6	0.0	0.0

\*The columns were conditioned with 25 mL distilled water, NaOH (0.2M) and HCl (0.2M) before adsorption tests. Weight of adsorbent (SD/PAn) = 1.0g, 50 mL of 50 mgL<sup>-</sup>Cr(VI) in distilled water used as test solution. Flow rate = 5mL min<sup>-</sup>, experiments were carried out at room temperature. The data reported are the average of three parallel experiments. Maximum uncertainty was less than 1%.

High concentration of Cr(VI) should also be avoided because of the oxidative nature of Cr(VI) in acidic media which is leaded to some degradation of PAn. For this reason we used test solutions with low concentration of Cr(VI). Although, Cr(VI) removal by SD can be partly due to the oxidative nature of Cr(VI) and existence of some easily oxdizable materials in wood (e.g. lignin). No measurable Cr(VI) sorption was observed when the treatment media was neutral or alkaline (pH  $\geq$  6). Under alkaline conditions (pH > 7), the polymer (PAn) became completely undoped and the polymer changed into its deprotonated emeraldine base (EB) form, with no chloride anions or other counter anions in the polymer to be exchanged with Cr(VI) anions in solution. Therefore, the adsorption could not occur. High removal of Cr(VI) by SD/PAn sorbent in acidic media might also be accompanied by some bioreduction of Cr(VI) to Cr(III).<sup>23</sup> Since Cr(III) is not toxic, we did not analyze the solution for presence of Cr(III).

#### Comparison of SD/PAn with other adsorbents

In order to have a better understanding of the sorption capacity of SD/PAn columns, adsorption experiments were repeated for polyaniline composites with nylon 66 and polyurethane under acidic conditions (HCl 0.1 M). In addition uncoated sawdust (SD) and a commercial grade of activated charcoal (AC) were used for Cr(VI) sorption studies. The results obtained are summarized in Table 2.

Table 2. Cr(VI) sorption by different adsorbents

Adsorbent	% Sorption
Cotton	0.0
RH	70
SD	85
AC	98
SD/PAn	100
SD/PAn/Ny	100
SD/Ny	55
SD/PAn/Pu	30

\*50 mL solution of Cr(VI) in with concentration of 50 ppm in HCl 0.1M was used as test solution. AC stands for activated carbon, SD stands for sawdust, RH stands for rice husk and SD/Ny stands for sawdust coated by nylon66 (5% coating). All the other experimental conditions were the same as described for Table 1.

Our preliminary studies showed that among the different tested adsorbents, the highest sorption percent was observed for SD/PAn. Untreated sawdust was also found to be a better choice for removal of Cr(VI) ion compared to other agricultural wastes such as rice husk. Cr(VI) removal by SD appears to be partially related to the chemical reactions like the oxidation

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of the organic constituents inherently associated with the cellulose such as lignins, tannins and pectins in SD. Using pure cellulose (cotton), no adsorption of Cr(VI) was observed even in acidic media. When SD was treated with a bleaching solution, the percentage of Cr(VI) sorption was much lower than unbleached SD (~ 30%).

Activated carbon is a popular adsorbent for removing of broad range organic and inorganic contaminants from air, soil and liquids. Its high sorption capacity is due to its abundant pores and large internal surface area. Its application for Cr(VI) removal has also been suggested by some investigators. It was also observed that removal of Cr(VI) by AC in acidic media is accompanied by catalytic reduction of Cr(VI) to Cr(III) (the color of treated solution changed to green). Therefore, the removal of Cr(VI) by activated carbon involve both reduction and adsorption. The catalytic reduction of Cr(VI) into Cr(III) in acidic media by activated carbon as sorbent seems to be an important drawback of its application for treatment of Cr(VI) polluted water or wastewaters. However, in the case of SD/PAn sorbent, complete removal of Cr(VI) (without side products) is achieved.

Our results interestingly show that the sorption percentage of Cr(VI) by activated carbon is lower than our introduced sorbent (SD/PAn). Application of SD/PAn columns for Cr(VI) removal is simple, more economical and even more efficient than other popular and commonly used adsorbents such as activated carbon. Adsorption of Cr(VI) by polyaniline composites were inferior to poyaniline itself. SD/PAn/Pu was found unsuitable sorbent because of its very poor sorption property.

The poor sorption capacity of SD/PAn/Pu, compared to SD/PAn or SD/PAn/Ny can be due to the hydrophobic nature of polyurethane. Due to the hydrophobicity of SD/PAn/Pu, the flow rate of liquid in column was also very low. Due to high hydrophilic nature of SD/PAn sorbent, it can be used in continuous flow systems (column systems) without any important pressure drop which is common when very small size particles are used in column systems.

### Sorption capacity of polyaniline (EB/HCl)

In order to obtain the maximum sorption capacity of SD/PAn for Cr(VI), different volumes of Cr(VI) solutions prepared in HCl 0.1 M were treated with SD/ PAn column under the same conditions used for Table 1. The results of Cr(VI) removal by SD/PAn in acidic media (0.1M HCl) are summarized in Table 3.

As our results show, each gram of SD/PAn adsorbent is able to complete decontamination of 300 mL of 50 ppm Cr(VI) solution from acidic aqueous solutions. The mechanism of Cr(VI) sorption by SD/

Table 3. Cr(VI) removal by SD/PAn column

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Cr(VI) solution (Conc. = 50 mg L <sup>-1</sup> )	% Adsorption
50 mL (2.5 mg)	100
100 mL (5 mg)	100
150 mL (7.5 mg)	100
200 mL (10 mg)	100
250 mL (12.5 mg)	99.5
300 mL (15 mg)	99
350 mL (17.5 mg)	80

Cr(VI) solutions were prepared in HCl 0.10 M. All the other experimental conditions were the same as used in Table 2.

PAn, seems to be mostly occurred via anion exchange process. When the acid doped polyaniline (EB/HCl) is treated with an aqueous solution of Cr(VI) ions in acidic media, the chloride ion (mobile dopant anion, shown in Figure 1) in the polymer is readily exchanged for dichromate or  $HCrO_4^-$  ions, so the removal of the Cr(VI) resultes.

$$Cr_2O_7^{2-} + H^+ \rightarrow 2HCrO_4^{-} + H_2O \ (pH \le 2),$$

then

EB/HCl (polymer) + HCrO<sub>4</sub><sup>-</sup> (solution)  $\rightarrow$ EB/HCrO<sub>4</sub><sup>-</sup> (polymer) + Cl<sup>-</sup> (solution)

Exchangeable anions (e.g. Cl<sup>-</sup>) in the polymer (PAn) exist only in the acid doped state. So, undoped polyaniline (EB form) does not adsorb Cr (VI). It was also observed that when a weak acid dopant such as phosphoric acid or acetic acid is used instead of HCl for doping polyaniline, the sorption percent of Cr(VI) decreased considerably.

# Effect of initial concentration on Cr(VI sorption by SD/PAn column

In order to investigate the effect of initial concentration of Cr(VI) on sorption percent by SD/PAn column, 10 mL of Cr(VI) solutions (in HCl 0.1M) with different initial concentrations( 100-1500 ppm) were treated with 1.0 g of SD/PAn. The results obtained are shown in Table 4.

 Table 4. Effect of initial Cr(VI) concentration on adsorption by SD/PAn column.

Initial Cr(VI) concentration (mg L <sup>-1</sup> )	Percentage of Cr (VI) sorption
100	100
300	100
500	100
1500	95
2000	80

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As our findings show, SD/PAn column can be used for Cr(VI) ions from aqueous solutions in both low and high initial concentrations effectively. It was found that increasing initial concentration of Cr(VI), percent of polymer loading and decreasing of pH increases Cr(VI) removal substantially.

#### **Desorption Study**

Using distilled water, HCl and HNO<sub>3</sub> with different concentrations (0.1 M - 1 M), recovery of Cr(VI) observed was not considerable (less than 0.5%). Then we used NaOH solution with different concentrations (0.1M-1M) and flow rates (1-5 mL min<sup>-1</sup>) for regeneration of the exhausted columns. It was found that desorption of Cr(VI) from the column started at pH  $\geq$  8. Regeneration percent of Cr(VI) treated SD/PAn column was from 10-70 percent depending on parameters such as the concentration of regenerant solution and flow rate.

Incomplete regeneration of SD or SD/PAn can be related to some chemical reactions (e.g. oxidation). With increasing the concentration of regenerant solution (NaOH) and decreasing the flow rate, higher regeneration can be obtained. It should also be reminded that in general, biomaterials such as SD are not chemically stable at very low or high pH values (some carbonizing or dehydrating reaction of sawdust might be occurred). The results obtained using a previously used SD/PAn for Cr(VI) adsorption indicate that SD/PAn column can be reused after regeneration without important loss of its sorption capability (Table 5). However; some decrease in its sorption capacity is observed (maximum loss was 10%).

Table 5	Cr(VI)	removal by a	regenerated SD/PAn column
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$Cr(VI)$ solution ( $C_o = 50 \text{ mg L}^{-1}$ )	% Adsorption
50 mL (2.5 mg)	100
100 mL (5 mg)	100
150 mL (7.5 mg)	95
200 mL (10 mg)	90
250 mL (12.5 mg)	80
300 mL (15 mg)	70

(i) The SD/PAn column and the experimental conditions were the same as used for Table 3. The regeneration procedure was performed using 50 mL of 0.2M NaOH with flow rate of 2 mL min.<sup>-1</sup>. The column was then conditioned using HCl (0.1 M) before adsorption experiments.

# **Conclusions**

SD/PAn adsorbent is cheap and simple to prepare and can be used successfully for removal of Cr(VI) ion from aqueous solutions. Sorption capacity of polyaniline toward Cr(VI) is greatly affected by pH of the treated solution. It was found that SD/PAn column was a useful

sorbent for Cr(VI) elimination at relatively low acidic solutions (pH=1-2). Adsorption was negligible at pH values higher than 4. The rate of adsorption decreased severely under alkaline conditions (pH > 6). As a result, adsorption/desorption of Cr(VI) by SD/PAn column can be achieved by simple pH control.

Adsorption of Cr(VI) by PAn is supposed to be based on anion exchange properties of acid doped polyaniline (replacement of Cl<sup>-</sup> by HCrO<sub>4</sub><sup>-</sup> or Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) and some chemical reactions such as complex formation or redox reactions. Formic acid is a suitable solvent of choice for processing of polyaniline using cast method for coating or preparation of polyaniline composites with conventional polymers. It is cheap, available, and volatile compared to other solvents for polyaniline (e.g. NMP). However it is very odorous and should be handled carefully.

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# Povzetek

Proučevali smo adsorpcijo Cr(VI) iz vodnih raztopin na žagovini, prevlečeni s polianilinom in polianilinskimi kompoziti z najlonom 66 in poliuretanom. Ugotovili smo, da polianilin v kislinski obliki lahko uporabljamo za adsorpcijo Cr(VI) ionov iz kislih raztopin (pH  $\leq$  2). Z višanjem pH-ja se adsorpcija bistveno poslabša. Predpostavili smo, da adsorpcijski mehanizem poteka v glavnem na osnovi ionske izmenjave. Izvedba tega procesa v koloni s predstavljenim adsorpcijskim materialom je enostavna in učinkovita v primerjavi z materiali, ki so jih proučevali drugi avtorji.