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ORIGINAL PAPER

Removal of Cr(VI) Ions from Aqueous Solutions Using Poly 3-Methyl Thiophene Conducting Electroactive Polymers

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Abstract This paper deals with a new application of poly 3-methyl thiophene synthesized chemically onto sawdust (termed as P3MTh/SD) as an effective adsorbent for removal of Cr(VI) ions from aqueous solutions using column system. Chemical synthesis of poly 3-methyl thiophene was performed by addition of ferric chloride (in chloroform) as oxidant to sawdust which had previously been soaked in monomer solution. All the sorption experiments were conducted using dynamic or column system at room temperature. The effect of important parameters such as pH and initial concentration on uptake of Cr(VI) was investigated. In order to find out the possibility of the regeneration and reuse of the exhausted adsorbent, desorption studies were also performed. The currently introduced adsorbent was found to be an efficient adsorbent for removal of highly toxic and hazardous Cr(VI) ions from aqueous solutions. As our breakthrough analysis has indicated, each gram of P3MTh/SD is able to remove more than 95% of Cr(VI)ions from 300 mL of Cr(VI) polluted solution with the initial concentration of 25 mg L^{-1} in column system. Sorption/desorption of Cr(VI) ions was found to be a highly pH dependent processes.

Keywords Removal · Cr(VI) ion · Poly 3-methyl thiophene · Sawdust · Desorption

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Introduction

Chromium is most commonly found in two oxidation states, Cr(III) and Cr(VI), and all other oxidation states are not stable in aerated aqueous media. Chromium (VI) is a common waste product generated from various industrial processes such as electroplating, wood preservation, metal finishing, chrome plating and leather tanning, and is highly toxic as compared to Cr(III) to biological activities [1]. The threshold value for Cr(VI) has been reported 0.1 mg L^{-1} [2]. Because of high toxicity of Cr(VI) to living systems it should be removed from wastewaters before it can be discharged into the sea. Cr(III) is a more stable, less toxic, and listed as an essential element (in trace concentration) to provide good health [3]. It is poisonous only at high concentration [4]. while the toxicity and carcinogenic properties of chromium (VI) have been known for a long time [5]. The chemistry of Cr(VI) is greatly dependent on pH of the solution. Cr(VI) normally exists in the anionic form, as $Cr_2O_7{}^{2-}$, $HCrO_4{}^{-}$ or $CrO_4{}^{2-}$ forms depending on pH and concentration (Eqs. 1–3). At pH value below 1, the predominant species is chromic acid (H_2CrO_4) with dissociation constants of $K_1 = 4.1$, and $K_2 = 1.2 \times 10^{-6}$ respectively. In acidic media with pH value of 2–4, Cr(VI) exists mostly in the form of dichromate ($Cr_2O_7{}^{2-}$) ions. At pH between 4 and 6, $Cr_2O_7{}^{2-}$ and $HCrO_4{}^{-}$ ions exist in equilibrium, and under alkaline conditions (pH > 8) it exists predominantly as chromate anion ($CrO_4{}^{2-}$). Chromium (VI) is most commonly encountered in the chromate ($CrO_4{}^{2-}$) and dichromate ($Cr_2O_7{}^{2-}$) anions. The chromate and dichromate anions are in equilibrium:

$$Cr_2O_7{}^{2-}H_2O \rightleftharpoons 2HCrO_4{}^{-} \quad K_{eq} = 10^{-2.2} \qquad (1)$$

$$2CrO_4{}^{2-}(\text{yellow}) + 2H^{+}(aq) \rightleftharpoons Cr_2O_7{}^{2-}(\text{red orange}) + H_2O \quad K_{eq} = 10^{14} \qquad (2)$$

$$Cr_2O_7{}^{2-} + 2OH^- \rightleftharpoons 2CrO_4{}^{2-} + H_2O \quad K_{eq} = 10^{14} \qquad (3)$$

The dominant species is therefore, by the law of mass action, determined by the pH of the solution. The change in equilibrium is visible by a change from yellow (chromate) to orange (dichromate). The various treatment techniques available for the removal and recovery of chromium (VI) from wastewaters are reduction precipitation, ion-exchange, reverse osmosis, lime coagulation and carbon adsorption, solvent extraction, chemical precipitation, evaporation and electrolytic reduction [2, 6–10]. However, most of the methods suffer from drawbacks such as high capital and operational cost of the disposal of the residual metal sludge.

The traditional treatment is reduction to trivalent chrome followed by precipitation. The Cr(III) is precipitated as hydroxide at alkaline conditions using either caustic or lime [11]. The pH of solution strongly affected the degree of adsorption of chromium species. The higher pH, the more removal of Cr(III) and the less removal of Cr(VI) is resulted.

Conducting electroactive polymers such as polypyrrole (PPy), polyaniline (PAni) and polythiophene (PTh) have attracted a great deal of attention in recent years due to their interesting electrical and electrochemical behaviors [11–19]. The electroactive nature or the switching properties of polymers have been utilized as the basis of most proposed applications such as sensors, separation devices, rechargeable batteries and controlled drug-release [14, 20–22].

In our previous studies, we have also shown that PPy and PAni electroactive polymers can be used to remove Cr(VI) ion from aqueous solutions effectively compared to other adsorbents reported so far [23, 24]. Poly (3-alkyl thiophenes) are both soluble and melt processable. They have good chemical and environmental stability with excellent electronic and optical properties suitable for various device applications. Polythiophenes can be prepared both by electrochemical polymerization and chemical oxidative polymerization technique. However, the polymers prepared by electrochemical method are not processable. The mechanism of the oxidative polymerization using ferric chloride has been proposed a radical mechanism (Scheme 1) [13–16].

In overall oxidative doping of polythiophene conducting polymers Electron are delocalized along the conjugated backbone of conducting polymers, usually through overlap of π-orbitals resulting in an extended π-system with a filled valence band. By removing electrons from the π-system ("p-doping"), a charged unit called a bipolaron is formed (see Scheme 2). The oxidation process is accompanied by the insertion of anions of acid electrolyte (y^-) in order to maintain the charge neutrality of the final polymer [16, 25]. In this study poly 3-methyl thiophene was prepared by chemical oxidative polymerization technique using iron (III) chloride ($FeCl_3$) in chloroform. The polymer was used as coated onto sawdust for removal of Cr(VI) from aqueous solution and is reported for the first time.

Experimentals

Determination of Cr(VI)

The Cr(VI) determination was carried out spectrophotometrically using a calibration curve (Figs. 1, 2). The calibration curve obtained from standard solutions of potassium dichromate (1–20 mg L^{-1} vs. Cr) prepared in 0.1 M NaOH. At pH value of 12 the Cr(VI) ions exist as chromate form ($\lambda_{max} = 370$ nm, $\varepsilon = 4900$). A Spectrophotometer (Perkin Elmer model 35, USA) was employed for analysis of Cr(VI). A Metrohm pH meter (model 827) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for showing pH values.

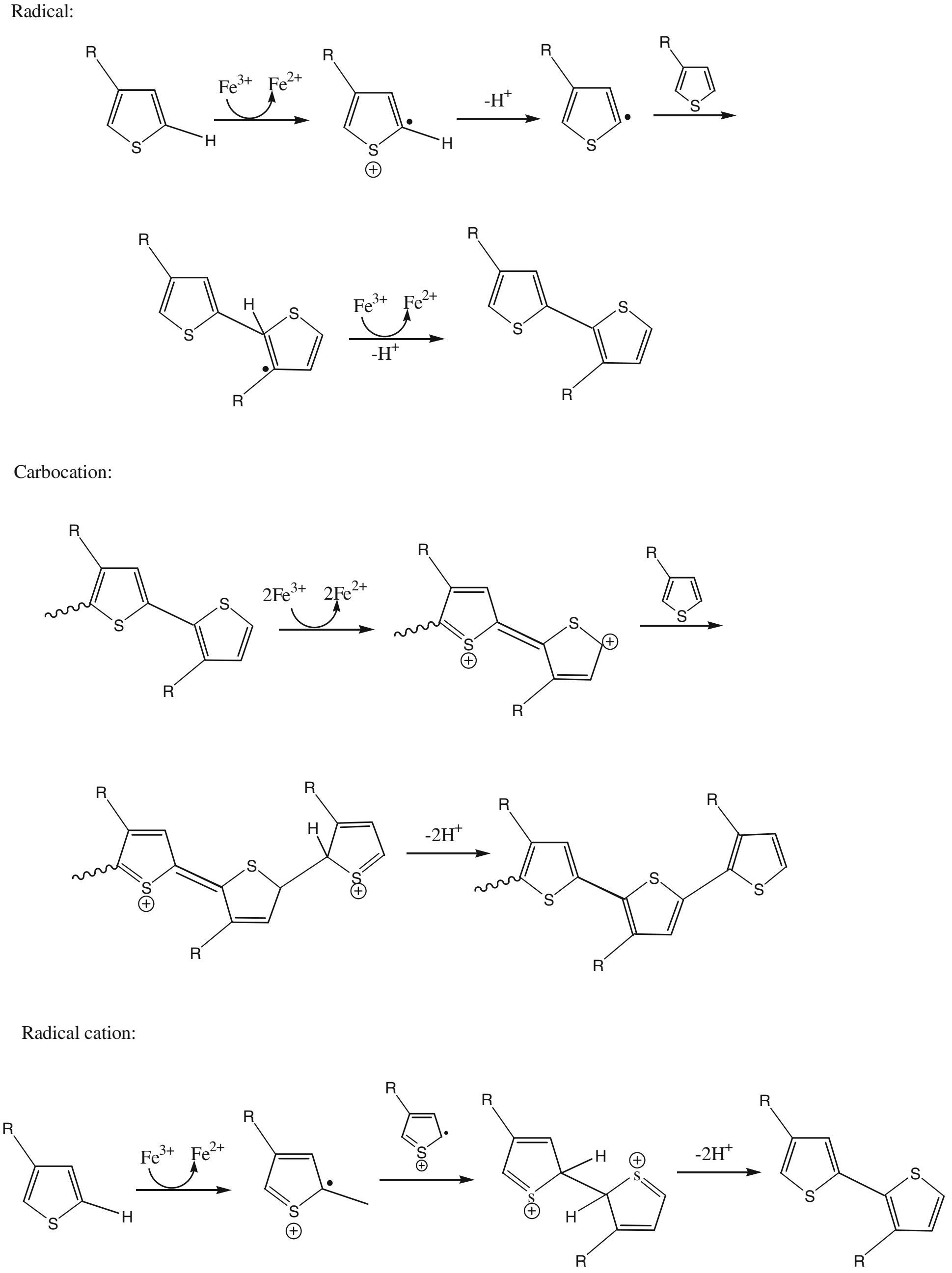
Using high concentration of Cr(VI) was avoided, because of oxidative nature of dichromate anions (Eq. 2), which may damage the polymer structure. However, they are only moderately oxidizing at high pH (Eqs. 4, 5).

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (E^o = 1.33\ V) \qquad (4)$$

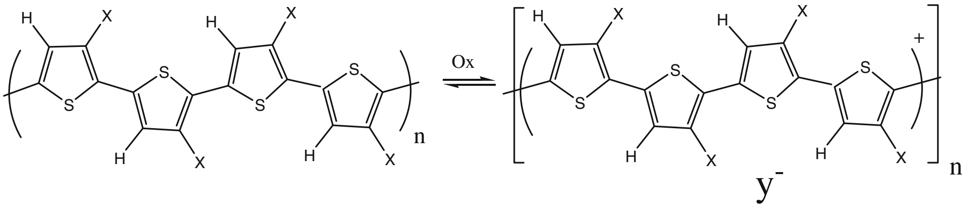
$$CrO_4{}^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3(s) + 5OH^-(E^o = -0.13\ V) \qquad (5)$$

Coating of Sawdust by Poly 3-Methylthiophene

Polymerization of 3-methyl thiophene was carried out in non aqueous solution [15, 26]. 4 mL freshly distilled 3-methyl thiophene was dissolved in 100 mL chloroform ($CHCl_3$). In order to prepare poly (3-methyl thiophene) (P3MTh/SD), 10.0 g sawdust (35–50 mesh) immersed in 100 mL of 3-methyl thiophene monomer solution (0.4 M) was prepared in chloroform at nitrogen atmosphere for 12 h before polymerization. 100 mL of oxidant solution (0.8 M $FeCl_3$ in chloroform) was added via a dropping funnel while the reaction mixture was stirred vigorously, and then the reaction was allowed to continue for 4 h at room temperature. The sawdust was coated by the polymer and the color of the sawdust changed into black. The coated sawdust with the polymer was then washed with copious amounts of deionized water and methanol and was allowed to dry for 2 days at room temperature. The particles were dried in an oven at 50–60 °C for 2–3 h. The polymer coated sawdust was sieved before use in order to have uniform particles for packing of the column and achievement of better reproducibility.



Scheme 1 Proposed mechanism for oxidative polymerization of poly 3-alkyl thiophene by ferric chloride



Scheme 2 Overall oxidative doping of polythiophene conducting polymers (X = H or alkyl)

Sorption Experiments

Cr(VI) solutions for sorption experiments were prepared from $K_2Cr_2O_7$ salt. In column experiments a glass column with dimensions of 1 cm diameter and 15 cm length was employed. 1.0 g sorbent (P3MTh/SD) was packed in the column (5 cm height), and then the Cr(VI) solution (25 mg L^{-1}) was passed through the column with flow rate of 3 mL min^{-1} at room temperature. The outlet solution was analyzed for unabsorbed Cr(VI) ion after each 10 mL.

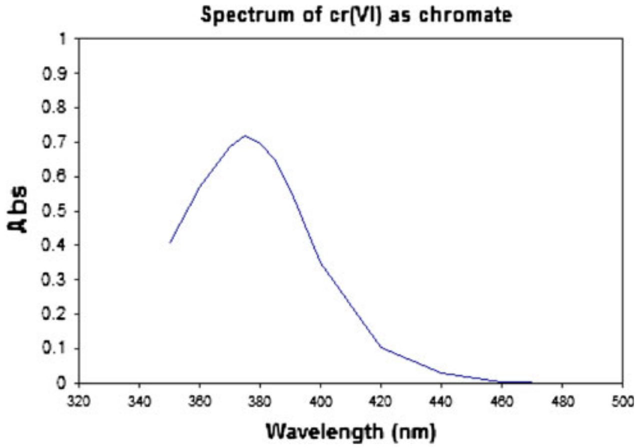


Fig. 1 The vis spectrum obtained for Cr(VI) in 0.1 M NaOH

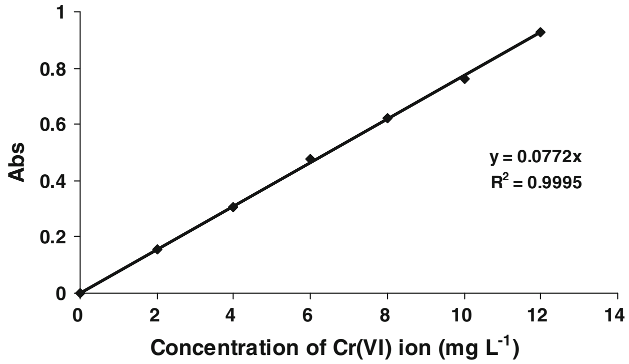


Fig. 2 Calibration curve obtained for spectrophotometric determination of Cr(VI)

The percentage of sorption was calculated using the relationship:

$$\%\text{Sorption} = \frac{C_0 - C_e}{C_0} \times 100 \tag{6}$$

where C_0 and C_e are initial (inlet) and final (outlet or effluent) concentration of Cr(VI) ion (mg L^{-1}). Sorbed Cr(VI) ions was determined using the following equation:

$$\frac{x}{m} = \frac{C_0 - C_e}{m} \times V \tag{7}$$

x/m stands for mg of Cr(VI) sorbed per gram of sorbent. C_0 and C_e are the initial (inlet) and final (outlet or unsorbed) concentrations of Cr(VI), respectively. V is the volume (mL) of Cr(VI) test solution. Alternatively, the following equations were used to calculate desorption percentage of the used adsorbent:

$$\%\text{Desorption} = \frac{m}{m_0} \times 100 \tag{8}$$

$$\text{Subsequently, } m_0 = \frac{(C_0 - C_e)V}{W} \quad \text{and} \quad m = C \times V \tag{9}$$

where m_0 is mg of the sorbed Cr(VI) onto adsorbent, m is the mg of desorbed Cr(VI) in regenerated solution and V is the volume of regenerant solution (dm^3).

Results and Discussions

Sorption of Cr(VI) Ion by P3MTh/SD and SD (Column System)

Effect of pH

In order to investigate the effect of pH on sorption of Cr(VI) ion by 1.0 g of sorbent (SD and P3MTh/SD) packed in glass column. The column was first washed with solutions with the same pH value of Cr(VI) solutions that must pass through the column, separately. The column was finally washed with distilled water. Then 25 mL of Cr(VI) solution (25 mg L^{-1}) at different pH (from 1 to 11 using HCl and NaOH dilute solutions) passed through the column with flow rate of 3 mL min^{-1}. The results obtained are shown in Table 1.

As our results show, removal percentage of Cr(VI) using both SD and modified SD by poly 3-methylthiophene is strongly affected by pH of the solution. They are effective only at acidic conditions. Sorption of Cr(VI) ion decreases as pH of treated solution increases. As we have already explained the dominant form of Cr(VI) at pH 2.0 is $HCrO_4^-$. So, this anion can be exchanged with the releasable chloride ion in the polymer because of higher affinity and stronger interaction of $HCrO_4^-$ ions with the polymer. Based on this result, removal mechanism might be due to ion exchange or redox processes as shown by the following equations:

$$\begin{aligned} &\text{P3MTh}^+\text{Cl}^-/\text{SD}_{(\text{solid})} + \text{HCrO}_{4(\text{solution})}{}^- \\ &\quad \rightarrow \text{P3MTh}^+\text{HCrO}_4{}^-/\text{SD}_{(\text{solid})} + \text{Cl}_{(\text{solution})}{}^- \end{aligned} \tag{10}$$

$$\begin{aligned} &\text{Cr}_2\text{O}_7{}^{2-}(\text{aq}) + 14\text{H}^+ + 6\text{P3MTh}^0 \\ &\quad \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 6\text{P3MTh}^+(\text{aq}) + 7\text{H}_2\text{O} \end{aligned} \tag{11}$$

Cr^{3+} ions produced in the course of redox reaction are entrapped in polymer matrix due to chelating properties of polymer. In basic condition, the polymer becomes undoped, so there will be not any anion to be exchanged, so

Table 1 Effect of pH on sorption percentage of Cr(VI) by SD and P3MTh/SD

Sorbent	pH					
	1	3	5	7	9	11
SD	80.0	2.0	0	0	0	0
P3MTh/SD	95.0	70.0	57.0	28.0	13.0	2.0

the uptake of Cr(VI) anions is decreased dramatically. With increasing pH of treated solution, Cr(VI) will be in the form of chromate and the surface of sorbent will be covered with OH^- group. As a result, the electrostatic interaction (repulsion) between chromate ions and negative sites in the polymer leads to a decrease of Cr(VI) ion sorption.

As we have shown by Eq. 11, due to oxidative nature of Cr(VI) ion under acidic conditions and the electroactive nature of poly 3-methyl thiophene [14] and also presence of oxidizable functional groups in sawdust, the importance of some redox reactions in removal of Cr(VI) can not be ignored.

Effect of Initial Concentration of Cr(VI)

In this experiment, 1.0 g of sorbent (P3MTh/SD and SD) packed in a glass column. The column was first washed with 0.1 M HCl. The column was finally washed with distilled water. Then 25 mL of Cr(VI) solution with different initial concentrations (10–100 mg L^{-1}) passed through the column with flow rate of 3 mL min^{-1} at room temperature. The results obtained are shown in Table 2 and Fig. 3.

As our data show, with increasing of the initial concentration of Cr(VI) the total amount of Cr(VI) uptake using both SD and polymer coated SD is increased. However the Chromium removal by polythiophene coated SD is more than uncoated SD. Removal of Cr(VI) by SD can be due to redox reaction between lignin impurities in sawdust and subsequent complex formation of the Cr(III) ion (the reduced product of chromium hexavalent) and the various surface functional groups (e.g. phenolic, carboxylic, carbonyl and hydroxyl) present in lignin compartment of sawdust [27–29].

Breakthrough Curve

Plotting breakthrough curves is needed to evaluate the performance of an adsorbent using column or flow test. The design of fixed packed bed adsorbent in continuous systems, concentration versus time or volume of solution usually yields as S-shaped curve, at which the solute concentration reaches its maximum allowable value referred to as a breakthrough curve. The point where the effluent solute concentration reaches 95% of its influent value is usually called the point of column exhaustion [30].

Table 2 Effect of initial concentration on sorption percentage of Cr(VI) by SD and P3MTh/SD

Sorbent	C_0 (mg L^{-1})					
	10	25	40	50	75	100
SD	100	80.0	65.0	60.0	54.0	50.0
P3MTh/SD	100	95.0	92.0	88.0	83.0	76.3

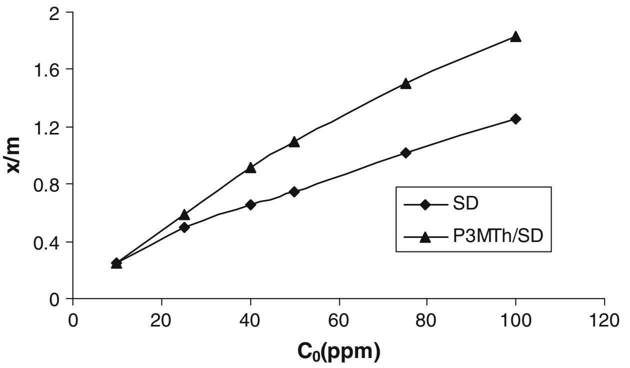


Fig. 3 Effect of initial Cr(VI) concentration on its sorption by SD (*filled square*), P3MTh/SD (*filled triangle*)

For performing this experiment, 1.0 g of SD and P3MTh/SD packed in a glass column, and then Cr(VI) solution with concentration of 25 mg L^{-1} passed through the column with constant flow rate (3 mL min^{-1}). Each time 10 ml was poured into the column. The outlet solution was analyzed for unsorbed Cr(VI) ion in order to obtain the breakthrough curve. The breakthrough curves obtained for the examined sorbents used for sorption of Cr(VI) in a column system are shown in Fig. 4. As it is evident from our results obtained in this experiment, the break point for P3MTh/SD is observed after treatment of about 300 mL of 25 mg L^{-1} Cr(VI) polluted solution. Complete exhaustion of the used column is occurred after passing of about 600 mL Cr(VI) solution. With increasing the volume of the sorbent bed in the column, it is quite possible to increase the chromium removal efficiency. As we have previously shown the breakthrough curve obtained for SD toward Cr(VI) adsorption, was very sharp and the break point or column exhaustion occurs very quickly. Therefore, P3MTh/SD seems to be much more effective sorbent

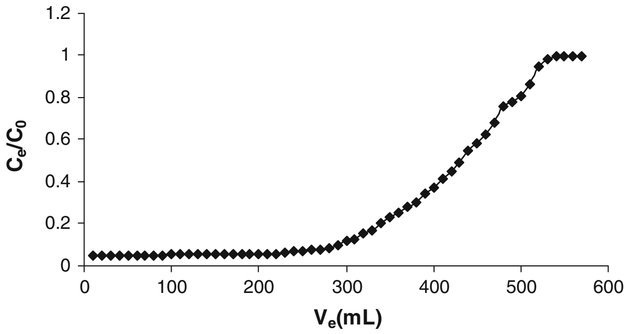


Fig. 4 Breakthrough curves obtained for uptake of Cr(VI) by P3MTh/SD

compared to SD for removal of Cr(VI) ion in column or flow systems [23].

Desorption Studies

For performing desorption studies, 1.0 g of adsorbent (P3MTh/SD) was first treated with 25 mL of Cr(VI) with initial concentration of 25 mg L^{-1} at pH value of 1 and flow rate of 3 mL min^{-1} at room temperature. Under these conditions it was found that about 95.0% of Cr(VI) was removed under acidic conditions. The exhausted column was then treated with 0.01 M NaOH solution for regeneration. Higher concentration of acid was avoided since SD is not very stable in highly acidic (or basic) solutions. Desorption percentage was calculated using Eqs. 8 and 9.

It was found that about 75% of the sorbed Cr(VI) was recovered from the column. In a separate experiment, when the regenerated column after neutralization and conditioning was employed for adsorption of Cr(VI) under the same conditions ($pH = 1$, $C_0 = 25$ mg L^{-1}), sorption percentage observed was 94%. Desorption investigation shows, the introduced column can be used frequently without any significant reduction in sorption capacity performance.

Conclusions

It was found that P3MTh/SD as coated form onto sawdust can be effectively and efficiently employed for removal of Cr(VI) ions from aqueous solutions. Sawdust is a very cheap, economical and environmentally friendly substrate for coating of this polymer. It was also found that sorption/desorption of Cr(VI) processes are strongly pH dependent and are occurred with high efficiency. Sorption of Cr(VI) is occurred under acidic conditions and subsequent desorption is readily achieved upon alkaline treatment of the sorbent. Removal of Cr(VI) ions by the introduced adsorbent in this paper seems to be a complex process. Redox, complex or chelation and ion exchange reactions are possible mechanisms for removal of Cr(VI) ions from aqueous solutions. The finding in this paper seems to be important for pollution control in treatment of water or wastewaters polluted with the highly toxic Cr(VI) ions.

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References

1. Katz F, Salem H (1994) The biological and environmental chemistry of chromium. VCH Publisher, New York, p 51
2. Ajmal Alikhan M, Siddiqui BA (1996) Water Resour 30:1478
3. Walter M (1993) Chromium in human nutrition: a review. J Nutr 123(4):626
4. Bobrowski A, Mocak J, Dominik J, Pereira H, Bas B, Knap W (2004) Acta Chim Slov 51:77
5. Donald B (1999) Chromium Clin Toxicol 37(2):173
6. Metcalf and Eddy Inc (1991) In: Tchobanoglous G, Burton FL (ed) Wastewater engineering, treatment, disposal and reuse, 3rd edn. McGraw-Hill, New York
7. Rengaraj S, Kyeong-Ho Y, Seung (2001) J Hazard Mater B87:273
8. Sharma DC, Foster CF (1994) Bioresour Technol 47:257
9. Dokken K, Gomez G (1999) In: Proceeding of the conference on hazardous waste research, pp 101–114
10. Hassan S, Krishpajah A, Ghosh TK, VisNanath DS, Boddu VM, Smith ED (2003) Sep Sci Technol 38:3775
11. Udaybhaskar P, Iyengar L, Prabhakara RA (1990) J Appl Polym Sci 39:739
12. Ansari R (2006) E-J Chem 3:186
13. Singh R, Kaur A, Lal Yadav K, Bhattacharya D (2003) Curr Appl Phys 3:235
14. Wallace GG, Spinks GM, Kane Maguire L, Teasdale PR (2009) Conducting Electroactive Polymers. CRC Press/Taylor and Francis, Boca Raton/London, p 197
15. Niemi VM, Knuuttila P, Österholm JE, Korvola J (1992) Polymer 33:1559
16. McCullough RD, Tristramnagle S, Williams SP, Lowe RD, Jayaraman M (1993) J Am Chem Soc 115:4910
17. Loponen MT, Taka T, Laakso J, Väkiparta K, Suuronen K, Valkeinen P, Österholm JE (1991) Synth Met 41:479
18. Bartus JJ (1991) Macromol Sci Chem A28:917
19. Ivaska A (1991) Electroanalysis 3:247
20. Weidlich C, Mangold KM, Juttner K (2001) Electrochem Acta 47:741
21. Rowley NM, Mortimer RJ (2002) Sci Prog 85:243
22. Machida S, Miyata S (1989) Synth Met 31:311
23. Ansari R, Khoshbakht FN (2007) React Funct Polym 67:367
24. Ansari R, Aliakbar AR, Masoudi M (2005) J Polym Mater 21:75
25. Mastragostino M, Soddu L (1990) Electrochim Acta 35:463
26. Ansari R, Fallah Delavar A (2009) J Appl Polym Sci 113:2293
27. Kobya M (2004) Bioresour Technol 91:317
28. Lebo SE, Gargulak J, Jerry D, McNally TJ (2001) “Lignin”. Kirk—Othmer encyclopedia of chemical technology. Wiley, New York
29. El Mansouri N, Salvado J (2007) Ind Crop Prod 26:116
30. Pan BC, Meng FW, Chen XQ et al (2005) J Hazard Mater 124 (1–3):74