

Application of Poly 3-methylthiophene for Removal of Silver Ion from Aqueous Solutions

Reza Ansari, A. Fallah Delavar

Department of Chemistry, University of Guilan, Rasht, Iran

Received 13 August 2008; accepted 8 February 2009

DOI 10.1002/app.30239

Published online 27 April 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article deals with application of poly (3-methyl thiophene) synthesized chemically on the surface of wood sawdust (termed as P3MTh/SD) and then was used for removal of silver ions (Ag^+) from aqueous solution. The polymer was synthesized directly on the surface of sawdust, which has previously soaked in monomer solution using ferric chloride as chemical oxidant. The sorption experiments were performed on both batch and column systems under simple open circuit conditions. The effects of some important parameters such as pH, initial concentration, sorbent dosage, and exposure time on uptake of silver ion were

investigated. The treatment of the data was also carried out using both Freundlich and Langmuir adsorption isotherms. To find out the possibility of the regeneration and reuse of the exhausted adsorbent, desorption studies were also performed. It was found that sawdust modified with polythiophene is an efficient system for uptake or recovery of the silver ions from aqueous solutions. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2293–2300, 2009

Key words: silver ion; poly (3-methyl thiophene); sorption; desorption; isotherm

INTRODUCTION

Environmental contamination by heavy metals is a widespread problem, with sources of pollution arising from industrial activities.¹ The free silver ion (Ag^+) has been reported to be extremely toxic to a variety of aquatic organisms even at trace concentrations. Silver and its salts are extensively utilized in the photographic and imaging industry, battery manufacture, jewelry and silver tableware manufacture, cloud seeding, catalysts as well as in electronics and electrical applications and other lesser uses.^{2,3} The increasing use of silver compounds and silver containing preparations in industry and medicine has resulted in an increased silver content of environmental samples.^{4,5} It has been reported that about 2.47 million kg of silver are lost each year to the environment. About 150 t of silver enter the aquatic environment every year from the mine tailings, photography, and electroplating industries. It is known that silver ion to be discharged to the environment from its industrial applications, and this leads to the possibility for exposure to aquatic and terrestrial organisms.

The adverse effects of chronic exposure to silver are a permanent bluish-gray discoloration of the skin or eyes. Exposure to soluble silver compounds

may produce some other toxic effects, including liver and kidney damage, irritation of the eyes, skin, respiratory, and intestinal tract, and changes in blood cells. Recommended exposure limit set by the national institute for occupational safety and health is 0.1 mg L^{-1} for all forms of silver.⁶ So, there is a need for introducing an efficient method for the removal or recovery of silver ion as a precious metal from waste solutions generated from the mentioned industries due to the both economical and environmental points of views. Different treatment techniques (adsorption, extraction, ion-exchange resins, reverse osmosis, metal replacement, precipitation, electrolysis, and electro dialysis) have been developed for removal of silver ions from wastewaters.^{7–10} We have already shown that polypyrrole (PPy) and polyaniline (PAni)-conducting electroactive polymers can be effectively used for removal of some heavy metal ions (e.g., Hg^{2+} , Pb^{2+} , Ag^+) from aqueous solutions.^{11–13} Conducting polymers such as PPy, PAni, and polythiophene have been the focus of numerous theoretical and experimental investigations in the last 2 decades.¹⁴ Their structural versatility is attracting researchers for their multiple applications such as in rechargeable batteries, light emitting diodes, super capacitors, biological and microbial sensors, solar cells, and actuators.^{15–20} Polythiophene and its derivatives have attracted considerable attention because they are stable in the oxidized and neutral state. Relative ease of substitution at the third position of the thiophene ring has enabled the synthesis of a large number of derivatives, resulting in

Correspondence to: R. Ansari (ransari@guilan.ac.ir).
Contract grant sponsor: University of Guilan.

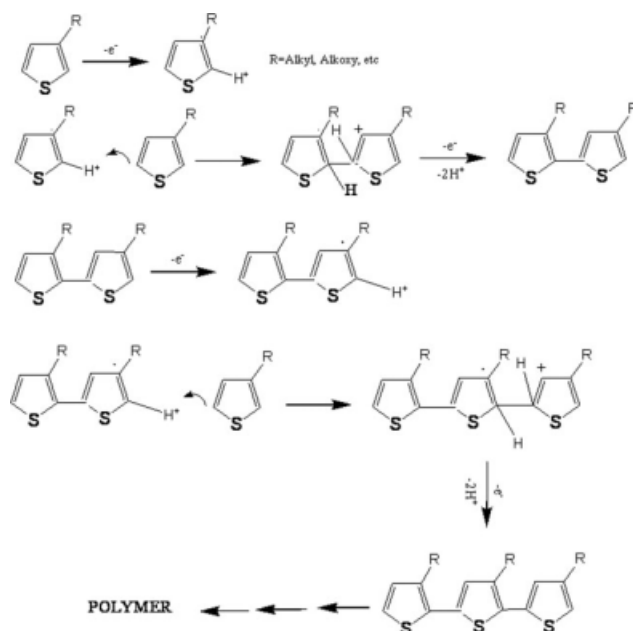


Figure 1 The proposed polymerization reaction of 3-alkyl thiophene.

numerous polymers with different degrees of stabilities, conductivities, solubility, and band gaps. Poly (3-methyl thiophene) has been the subject of extensive investigation due to its good environmental stability, relatively high electrical conductivity with excellent electronic and optical properties.^{21–28}

Thiophene and its derivatives is oxidized to form a conducting electroactive polymer with the greatest conductivity obtained from α - α linkages. However, because of the limited solubility of thiophene, in contrast to PPy and PANi conducting polymers, which can be prepared in aqueous solutions, this reaction must be carried out in nonaqueous media.²¹ Various substituted thiophenes have also been oxidized to the corresponding polythiophenes, the most commonly studied being 3-alkyl thiophenes.²² All monomers could be oxidized to form conducting polymers but the oxidation potentials increased according to: MTh < ETh < Th. Poly (3-alkyl thiophenes) are both soluble and melt processable. Polythiophenes can be prepared both by electrochemical polymerization and chemical oxidative polymerization techniques. However, the polymers prepared by electrochemical method are not processable. Chemical synthesis offers two advantages compared with electrochemical synthesis of polythiophenes, a greater selection of monomers and, using the proper catalysts, the ability to synthesize perfectly regioregular substituted Poly (3-alkyl thiophenes).

Poly (3-alkyl thiophenes) can be synthesized either electrochemically or chemically using a simple oxidation process.²¹ Chemical oxidative polymerization

of 3-methyl thiophene with iron (III) chloride (FeCl_3) produces polymers in high yield. The mechanism of the oxidative polymerization using ferric chloride has been proposed a radical mechanism as shown in Figure 1. As with PPys, the mechanism of polymerization involves formation of radical cations that react with each other or the starting monomer to develop the polymeric structure. The direct oxidative polymerization of 3-alkylthiophenes with FeCl_3 in an organic solvent such as chloroform has also been widely used to prepare P3MTh, with molecular weights between 30,000 and 300,000.^{24,25} The overall polymerization reaction of polythiophene can be shown as the following (Fig. 2).

Where n is usually between 2 and 4; A^- is a counterion incorporated into the polymer during growth to balance the charge on the polymer backbone, and m is a parameter proportional to the molecular weight.²³ All of the previous applications of polythiophenes are based on their interesting electrical and electrochemical properties. However, in this article we have introduced a new application of polythiophene in which is mainly based on its chemical structure and also redox activity of the polymer as we have previously reported for PPy and PANi conducting electroactive polymers.¹³ However, the currently introduced adsorbent behaves more effective for uptake of silver ion from aqueous solution than PPy and PANi electroactive polymers. This might be due to the stronger interactions between sulfur atoms (in PTh) and silver ions compared to N-H groups in PPy or PANi.¹³

EXPERIMENTAL

Materials and equipments

All chemicals used were analytical reagents grade and prepared in deionized water. 3-methylthiophene was obtained from Merck and distilled before use. Wood sawdust sample (SD) prepared by walnut obtained from a local carpentry workshop. Silver nitrate (AgNO_3) solution with the concentration of 140 mg L^{-1} vs. silver ion was prepared in deionized water, used as stock solution. To prevent the photodecomposition of the stock solution of silver stored in a dark dish. A single beam Perkin-Elmer UV-vis

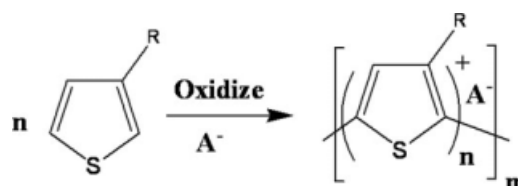


Figure 2 The overall polymerization reaction of polythiophene conducting polymers (R=H or alkyl).

spectrophotometer with a 1 cm cell was used for measuring all of absorption data. 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. The structure of polymer samples was studied using X-ray diffraction (XRD) technique (Model Philips, X'PERT-MPD system).

Determination of silver ion

The measurement of silver ion was carried out spectrophotometrically based on the formation of a ternary complex between the silver ions, 1, 10-phenanthroline, and 2, 4, 5, 7-tetra-bromofluorescein (Eosin Y) in aqueous media ($\lambda_{\max} = 550 \text{ nm}$ at pH 6).²⁹ Quantitative analysis of silver ion was carried out using a calibration curve obtained by means of the silver ion standard solutions prepared in deionized water in the ranges: 0.0–2.0 mg L^{-1} . The calibration curve shows that Beer's law is obeyed in this concentration range. The pigment Eosin (Y) does not interfere in our analysis ($\lambda_{\max} = 515 \text{ nm}$ at pH 6). pH adjustments were carried out using dilute NaOH and HNO_3 solutions. All the experiments were carried out at least in triplicate. The results were average of these measurements. The linear regression analysis was carried out for treatment of the data. The relative standard deviation was less than 1.0% and the detection limit value, based on the three times the standard deviation of the blank, was 0.02 mg L^{-1} .

Coating of sawdust by poly (3-methylthiophene)

Polymerization of 3-methyl thiophene was carried out in nonaqueous solution. A 4.0 mL freshly distilled 3-methyl thiophene was dissolved in 100 mL chloroform (CHCl_3). 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 (0.4M) was prepared in chloroform at nitrogen atmosphere for 12 h before polymerization. A 100 mL of oxidant solution (0.8M 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. Because of the polymerization, the solution yielded a greenish black precipitate. Methanol was added in the copious amount in the precipitate,

and the polymer was collected using vacuum filtration technique.^{22,23} The precipitate was then washed with copious amounts of deionized water and methanol and the resulting precipitate was allowed to dry for 2 days, in which time it formed a solid cake of flat-black 3- methylthiophene polymer.

RESULTS AND DISCUSSIONS

Sorption experiments

In batch experiment, fixed amounts of sorbent were treated with silver polluted solution (0–140 mg L^{-1}) at room temperature. During each experiment, the solutions were agitated using a mechanical shaker. In column experiments, a glass column with dimensions of 1 cm diameter and 15 cm length was employed. A 1.0 g sorbent (P3MTh/SD) was packed in the column (5 cm height), and then the silver solution (conc. 50 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 silver ion after each 10 mL. The percentage of sorption was calculated using the following relationships:

$$\% \text{ Sorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$\frac{x}{m} = \frac{C_0 - C_e}{m} \times V \quad (2)$$

where C_0 and C_e are initial and equilibrium concentrations of Ag^+ ion (mg L^{-1}), respectively, V is the volume (L) of silver test solution. x/m stands for mg of silver ion sorbed per gram of adsorbent.

Sorption of silver ion by P3MTh/SD and SD (batch system)

Effect of initial concentration

For performing this experiment, 1.0 g of P3MTh/SD and SD were treated with 25 mL of silver solution with concentration of 10–140 mg L^{-1} for 1 h accompanied by mild shaking at room temperature. The results obtained are summarized in Table I. The graphical form of the data has been shown in Figure 3.

As our results show (Figure 3 and Table I), with increasing the initial concentration of silver ion, total

TABLE I
Effect of Initial Concentration on Sorption Percentage of Ag^+ Ion by SD and P3MTh/SD

Adsorbent	C_0 (mg L^{-1})										
	10	20	30	40	50	60	80	100	110	120	140
SD	50.2	51.6	52.4	54.3	53.2	50.5	46.2	43.5	39.5	37.0	34.0
P3MTh/SD	99.1	98.3	98.5	98.7	98.4	97.8	96.0	93.0	90.2	88.0	77.6

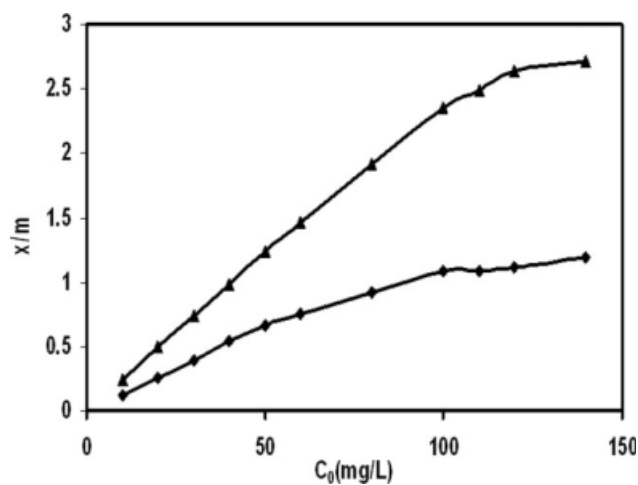


Figure 3 Effect of initial silver concentration on its sorption by SD ■ and P3MTh/SD ▲.

amount of metal sorption (x/m) also increases linearly. However, in the case of P3MTh/SD, metal uptake or sorption is much higher than SD. It is also interesting to note that even uncoated sawdust (SD) can be used to remove silver ion from aqueous solutions effectively. Silver sorption or uptake by SD seems to be based on partly due to redox or complex reactions between silver ion (as oxidizing agent) and noncellulosic constituents such as hemicellulose (a disordered array of several sugar polymers), lignin (which possess many oxidizable functional groups), and aldehyde or ketone groups that this case shown in our previous literature, which lead to silver deposition might be a possible explanation of mechanism for silver removal.

In the case of P3MTh/SD, sorption capacity of silver ion was much higher than SD and even higher than sawdust coated by PANi and PPy as we have previously reported.¹³ The proposed mechanism for removal of silver ion employing our currently introduced adsorbent may be ionic, chelation, redox reactions. Higher sorption of silver ion by P3MTh/SD can also be explained using Pearson hard-soft acid-base theory.³⁰ According to Pearson concept, the hard O— (or N—) bases are preferred to their S— (or P—) analogs by hard acids. Conversely a "soft acid" possesses an acceptor center of high polarizability and exhibits the reverse preference for coordination of a soft base. However, these preferences are not defined in a quantitative sense. Therefore, complex formation of silver ion (as a soft acid) with P3MTh (as a soft base) can be considered as a type of Lewis acid/base (termed as soft acid–soft base reactions) might be a possible description for high-sorption capacity of P3MTh/SD toward silver ion.

It was also interesting to notice that some silver deposition (by visual inspection) is formed on the surface of polymer when it was exposed to silver

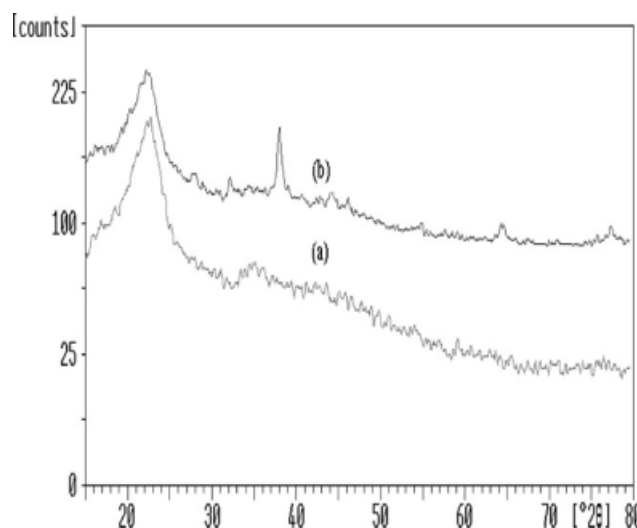


Figure 4 The X-ray diffractograms (XRD) patterns obtained for: (a) untreated polymer, (b) treated polymer to silver ion solution. Anode tube: Cu K_{α} radiation (β_1 : 1.54056 \AA° , β_2 : 1.54439 \AA°), intensity ratio (Alpha 2/1): 0.500. Generator tension: 40 kV, generator current: 40 mA.

ion solution. To have a more accurate conclusion, the samples were further studied using XRD technique. Inspection of XRD patterns obtained from silver ion treated and untreated adsorbent (P3MTh/SD) are shown in Figure 4. As our XRD patterns indicate, P3MTh polymer showed an amorphous nature with a characteristic weak peak at $2\theta = 22.69^\circ$ [Fig. 4(a)]. Silver-treated polymer also showed an amorphous nature (weak peak at $2\theta = 22.21^\circ$) and with a new recognized peak at $2\theta = 38.05^\circ$ [Fig. 4(b)] corresponding to the presence of metallic silver particles on the polymer surface. The calculated intracrystalline d -spacing ($d = 2.359$) using Bragg's Law confirms the presence of silver deposition during treatment of the polymer with silver ion

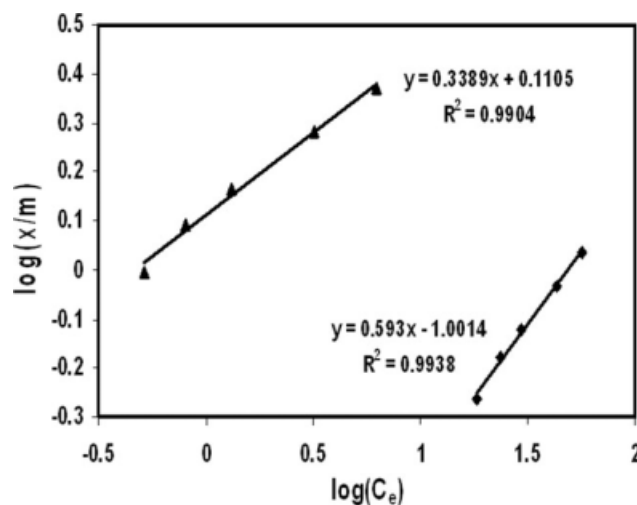


Figure 5 Freundlich linear isotherm for sorption of silver ion by SD ■ and P3MTh/SD ▲.

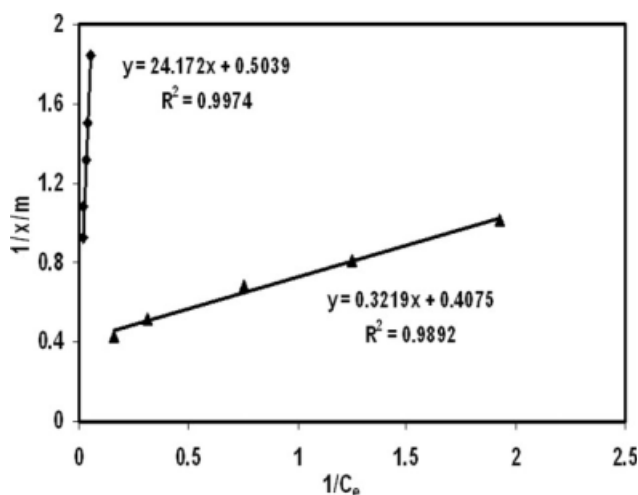


Figure 6 Langmuir linear isotherm for sorption of silver ion by SD ■ and P3MTh/SD ▲.

solution.^{31–33} On the other hand, a redox reaction seems to be important in the course of adsorption process.

Therefore, silver removal by P3MTh seems to be partly due to the redox reaction between electroactive polymer (P3MTh) and silver ion, which leads to some deposition of silver particles on the polymer surface. Synthesis of polymer/nanoparticles composite materials seems to be important in advanced material science. These materials combine both the unique properties of nanoparticles and polymers and possess new properties, which are not specific to the original components.

Adsorption isotherms

To model the sorption behavior, adsorption isotherms were studied at room temperature. Both Langmuir and Freundlich equations were employed to plot the isotherms.^{12,13} For plotting the sorption isotherms, 1.0 g of the selected adsorbents were treated with constant volume (25 mL) of silver ion possessing different concentrations (40–100 mg L⁻¹) at room temperature and pH 6. As our results show (Figs. 5, 6), the data obtained for Ag⁺ ion sorption fit with both the linearized form of Langmuir and Freundlich adsorption isotherm models (linearized form). The k and n constants (in adsorption equation of Freundlich) and b and X_m constants (in adsorption equation of Langmuir) and the correlation coefficient

TABLE II
Comparison of Freundlich and Langmuir Constant Values Obtained for SD and P3MTh/SD

Sorbent	n	K	b	X_m
SD	1.70	0.10	0.02	1.98
P3MTh/SD	2.95	1.29	1.26	2.45

TABLE III
Effect of pH on Removal Percentage of Silver Ion by SD and P3MTh/SD

Adsorbent	pH					
	1	2	3	4	5	6
SD	53.2	50.2	45.3	40.0	34.1	25.3
P3MTh/SD	71.2	76.3	84.2	91.1	95.3	98.4

coefficients (R^2) were determined by using linear regression analysis and have been summarized in Table II. As our data show, the constant n calculated for P3MTh/SD are higher than the n obtained for SD. Higher values of k indicate a higher adsorption capacity. The high values of correlation coefficients obtained for these adsorbents (SD, P3MTh/SD) indicate that both Langmuir and Freundlich models can be applied to these sorbent systems. The removal rates of silver (x/m) for a unit gram of SD, P3MTh/SD were 1.98 and 2.45, respectively. The values of n obtained for P3MTh/SD indicate (Table II) that it is a suitable adsorbent for sorption of silver ion from aqueous solutions. For a suitable sorbent, value of n is normally between 2 and 10.

Effect of pH

For this investigation, fixed amounts of the selected sorbents (1.0 g) were treated separately with 25 mL of Ag⁺ ion (50 mg L⁻¹) in various pH values from 1 to 6. The results obtained are shown in Table III and Figure 7. According to the results, the sorption of Ag⁺ ion increases as pH of treated solution increases. To prevent the precipitation of silver ion in alkaline media, all of our further experiments were carried out at pH 6. The increase of Ag⁺ sorption with the increase in pH can be attributed to the increase in free surfaces sites in polymers, with the

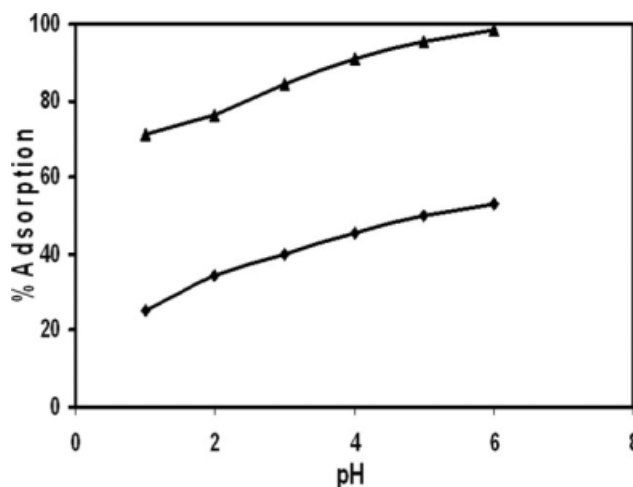


Figure 7 Effect of pH on sorption of silver ion by SD ■ and P3MTh/SD ▲.

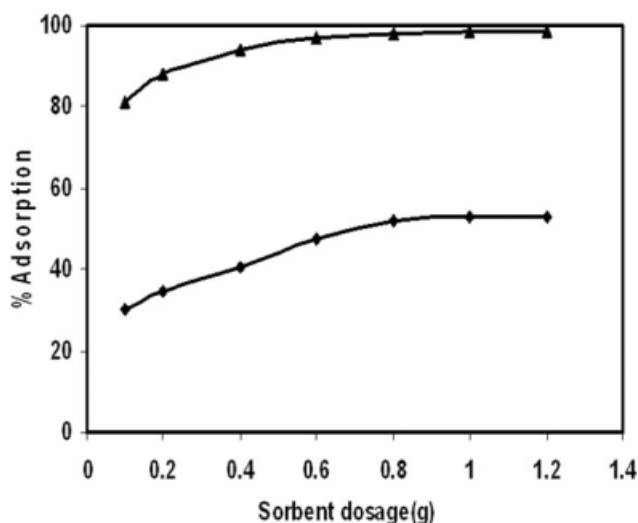


Figure 8 The effect of sorbent dosage on Ag^+ sorption percentage by SD ■ and P3MTh/SD ▲.

increase of pH. In addition to, under neutral conditions, the free $-\text{S}$ groups will be available for complex formation or metal chelating.

Effect of sorbent dosage

In this experiment, different weights of sorbents (0.1–1.0 g) were treated with 25 mL silver ion solutions with concentration of 50 mg L^{-1} . The results obtained have been summarized in Figure 8. As our results show (Table IV and Fig. 8), higher sorption or silver uptake is observed in the case of P3MTh/SD. With increasing sorbent dosage up to 1.0 g, sorption percentage is also increased gradually.

Effect of exposure time

For performing this experiment, 1.0 g of adsorbents (P3MTh/SD and SD) were treated with 25 mL of 50 mg L^{-1} silver ion for different periods (10–70 min) accompanied by stirring at room temperature. The results of adsorption obtained from the analysis of unadsorbed Ag^+ ion in solution are shown in Table V and Figure 9. As the results indicate, removal of silver using the selected sorbent occurs quickly and is not a very time dependent process.

TABLE IV
Effect of Sorbent Dosage on Sorption Percentage of Silver Ion by SD and P3MTh/SD

Adsorbent	Sorbent dosage (g)						
	0.1	0.2	0.4	0.6	0.8	1.0	1.2
SD	30.0	34.6	40.4	47.3	52.1	53.2	53.2
P3MTh/SD	81.2	88.1	94.2	97.1	98.2	98.4	98.4

TABLE V
Effect of Exposure Time on Sorption Percentage of Silver Ion by SD and P3MTh/SD

Adsorbent	Contact time (min)						
	10	20	30	40	50	60	70
SD	47.0	49.2	51.8	52.0	53.2	53.2	53.2
P3MTh/SD	83.6	90.2	94.3	97.1	98.4	98.4	98.4

Desorption studies (column system)

In this study, 1.0 g of adsorbent (P3MTh/SD and SD) was first treated with 25 mL of Ag^+ ion with concentration 50 mg L^{-1} . The exhausted column was then treated with 0.01–0.5M HNO_3 solution for 1 h for regeneration. As our data show, increasing concentration of acid, recovery percentage was increased. Higher concentration of acid was avoided because SD is not very stable in highly acidic (or basic) solutions. Desorption percentage was calculated from the following expression:

$$\% \text{ Desorption} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed onto sorbent}} \times 100 \quad (3)$$

Maximum recovery achievable was 40% for P3MTh/SD and 33.5% for SD when a solution of 0.50M HNO_3 was used as regenerant. In separate experiments, we also used EDTA (0.05 and 0.10M) and ammonia (1.0M) solutions for recovery of silver ion from the exhausted column (containing P3MTh/SD). Low-soluble silver compounds are possibly formed between the polymer dopant anions (e.g., Cl^-) and silver cation should be dissolved in EDTA or ammonia solution. In the case of EDTA as regenerant, maximum recovery observed was about 33%.

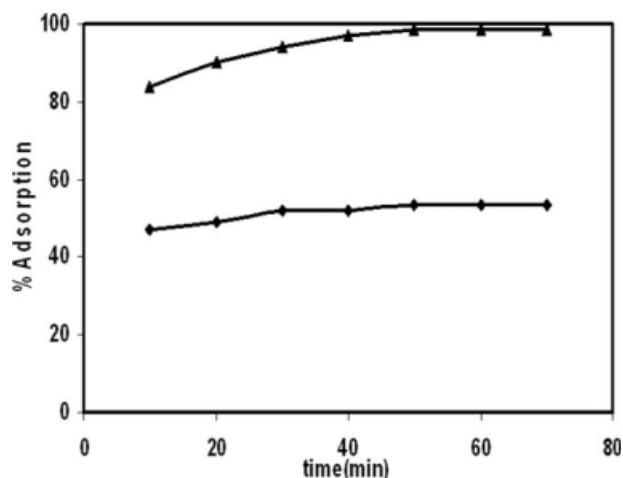


Figure 9 The effect of exposure time in sorption of Ag^+ ion SD ■ and P3MTh/SD ▲.

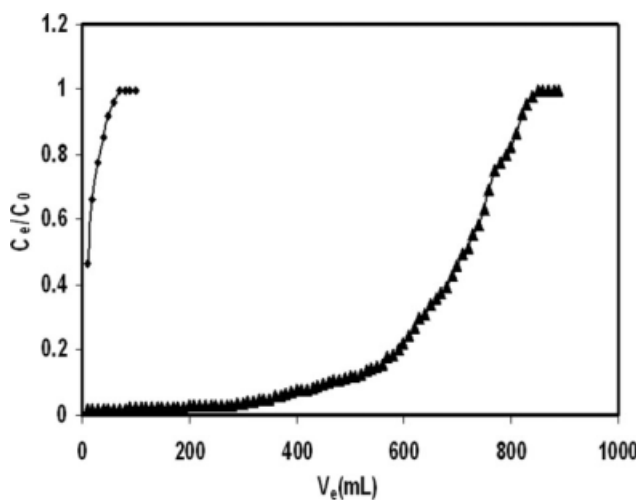


Figure 10 Breakthrough curves obtained for SD ■ and P3MTh/SD ▲.

When ammonia solution (1.0M) was used as regenerant solution, maximum recovery observed was 42% in the case of P3MTh/SD. These findings clearly show that silver ion is not just sorbed via reduction process. Some other reactions such as complex formation, precipitation, chelation might be occurred during silver removal by P3MTh conducting polymers. Incomplete desorption of the sorbed silver ion from the sorbent materials used in this research also express the strong interactions between the silver (both metallic and ionic forms) with the polymer matrix or sawdust.

Breakthrough curve (column system)

When working sorption experiments with columns, the breakthrough curves are very useful. A plot of effluent solute concentration vs. time 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. For performing this experiment, 1.0 g of P3MTh/SD and SD packed in a glass column, and then Ag^+ solution with concentration of 50 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 then analyzed for unsorbed Ag^+ ion to obtain the breakthrough curve. The breakthrough curves obtained for the examined sorbents used for sorption of silver in a column system are shown in Figure 10.

As it is evident from our results obtained in this experiment, the break point for P3MTh/SD is observed after treatment of about 400 mL of 50 mg L^{-1} silver polluted solution and the breakthrough curve

for SD is very sharp and the break point or column exhaustion occurred very quickly. As the results show that P3MTh/SD seems to be much more effective sorbent compared with SD for removal of silver ion in column or flow systems. According to the results shown in Figure 10, 1.0 g of P3MTh/SD can remove more than 95% of silver ion from 400 mL silver polluted solution under the used experimental conditions.

CONCLUSIONS

Sawdust was found a very cheap, economical, and environmentally friendly substrate for coating of high performance conducting electroactive polymers such as poly (3-methyl polythiophene) as an effective adsorbent for removal of silver ion from aqueous solutions. High uptake of silver ion by the currently introduced adsorbent can be due to the high tendency of silver ion toward sulfur containing compounds (e.g., complex or chelation reactions). According to our XRD analysis, the importance of the redox reaction cannot be ignored. The treatment of data using adsorption isotherms shows that the data obtained for silver ion sorption using P3MTh/SD fit better with Freundlich equation. The high-sorption capacity (obtained from breakthrough curve), high Freundlich constants (k , n), and the position of the isotherm obtained for P3MTh/SD, all imply that it is a suitable and efficient adsorbent for removal of silver ion from aqueous solutions.

References

1. Alloway, B. J.; Ayers, D. C. *Chemical Principles of Environmental Pollution*; Blackie Academic & Professional: London, 1993.
2. Janes, N.; Playle, R. C. *Environ Toxicol Chem* 1995, 14, 1847.
3. Ratte, H. T. *Environ Toxicol Chem* 1999, 18, 89.
4. Won, M.; Yeom, J.; Yoon, J.; Jeong, E.; Shim, Y. *Bull Korean Soc* 2003, 24, 948.
5. Grayson, M. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley: New York, 1980; Vol. 21.
6. Drakei, P. L.; Hazelwood, K. J. *Annal Occup Hyg* 2005, 49, 575.
7. Calace, N.; Nardi, E.; Petronio, B. M.; Pietroletti, M.; Tosti, G. *Chemosphere* 2003, 51, 797.
8. Akgül, M.; Karabakan, A.; Acar, O.; Yürüm, Y. *Micropor Mesopor Mat* 2006, 94, 99.
9. Dimeska, R.; Murray, P. S.; Ralph, S. F.; Wallace, G. G. *Polymer* 2006, 47.
10. Yirikoglu, H.; Gülfen, M. *Sep Sci Technol* 2008, 43, 376.
11. Ansari, R. *E J Chem* 2006, 3, 186.
12. Ansari, R.; Khoshbakht Fahim, N. *React Funct Polym* 2007, 67, 367.
13. Ansari, R.; Fallah Delavar, A. *J Iran Chem Soc* 2008, 5, 657.
14. Wallace, G. G.; Spinks, G. M.; Teasdale, P. R. *Conductive Electroactive Polymers: Intelligent Materials Systems*, 2nd ed.; CRC Press LLC, USA, 2003.
15. Singh, R.; Kaur, A.; Yadav, K.; Bhattacharya, D. *Curr Appl Phys* 2003, 3, 235.

16. Udum, Y. A.; Pekmez, K.; Yildiz, A. *J Solid State Electrochem* 2006, 10, 110.
17. Saoudi, B.; Jammul, N.; Abel, M. L.; Chehimi, M. M.; Dodin, G. *Synth Met* 1997, 87, 97.
18. Wang, Y.; Jing, X. *Polym Advan Tech* 2005, 16, 344.
19. Gurunathan, K.; Murugan, A. V.; Marimuthu, R.; Mulik, U. P.; Amalnerkar, D. P. *Mat Chem Phys* 1999, 61, 173.
20. De Paoli, M. A.; Gazotti, W. A. *J Braz Chem Soc* 2002, 13, 410.
21. Niemi, V. M.; Knuutila, P.; Österholm, J. E.; Korvola, J. *Polymer* 1992, 33, 1559.
22. Sugimoto, R.; Taketa, S.; Gu, H. B.; Yoshino, K. *Chem Express* 1986, 1, 635.
23. Sato, M. A.; Tanaka, S.; Am, K. *J Synth Met* 1986, 14, 279.
24. Yoshino, K.; Hayashi, S.; Sugimoto, R. *Jpn J Appl Phys* 1984, 23, L899.
25. Jen, K. Y.; Oboodi, R.; Elsenbaumer, R. L. *Polym Mater Sci Eng* 1985, 53, 79.
26. Qi, L.; Sun, M.; Dong, S. *J Appl Polym Sci* 2006, 102, 1803.
27. Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol Chem* 1989, 190, 3105.
28. McCullough, R. D.; Williams, S. P.; Tristam-Nagle, S.; Jayarman, M.; Ewbank, P. C.; Miller, L. *Synth Met* 1995, 69, 279.
29. El-Ghamry, M. T.; Frei, R. W. *Anal Chem* 1968, 40, 1986.
30. Pearson, G. R. *J Amer Chem Soc* 1963, 85, 3533.
31. Sinha, A.; Sharma, B. P. *Bull Mater Sci* 2005, 28, 213.
32. Iglesias-Silva, E.; Rivas, J.; Leon Isidro, L. M.; Lopez-Quintela, M. A. *J Noncryst Solids* 2007, 353, 829.
33. Available at: <http://www.geologynet.com/geolbases.htm>.