IAU-ARAK

J. Iran. Chem. Res. 2 (2009) 163-171

**Journal of the Iranian Chemical Research**

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# Removal of thiocyanate ions from aqueous solutions using polypyrrole and polyaniline conducting electroactive polymers

Reza Ansari [*], Nilofar Khoshbakht Fahim, Ali Fallah Dellavar

*Chemistry Department, University of Guilan, P.O. Box 41335-1914, Rasht, Iran*

**Received 9 January 2009; received in revised form 19 August 2009; accepted 24 August 2009**

## Abstract

Polypyrrole (PPy/Cl) and polyaniline (PAni/Cl) synthesized chemically onto sawdust (SD) was used for removal of thiocyanate ($SCN^-$) ions from aqueous solutions. The effect of some important parameters such as pH, initial concentration, sorbent dosage, and contact time on uptake of $SCN^-$ was investigated. PPy/SD was found to be much more effective sorbent than PAni/SD for uptake $SCN^-$ from aqueous solutions. Removal of $SCN^-$ ions using PPy/Cl is supposed to be occurred mostly via ion exchange process at the surface of polymer coated onto sawdust as a very thin film. Desorption studies were also carried out for figuring out the possibility of the regeneration and reuse of the exhausted adsorbent. A proposed mechanism based on interesting anion exchange properties of the PPy/Cl has been discussed. It was found that polypyrrole conducting polymers doped with releasable counterions can be used for used to remove some anions via ion exchange process under simple open circuit conditions. The finding in this paper shows the promising application of polypyrrole conducting polymers in future water or wastewater purification technology.

***Keywords:*** Thiocyanate ion; Removal; Polypyrrole; Polyaniline; Sawdust; Desorption.

## 1. Introduction

Thiocyanate ($SCN^-$) is found in various foods and plants. They are present in water primarily because of discharges from coal processing, extraction of gold and silver, and mining industries. Thiocyanates in soil result from direct application of herbicides (weed killers), insecticides, pesticides and from disposal of byproducts from industrial processes. Less important sources include release from damaged or decaying tissues of certain plants, such as mustard, kale, and cabbage. Thiocyanates are known to affect the thyroid glands, reducing the ability of the gland to produce hormones that are necessary for the normal function of the body [1-3]. Ion exchange, reverse osmosis, electrodialysis, distillation and activated carbon adsorption are processes that have been employed for uptake of thiocyanate from drinking water supplies, but these processes are expensive and a brine of difficult management is generated [4-6]. Conducting electroactive polymers (CEP) such as Polypyrrole (PPy) and polyaniline (PAni) are a subject of intense investigation of many research groups worldwide because of their interesting and unique electrical and electrochemical properties [7-13].

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[*] Corresponding author. Tel.: +98 131 3233262; fax: +98 131 3233262.
*E-mail address:* ransari@guilan.ac.ir (R. Ansari)

Polyaniline can be easily synthesized chemically from bronsted acidic aqueous solutions. On the basis of conductivity, HCl and $H_2SO_4$ were found the best dopants for protonation of polyaniline. Ammonium persulfate have been found the most popular oxidant for chemical of aniline in aqueous acidic media. Besides being easily synthesized, this polymer shows high electric conductivity, high thermal and environmental stabilities [14-18]. The overall polymerization reaction of polyaniline can be simply shown as (Fig. 1):

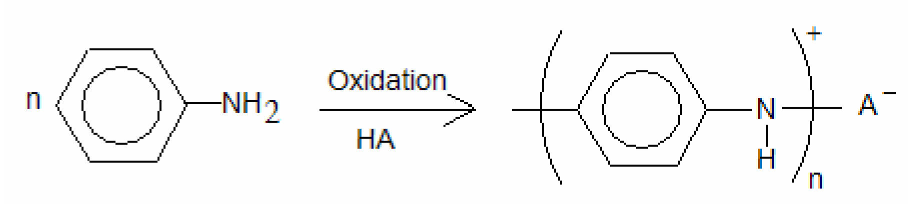

**Fig. 1.** The overall polymerization reaction of polyaniline (PAni).

Polypyrrole (PPy) is another important class of conducting polymers that can be synthesized both chemically and electrochemically from both aqueous and non-aqueous solvents [19-26]. PPy can be prepared from neutral or weakly acidic aqueous solutions but the efficient polymerization of aniline is achieved only in an acidic media. Iron (III) chloride has been found to be the best chemical oxidant and water is the best solvent for chemical polymerization with respect to desirable conductivity characteristics. By performing the polymerization of PPy in electrolytes containing different counter ions, the functionality and properties of the polymer can readily be changed [26-28]. Although PPy only exists in a neutral reduced state and a positive oxidized state, it is possible to create both anion and cation sensitive films using small inorganic anions or large organic anions as counter ions during the synthesis. Polymerisation reaction of polypyrrole can be simply shown as (Fig. 2):

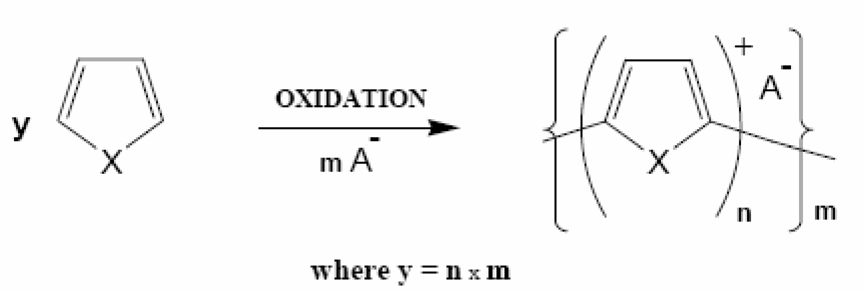

**Fig. 2.** The overall polymerization reaction of polypyrrole.

Where $A^-$ is the counterion or anion of the electrolyte incorporated during polymerization in order to maintain charge balance. Depending on the type and the charge of the incorporated anion corresponding to one anion for every 3-4 pyrrole units in order to achieve electroneutrality, and this makes up 30-40% of the final weight of the polymer [25]. Polypyrrole is electroactive and can act as ion exchanger during redox reaction. The charging and discharging (doping-dedoping) processes of polypyrrole, are accompanied by the exchange of ions (anions, cations or both) depending on the size of the dopant and potential applied on the membrane [11]. This effect was used for the development of an electrochemically switchable ion-exchanger for water purification, especially for softening drinking water [29-36]. The ion-exchange behavior and capacity of electrochemically and chemically prepared polypyrrole (PPy) in dependence on the incorporated counterions are characterised using an electrochemical quartz crystal microbalance and cyclic voltammetery (CV) techniques [7, 10, 20]. Almost all the previously reports in applications of conducting polymers in separation devices rely on mainly their electrical and electrochemical properties. In this paper we have taken advantage of the interesting ion exchange properties of these polymers for removal of $SCN^-$ ions under simple open circuit conditions and the new system used in this investigation is reported for the first time.

## 2. Experimental

### 2.1. Materials and equipments

All chemicals used were analytical reagents grade and prepared in deionized water. Pyrrole and aniline were obtained from Merck and distilled before use. Sawdust sample (SD) obtained from a local carpentry workshop. $Fe(NO_3)_3$ solution prepared in nitric acid 1.0 mol $L^{-1}$ and standard solution of thiocyanate with the concentration of 125 mg $L^{-1}$. A single beam Perkin-Elmer UV–Vis 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. Dilute NaOH and HCl solutions were used for pH adjustments.

### 2.2. Preparation of the polymers

The polymers were synthesized directly on the surface of the sawdust which has previously soaked in monomer solutions (0.2 mol $L^{-1}$) by slow addition of chemical oxidants (chloride ferric for PPy and ammonium persulfate for PAni) at room temperature as we have described the details in our previous publications [38-40]. Sawdust was first washed with enough distilled water, dried at room temperature at 80-90 °C for 1 h for removing the moisture and sieved (35-50 mesh size) before use. Polyaniline (PAni/SD) and polypyrrole (PPy/SD) obtained were filtered, washed with copious distilled water, then dried at temperature about 60 °C (in an oven), and sieved before using.

### 2.3. Determination of thiocyanate anion

The concentration of thiocyanate ion in the filtrate was determined using a Perkin-Elmer UV-Vis Spectrophotometer, at the $FeSCN^{2+}$ complex absorption maxima ($\lambda_{max}$= 447 nm) and computing from the calibration curves (Fig. 3).

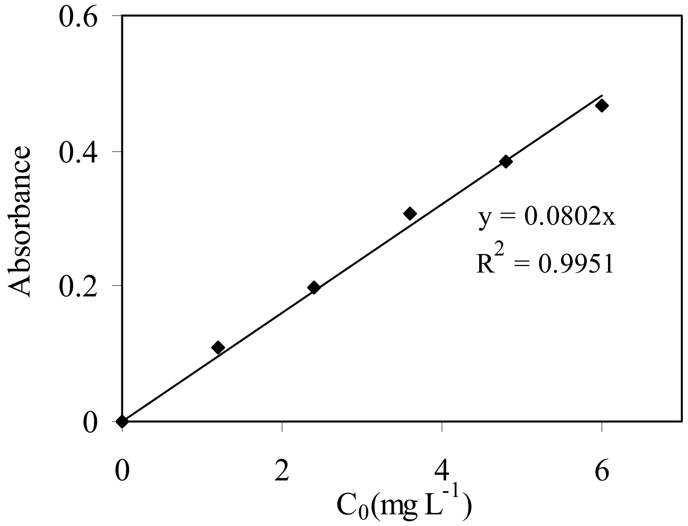

**Fig. 3.** Calibration curve obtained for spectrophotometric determination of $SCN^-$.

Iron (III) reacts with the thiocyanate ion ($SCN^-$) to produce the bright red $FeSCN^{2+}$ ion. The relative standard deviation (RSD) was less than 1.0% and the detection limit value, based on the three times the standard deviation of the blank was 0.01 mg $L^{-1}$.

### *2.4. Sorption experiments*

In batch experiment, a fixed amount of adsorbents were treated with anionic polluted solution (0-125 mg $L^{-1}$) at room temperature. During each experiment, the solutions were agitated using a mechanical shaker. The solutions were filtered with Whattman filter paper (number 42) and uptake of thiocyanate ion was analyzed spectrophotometrically at $\lambda_{max}$. In column experiments a glass column with dimensions of 1.0 cm diameter and 15 cm height was employed. 1.0 g sorbent (PPy/SD or PAni/SD) was packed in the column (bed volume ~5 $cm^3$), and then the anion solution was passed through the column with flow rate of 3 mL $min^{-1}$. The outlet solution was analyzed for residual adsorbate ion. The values of percentage removal and the amount of dye adsorbed were calculated by using following relationships:

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

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

where $C_o$ and $C_e$ are the initial and equilibrium concentrations of the anion, respectively (mg $L^{-1}$); X/m is the amount of anion sorbed onto unit amount of the adsorbent (mg $g^{-1}$) at equilibrium; and V is the volume of the solution used in the adsorption experiment (L). The percentage of desorption of $SCN^-$ was calculated from the following expression:

$$\%\text{Desorption} = \frac{m_r}{m_o} \times 100 \qquad (3)$$

where $m_r$ is the amount of $SCN^-$ desorbed (mg) and $m_o$ is the amount of $SCN^-$ adsorbed (mg). Each adsorption and desorption experiment was carried out in triplicate and the average results are presented in this work.

## 3. Results and discussion

### *3.1. Removal of thiocyanate by PAni/SD and PPy/SD (Batch system)*

### *3.1.1 Effect of pH*

In this experiment, 1.0 g dried sorbents (PAni/SD and PPy/SD) and sawdust as a blank were treated separately with 25 mL of 60 mg $L^{-1}$ thiocyanate solution at different pH values (2-11). Since uncoated sawdust did not show any removal of $SCN^-$ ions. Maximum adsorption of $SCN^-$ ions measured using uncoated sawdust (SD), was less than 5%. Sawdust as other biomaterials is more effective for uptake of cationic species such as heavy metal ions rather than inorganic anions, because of the presence of different polar functional groups in its structure capable to make chemical binding. So in our further study in this paper we used only coated form of sawdust by PPy and PAni (termed as PPy/SD, PAni/SD). The results obtained for removal of $SCN^-$ ions using PAni/SD and PPy/SD have been shown in Fig. 4.

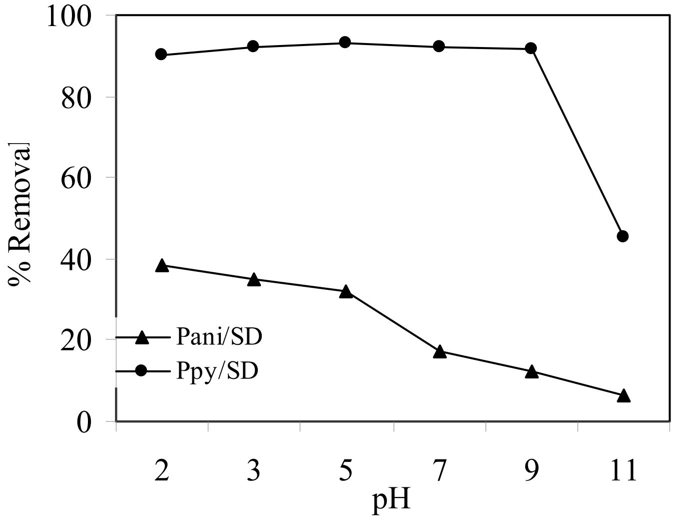

**Fig. 4.** The effect pH on removal percentage using PPy/SD and PAni/SD.

As the results obtained show (Fig. 3), PPy/SD seems to be more effective adsorbent for removal of $SCN^{-1}$ than PAni/SD. Higher sorption capacity of $SCN^-$ ions was observed using PPy/SD. Removal of $SCN^-$ ions by PPy/SD is less dependent to pH than PAni/SD at least at pH values from 2 to 9. The following mechanisms (Eqs. 4, 5) are suggested for removal of $SCN^{-1}$ ions by PPy and PAni conducting electroactive polymers:

$$PPy^+/Cl^- \quad + \quad SCN^-_{(sol)} \leftrightarrows PPy^+/SCN^- \quad + \quad Cl^-_{(sol)} \qquad (4)$$

$$PAni^+/Cl^- \quad + \quad SCN^-_{(sol)} \leftrightarrows PAni^+/\,SCN^- \quad + \quad Cl^-_{(sol)} \qquad (5)$$

The removal of $SCN^-$ ions with PPy or PAni can be mostly due to the anion exchange properties of these polymers. Higher removal percentage of PPy might be due to the higher anion exchange properties of PPy compared to PAni. Polypyrrole doped with small size dopants or counterions can act as anion exchanger. The dopant anions in the polymer matrix can be exchanged with other anions in solution if they are small size or releasable (e.g. $Cl^-$, $NO_3^-$). With increasing pH of solution (pH ≥ 4), PAni/Cl become undoped (forming emeraldine base), and then less anion will be available to be exchanged with $SCN^-$ ions in solution. Therefore, the removal percentage of $SCN^-$ decreased considerably. Decreasing removal percentage of $SCN^{-1}$ by PPy/Cl at pH > 10 can be due to the dedoping of PPy/Cl (possibly formation of $PPy^+/OH^-$) which occurs at more alkaline conditions. Consequently its anion exchange property is decreased. Hydroxide anions stabilize the positive charges in PPy by H bonding and the interaction is so strong that ion exchange properties of PPy decreased markedly. The same behavior for PPy was observed for removal of nitrite ions as we have reported it recently [41]. It has already been reported that PAni is more effective for uptake or removal of heavy metal ions [42-44]. Chelating and electron donating properties of the amine groups on the PAni conducting polymers seems to make them more useful for the collection of heavy metal ions such as $Pb^{2+}$ and $Hg^{2+}$ from aqueous solutions. Anion exchange property of PAni has also been reported recently [45].

### *3.1.2. Effect of initial concentration*

In this investigation 1.0 g of sorbents (PAni/SD and PPy/SD) were placed in contact with 25 mL of different concentrations of $SCN^1$ for 1 h. The results obtained are shown in Fig. 5.

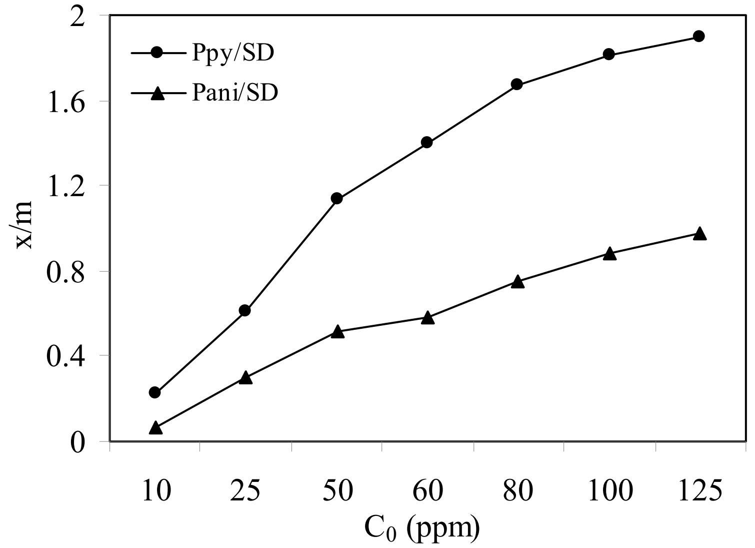

**Fig. 5**. Effect of initial concentration of SCN$^-$ ion on removal percentage by PPy/SD and Ani/SD.

As the results show, with increasing the initial concentration of thiocyanate ion ($C_o$), total amount of SCN$^{-1}$ sorption (x/m) is also increased. At all of the initial concentrations of adsorbate, higher removal percentage was observed for PPy/SD.

### 3.1.3. *Effect of exposure time*

In the investigation of the effect of shaking time, 1.0 g of sorbents (PAni/SD and PPy/SD) were exposed to 25 mL of thiocyanate ion solution with concentration of 60 mg L$^{-1}$ at different equilibration times (10-70 minutes).

The samples were stirred during exposure at room temperature. Then the solutions were filtered and the filtrates were analyzed for un-adsorbed SCN$^-$ . The results are illustrated in Fig. 6.

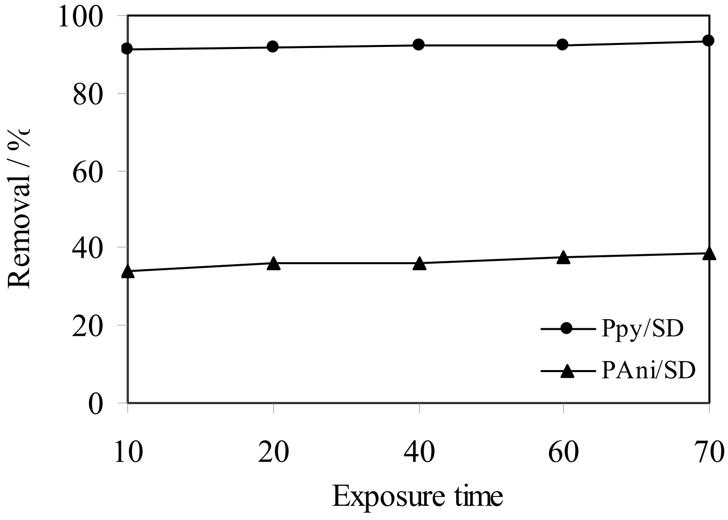

**Fig. 6.** Effect of exposure time on SCN$^-$ removal percentage by PPy/SD and PAni/SD.

As the results indicate, removal of thiocyanate using the selected adsorbents occurs quickly and removal percentage of SCN$^-$ using PPy/SD is also much higher than PAni/SD.

### *3.1.4. Effect of sorbent dosage*

The effect of variation of sorbent dosage on the removal of thiocyanate by PAni/SD and PPy/SD are shown in Figure 7. Dosages were varied from 0.1 to 1.2 g and equilibrated for 1 hour. The initial concentration was 60 mg $L^{-1}$.

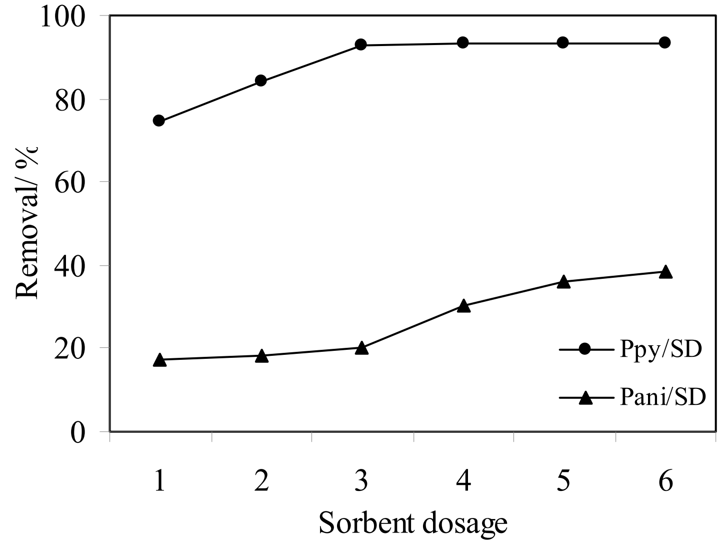

**Fig. 7.** Effect of adsorbent dosage on $SCN^-$ removal percentage by PPy/SD and PAni/SD.

As our data obtained show here, PPy/SD is a much more efficient sorbent in compared to PAni/SD for $SCN^-$ removal. With increasing sorbent dosage up to 1.0 g, sorption percentage is also increased gradually because of higher adsorption sites will be available with increasing of sorbent dosage. As our investigation in the current study show, polypyrrole doped with chloride ion as dopant is more efficient for removal or adsorption of $SCN^-$ from aqueous solutions in compared to PAni.

### *3.2. Desorption Study*

In this part of study, 1.0 g of sorbent (PAni/SD and PPy/SD) was first treated with 25 mL of $SCN^-$ ion with concentration 100 ppm at a fixed flow rate (3 mL $min^{-1}$). After the column was completely exhausted, desorption of solute from loaded adsorbent was carried out by solvent elution method, using 0.01 M NaOH as an regenerate solution through the column maintained at constant temperature. From the start of the experiment effluent samples at different time intervals (5, 10, 20, 30 min and so on) were collected at the bottom of the column for analysis. Maximum desorption percentage of $SCN^-$ ions for PAni/SD and PPy/SD under the used conditions was found 30% and 60% respectively. Incomplete desorption might be due to the strong interactions between the polymers and thiocyanate. With increasing the alkalinity of the regenerate solution, it might be possible to increase regeneration or recovery percentage.

## 4. Conclusions

Sawdust was found as a suitable substrate or support for chemical coating of conducting polymers from aqueous solutions. Removal of anions such as $SCN^-$ by biomaterials such as wood sawdust is very poor. Conducting electroactive polymers such as polypyrrole (PPy) doped with small size dopant anions can be used for removal of anions such as $SCN^-$ from aqueous solutions effectively. The removal mechanism of the $SCN^-$ ions by PPy/SD is supposed to be mostly based on anion exchange properties of polypyrrole conducting polymers doped with small size dopants (e.g. $Cl^-$). PPy is more effective and efficient than PAn in order to be used for adsorption of thiocyanate ion from aqueous solutions. Regeneratability percentage of PPy after use was also much higher than PAni. It might be concluded that polypyrrole conducting polymers doped with small size or releasable dopants are promising adsorption system in future water and wastewater treatment in order to remove toxic anions or water softening as anion exchanger resins.

## Acknowledgement

The authors would like to thank for the financial support of post graduate studies of the University of Guilan, Rasht, Iran.

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