

Sorption of Silver Ion from Aqueous Solutions Using Conducting Electroactive Polymers

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(Received 13 December 2007, Accepted 29 January 2008)

In this research polypyrrole (PPy) and polyaniline (PAni) conducting polymers which were synthesized chemically on the surface of wood sawdust (SD). These electroactive polymers as coated form on sawdust then were used for sorption or removal of silver ion from aqueous solutions under simple open circuit conditions. The effects of some important parameters such as pH, initial concentration, sorbent dosage, and contact time on uptake of silver ion were also investigated in this research. The experiments were carried out using both batch and column systems at room temperature. The treatments of the data were carried out using both Freundlich and Langmuir adsorption isotherms. In order to find out the possibility of the regeneration and reuse of the exhausted adsorbent, desorption studies were also performed. It was found that conducting electroactive polymers such as PPy or PAni are efficient sorbents for removal of the silver ions from aqueous solutions. Sorption/desorption processes can be simply carried out with pH control with satisfactory performance. Recovery percentage observed for PAni/SD in column study was more than PPy/SD and SD, under the same operational conditions.

Keywords: Silver ion, Sorption, Sawdust, Polypyrrole, Polyaniline, Desorption

INTRODUCTION

Silver (Ag) is a white and precious metal. It is a stable element and is not affected by air or water at ordinary temperatures. As a conductor of heat and electricity, it is superior to all other metals. It is insoluble in HCl but soluble in HNO₃ and hot H₂SO₄ but is inert to alkalis. Silver and its salts have a broad range of industrial and commercial applications. Small fraction of silver and its salts consumption in modern technology are, in photographic films, electrical contacts, batteries, conductive paints, brazing alloys, silverware, medical products, as coinage metal, jewelry, catalysis, chemistry laboratories, water purification and cloud seeding [1,2]. Silver is widely distributed throughout the world and occurs as the metal and also as sulfide ores (*e.g.* argentite).

It is found in the environment in four oxidation states: 0, 1+, 2+ and 3+, with 0 and 1+ being the most common, while 2+ and 3+ are seldom seen naturally in the environment. Nearly all silver minerals are compounds of silver with sulfur, or the homologues (*e.g.*, selenium and tellurium) and neighbors on the periodic chart (arsenic, antimony and bismuth). Other minerals include halides and free metal.

In wastewaters, the free silver ion is extremely toxic to aquatic organisms even at trace concentrations [2]. The major source of silver in the environment is wastewaters from the photographic and imaging industry (47%). It has been reported that about 2.47 million Kg of silver are lost each year to the environment. About 150 tons of silver enter the aquatic environment every year from the mine tailings, photography and electroplating industries [3-5].

Different treatment techniques (adsorption, extraction, ion-

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exchange resins, reverse osmosis, metal replacement, precipitation, electrolysis and electro dialysis) have been developed for removal of silver ions from wastewaters [6-14]. Thus, there is a need for introducing an efficient method for the removal or recovery of silver ion from waste solutions generated from the mentioned industries due to the both economical and environmental points of view.

Conducting electroactive polymers such as polyaniline (PAni) and polypyrrole (PPy) have attracted a great deal of attention in recent years [15-22]. These polymers can be synthesized chemically or electrochemically from aqueous and non-aqueous solvents. PPy and PAni are two electronically conducting polymers that can be prepared in aqueous solutions. However, polyaniline should be synthesized from acidic aqueous media. Ferric chloride and ammonium persulfate are the most popular oxidants for chemical synthesis of PPy and PAni in water, respectively.

Oxidation of pyrrole and aniline yield cationic charged polymer products with incorporated anions. During polymerization of pyrrole and aniline, electroneutrality of the polymer matrix is maintained by incorporation of anions (called dopant) from the reaction solution, corresponding to one anion for every 3-4 monomer units, making up 30-40% of the final weight of the polymer. The dopant or counterion, in fact plays the most important role in characterizing the polymer product. Polymerization reaction of PPy is also limited to high nucleophilic environments, since polymerization mechanism involves radical cation coupling

[22].

In chemical polymerization, these counter ions are usually the anion of the chemical oxidant or reduced product of the oxidant. The overall stoichiometry resulting from chemical polymerization of PPy with ferric chloride as oxidant and the overall polymerization reaction of PAni can be simply shown in Figs. 1a and 1b, respectively.

The electroactive nature or the switching properties of PPy and PAni have been utilized as the basis of most proposed applications such as sensors, separation devices, rechargeable batteries and controlled drug-release [22-26]. All of the previous applications of these polymers are based on their electrically conductivity [27] and unique electrochemical properties [28-30]. However, this paper deals with a quite different application of these reactive and functional polymers. Our recent studies have shown that these polymers can effectively remove or uptake the precious metals such as silver ions from aqueous solutions under simple open circuit conditions. Adsorption of silver ion onto various solids is important from purification, environmental and economical points of view. The main advantages of adsorption are its simplicity, selectivity, efficiency and the separation of trace amount of elements from large volumes of solutions.

EXPERIMENTAL

Materials and Equipments

All chemicals used were analytical reagents grade and

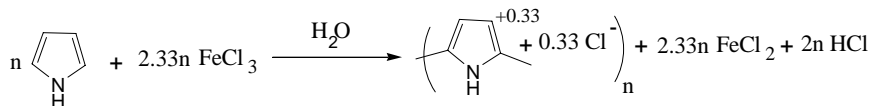


Fig. 1a. Chemical polymerization of pyrrole.

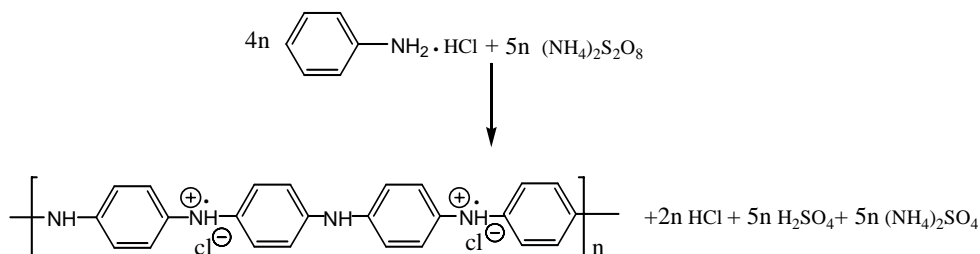


Fig. 1b. Chemical polymerization of polyaniline.

prepared in deionized water. Pyrrole and aniline were obtained from Merck and distilled before use. Sawdust sample (SD) obtained from walnut wood obtained from a local carpentry workshop. Silver nitrate (AgNO_3) solution with the concentration of 120 mg l^{-1} vs. silver ion was prepared in deionized water, used as stock solution. The stock solution of silver stored in a dark dish in order to prevent of photodecomposition.

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. pH adjustments were carried out using dilute NaOH and HNO_3 solutions.

Preparation of the Polymers

The polymers were synthesized directly on the surface of the sawdust which has previously soaked in monomer solutions by slow addition of chemical oxidants at room temperature as we have described in our previous publications [31-33]. 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.

PAni/SD and PPy/SD obtained were filtered, washed with copious distilled water, then dried at temperature about 60 °C (in an oven) and sieved before use.

Determination of Silver Ion

Determination of silver ion was carried out spectrophotometrically as described in the literature with a little modification [34]. The measurement of silver ion is based on the formation of a ternary complex between the silver ions, 1,10-phenanthroline and 2,4,5,7-tetra-bromo-fluorescein (Eosin Y) in aqueous media ($\lambda_{\text{max}} = 550 \text{ nm}$ at pH 6.0). The compound's formula could be suggested as: $[\text{Phen.Ag-phen}]_2^+ \text{TBF}_4^{2-}$. 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 ppm (Fig. 2). The calibration curve shows that Beer's law is obeyed in this concentration range.

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 (RSD) was less than 1.0% and the detection limit value, based on the three times the standard deviation of the blank [35], was 0.02 mg l^{-1} .

Sorption Experiments

In batch experiment, a fixed amount of sorbents were treated with silver polluted solution (0-120 ppm) at room temperature. During each experiment, the solutions were agitated using a mechanical shaker. In column experiments a glass column with dimensions of 1.0 cm diameter and 15 cm height was employed. 1.0 g sorbent (SD, PPy/SD or PAni/SD)

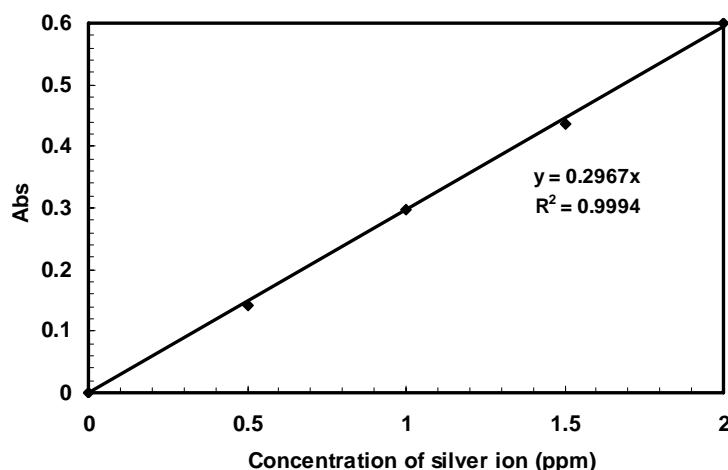


Fig. 2. Calibration curve obtained for analysis of Ag(I).

was packed in the column (bed volume $\sim 5 \text{ cm}^3$), and then the silver solution (50 ppm) was passed through the column with flow rate of 3 ml min^{-1} at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$). The outlet solution was analyzed for residual silver ion. The following equations were used to calculate the percentage of sorption and the amount of adsorbed silver ion, respectively:

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

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

where C_0 and C_e are the initial and equilibrium concentrations of the silver ion, respectively (mg l^{-1}); x/m is the amount of silver ion adsorbed 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). All of adsorption experiments were carried out at room temperature and pH 6.

RESULTS AND DISCUSSION

Sorption of Silver Ion by Sawdust (SD), PANi/SD, and PPy/SD (Batch System)

Effect of initial concentration. For performing this experiment, 1.0 g portions of dried above mentioned adsorbents were treated with 25 ml of silver solution with concentration of 10-120 ppm at pH 6 for 1 h accompanied by mild shaking at room temperature. The results obtained are summarized in Table 1 and the corresponding graphical form has been shown in Fig. 3. As our results show, with increasing initial concentration of silver ion (C_0), total amount of metal sorption (x/m) also increases linearly. It is also interesting to note that even uncoated sawdust can be used to remove silver ion from aqueous solutions effectively.

Silver 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 (a complex amorphous polyphenol polymer which, possess many functional groups such as OH (either the alcoholic OH's on the chains or the phenolic OH's on the aromatic rings) and aldehyde or ketone groups [36]. It is interesting to note that even pure cellulose (cotton) is able to adsorb silver ion ($\sim 30\%$) under the operational conditions. However, in the case of

PPy/SD and PANi/SD sorbents, sorption capacity of silver ion was much higher than SD.

In order to elucidate the mechanism of metal uptake by polypyrrole conducting polymers, some PPy sample prepared electrochemically as free standing films as we have previously described [27]. These films were treated with silver solutions without application of potential or current. After a while it was observed that a thin silver layer was deposited on the surface of polymer. It can also be concluded that the conductivity and sensing behavior of PPy and PANi conducting electroactive polymers could be further improved by silver deposition in polymer matrix. This finding might be important from analytical and electroanalytical point of view in the field of preparation of conducting polymer modified electrodes and electrocatalysis.

It might be concluded that silver removal by PPy conducting polymers can be due to mostly redox reaction (leading to silver deposition and polymer oxidation).

Another possible reason for metal uptake by PPy can be due to oxidizing nature of Ag^+ ion ($E^\circ = 0.80 \text{ V}$), and overoxidation of the polymer (PPy). As we have already shown [30], applying anodic potentials more positive than $+0.80 \text{ V vs. Ag/AgCl}$ will lead to overoxidation of the polymer. Overoxidation of PPy is accompanied by the loss of its conjugation system and also conductivity. It also causes the loss of the positive charge, which releases the dopant out of the polymer texture to maintain electroneutrality (Fig. 4). Therefore, it seems that, prolonged exposure of PPy to Ag^+ ion (oxidizing agent) because of overoxidation process, silver ion is reduced. Dedoping (removal of anions) of the polymer in the course of overoxidation, creates also a cavity for entrapping of the silver.

Adsorption isotherms. An isotherm plot can be analyzed to determine the performance of a given adsorbent or to compare the performance of two or more adsorbents. In order to make a model for the sorption behavior of silver ion by the introduced adsorbents, adsorption isotherms were studied at room temperature.

Both Langmuir and Freundlich equations were employed to plot the isotherms. Non-linear Langmuir and Freundlich isotherms can be expressed, respectively, as:

$$X = \frac{X_m b C_e}{1 + b C_e} \quad (3)$$

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Table 1. Effect of Initial Ag(I) Concentration on Sorption Percentage^a

Adsorbent	C ₀ (ppm)									
	10	20	30	40	50	60	80	100	110	120
SD	50.2	51.6	52.4	54.3	53.2	50.5	46.2	43.5	39.5	37.0
PPy/SD	93.9	94.8	95.0	96.9	96.2	95.1	92.3	89.0	86.3	81.9
PAni/SD	95.0	95.8	96.8	98.2	97.8	97.0	94.8	92.0	87.0	83.5

^aAll results reported in this paper are the average of at least triplicate measurements and the maximum expected error was less than ±5%.

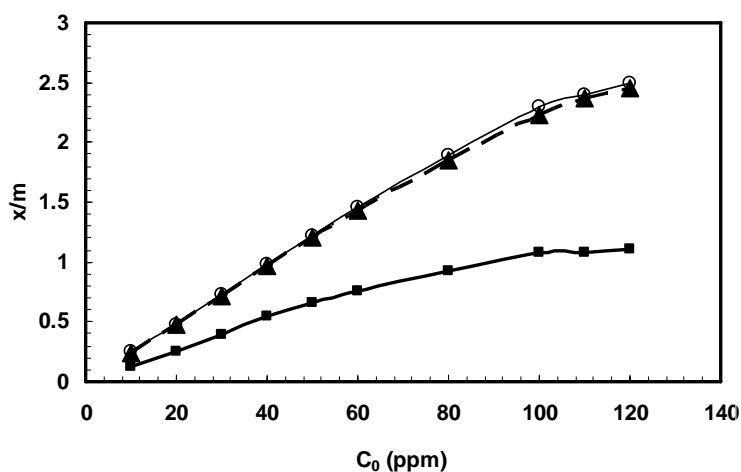


Fig. 3. Effect of initial Ag(I) concentration on its sorption onto (■) SD, (▲) PPy/SD and (○) PAni/SD.

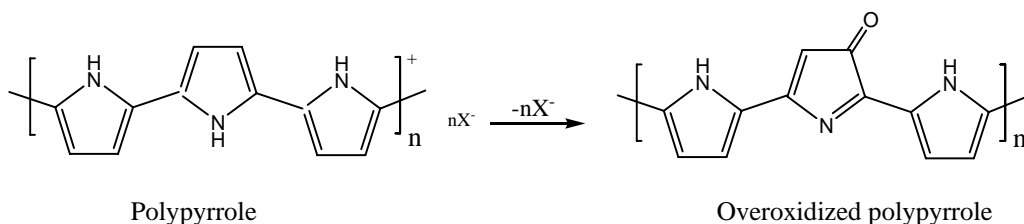


Fig. 4. Formation of polypyrrole and its overoxidation.

$$X = kC_e^{\frac{1}{n}} \quad (4)$$

where X is the amount of silver ion adsorbed (mg g⁻¹), represents the adsorptive capacity of the adsorbent for the equilibrium effluent concentration, X_m is the maximum amount sorbed, b is a Langmuir's constant signifying energy of sorption, C_e is equilibrium concentration of Ag⁺ in the

aqueous phase (mg l⁻¹), k and n are Freundlich constants, indicating sorption capacity and intensity of the adsorbent, respectively. The Langmuir equation (Eq. 3) makes several assumptions, such as monolayer sorption on a surface containing a limited number of sites, predicting a homogeneous distribution of sorption energies, while the Freundlich empirical equation (Eq. 4) deals with

physicochemical adsorption on a very heterogeneous adsorption surface [37-39].

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 ppm) at room temperature and pH 6.0. As our results show (Figs. 5 and 6), the data obtained for Ag⁺ sorption fit with the both linearized form of Langmuir and Freundlich adsorption isotherm models. The agreement of the experimental data for silver sorption by the used adsorbents with both Langmuir and Freundlich adsorption models (Figs. 5 and 6) implied that both monolayer

adsorption and heterogeneous surface conditions existed under the experimental conditions used.

PAni/SD is obviously better than PPy/SD and SD, since its isotherm lies above the isotherms for PPy/SD and SD. For any equilibrium concentration of silver, the amount of silver adsorbed is greater for PAni than for SD or PPy/SD. Furthermore, the Langmuir isotherm for PAni/SD (Fig. 5), has steeper slope indicates that its adsorptive capacity increases at higher equilibrium concentration of silver. It might be concluded that PAni/SD will be more efficient for column applications in continuous flow systems too.

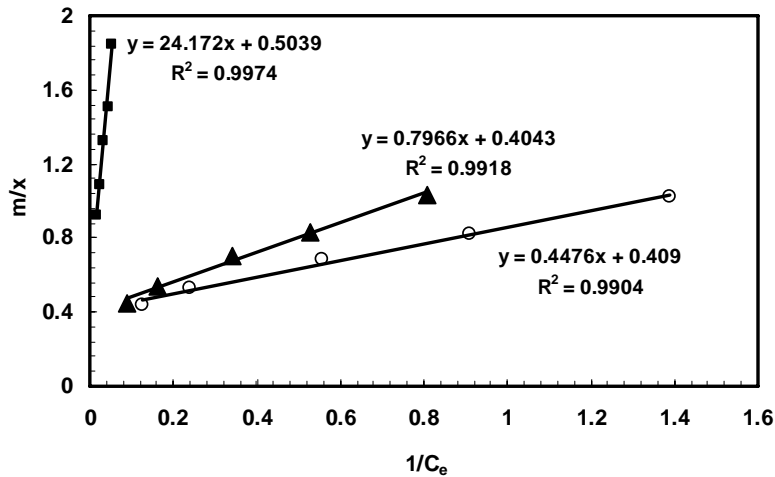


Fig. 5. Langmuir plot for the sorption of Ag(I) onto (■) SD, (▲) PPy/SD and (○) PAni/SD.

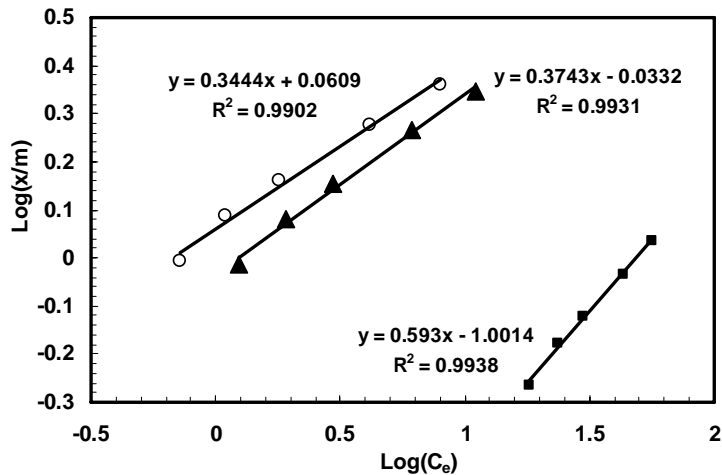


Fig. 6. Freundlich plot for the sorption of Ag(I) onto (■) SD, (▲) PPy/SD and (○) PAni/SD.

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A log-log plot of the data was used to linearize the Freundlich equation in order to determine adsorbents capacity at a specified equilibrium concentration (Eq. 5). The intercept of such a line ($\log k$), signifying the adsorption capacity, will occur at a value of $C = 1.0 \text{ mg l}^{-1}$. The slope of this line ($1/n$) provides adsorption intensity.

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log C_e \quad (5)$$

Alternatively, using Langmuir equation, a plot of $1/C_e$ vs. $1/x$ yields a straight line with intercept of $1/x_m$ and the slope of $1/bx_m$, confirming the applicability of the Langmuir adsorption isotherm.

$$\frac{1}{x} = \frac{1}{x_m} + \frac{1}{x_m b C_e} \quad (6)$$

Parameters related to each isotherm and the correlation coefficients (R^2) were determined by using linear regression analysis. As the results show (Table 2), the constant k obtained for both PPy/SD and PAni/SD adsorbents is higher than the k obtained for SD. Higher values of k indicate a higher adsorption capacity. The high values of correlation coefficients obtained for all the adsorbents (SD, PPy/SD and

PAni/SD), indicates that both Langmuir and Freundlich models can be applied to this sorbent systems (Figs. 5 and 6). The removal rates of silver (x/m) for a unit gram of SD, PPy/SD and PAni/SD were 1.98, 2.47 and 2.44, respectively. The values of n obtained for PPy/SD and PAni/SD indicates (Table 2) that they are good adsorbents for free silver ion from aqueous solutions. For a suitable sorbent, the value of n are normally between 2 and 10 [40].

Effect of pH on silver uptake. For this investigation, 1.0 g portions of dried sorbents (PAni/SD, PPy/SD and SD) were treated separately with 25 ml of Ag^+ ion (50 ppm) in various pH values. The results obtained are shown in Table 3. These results show (Table 3), sorption of Ag^+ ion increases as pH of treated solution increases. The increase of Ag(I) sorption with the increase in pH can be attributed to the increase in free surfaces sites in polymers, with the increase of pH. At $\text{pH} > 4$, PAni is changed into deprotonated form, then more active sites ($-\text{N}$ groups) will be available for metal binding. However, under low pH conditions, these sites are protonated. Therefore, they are not available for Ag(I) sorption, resulting in a decrease in the silver sorption. PAni in fact can exist in various oxidation states characterized by the ratio of imine to amine nitrogen. Transformation between doped and undoped states is readily occurred *via* simple acid-base treatment [21].

Table 2. Freundlich and Langmuir Constant Values Obtained for SD, PPy/SD and PAni/SD

Adsorbent	n	k	b	x_m
SD	1.7	0.10	0.041	1.98
PPy/SD	2.7	0.93	1.25	2.47
PAni/SD	2.9	1.15	2.23	2.44

Table 3. Effect of pH on Sorption Percentage of Ag(I) by the Used Adsorbents

Adsorbent	pH					
	1	2	3	4	5	6
SD	25.3	34.1	40.0	45.3	50.2	53.2
PPy/SD	60.0	72.1	76.6	83.2	91.8	96.3
PAni/SD	61.3	73.0	78.3	86.1	93.1	97.8

*The pH of solutions was adjusted using dilute nitric acid solution. Alkaline media were avoided because of chemical precipitation of silver ion which occurs at $\text{pH} > 8$.

Under neutral conditions, PANi exists in deprotonated form, so the free -N groups will be available for complex formation or metal chelating.

Effect of sorbent dosage. In this experiment different weights of the selected sorbents (0.10-1.0 g) were treated with 25 ml silver ion solutions with concentration of 50 ppm. The results obtained have been summarized in Fig. 7. As our results, higher sorption or silver uptake is observed in the case of PPy/SD and PANi/SD. With increasing sorbent dosage up to 1.0 g, sorption percentage is also increased gradually.

Effect of contact time. For performing this experiment, 1.0 g of adsorbents (PANi/SD, PPy/SD and SD) were treated

with 25 ml of 50 ppm 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 Fig. 8. As the results indicate, removal of silver using the selected adsorbents occurs quickly and is not a very time dependent process. However, in comparison to SD, silver removal is much higher when PPy or PANi are used.

Effect of flow rate on silver removal. The adsorption capacity parameters obtained from the batch system are useful on a small scale for predicting the design parameters. Therefore, it is necessary to carry out flow test using columns

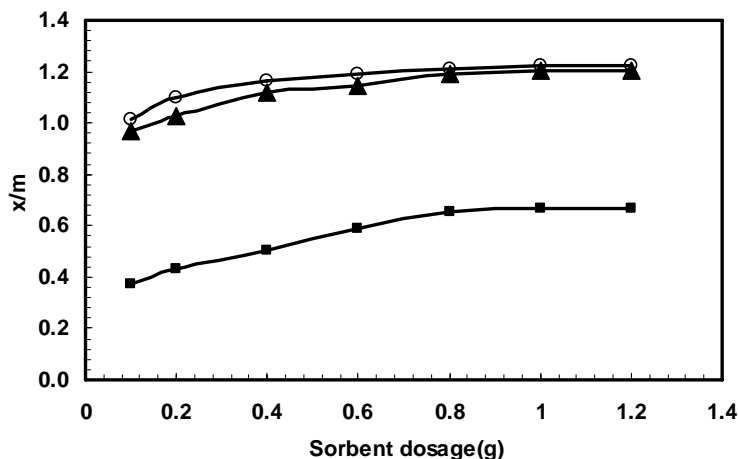


Fig. 7. Effect of sorbents dosage on percent sorption of Ag(I) onto (■) SD, (▲) PPy/SD and (○) PANi/SD.

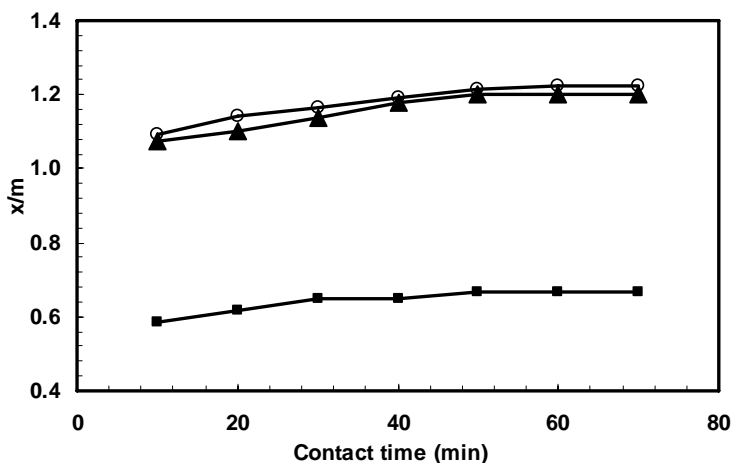


Fig. 8. Adsorption percentage of Ag(I) vs. contact time for the three adsorbents: (■) SD, (▲) PPy/SD and (○) PANi/SD.

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Table 4. Effect of Solution Flow Rate on Percent Sorption of Ag(I)

Adsorbent	Flow rate (ml min ⁻¹)			
	2	3	4	5
SD	53.5	53.2	44.1	35.0
PPy/SD	97.1	96.9	92.1	83.4
PAni/SD	98.4	98.2	93.5	84.1

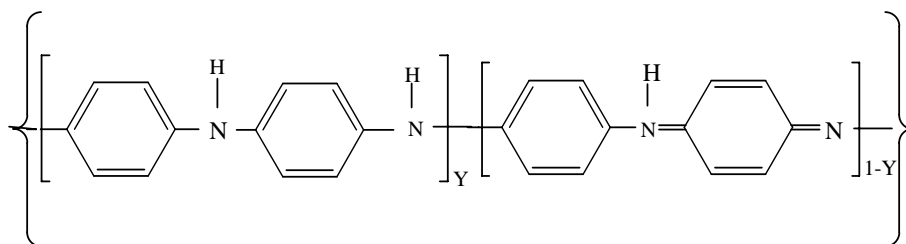


Fig. 9. Structure of emeraldine base form of polyaniline (EB).

to obtain design models which would be applicable to commercial systems.

In this study a fixed bed (~5 cm³) operation conditions used for the three adsorbents. The flow rate was studied in the range of 2-5 ml min⁻¹ since flow rate in the systems used, did not exceed 5 ml min⁻¹. As the data indicate (Table 4), with increase in flow rate of the Ag(I) solution through the column, sorption percentage is decreased for all of the adsorbents. Therefore, a flow rate of 3 ml min⁻¹ was used for all of our further investigation in this paper. The data obtained in column study are also in good agreement with the data obtained in our batch experiments (Fig. 8).

Effect of dopant in the case of PAni/SD on Ag(I) removal. For performing this experiment, PAni/SD prepared in the presence of HCl was treated with ammonia solution (0.5 M) for 1 h. The polymer was then dried at 60-70 °C till complete removal of excess ammonia. During base treatment, polyaniline will be changed into undoped state (termed as emeraldine base). Emeraldine base form of PAni (EB) consists of equal numbers of reduced and oxidized repeat units (Fig. 9). Where, the value for Y can be between 0 (completely oxidized state) to 1 (completely reduced state) [21]. The undoped and doped state of polyaniline with different bronsted acids (HCl, H₂SO₄, H₃PO₄, HNO₃ and *p*-toluene sulfonic acid or PTS) with concentration of 0.5 M were then used for silver sorption

Table 5. Influence of Dopant Acids on Sorption Percentage of Ag(I) by PAni/SD

Adsorbent	Adsorption percentage
PAni (EB)	96.1
PAni/Cl	94.5
PAni/SO ₄	95.8
PAni/PTS	96.0
PAni/PO ₄	87.1
PAni/NO ₃	91.5

experiment. The experiment was carried out with treatment of 1.0 g adsorbent with 25 ml of silver solution (50 ppm) for 1 h at room temperature. As our data show (Table 5), Ag⁺ ion uptake by polyaniline is not much dependent on the nature of the dopant acid. It was found that PAni in both undoped (EB form) and acid doped states, showed high sorption capacity for silver. Due to the partially oxidized structure of PAni, and free -N groups in polymer structure, silver uptake might be occurred *via* both redox and metal chelating reactions.

Desorption Studies

In this study, 1.0 g of adsorbent (PAni/SD, PPy/SD and SD) was first treated with 25 ml of Ag⁺ ion with concentration

50 ppm. The used column was then treated with different chemicals (used as eluent or desorption agent). HCl was not employed because of AgCl precipitation. Higher concentration of acid was also avoided since sawdust, the same as any biomaterial, is not very stable in highly acidic (or basic) solutions. Desorption percentage was calculated from the following expression:

$$\% \text{ Desorption} = \frac{\text{Amount of metal ion desorbed}}{\text{Amount of metal ion adsorbed onto sorbent}} \times 100 \quad (7)$$

The concentration of the silver ion in aqueous phase was analysed as described before. As the data show (Table 6), when HNO₃ 0.50 M was used as eluent solution, 33.5%, 37% and 35% of the silver is recovered for SD, PPy/SD and PAni/SD, respectively. When a 1 M ammonia solution was used as eluent, maximum recovery percentage of silver ion was 31.5%, 44.1 and 50% for the three adsorbents, respectively. Higher recovery percentage of silver ion from PAni/SD and PPy/SD, using ammonia solution may indicate that some of metal uptake by these polymers can be due to complex formation. Incomplete desorption of the silver from the sorbents employed in this investigation, also express the importance of chemical adsorption accompanied by the strong interactions between the silver (both metallic and ionic forms) with the polymer matrix or sawdust can not be ignored.

Therefore, complex chemical reactions such as complex or chelate formation, redox and precipitation, are occurred during silver removal by PAni or PPy conducting/electroactive polymers.

Breakthrough Curves

Sorption isotherms which are obtained from batch study do not give accurate scale-up data for industrial treatment systems since sorption in a column is not normally in a state of equilibrium. Consequently, there is a need to perform flow tests using columns to evaluate the performance of adsorbent. The design of packed bed adsorbent in continuous systems, involves mainly the calculation of the breakthrough curve. A plot of effluent solute concentration vs. 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. For performing this experiment, 1.0 g of PAni/SD, PPy/SD and SD packed in a glass column (fixed bed depth of 5 cm), and then Ag⁺ solution with concentration of 50 ppm passed through the column with constant flow rate (3 ml min⁻¹) at pH 6.0. Each time 10 ml was poured into the column. The outlet solution was analyzed for unadsorbed Ag⁺ ion in order to obtain the breakthrough curve. The breakthrough curves obtained for the examined adsorbents used for sorption of silver in a column system are shown in Fig. 10.

As it is evident from our results obtained in this experiment, the break point for PAni/SD is observed after treatment of about 400 ml of silver polluted solution with initial concentration of 50 mg l⁻¹. The breakthrough curve for SD is very sharp and the break point or column exhaustion occurred very quickly. In the case of PPy/SD break point occurs faster than PAni/SD. Therefore, PAni/SD seems to be much more effective sorbent compared to SD and better sorbent than PPy/SD for removal of silver ion in column or flow systems. According to the results shown in Fig. 10, 1.0 g of PAni/SD can remove more than 95% of silver ion from 400 ml silver polluted solution under the used experimental conditions.

CONCLUSIONS

Polyaniline and polypyrrole conducting polymers can be easily synthesized *via* chemical oxidation directly on the surface of sawdust from aqueous solutions. Sawdust is a very cheap, environmental friendly material and suitable substrate for coating of conducting/electroactive polymers in order to be used for adsorption of heavy metal ions from aqueous solutions. Sorption or silver ion uptake by the three adsorbents (SD, PPy/SD and PAni/SD) employed in this investigation seems to be occurred *via* complex chemical reactions such as reduction-oxidation, complex formation and chelating. The findings in this paper are very important from application point of view for water and wastewater treatments in order to remove heavy metal ions.

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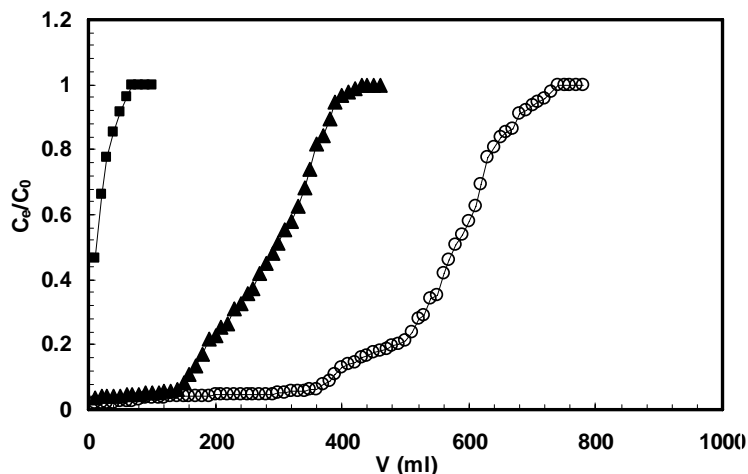


Fig. 10. Breakthrough curves for the uptake of Ag(I) by (■) SD, (▲) PPy/SD and (○) PANi/SD. C_0 and C_e are the initial and residual Ag(I) concentration, respectively, and V is the volume of the treated solution.

Table 6. Effect of Different Chemicals on Desorption Percentage of Ag(I)

Adsorbent	Eluent Solutions					
	EDTA (0.1 M)	NH ₄ OH (0.5 M)	NH ₄ OH (1 M)	HNO ₃ (0.1 M)	HNO ₃ (0.2 M)	HNO ₃ (0.5 M)
SD	20.0	30.0	31.5	24.6	26.0	33.5
PPy/SD	22.0	35.2	44.1	25.0	27.0	37.0
PANi/SD	34.0	40.4	50.0	24.8	26.4	35.0

ACKNOWLEDGEMENTS

The authors are thankful to the reviewers for their critical comments and useful suggestions, which significantly improved the quality of the manuscript. The authors would also like to acknowledge financial support from the Postgraduate Studies of University of Guilan.

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