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Removal of Arsenic Ions from Aqueous Solutions Using Conducting Polymers

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Abstract: In this study, polypyrrole (PPy), polyaniline (PANi) and poly 3-methyl thiophene (P3MTh) conducting polymers were synthesized chemically as coated on the surface of wood sawdust (SD), then used for removal of arsenic ions (As^{3+}) from aqueous solutions. The experiments were performed using both batch and column systems. In order to find out the possibility of desorption for frequent application, the chemical regeneration of the used column was also investigated

Keywords: Arsenic, Removal, Conducting polymers, Sawdust, Aqueous solution.

Introduction

Arsenic is one of the well established toxic elements and has been recognized to have an adverse human health hazards such as possible carcinogenic activity. It is widely distributed in human tissues, hair, skin and nail¹. Drinking water is a major source of arsenic for most people. The recommended tolerance limit of its uptake is up to 0.4 mg per day. Inorganic arsenic predominates in drinking water and is present as arsenite [(As(III))] and arsenate [As(V)]. Different levels of toxicity for various arsenic compounds (organic and inorganic) have been reported by some investigators²⁻⁶. The major sources of arsenic in natural waters are also from its widespread use in herbicides, pesticides, fungicides and insecticides³⁻⁶.

The allowed concentration of arsenic in drinking water reported by the US Environmental Protection Agency (USEPA) is 50 ppb. Living organisms are exposed to the toxic arsenic species primarily from food and water. However, there is also some scientific evidence that suggests arsenic is a necessary part of the diet. The toxicity of arsenic arises from its ability to react with the sulphhydryl groups of the enzyme system thereby blocking the action of the thiol groups of enzymes. Inorganic arsenic predominates in drinking water and is present as arsenite [(As(III))] and arsenate [As(V)]. Arsenic occurs in the natural

environmental in four oxidation states: As(V), As(III), As(0) and As(-III) depending on pH and redox conditions. Among the different oxidation states, because of the ability to complex with certain co-enzymes, arsenite, As(III) is more toxic to animal and plants than As(V) (~10 times) and methylated species (~70 times)⁶⁻⁹. The mobility and toxicity of arsenic are determined by its oxidation state. The valence and species of inorganic arsenic are dependent on the oxidation-reduction conditions and the pH of the water.

The reduced form [As(III)] is normally found in groundwater (anaerobic conditions) under reducing conditions and the oxidized form [As(V)] is mostly found in surface water or oxidizing waters (as H_2AsO_4^- or HASO_4^{2-}). As(III) is not very stable in aqueous solutions and can be easily oxidized chemically (*e.g.* KMnO_4 , Cl_2), solid phase oxidizing media, electrochemically and photochemically (UV radiation) into As(V). Biotransformation of arsenic can produce highly volatile compounds such arsine (AsH_3) and methylated compounds which are extremely toxic¹⁰. Many aquatic organisms (bacteria, fungi) are capable of accumulating arsenic and may catalyze the oxidation of arsenite to arsenate while also promoting the formation methyl arsines through biomethylation reaction¹⁰. In aqueous systems, arsenic (arsenite, arsenate) exhibit anionic forms depending on pH. As(V) is generally more efficiently removed than As(III), so pre-oxidation of As(III) to As(V) is mandatory for high arsenic removal from drinking water supplies containing high concentration of As(III). Several technologies such as reverse osmosis, ion exchange, adsorption, are available for removal of arsenic from aqueous solutions⁹⁻¹³. A relatively new and promising method for reducing arsenic levels (both trivalent and pentavalent) in drinking water is the use of iron oxide filters^{10,12}. Like activated carbon, these granular filters have large amounts of surface area and an affinity for arsenic to adhere to its surface. Although these filters are fairly new to the home treatment market, the principals behind them have been used by public water suppliers for many years.

We have already shown¹³ that impregnation of activated carbon with copper or silver salts leads to some improvement in uptake of As(III) from aqueous solutions but the Fe(II) and Fe(III) salts also leads to some diminish in As(III) removal. Considerable improvement in arsenic removal was also observed when activated carbon impregnated with S- containing compounds was used¹³. This can be due to the high tendency of arsenic to bond with sulphur. Polypyrrole, polyaniline and polythiophene are three of the most well-known conducting electroactive polymers that have attracted a great deal attention in the last two decades¹⁴⁻¹⁸. Almost all the previously published paper of conducting polymers relies on their interesting electrical and electrochemical properties¹⁹⁻²³. However; this paper deals with their possible applications for uptake or removal of toxic anions from aqueous solutions. Removal of anions using conducting polymers can be due to the anion exchange or redox properties of these new classes of conjugated conductive electroactive polymers²⁴. PPy can be easily synthesized on the surface of any substrate chemically^{25,26}.

The overall polymerization reaction of pyrrole can be shown (Figure 1) as the following:

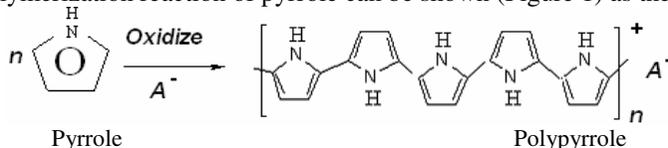


Figure 1. Overall polymerisation reaction of polypyrrole

Where; the A^- is the anion of oxidant in monomer solution or reduced product of oxidant. The value of n has been determined to be between 2.2 and 2.4. During chemical polymerisation of pyrrole, electroneutrality of the polymer matrix is maintained by incorporation of anions of oxidant from the reaction solution. Iron(III) chloride has been found to be the best chemical oxidant and water has been reported the best solvent for chemical polymerization of pyrrole with respect to desirable conductivity characteristics. During chemical polymerisation of pyrrole, electroneutrality of the polymer matrix is maintained by incorporation of anions from the reaction solution. These counterions are usually the anion of the chemical oxidant or reduced product of oxidant.

Polyaniline (PANi) is a poly aromatic amine that can be easily synthesised chemically from bronsted acidic aqueous solutions²⁷. It is one of the most potentially useful conducting polymers and has received considerable attention in recent years. Chemical polymerisation of aniline in aqueous acidic media can be easily performed using of oxidising agents such as $(NH_4)_2S_2O_8$ as shown in the following (Figure 2).

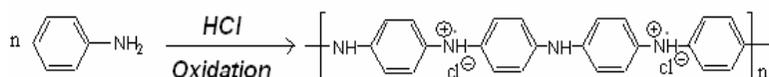


Figure 2. Overall polymerization reaction of polyaniline

The oxidation process is accompanied by the insertion of anions of acid electrolyte in order to maintain the charge neutrality of the final polymer product. Ammonium persulfate is a popular and frequently used chemical oxidant for polymerization of aniline in acidic aqueous solutions. Poly (3- methyl thiophene) was prepared via chemical oxidation from nonaqueous solution which the monomer is soluble^{28,29}. The suggested mechanism for polymerization of 3-alkyl thiophene can be shown as in Figure 3.

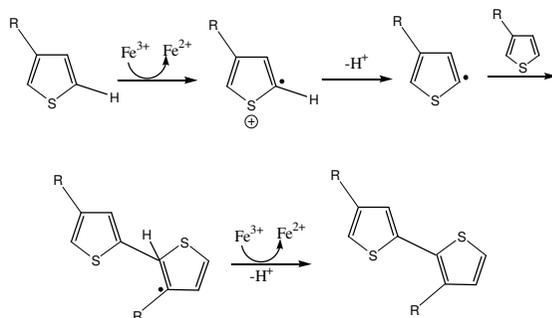
Experimental

The chemicals used were analytical grade and prepared in distilled water. A stock solution of As(III) (100 mg.L^{-1}) was prepared from As_2O_3 in distilled water. Pyrrole (C_4H_5N), thiophene (C_4H_4S) and aniline (C_6H_7N) monomers (Merck) were distilled before polymerization. Polymerization of polypyrrole and polyaniline were carried out in aqueous solutions and poly 3-methylthiophene was synthesized from non-aqueous solvent. In order to prepare PPy/SD, 5.0 g sawdust (35-50 mesh, 10% humidity) immersed in 50 mL of 0.2 M freshly distilled pyrrole solution for 12 hours before polymerization. The excess of the monomer solution was removed by simple decantation. 50 mL of oxidant solution (0.5M $FeCl_3$) was added into the mixture gradually (in 10 minutes) and then the reaction was allowed to continue for another 2h at room temperature. Then the coated sawdust polymer (PPy/SD) filtered, washed with distilled water, then dried at temperature about $60^\circ C$ (in an oven) and sieved again before use. PANi/Cl was synthesized with the same procedure used for preparation of PPy/SD. For polymerization of aniline in HCl solution (1 M) ammonium persulfate was employed as chemical oxidant.

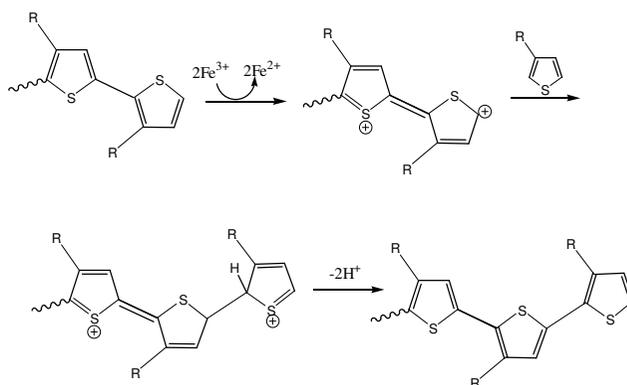
Poly (3-methyl thiophene) was synthesised as described in literature with minor modification²⁸. In order to prepare sawdust coated by poly (3- methyl thiophene) termed as P3MTh/SD, 4 mL freshly distilled 3-methyl thiophene was dissolved in 100 mL chloroform ($CHCl_3$). 10.0 g sawdust (35-50 mesh) immersed in 100 mL of 3-methyl thiophene monomer solution in chloroform (0.4M) for 12h before polymerisation. 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 4h 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. The precipitate was washed with copious amounts of deionized water and methanol and allowed to stay for 2 days at room temperature, then dried at 50- 60°C for 12 hour in an oven. In order to increase the reproducibility of the results, the sawdust coated polymers sieved again before adsorption experiments.

Radical:



Carbocation:



Radical cation:

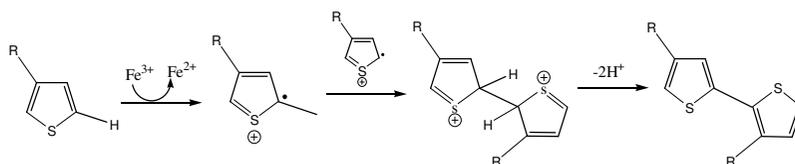
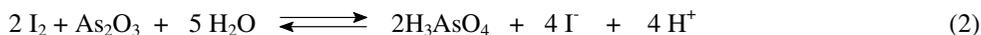


Figure 3. Proposed mechanism for oxidative polymerisation of poly 3-alkyl thiophene by FeCl_3

Sorption experiments were carried out using both batch and column systems at room temperature. Column experiments were carried out using a glass tube (1 cm \times 10 cm). The analysis of As(III) was carried out using coulometric titration in the presence of KI (2.5%) and NaHCO_3 . Electrolysis was carried out using a constant current of 5 mA.



The end point was detected using starch indicator or employing potentiometry technique using Pt and Ag/AgCl in NaCl 3 M as indicator and reference electrodes respectively. The details of the procedures can be found in analytical chemistry text books. The percentage of sorption was calculated using the following relationship:

$$\% \text{ Sorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (3)$$

Where C_i and C_f are initial (inlet) and final (outlet or effluent) concentrations of As(III). Alternatively the amount of sorption per unit mass of sorbent (x/m) can be calculated using the following relationship:

$$\frac{x}{m} = \frac{(C_0 - C)V}{m} \quad (4)$$

Where V is the volume of adsorbate (cm^3) and m is the amount of adsorbent (g).

Instrumentation

A digital coulometer (model ZCM 76, IRAN) was used for coulometric determination of As(III) and a digital desktop pH meter (Metrohm 827) was employed for the pH control.

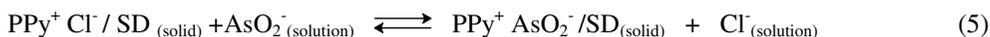
Results and Discussion

Removal of As(III) using SD, PPy/SD, PANi/SD and P3MTh/SD (batch system)

The effect of pH

The chemistry of arsenic in aqueous solutions is very pH dependent, so in this research we first investigated the effect of pH on adsorption of As(III) in order to find out the optimum pH for maximum removal efficiency. In this study, 25 mL of 100 ppm As(III) solution was prepared in different pH values (1-11) using dilute HCl and NaOH solution. The results obtained for SD, PPy/SD, PANi/SD and P3MTh/SD are shown in Figure 4.

According to our results (Figure 3), high efficiency in As(III) removal is observed under basic conditions for all the four sorbents used in this experiment. As(III) removal by PPy/SD, PANi/SD and P3MTh/SD sorbents seems to be mostly occurred via anion exchange process between the releasable polymer dopant (Cl^-) or OH^- (sorbed on the surface of positively charged polymer composite in alkaline conditions) and AsO_2^- in the treated solutions as shown by the following equations:



However, the exact mechanism for As(III) sorption by conducting polymers employed in this paper and SD (due to the variety of the functionalities exist on the surface of SD) is not very clear for us. It seems to be a complex processes. Processes such as anion exchange, chemical oxidation, chelation seems to be possible reactions which are occurred during As(III) removal. Further and more accurate investigations are needed in order to find out the exact mechanisms.

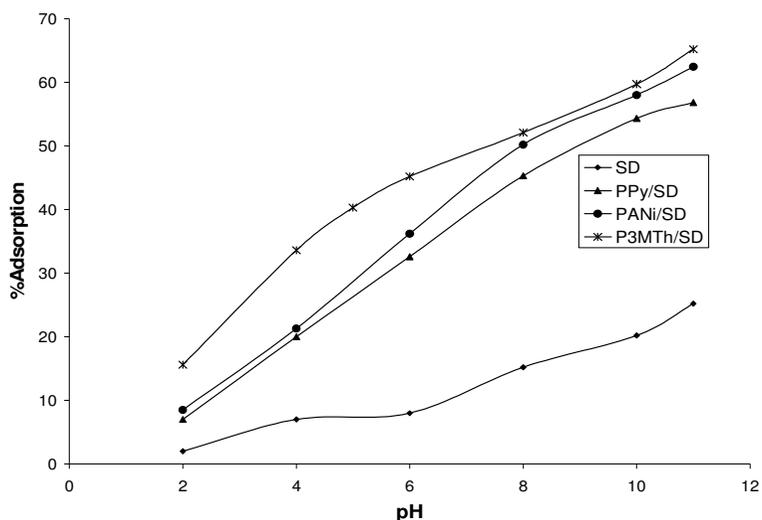


Figure 4. The effect of pH on As(III) sorption by SD, PPy/SD, PANi/SD and P3MTh/SD.

Effect of initial concentration

In this investigation, 1.0 g. of sorbents (SD, PPy/SD, PANi/SD and P3MTh/SD) was treated with 25 mL of As(III) solutions containing different initial concentration. The exposure /shaking time was selected one hour. Sorption experiments were carried out at the most suitable pH value (11) for each sorbent. The results are summarized in Table 1. Each data reported is the average of at least three measurements with maximum uncertainty of %5.

Table 1. Effect of the initial As(III) concentration on sorption by SD, PPy/SD, PANi/SD and P3MTh/SD (using batch system)

sorbent	C_0	%A	X/m
SD	10	37.2	0.09
	25	38	0.24
	50	32.5	0.41
	75	28.2	0.53
	100	25.2	0.63
PPy/SD	10	76	0.19
	25	74.5	0.46
	50	68.3	0.85
	75	63.8	1.2
	100	56.8	1.42
PANi/SD	10	82.6	0.21
	25	80.5	0.50
	50	73.8	0.92
	75	68.3	1.28
	100	62.4	1.56
P3MTh/SD	10	84.1	0.21
	25	84.9	0.53
	50	78	0.97
	75	69.4	1.30
	100	65.2	1.63

As our results show, none of the polymers used in this experiment seems to be a very efficient sorbent for removal of arsenic from aqueous solutions. However; P3-MTh/SD seems to be a better sorbent than PPy/SD and PANi/SD but is more expensive. With increasing the initial concentration, the total removal of arsenic increases in the case of all polymers used in this paper.

Treatment of data using adsorption isotherms

In order to model the sorption behavior, adsorption isotherms were studied at room temperature. Both Langmuir and Freundlich equations were employed to plot the isotherms. Langmuir and Freundlich equations can be shown as $1/X = 1/X_m + 1/bC_e$, $X/m = KC_e^{1/n}$ (or $\log X/m = \log K + 1/n \log C_e$) respectively. Where C_e is the equilibrium concentration of Cr(VI) solution (mg/L), X is the amount sorbed by adsorbent (mg/g), X_m is the maximum amount sorbed, b a Langmuir's constant signifying energy of sorption, K and n are Freundlich's constants indicating sorption capacity and intensity, respectively. The isotherm obtained (both Freundlich and Langmuir) as shown in Figures 5 and 6, indicate that adsorption of As(III) by PPy/SD, PANi/SD and P3MTh/SD can be modeled by both Freundlich and Langmuir isotherm equations (linear form). The Langmuir model deals with monolayer adsorption and constant adsorption energy, while the Freundlich equation deals with physicochemical adsorption on heterogeneous surfaces.

According to Freundlich equation, Plotting x/m vs. C_e , a straight line is obtained on a log-log paper. The slope of this line ($1/n$) provides adsorption intensity. The intercept of such a line will occur at a value of $C=1$ mg/L, such that $\log C=0$, then $K = X/m$. In Freundlich adsorption system, the value of n is determined experimentally from the slope of the line which is equal to $1/n$. For a good adsorbent it is between 2 and 10.

The isotherm obtained (both Freundlich and Langmuir) as shown in Figures 5 and 6, indicate that adsorption of As (III) by PPy/SD, PANi/SD and P3MTh/SD can be modeled by both Freundlich and Langmuir isotherm equations (linear form). Also, as our data show (Table 2), the PPy and PANi conducting polymers used for removal of arsenic do not possess a suitable n while P3MTh/SD has a better value for n . X_m observed for PPy seems to be higher than other used polymers in this investigation. Langmuir isotherm assumes that the number of adsorption sites is fixed and that adsorption is reversible. However; our desorption experiments showed that arsenic sorption process is not completely reversible.

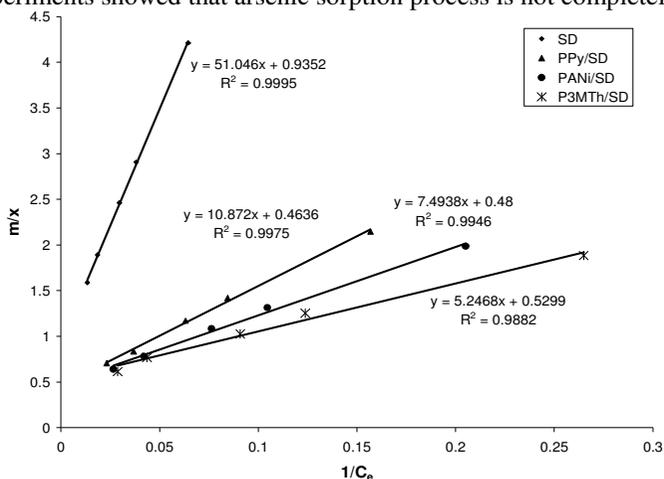


Figure 5. Lungmuir isotherm SD, PPy/SD, PANi/SD and P3MTh/SD for sorption of As(III)

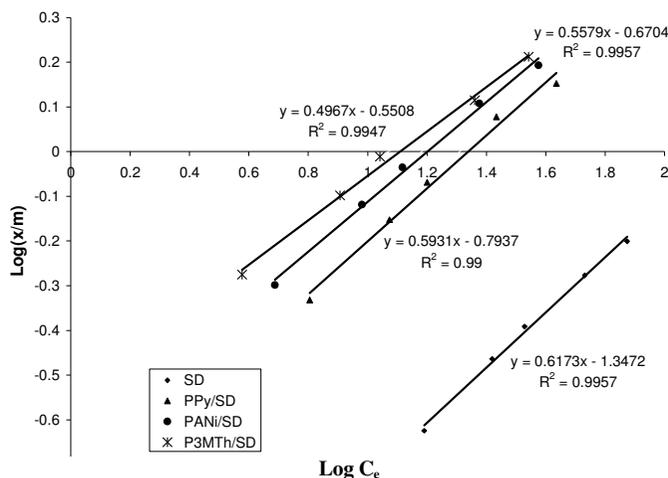


Figure 6. Freundlich isotherm SD, PPy/SD, PANi/SD and P3MTh/SD for sorption of As(III)

Table 2 Comparison of Freundlich and Langmuir constant values obtained for SD, PPy/SD, PANi/SD and P3MTh/SD

Sorbent	n	k	b	x_m
SD	1.62	0.04	0.02	1.07
PPy/SD	1.69	0.16	0.09	2.16
PANi/SD	1.79	0.21	0.13	2.08
P3MTh/SD	2.01	0.28	0.19	1.89

Effect of sorbent dosage

In this investigation, 25 mL of As(III) solution containing constant initial concentration of 100 ppm were treated with different amounts of sorbent (0.1 to 1.0 g) for one hour at room temperature accompanied by shaking. The effect of variation of sorbent dosage on the removal of As(III) is shown in Figure 7. As our results show, with increasing sorbent dosage a gradual increase in arsenic removal is occurred.

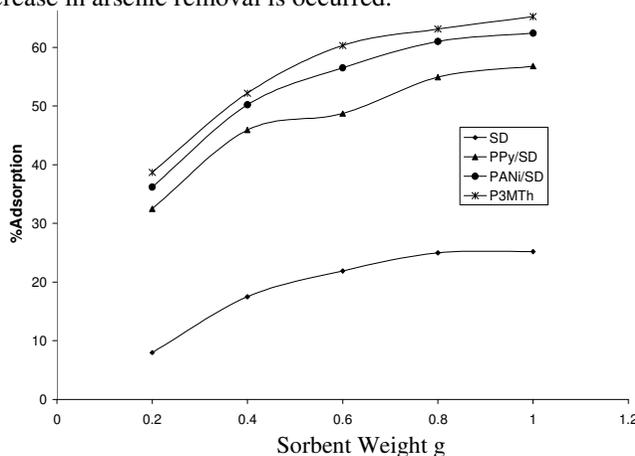


Figure 7. Effect of SD, PPy/SD, PANi/SD and P3MTh/SD dosage on the adsorption percentage of As(III). PH=11 and $C_0 = 100$ ppm

Effect of contact time

In order to carry out this experiment, 1.0 g of different selected sorbents were treated with constant volume of arsenic solution (25 mL) with the initial concentration of 100 ppm at room temperature accompanied by mild stirring using a mechanical shaker. The results obtained are shown in Figure 8.

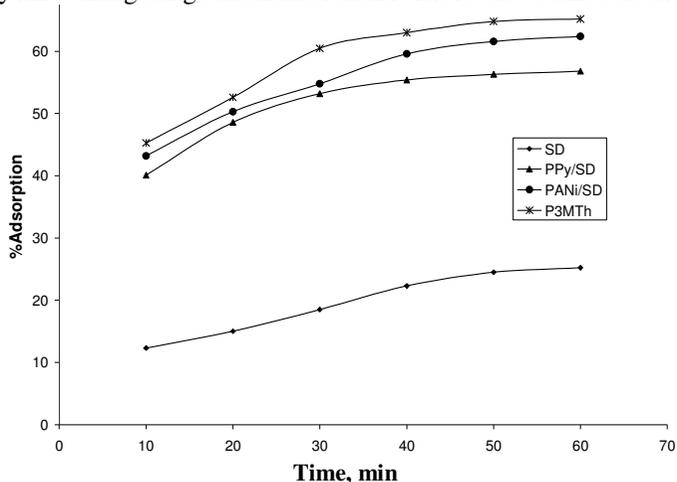


Figure 8. Effect of contact time on the adsorption of As(III). SD, PPy/SD, PANi/SD and P3MTh/SD.

As our data show (Figure 8), with increasing reaction or exposure time, a gradual increase in arsenic removal is occurred. Removal percentage of arsenic using P3MPTTh/SD is higher than other investigated polymers.

Breakthrough curves obtained for As(III) removal in 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. The breakthrough curves obtained for SD, PPy/SD and PANi/SD sorbents used for sorption of arsenic in a column systems are shown in Figure 9.

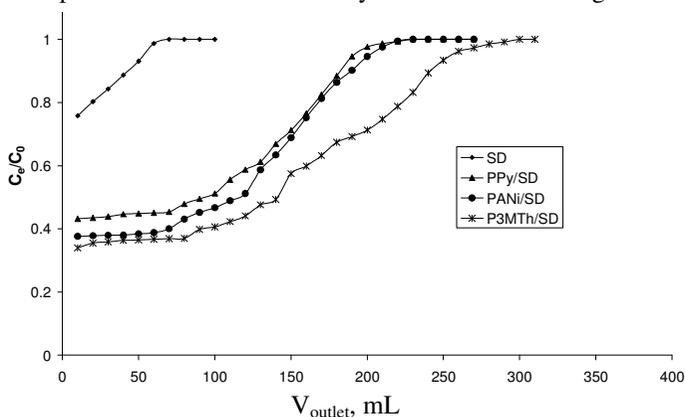


Figure 9. Breakthrough curves obtained for SD, PPy/SD, PANi/SD and P3MTh/SD

As our results show, poly 3-methylthiophene coated on sawdust seems better sorbent than other conducting polymers for removal of arsenic ions from aqueous solutions. However none of the investigated polymers are very efficient for uptake of As(III) ions. Higher uptake of As(III) observed in the case of P3MTh/SD might be due to the higher tendency of sulfur containing compounds for As(III) ions.

Conclusions

Polypyrrole and polyaniline conducting polymers are two classes of the most important conducting polymers that can be synthesized via simple chemical polymerisation as coated form on the surface of sawdust from aqueous solutions. Sawdust was also found to be a suitable substrate for coating of PPy and PANi conducting polymers. Its abundance, cheapness and environmentally friendly nature are the other advantages. Thiophene monomer is more expensive and has higher oxidation potential than pyrrole and aniline. Polythiophene conducting electroactive polymers should be prepared from non-aqueous solvents due to the insolubility of the monomer in water. In comparison to PPy and PANi, coating of sawdust by P3MTh, seems to be neither economical and nor very reproducible and uniform (by visual inspection). However, it was found that polythiophene based conducting polymers are better sorbent for removal of As(III) ions from aqueous solutions than other polymers investigated in this research. As(III) sorption using conducting electroactive polymers seems to be due to the ion exchange and also interactions between polymer matrix with the arsenic ion. Due to the dependence of the chemistry of arsenic species to pH, sorption percentage of arsenic is also a pH dependent process. Higher removal of As(III) was observed at alkaline pH values.

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