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Removal of Ce(IV) Ions from Aqueous Solutions Using Sawdust Coated by Electroactive Polymers

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In this work, adsorption of the Ce(IV) ions onto polypyrrole (PPy) and polyaniline (PAn) conducting electroactive polymers as coated form on sawdust has been investigated. The effect of some important parameters such as initial concentration of the Ce(IV) ion adsorbent dosage, and contact time was studied. The experiments were carried out using both batch and column systems at room temperature. The equilibrium adsorption capacity of sawdust coated by polypyrrole and polyaniline for the removal of Ce(IV) ion was measured and extrapolated using linear Freundlich and Langmuir isotherms. It was found that sawdust modified by PPy and PAn improved the removal efficiency of Ce(IV) ions from aqueous solutions greatly.

Keywords Ce(IV) ion; polyaniline; polypyrrole; removal; sawdust

INTRODUCTION

Cerium (Z = 58, AW = 140.12) is a lanthanide series rare-earth metals (elements in Row 6 of the periodic table) and is the most abundant of these rare earths (1). It presents at about 66 mgL^{-1} in the earth and ranks about number 26 in abundance among elements found in the earth's crust. Naturally occurring cerium (Ce) is composed of 4 stable isotopes: ^{136}Ce, ^{138}Ce, ^{140}Ce, and ^{142}Ce, with ^{140}Ce being the most abundant (88.48% natural abundance). The last of these isotopes is radioactive (2). Radioisotopes of cerium are a common constituent of liquid radioactive wastes arising from nuclear fission (U-235 nucleus) in power reactors (2). So, because of the radioactivity in the fission products, the separation of these byproducts from nuclear wastewaters before discharging them into the rivers is of great importance. Cerium can exist in either the free metal or oxide form, and can cycle between the cerous, Ce(III), ceric, Ce(IV), oxidation states (2). Although there are a lot of publications for the removal of heavy metal ions from aqueous solutions (3–13), but there are very limited reports for the removal of cerium ions from aqueous solutions (5,11,12).

Polypyrrole (PPy) and polyaniline (PAn) are two of the most well-known conducting electroactive polymers that have attracted a great deal of attention in the last two decades because of their high electrical conductivity, unique electroactivity, environmental stability, and ease of their synthesis from both aqueous and non-aqueous solutions (14–21). Chemical polymerization of conducting polymers is a simple route for bulk preparation and preparing of composites of conducting polymers with the conventional polymers. Polypyrrole (PPy) and polyaniline (PAn) conducting electroactive polymers can be readily synthesized from aqueous solutions using various chemical oxidants without a need for any special instruments. Ferric chloride and ammonium persulfate are two commonly used and most suitable chemical oxidants for chemical synthesis of PPy and PAn conducting polymers from aqueous media. The overall polymerization reaction of pyrrole and aniline based conducting electroactive polymers can be simply shown as in Figs. 1(a) and 1(b).

Where A$^-$ (termed as dopant or counterion) is the anion of the chemical oxidant incorporated during polymerization from solution in order to maintain charge balance in the polymer product. The resulting polymer is produced in the oxidized state with the incorporation of counterions and 0.25 to 0.33 cation centers per pyrrole unit (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. Doping of these polymers creates new bands in the energy gap, making it possible for the electrons to move to these new bands and increasing the conductivity of the materials.

Redox processes in conducting electroactive polymers, involves mass and resistance changes as well as electron transitions, and this makes these materials very different from other common redox systems in electrochemistry in which only electrons are involved during redox processes (19,22). Most of the previously published articles on conducting electroactive polymers relied on their interesting electrical and electrochemical properties (22–27).

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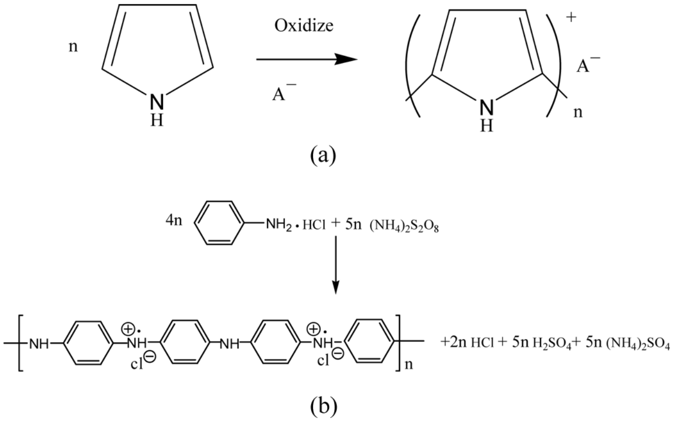

FIG. 1. The overall polymerization reaction of a) pyrrole and b) Aniline based conducting polymers.

Howevers, in this article we have taken advantage of the redox activity and chelating properties of these polymers for removal of Ce(IV) ion as we have recently reported the capability of these reactive and functional polymers for the uptake of some other heavy metal ions (silver, mercuric, and lead) from aqueous solutions (7,8). Since the chemical behaviors of different isotopes are similar and the difference in mass number does not affect the identity or chemical nature of the elements, so we used nonhazardous or nonradioactive salt of Ce(IV) ion in our investigation. Isotopes are in fact atoms of the same element that have different masses due to differences in the number of neutrons they contain and the chemistry of the atoms or ions is determined only by atomic number (number of protons) not mass number.

EXPERIMENTAL

Materials and Methods

The chemicals used were analytical grade and prepared in distilled water. Ce(IV) ion solution was prepared from $CeSO_4 \cdot 4H_2O$ (purity 99.99%). A solution of Ce(VI) ion with concentration of $100\,mg \cdot L^{-1}$ (100 ppm) was prepared in deionized water, used as stock solution. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ salt (AR grade) was used for the preparation of standard solution of Fe(II) ion for analysis of Ce(IV) ion. Pyrrole (C_4H_5N) and aniline (C_6H_7N) monomers were obtained from Merck and distilled, and stored in fridge before use. 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 the pH values. The pH adjustments were carried out using dilute NaOH and HCl solutions.

Sawdust was obtained from a local carpentry workshop washed with sufficient distilled water in order to remove any possible impurities, dried, and sieved (35–50 mesh size) before use.

Preparation of the Adsorbents (PPy/SD and PAn/SD)

Pyrrole and aniline monomers (Merck) were distilled before polymerization. Polymerization was carried out in aqueous solution. For preparing polymer coated onto sawdust (termed as SD), 5.0 g sawdust (35–50 mesh) immersed in 50 mL of 0.20 M of freshly distilled monomer solutions for 12 hours before polymerization. The excess of the monomer solution was removed by simple decantation. 0.50 M $FeCl_3$ and $(NH_4)_2S_2O_8$ were used as chemical oxidants for direct polymerization of PPy and PAn onto the sawdust (termed as PPy/SD and PAn/SD respectively). The oxidant solutions were added into the mixture gradually, and the reaction was allowed to continue for 4 hours at room temperature. The polymers coated sawdust was filtered, washed with sufficient distilled water, dried in an oven at 50°C, and sieved before use. A thin film of the conducting polymer grows at the surface as the polymerization proceeds. The coating percentage of PPy onto sawdust was calculated from the difference in mass of the sawdust before and after coating (3–4%).

Sorption Experiments

In batch experiment, a fixed amount of sorbents were treated with Ce(IV) solution ($10–100\,mg \cdot L^{-1}$) at room temperature. During each experiment, the solutions were agitated using a mechanical shaker (50 rpm). In column experiments a glass column with dimensions of 1.0 cm diameter and 15 cm height was employed. 1.0 g sorbents (SD, PPy/SD and PAn/SD) were packed in the column (bed volume $\sim 5\,cm^3$), and then the Ce(IV) solution ($10\,mg \cdot L^{-1}$) was passed through the column with a flow rate of $2\,mL\ min^{-1}$ at room temperature. The outlet solutions were analyzed for residual Ce(IV). In order to have uniform particles and reproducibility, the same particle size of the adsorbent (35–50) was used for both batch and column studies. It is well known that with decreasing particle size, the performance of adsorption is improved but it will result in flow resistance in the column.

All adsorption experiments were carried out at room temperature in 0.10 M H_2SO_4 ($pH = 0.6$) due to the high tendency of Ce(IV) ions to hydrolysis at pH above 2. The following equations were used to calculate the percentage of adsorption and the amount of adsorbed Ce(IV), respectively:

$$\%\ \mathrm{Re}moval = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (1)$$

$$\frac{X}{m} = \frac{(C_i - C_f)\,V}{m} \qquad (2)$$

Where, C_i and C_f are the initial and final concentrations of the Ce(IV), respectively ($mg\ L^{-1}$); X/m is the amount of

Ce(IV) adsorbed onto the unit amount of the adsorbent ($mg \cdot g^{-1}$) at equilibrium; and V is the volume of the solution used in the adsorption experiment (L). X/m ($mg \cdot g^{-1}$) can also be calculated using the following equations:

$$X/\mathrm{m} = \frac{m}{m_o} \tag{3}$$

$$\frac{X}{m} = \frac{R\% \times C_o \times V}{100\, m_o} \tag{4}$$

Where, m is the amount of adsorbed material by adsorbent (mg) and m_o is the weight of adsorbent (g), R% stands for removal percentage, C_o is the initial concentration of the adsorbate ($mg \cdot L^{-1}$) and V is the volume of the treated solution (L).

Analysis of Ce(IV) ion was carried out electrochemically (Biamperometric titration). Twin platinium microelectrodes were used to obtain end points for oxidation-reduction titration of Ce(IV) ion with Fe(II) in 0.10 M H_2SO_4 with applying a small potential (0.20 V). The end-point is marked by a sudden increase in the current from zero (28). Ce(IV) ion test solutions were prepared in H_2SO_4 solution with the pH value about 0.6.

RESULTS AND DISCUSSION

Effect of Initial Concentration

For performing this experiment 0.025 g of the selected adsorbents (SD, PPy/SD and PAn/SD) were treated with 50 mL of Ce(IV) solution with various initial concentrations (10–100 $mg\,L^{-1}$) for 40 min accompanied by mild shaking at room temperature. The results obtained from this investigation are summarized in Table 1. As our results show (Table 1), uncoated sawdust (SD) is an efficient adsorbent for the removal of Ce(IV) ions from aqueous solutions only at low initial concentrations. Removal of Ce(IV) ions by SD can be related to the redox reactions between Ce(IV) and SD due to the presence of different oxidizable surface functional groups present on the sawdust (e.g., lignin) and subsequent complex or chelating reactions between Ce(III) ions (reduced product of Ce^{4+}) and functional groups in SD (such as phenolic, methoxy, hydroxyl, carboxyl, and etc.) (29).

TABLE 1
Effect of initial concentration of Ce(IV) ion on adsorption percentage by the used adsorbents. Adsorbent dose = 0.025 g, Volume of test solution = 50.0 mL

	C_i ($mg \cdot L^{-1}$)				
Adsorbent	10	25	50	75	100
SD	98.0	97.0	66.0	52.0	40.0
PAn/SD	99.9	99.0	98.0	97.0	95.6
PPy/SD	99.9	99.9	99.0	98.0	96.4

TABLE 2
Effect of initial concentration of Ce(IV) ion on adsorption capacity (X/m) of the used adsorbents ($mg \cdot g^{-1}$)

	C_i (mgL^{-1})				
Adsorbent	10	25	50	75	100
SD	19.6	48.5	66.0	78.0	80.0
PAn/SD	20.0	49.0	98.0	145.5	191.0
PPy/SD	20.0	50.0	99.0	147.0	193.0

As our data in this investigation indicate, coating of sawdust by PPy or PAn polymers increased the removal efficiency of Ce(IV) ion considerably (Table 1). PPy/SD and PAn/SD adsorbents can be considered very effective in the removal of Ce(IV) ions especially at high initial concentrations of Ce(IV) ions. Sorption capacity of the used adsorbents toward Ce(IV) ions calculated from the data shown in Table 1 and the Eqs. (1–2), clearly indicate the superiority of PPy/SD or PAn/SD versus uncoated SD (Table 2). The data in Table 2 was derived from the data reported in Table 1 using Eq. (4).

Removal of Ce(IV) ion by PPy/SD or PAn/SD adsorbents is supposed to be mostly based on the strong interaction between the adsorbent and metal ions. Chemisorptions and complex reaction are possible mechanisms for the metal uptake. Due to the electroactive nature of PPy or PAn conducting electroactive polymers and Ce(IV) ion ($E^o = 1.44\,V$), the possibility of the redox reaction should also be considered. However, when the filtrate solution was analyzed for Ce^{3+} ion (reduced product of Ce^{4+}) using cyclic voltammetry technique (CV), no evidence for the presence of the Ce^{3+} ion in solution was found. So, it can be concluded that if redox reaction occurs; the Ce(III) ions are entrapped in the polymer matrices because of the reactive and chelating properties of PPy or PAn electroactive polymers.

Effect of Sorbent Dosage

In this investigation, 50 mL of Ce(IV) solution containing constant initial concentration of 100 $mg\,L^{-1}$ were treated with different amounts of sorbent (0.01 to 0.125 g) for a fixed period of time (40 min) at room temperature accompanied by mild shaking. The effect of variation of the sorbent dosage on the removal of Ce(IV) is shown in Fig. 2. As our results show (Fig. 2), both PPy/SD and PAn/SD are a much more efficient adsorbent for uptake of Ce(IV) ions than uncoated sawdust at whole sorbent dosages. It is very interesting to note that even 0.05 g of PPy/SD or PAn/SD adsorbent can completely decontaminate 50 mL of Ce(IV) solution with the initial

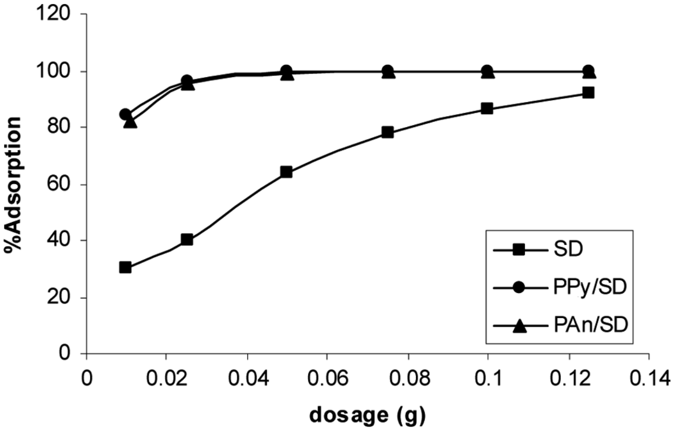

FIG. 2. Effect of dosage on the adsorption of Ce(IV) ion by SD and PAn/SD and PPy/SD. Initial pH: 0.6, agitation rate: 50 rpm, Ce(IV): 50 mL of 100 mg · L^{-1}.

concentration of 100 mg · L^{-1}. With increasing adsorbent dosage a gradual increase in Ce(IV) removal also occurs. Increasing of sorption percentage with sorbent dosage can be due to more availability of adsorption sites.

Effect of Contact Time

In this investigation 0.05 g of the selected adsorbents (SD, PPy/SD, and PAn/SD) were treated with 50 mL Ce(IV) ion solution with concentration of 50 mg.L^{-1}. The results obtained from the investigation of the effect of contact time on the removal of Ce(IV) ions by SD and PPy/SD and PAn/SD are shown in Fig. 3. As our results indicate (Fig. 3) both PPy/SD and PAn/SD are a much more efficient adsorbent for Ce (IV) ions and also require less residence time for the complete removal of Ce(IV) ions compared to the uncoated sawdust (SD). All the results obtained from the investigation of the effect of various parameters all implies the superiority of the removal performance of sawdust coated by PPy and PAn conducting polymers toward the Ce(IV) ion.

Treatment of Data Using Adsorption Isotherms

In order to model the sorption behavior, adsorption isotherms were studied at room temperature. Both the Langmuir and Freundlich equations were employed to plot the isotherms (14). Langmuir equation can be shown as $X/m = X_m bC_f/1 + bC_f$ and the linearized form is $m/X = 1/X_m + 1/X_m bC_f$), where X/m is the amount sorbed by adsorbent (mg/g), X_m is the maximum amount sorbed (1/intercept), C_f is the final concentration of Ce(IV) solution (mg · L^{-1}) and b (L · mg^{-1}), a Langmuir's constant signifying energy of sorption. The value of b is calculated from the linear equation of Langmuir's adsorption isotherm ($b = 1/\text{slope}.\ X_m$). Subsequently, Freundlich equation can be shown as: $X/m = KC_f^{1/n}$ and linearised form is $\log X/m = \log K + 1/n \log C_f$. Where, K (mg · g^{-1}) and 1/n are Freundlich's constants indicating adsorption capacity and intensity of adsorption, respectively.

The plot of m/X against $1/C_f$ gave straight lines for all the concentrations. High correlation coefficients obtained for SD, PAn/SD, and PPy/SD (0.9917, 0.9693, and 0.9666) implies that the adsorption is well fitted to the Langmuir isotherm (Fig. 4). The higher correlation coefficient indicates higher interactions between the adsorbent and Ce(IV) ions.

The Freundlich isotherm (linear forms) obtained for the three adsorbents employed in this research are shown in Fig. 5. From the correlation coefficient obtained for SD ($R^2 = 0.8589$) and PPy/SD ($R^2 = 0.891$), it could be

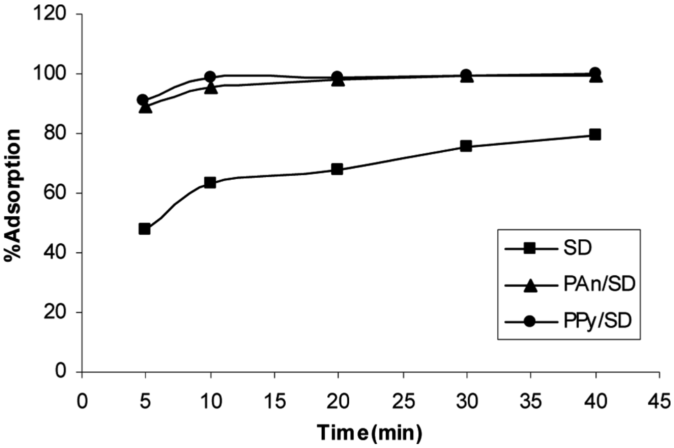

FIG. 3. Effect of contact time on the adsorption of Ce(IV) ion by SD, PAn/SD and PPy/SD. Initial pH = 0.6, agitation rate: 50 rpm, Ce(IV): 50 mL of 50.0 mg · L^{-1}, and sorbent dose: 0.050 g.

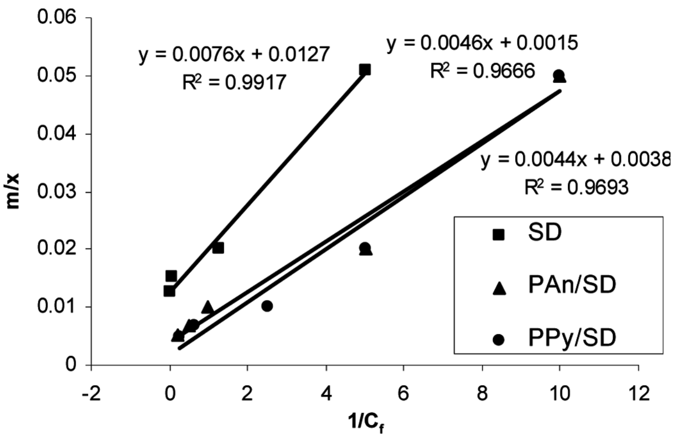

FIG. 4. Langmuir isotherms for adsorption of Ce(IV) ion by SD, PAn/SD and PPy/SD. Initial pH: 0.6, agitation rate: 50 rpm, and sorbent dosage: 0.0250 g.

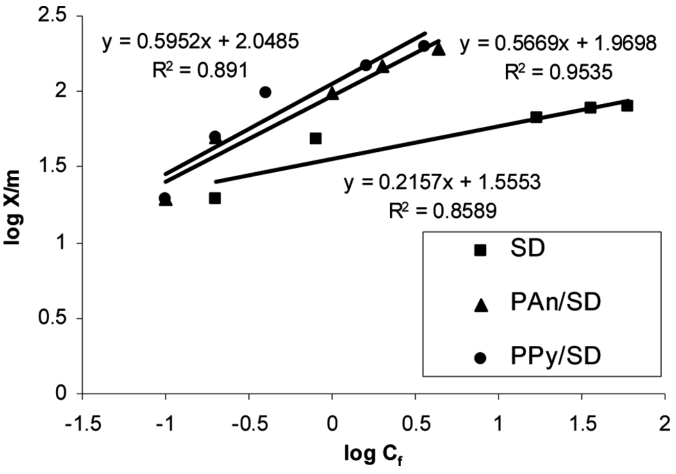

FIG. 5. Freundich adsorption isotherms for Ce(IV) ion by SD and PAn/SD and PPy/SD. Initial pH: 0.6, agitation rate: 50 rpm, and sorbent dosage: 0.0250 g.

concluded that the adsorption isotherm of Ce(IV) using these adsorbents does not fit to the Freundlich model well. The higher correlation coefficient obtained for PAn/SD ($R^2 = 0.9535$) implies that removal of Ce(IV) ion using PAn/SD fits better with Freundlich model compared to SD and PPy/SD.

On the basis of slopes and intercepts of the straight lines, Langmuir and Freundlich constants derived from these straight lines are presented in Table 3. The higher adsorption capacity (X_m) obtained for PPy/SD ($667\,\mathrm{mg \cdot g^{-1}}$) using the Langmuir model, indicate a higher sorption capacity and high performance of PPy/SD adsorbent for the removal of Ce(IV) ions from aqueous solution compared to untreated sawdust (SD) and PAn/SD.

The higher value for K also indicates the higher affinity of PPy/SD for Ce(IV) ion (Table 3). Freundlich's constant n calculated for the three adsorbents indicates the degree of favorability of adsorption. For a favorable adsorption the value of n should be in the range of 1 to 10 (30,31). The intensity of adsorption is in fact indicative of the bond energies between the metal ion and the adsorbent and the possibility of chemisorptions rather than physisorption.

TABLE 3
Freundlich and Langmuir constant values obtained for the used adsorbents

Adsorbent	n	K ($\mathrm{mg \cdot g^{-1}}$)	b ($\mathrm{L \cdot mg^{-1}}$)	X_m ($\mathrm{mg \cdot g^{-1}}$)
79	4.6	36	1.7	SD
263	1.8	93	0.86	PAn/SD
PPy/SD	1.7	112	0.33	667

Breakthrough Curves Analysis of Ce(IV) Ion Using SD, PPy/SD and PAn/SD

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. In order to plot this analysis, packed glass columns are configured to study the removal of Ce(IV) ions by 1.0 g of PPy/SD, PAn/SD, and SD adsorbents (as described in Section titled "Sorption Experiments" 2.3). The inlet Ce(IV) solution was $10\,\mathrm{mg \cdot L^{-1}}$. The results are shown in Fig. 6.

As is illustrated (Fig. 6), the adsorption curves obtained for the removal of Ce(IV) ions, using a column system employing the three adsorbents (SD, Pan/SD, and PPy/SD) are different. The breakthrough point of the SD curve appears much earlier than PAn/SD and PPy/SD, and the slope of the SD curve is steeper than PAn/SD and PPy/SD curves. On the other hand the PPy/SD adsorbent seems to be a much more effective sorbent compared to SD and an even better sorbent than PAn/SD for the removal of Ce (IV) ion in column systems (the same as observed in batch system). As it has been indicated (Fig. 6) each gram of SD, PAn/SD, and PPy/SD can completely clarify 300, 500, and 600 mL Ce(IV) ion polluted solution ($10.0\,\mathrm{mg \cdot L^{-1}}$) under the specified experimental conditions respectively.

As our breakthrough curves (Fig. 6) show, the breakthrough point and saturation of the SD bed occurred sooner than PPy/SD and PAn/SD. The breakthrough point ($C/C_o = 0.05$) happened after passing about 700 mL of Ce(IV) ion solution for PPy/SD. Complete exhaustion of the column containing 1.0 g of PPy/SD or PAn/SD occurred after the passage of about 1800 mL of Ce(IV) solution, which implies the high potential of the introduced adsorbents (PPy/SD or PAn/SD) for the removal of

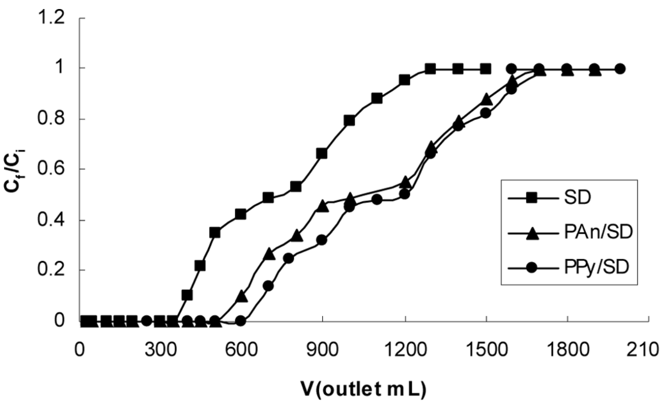

FIG. 6. Breakthrough curve obtained for removal of Ce(IV) ion using SD and PAn/SD and PPy/SD. Initial pH: 0.6, Flow rate: $2\,\mathrm{mL\ min^{-1}}$, and Ce(IV): $10\,\mathrm{mg \cdot L^{-1}}$.

Ce(IV) ions from aqueous wastes using both batch or column systems. No remarkable decrease of capacity was observed within 3 consequent runs (less than 10%) for the coated sawdust by the polymers. However, it is clear that exhaustion time or volume will be increased with increasing bed height or the sorbent dose as more binding sites are available for sorption.

CONCLUSIONS

It was found that the coating of sawdust (a very inexpensive biomaterial waste) by polypyrrole or polyaniline electroactive polymers can be used to remove Ce(IV) ions from aqueous solutions with high efficiency. As we have indicated in this article, each 25 mg of PPy/SD or PAn/SD can remove more than 96% of Ce (IV) from 100 mL of $50\,\mathrm{mg \cdot L^{-1}}$ of this solution. The adsorption of Ce(IV) ions is highly dependent on the amount of adsorbent, contact time, and initial metal concentration. The high values of adsorption capacity ($K = 112\,\mathrm{mg \cdot g^{-1}}$) and sorption capacity ($X_m = 667\,\mathrm{mg \cdot g^{-1}}$) calculated from the Freundlich and Langmuir adsorption equations for Ce(IV) ion imply that PPy/SD is an excellent adsorbent for the removal of Ce(IV) ions from aqueous solutions.

From the treatment of the data using Freundlich and Langmuir adsorption isotherms, it was found that sorption of Ce(IV) ions by PPy/SD fits better using the Freundlich adsorption equation. The breakthrough curve analysis also confirms the usability of the employed adsorbents, especially PPy/SD for the removal of Ce(IV) ions in continuous or column systems. Due to the chemical reactivity and electroactivity of the adsorbate and adsorbents, the elimination of Ce(IV) ions by the polymeric adsorbents used in this investigation is supposed to occur mostly via redox and subsequent complex and chemisorptions of the metal ions with the polymer matrix. The currently introduced adsorbents can be considered as a very efficient and cost-effective adsorbent for the removal of Ce(IV) ion from industrial wastewaters such as nuclear power plants.

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