Adsorption of ^{60}Co and $^{154+152}\text{Eu}$ using graft copolymer of starch-polyacrylic acid-polyvinylsulfonic acid

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Research Article

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Abstract

Graft copolymer of starch-polyacrylic acid-polyvinylsulfonic acid (St-g-PAA-PVSA) was synthesized by gamma radiation as an initiator. The chemical structure, morphology, and thermal stability of the graft copolymer were investigated using FTIR, SEM, and TGA. St-g-PAA-PVSA graft copolymer was employed as an adsorbent for the removal of cobalt(II) and europium(III) radionuclides from their aqueous solutions by batch adsorption method. Several experimental factors such as pH, contact time, initial concentration of adsorbate, and temperature were used to find the best conditions for the removal of cobalt(II) and europium(III) radionuclides. The pseudo-second order kinetic model better fit the adsorption kinetic data of radionuclides. Langmuir models had the ability to well describe the equilibrium data of adsorption of radionuclides. Thermodynamic parameters were calculated and suggested the adsorption process was endothermic and spontaneous in nature. Among the examined desorbing agents, both AlCl_3 and HCl were succeeded to desorb most of radionuclides.

Introduction

Recently, many papers have shown an increasing interest in modifying the renewable source-based biodegradable polymers as a substitution of conventional synthetic materials because they are non-toxic, biodegradable, cheap, and easy to develop [1, 2]. Starch (St) is a polysaccharides polymer and has advantages above other biodegradable polymers such as its low cost, wide using and total composability without toxic remains. Because of the drawbacks of starch such as lowly process capacity and poor long-standing stability, high sensitivity to water, and weak mechanical properties [3–6]. Many study attempts had been utilized both in industrial and academic organizations to solve these problems through chemical modification or cross-linking starch. Also, modification of starch was tested with various synthetic monomers, e.g., acrylamide, methacrylamide, acrylic acid, vinyl imidazole, acrylonitrile, vinyl alcohol, styrene [6–8].

Polyacrylic acid (PAA) is a high-absorbency polymer that can absorb and retain water while swelling to many times its original volume. It has been employed in water treatment as a result of this unique property [5, 7, 9–11]. Polyvinylsulfonic acid (PVSA) (as sodium salt) is a polyelectrolyte with negatively charged sulfonate groups. Vinylsulfonic acid (VSA) is a monomer used to make extremely acidic and anionic homopolymers and copolymers. These polymers are employed as photoresists and ion-conductive polymer electrolyte membranes for fuel cells in the industry. Polyvinylsulfonic acid, for example, can be used to make translucent membranes with high ion exchange capacity and proton conductivity [5, 7, 9–13].

The applications of radioactive materials in many industrial studies are a widespread and rapid increase such as industrial radiography, nuclear medicine, agriculture, and oil processing, and academic study. Therefore, radioactive waste management becomes a worldwide problem. ^{60}Co and $^{152+154}\text{Eu}$ are among the most dangerous radionuclides. These isotopes emit γ -rays of high energies and have long half-lives. They may cause dangerous human disorders. As a result, removing such nuclides from radioactive wastewater is critical. Various technologies are existing to remove the radionuclides such as ion exchange, chemical precipitation, flocculation, coagulation, and reverse osmosis. Unfortunately, these technologies' generality is expensive and/or environmentally unfriendly. Adsorption has been popular as a method for eliminating radionuclides because of its many benefits, including high efficiency, environmental friendliness, and low cost [10, 14–17]. The goal of this research is to develop and test a low-cost starch-grafted poly(acrylic acid-vinylsulfonic acid) (St-g-PAA-PVSA) graft copolymer for removing Co(II) and Eu(III) from radioactive waste under various experimental settings. The physical and chemical characterisation of the St-g-PAA-PVSA can aid in determining the sorption mechanism as well as provide information on heat stability.

Experimental

Materials

Starch was obtained from Nice Chemical Pvt. Ltd. (India). Cobalt Chloride, Europium(III) Oxide, N, N'-Methylenebisacrylamide (NMBA), and Acrylic acid (AA), were purchased from Merck (Germany). Vinyl sulfonic acid sodium salt solution monomer (VSA) was purchased from Aldrich. Methanol was obtained from ADWIC, Egypt. Bi-distilled water was used in all experiments, for preparation, dilution, and analytical purposes. All chemicals and reagents were of the highest purity grade.

Synthesis of St-g-PAA-PVSA graft copolymer.

St-g-PAA-PVSA graft copolymer was synthesized by dispersing 2.50 g of starch in 40 mL deionized water and heated at 80°C in a water bath until a homogeneous solution was obtained. Then, 8.75 g of AA, 3.75 g of VSA monomers, and 0.25 g of NMBA were added to the suspension via stirring and the mixture was completed to 60 mL and sonicated for 30 min. The mixture was subjected to gamma-irradiation at room temperature with a dose of 20 KGy using a ^{60}Co γ -ray field (Cobalt - 60 gamma cell of type MC -20, Cyclotron Project, Inshas, Egypt). The sample was then cut into small pieces and washed in a water-methanol solution. The grafted material was separated, filtered, and dried at 75°C overnight to a constant weight.

Characterization

The structural features of the produced graft copolymer were released by Fourier transform infrared analysis (FT-IR). The FT-IR spectrum was recorded in the midinfrared range ($4000\text{--}400\text{ cm}^{-1}$) using a Shimadzu infrared spectrometer (BOMEM, FT-IR, Japan) by KBr disc method. The morphological structure was obtained by scanning electron microscope (SEM) (JEOL -JSM 6510 LA, Japan) at high magnification and resolution. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed at a heating rate of $20^\circ\text{C}/\text{min}$ using a Shimadzu DTG-60 thermal analyzer, Japan.

Adsorption studies of radioactive isotopes

The adsorption behavior of Co(II) and Eu(III) toward the St-g-PAA-PVSA graft copolymer was investigated using the batch technique. 0.01 g of graft copolymer was equilibrated individually with 5 mL of the solution containing definite volumes of $^{60}\text{Co}(\text{II})$ or $^{152+154}\text{Eu}(\text{III})$ stock solution, individually, by mechanical shaking at $25 \pm 1^\circ\text{C}$ for 24 h. Aliquots of the solution before and after the equilibration were taken, and the radioactivity was assayed radiometrically by a single-channel analyzer (Spetech ST 360 to crystal, USA). Removal percentage of radionuclides was calculated using the equation[16]:

$$R = \frac{C_o - C_e}{C_o} \times 100$$

The removal capacity (q) (mg/g) was obtained from:

$$q = \frac{C_o - C_e}{m} \times V$$

where C_o and C_e (mg/L) are the beginning and final radionuclides concentration, V is the volume of the radionuclide solution (L), and m is the adsorbent mass (g).

Desorption experiments

Desorption investigations were carried out in order to recover and reuse adsorbent in a variety of adsorption processes. 0.05 g of St-g-PAA-PVSA graft copolymer was contacted with 5 mL of 250 mg/L of cobalt(II) and europium(III) ion, spiked with ^{60}Co and $^{152+154}\text{Eu}$ at pH ~ 5 and ~ 4 , respectively, for 24 h. The cobalt(II)-loaded St-g-PAA-PVSA graft copolymer and europium(III) loaded St-g-PAA-PVSA graft copolymer were separated by centrifugation and dispersed into 5 mL of the desorbing agent (0.001–0.1 M of HCl, NaCl, MgCl_2 , and AlCl_3) and aged under shaking at 120 rpm for 24 h. After centrifugation and measuring the radioactivity of cobalt(II) and europium(III) radionuclides in the supernatant, the desorption percentage of the concerned radionuclide was calculated using the following equation.

$$\% \text{Desorption} = \frac{\text{Amount of adsorbate desorbed}}{\text{Amount of adsorbate absorbed}} \times 100$$

Results And Discussion

Synthesis of St-g-PAA-PVSA adsorbent

The St-g-PAA-PVSA graft copolymer was prepared by gamma radiation for initiating the graft copolymerization of AA/VSA onto starch in the presence of NMBA as crosslinker. Figure 1 shows a schematic diagram for the synthesis processes as well as a suggested structure.

Structural analysis

FT-IR

FT-IR spectrum of starch and St-g-PAA-PVSA graft copolymer is shown in Fig. 2. A weak absorption band at 1368 cm^{-1} is the characteristic absorbance band of $-\text{C}-\text{OH}$, $\text{O}-\text{C}-\text{H}$ and $\text{C}-\text{C}-\text{H}$ on the starch chain, the peak at 1645 and 1634 cm^{-1} is ascribed to the $\delta(\text{OH})$ bending of tightly bound water present in starch and St-g-PAA-PVSA graft copolymer, respectively. The peak at 1459 cm^{-1} indicates symmetric stretching of $-\text{COO}-$ group and the band at 1634 cm^{-1} indicates asymmetric stretching of $-\text{COO}-$ group of AA. The absorption band at 1740 cm^{-1} , $2853\text{--}2924\text{ cm}^{-1}$, and the strong and wideband at 3443 cm^{-1} are assigned to the asymmetric stretching vibration of COOH group, $-\text{C}-\text{H}$, $-\text{OH}$, and $-\text{COOH}$ group, respectively of starch, and AA, overlap each other. The absorption band at 1403 cm^{-1} which is due to $-\text{SO}_3$ and $\text{S}=\text{O}$ vibration is typical of stretching vibration[10].

SEM

Figure 3 shows SEM images of St and St-g-PAA-PVSA graft copolymer. St micrographs show spherical or oval granules with smooth surfaces free of scratches or cracks. The SEM micrographs of starch-g-AA-VSA graft copolymer contains irregular morphology with different size granules and appeared as a porous surface with interconnected pores. This irregular morphology is caused by exposure to heat during the produce of the graft copolymer. Rough surfaces of the graft copolymer lead to enhancement of its surface area and increase the interaction between the adsorbent and the radionuclides and decrease the diffusion limitations in radionuclides adsorption[10].

TGA

Figure 4 shows the TGA and TDA of St and St-g-PAA-PVSA graft copolymer. St shows three-step thermal degradation. The first step occurs in the temperature range 81–172°C with 11.82% weight loss due to dehydration and pyrolytic volatilization processes. The second and third stages are consecutive overlapping steps that occurred in the temperature range 275–490°C with 72.53% weight loss. This is attributed to loss by depolymerization and oxidation of the organic matter. St-g-PAA-PVSA graft copolymer shows the fifth decomposition stage, the first stage continued up to the temperature of 200°C and count for about 7.15% weight loss. This corresponds to a loss of moisture. The second stage of degradation was observed from 200 to 290°C with weight loss of about 14.13%. It is mostly contributed to the decomposition of starch. In the third stage, the decomposition is characterized by a weight loss of 16.97% due to the chain scission of the PAA and PVSA molecules, which has a maximum temperature of 385°C. The fourth and fifth stages occurs with the temperature range 385–470°C with 21.7% weight loss due to the breaking up of covalent bonds. DTA curves released the TGA results; starch exhibited endothermic peaks at 142.38 °C and exothermic at 300.92. However, St-g-PAA-PVSA showed endothermic decomposition at 156.90, 212.35, 313.50, 441.08, 525.12, and 567.05°C, and exotherm peaks at 247.84, 405.70, 546.69, and 581.87 °C. TGA-DTA studies revealed that the decomposition temperature of the graft copolymer was higher than that of native starch[5, 6, 8, 10].

Batch adsorption optimization

Effect of pH

Figure 5 shows how the pH values influence the adsorption of Co(II) and Eu(III) radionuclides on the St-g-PAA-PVSA graft copolymer. The adsorption capacity for both cations is very low at low pH values then increases with an increase in the pH values, clearly owing to the nature of the functional groups in the St-g-PAA-PVSA graft copolymer. At low pH, the surface charge of the graft copolymer will become positive and competition between H^+ and Co(II) or Eu(III) ions for occupancy of the active sites was increased. Whereas at higher pH values the surface charge of the graft copolymer becomes negative, increasing radionuclides adsorption. The adsorption capacity of Eu (III) is higher than that of Co(II), this may be attributed to the adsorption capacity values are proportional to the ionic potential, i.e., Z/r of ions; along with other factors, especially in the case of Eu(III) (as an f-block element) whose coordination bonds are predominantly electrostatic. Consequently, it can be expected that the adsorption capacity of Eu^{3+} should be higher than that of Co^{2+} [16–18].

Adsorption kinetics

Figure 6 shows the influence of the contact time on the adsorption of Co(II) and Eu(III) radionuclides. The results showed that adsorption has occurred rapidly. Then the adsorption nearly remains at a constant with increasing time, the adsorption was appeared to proceed rapidly when the numbers of available sites are larger than the number of adsorbed radionuclides. Lagergren's pseudo-first-order, pseudo-second-order, and Intraparticle diffusion models were applied to examine the adsorption kinetic behavior of Co(II) and Eu(III) radionuclides. The linearized equations of the models can be expressed as in Table 1[10, 13, 16].

The data given in the Table 2 indicated the experimental kinetic data of adsorption of Co(II) and Eu(III) radionuclides were closer and have high correlation coefficient (R^2) to those calculated from the pseudo-second-order model. The chemisorption of Co(II) and Eu(III) is assumed in these studies.

Table 1
The linearized equations of the used models

Models	Equations	Parameters
Lagergren's pseudo first-order model	$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$	q_e (mg/g) is the amount of absorbed radionuclides at equilibrium, q_t (mg/g) is the amount of absorbed radionuclides at t , t is the time, and k_1 is the Lagergren's rate constant (min^{-1}). k_1 is determined from the slope of the plots of $\log(q_e - q_t)$ versus t
Lagergren's Pseudo-second-order model	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	q_e and q_t is mentioned previously. K_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second order rate constant. K_2 were calculated from the slope and intercept of the plot t/q_t versus t
Intraparticle diffusion	$q_t = k_i t^{0.5} + C_i$	C_i is the boundary-layer thickness and K_i ($\text{mg g}^{-1} \text{min}^{0.5}$) is the intra-particle diffusion rate constant. K_i and C_i were calculated from the slope and intercept of the plot q_t versus $t^{0.5}$
Langmuir isotherm model	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	C_e is the radionuclides concentration at equilibrium in solution (mg/L), q_m is the maximum capacity of monolayer coverage (mg/g), and K_L is Langmuir constant (L/g). q_m and K_c values are calculated from the slope and the intercept of the linear plot of C_e/q_e against C_e .
Freundlich isotherm model	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	n represents a constant of the adsorption intensity. K_f and n are the Freundlich constants and counted from the intercept and the slope of the linear plot.
Temkin model	$q_e = \frac{RT}{b_T} \ln k_T + \frac{RT}{b_T} \ln C_e$	K_T is equilibrium binding constant (L g^{-1}), b is related to heat of adsorption (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), and T is the absolute temperature (K). K_T and b_T are calculated from the slope and intercept of the q_e versus $\ln C_e$ plot.
Dubinin–Radushkevich model	$\log q_e = \ln x_m + \frac{1}{n} \beta \epsilon^2$	X_m is the theoretical saturation capacity (mg g^{-1}), β is a constant related to mean free energy of adsorption per mole of the adsorbate (mol^2/kJ^2), and ϵ is the Polanyi potential which is related to equilibrium
Thermodynamic study	$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$ $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$	Changes in enthalpy (ΔH , kJ mol^{-1}) and entropy (ΔS , kJ mol^{-1}) were calculated from the slop and intercept of the Van't Hoff plot.

Table 2
Adsorption kinetic parameters

Parameters	Pseudo-First-Order			Pseudo-Seond-Order			Intraparticle diffusion model			Exp.
	k_1	q_e	R^2	k_2	q_e	R^2	K	C_i	R^2	
	(min^{-1})	(mg/g)		($\text{g mg}^{-1} \text{min}^{-1}$)	(mg/g)		($\text{mg g}^{-1} \text{min}^{0.5}$)	(mg/g)		
^{60}Co	2.44E-03	18.580	0.270	4.50E-04	95.147	0.998	0.338	-10.429	0.467	93.422
$^{152+154}\text{Eu}$	3.02E-03	62.400	0.881	8.75E-05	132.275	0.952	2.894	38.629	0.528	123.587

Adsorption isotherms

The adsorption isotherm is helping in understanding the interaction between the graft copolymer and the radionuclides in the adsorption process. Figure 7 shows that the adsorption capacity of ^{60}Co and $^{152+154}\text{Eu}$ radionuclides increases by increasing the initial concentration of radionuclides. It is maybe a result of an increase of driving force for mass transfer at high initial concentration.

In this study, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models were investigated to analysis of the equilibrium data of sorption of Co(II) and Eu(III) radionuclides onto St-g-PAA-PVSA graft copolymer. The linear equations are given in Table 1[10, 11, 16]. The parameters of the studied isotherm models were summarized and are listed in Table 3. The high correlation coefficient (R^2) value indicated that the experimental data for the adsorption of $^{152+154}\text{Eu}$, and ^{60}Co radionuclides by St-g-PAA-PVSA graft copolymer follow the Langmuir model better than other models. According to the Langmuir model, adsorption happens by monolayer adsorption onto a homogenous surface.

Table 3
Adsorption isotherm parameters

Parameters	Langmuir Isotherm:			Frundlich Isotherm:			Dubinin- Radushkevich Isotherm:			Temkin Istherm		Exp.
	$q_{\max}$ (mg/g)	K_L (L/g)	R^2	$1/n$	k_f	R^2	E (kJ/mol)	B (mol ² /kJ ²)	$q_{\max}$ (mg/g)	$\ln K_T$ (L/g)	bt kJ/mole	$q_{\max}$ (mg/g)
⁶⁰ Co	105.374	0.175	0.999	0.238	28.493	0.853	6.72E + 02	1.11E-06	35.303	1.802	174.710	103.980
¹⁵²⁺¹⁵⁴ Eu	206.185	9.00E-02	0.993	0.4759	22.050	0.700	7.71E + 02	8.41E-07	0.54104	1.559	0.094	198.770

Thermodynamic studies

The effect of temperature on the adsorption of cobalt and europium onto St-g-PAA-PVSA graft copolymer was determined by varying the temperature between 20 and 70°C. Figure 8 shows that the capacities slightly increase with the increasing temperature this may be attributed to decreases the viscosity of the solution and correspondingly increases the diffusion rate of the radionuclides within the pores of the graft copolymer by increasing temperature.

Thermodynamic parameters are given in Table 1[19, 20, 20, 21] and the values of ΔH° , ΔS° , and ΔG° are given in Table 4. The positive value of ΔH° indicated that the adsorption was endothermic. The positive value of ΔS° for Co(II) radionuclides indicated that the randomness is increased at the solid–solute interface, while the negative value of ΔS° for Eu(III) radionuclides assumed is the arrangement of Eu(III) radionuclides is shaped more ordered onto the surface of the graft copolymer after adsorption. The negative value of ΔG° indicated the feasibility of the reaction and spontaneous nature of the adsorption at a given temperature.

Table 4
Thermodynamics adsorption data

Radionuclides	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (KJ/mol.K)
⁶⁰ Co	303	-0.0091	1.24718E-05	3.01816E-05
	313	-0.0094		
	323	-0.0097		
	333	-0.001		
¹⁵²⁺¹⁵⁴ Eu	303	-9.788	-30.928	-0.0698
	313	-9.089		
	323	-8.392		
	333	-7.693		
	343	-6.996		

Desorption study- batch method

Figure 9 illustrates the influence of desorbing agent concentrations (0.001–0.1 M of HCl, NaCl, MgCl₂ and AlCl₃) on the desorption percentage of cobalt(II) and europium(III). the data in the figure show that the desorbing agent concentration played a significant role in the desorption of cobalt(II) and europium(III). Increasing the desorbing agent concentration, concentration resulted in an increase in the desorption percentage of cobalt(II) and europium(III) radionuclides. The maximum desorption percentage of cobalt(II) ions about 59.60 and 54.72% is achieved by AlCl₃ and HCl, respectively, at concentrations ≥ 0.1 M. while The maximum desorption percentage of europium(III) ions about 63.72 and 63.05% is achieved by AlCl₃ and HCl, respectively, at concentrations ≥ 0.1 M. This desorption results proposed that the radionuclides are adsorbed onto the active sites of the graft copolymer. While the fraction remained onto the adsorbent, 45 – 40% of adsorbate could not be desorbed, clarified that insignificant amount of radionuclides are adsorbed onto the internal adsorption sites[22, 23].

Conclusion

St-g-PAA-PVSA graft copolymer was successfully synthesized and its chemical structure, morphology and thermal stability were investigated by FTIR, SEM, and TGA. St-g-PAA-PVSA graft copolymer was applied as an adsorbent for cobalt(II) and europium(III) radionuclides from their aqueous solutions. Modeling of the kinetic data showed that the pseudo-second-order model was the best one for describing the present adsorption process. Langmuir isotherm models had the ability to represent the equilibrium isotherms data. Thermodynamic parameters deduced that cobalt(II) and europium(III) radionuclides were endothermic and spontaneous in nature. At concentrations of 0.1 M, AlCl_3 and HCl obtain a maximum desorption percentage of cobalt(II) ions of about 59.60 and 54.72%, respectively, whereas AlCl_3 and HCl achieve a maximum desorption percentage of europium(III) ions of about 63.72 and 63.05%, respectively.

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Figures

Figure 1

Schematic diagram of St-g-PAA-PVSA graft copolymer

Figure 2

FTIR spectra of starch and St-g-PAA-PVSA graft copolymer

St

St-g-PAA-PVSA graft copolymer

Figure 3

SEM images of starch and St-g-PAA-PVSA graft copolymer

Figure 4

TGA curves of starch and St-g-PAA-PVSA graft copolymer

Figure 5

Effect of pH on the adsorption capacity

Figure 6

Effect of contact time on the adsorption capacity

Figure 7

Effect of initial radionuclides concentration on the adsorption capacity

Figure 8

Effect of temperature on the adsorption capacity

Figure 9

Desorption of cobalt(II) and europium(III) radionuclides loaded onto St-g-PAA-PVSA graft copolymer using various desorbing agents