



## THE REMOVAL OF $^{210}\text{Po}$ AND $^{210}\text{Pb}$ FROM AQUEOUS SOLUTION USING SULPHONATED POLYSTYRENE WASTE

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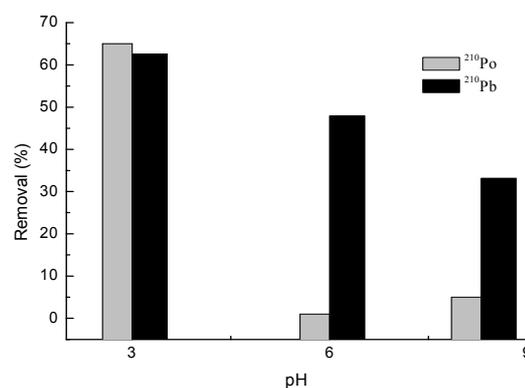
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Received October 31, 2018

Functionalized polymers are effective adsorbents for removing various radionuclide contaminants. In this study, sulphonated polystyrene waste particles were used to investigate the removal of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  from contaminated solutions. The adsorption kinetics well fitted using a pseudo second-order kinetic model. The intraparticle diffusion model described that the intraparticle diffusion did not occur. The adsorption isotherm data could be well described by the Freundlich equation. These results suggest that functionalized polymer wastes could be utilized as an efficient adsorbent for the removal of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  from contaminated waters sources or to separate them from each other at neutral and base solutions.



### INTRODUCTION

Heavy metals and radionuclides pollutions have become one of the most environmental and health problems, due to the rapid development of various industries producing large quantities of wastes containing heavy metals and radionuclides especially naturally occurring radionuclides that are directly or indirectly discharged into the aquatic environment.<sup>1-2</sup> Many possibilities to reduce their emissions to environment or remove them from the environment have been studied.<sup>3</sup> Conventional methods for removing metal ions from aqueous solutions include chemical precipitation, electrochemical treatment, membrane technologies and adsorption on activated carbon.<sup>4</sup> These methods do not seem to be effective in many cases. In addition, large quantities of sludge, which require treatment and disposal, are generated.

Ion exchange, membrane technologies and activated carbon adsorption processes are extremely expensive for treating large quantities of water and wastewater containing heavy metal in low concentration.<sup>2</sup>

Polonium-210 (half-life = 138.4 days) is directly produced during the radioactive decay of its parent radionuclide,  $^{210}\text{Pb}$ ; which is, in turn, a member of  $^{238}\text{U}$  decay series.  $^{210}\text{Po}$  is found at elevated concentrations in association with  $^{226}\text{Ra}$  sources, but it is often detected at some distance from sites of release due to the extreme mobility of the noble radon gas,  $^{222}\text{Rn}$  (half life = 3.8 days). The rapid decay of  $^{222}\text{Rn}$  in the atmosphere generates  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ , which are rapidly adsorbed by aerosols and returned to earth surface.<sup>5-6</sup> In addition  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are found in the presence of uranium-bearing ores such as in phosphate and uranium mines and it also occurs in other minerals such as shale, coal and

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industries products and wastes such as phosphate and the oil and gas industry.<sup>7-9</sup>

Global world production of plastics rose in the last decades from 204 M tone in 2002 to 288 M tone in 2012.<sup>10</sup> Polystyrene (PS) is one of the most six common types of plastics, and forms 7.3% of this production.<sup>11</sup> Polymer waste generally can be modified/ treated using different ways depending on the chemical structure of the backbone chain to obtain valuable raw materials, which would account for several applications.<sup>12-18</sup>

Functionalizing of the benzene ring in PS supports the formation of new polymer derivatives having different behaviour and applications.<sup>15</sup> The sulphonate group is one of these functional groups, and the sulphonation reaction has been studied by many researchers.<sup>19-25</sup>

The present work reports on the use of sulphonated expanded polystyrene waste for

removing <sup>210</sup>Po and <sup>210</sup>Pb from contaminated waters.

## RESULTS AND DISCUSSION

### 1. Chemical characteristics of the polymer

Expanded polystyrene waste has been sulphonated using commercial sulphuric acid, and the yield of the sulphonation reaction have been reported previously with regards to different parameters.<sup>25</sup> Figure (1) shows the DSC thermogram of the used PS waste; the glass transition temperature (T<sub>g</sub>) was determined from the second DSC run. The T<sub>g</sub> of the used PS waste is equal to 103.2 °C. The endothermic process appeared in the first run corresponds to the decomposition of the polymer, and the onset point is 391.2 °C.

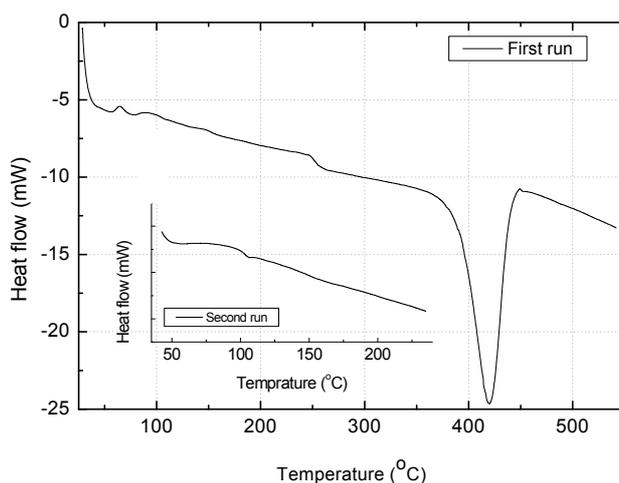


Fig. 1 – DSC thermogram of the used PS waste.

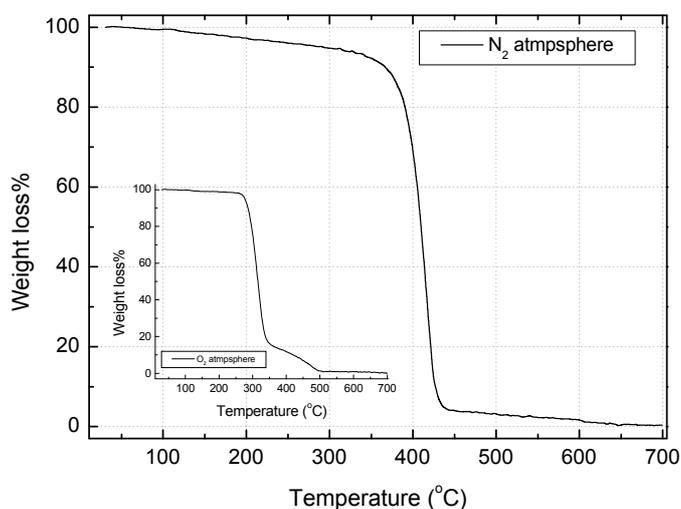


Fig. 2 – TGA thermogram of the used PS waste.

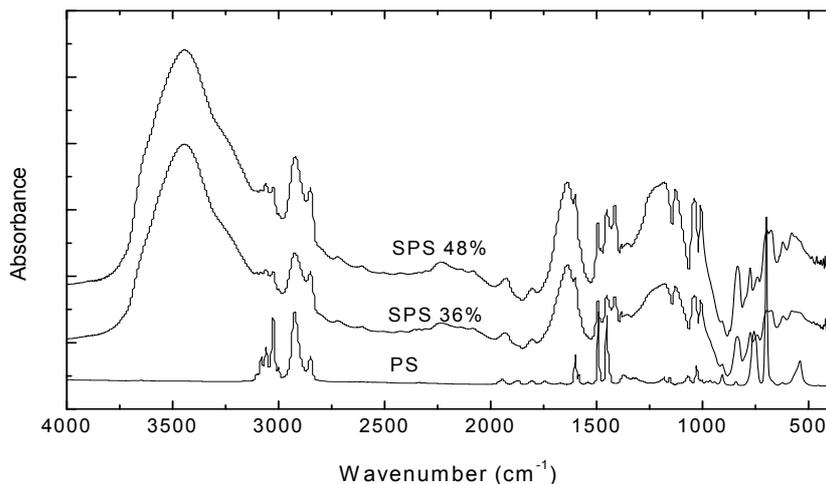


Fig. 3 – IR spectra of polystyrene (PS) and sulphonated polystyrene (SPS).

Figure (2) represents the TGA thermograms of the used PS waste under nitrogen and oxygen atmospheres. The onset of the decomposition temperature was determined, and it is  $394.2\text{ }^{\circ}\text{C}$  under the nitrogen atmosphere and  $289.1\text{ }^{\circ}\text{C}$  under the oxygen atmosphere. The presence of oxygen accelerates the decomposition process.

The sulphonation reaction was followed by Fourier Transform Infrared (FTIR) Spectroscopy. Figure 3 shows the FTIR spectra of polystyrene and sulphonated polystyrene, and changes in the structures of polystyrene via the sulphonation reaction could be deduced. These corresponded with the appearance of new absorption bands and the splitting of others, consistent with the presence of  $-\text{SO}_3\text{H}$  group on the aromatic ring. New absorption bands at  $3340$ ,  $1250$ , and  $1078\text{ cm}^{-1}$  were assigned to the stretching of the  $-\text{OH}$  in the  $-\text{SO}_3\text{H}$  group and to the asymmetric and symmetric stretching of the  $\text{O}=\text{S}=\text{O}$  group respectively.

## 2. Equilibrium studies on sorption

### 2.1. Effect of agitation time and pH

The effect of agitation time on the adsorption of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  by the polymer was studied from 15 to 1440 min; it was found that the time required to reach sorption equilibrium is around 300 min at room temperature. Both radionuclides were adsorbed in acid medium, and the removal was more than 60% using the polymer samples no. 2 as an example. The increase in pH has led to a decrease in the removal of  $^{210}\text{Po}$  from 65% to 4% when the pH increased from 3 to 6. While  $^{210}\text{Pb}$  removal decreased from 63 to 50 when pH increased from 3 to 6 (Figure 4). This fact let suggest that these radionuclides could be separated from each other using the prepared sulphonated polymer at a pH value of 6 of the solution.

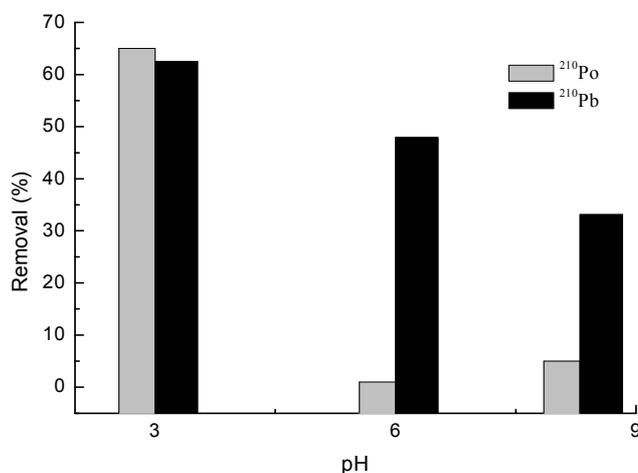


Fig. 4 – Effect of pH on  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  removal onto polymer no. 2.

Pseudo first-order adsorption kinetic model could not be applied for the resulted data. So the pseudo second-order adsorption parameters  $q_e$  and  $K$  were determined by plotting  $t/q_t$  versus  $t$ . The coefficient of determination ( $R^2$ ) for the pseudo second-order kinetic model fits are 1.00, these suggests that  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  adsorption follow pseudo second-order kinetics and  $^{210}\text{Po}^{+2}$  and  $^{210}\text{Pb}^{+2}$  ions were adsorbed onto the polymer surface via chemical interaction.

## 2.2. Adsorption mechanisms

A detailed understanding of adsorption mechanisms facilitates the determination of the rate-limiting step. This information can then be used to optimize the design of adsorbents and adsorption conditions. The overall rate of adsorption can be described by the following three steps:<sup>26</sup> (1) film or surface diffusion where the sorbate is transported from the bulk solution to the external surface of sorbent, (2) intraparticle or pore diffusion, where sorbate molecules move into the interior of sorbent particles, and (3) adsorption on the interior sites of the sorbent. Since the adsorption step is very rapid, it is assumed that it does not influence the overall kinetics. The overall rate of adsorption process, therefore, will be controlled by either surface diffusion or intraparticle diffusion. The Weber–Morris intraparticle diffusion model has often been used to determine if intraparticle diffusion is the rate-limiting step.<sup>27,28</sup> According to this model, a plot of  $q_t$  versus  $\sqrt{t}$  should be linear if intraparticle diffusion is involved in the adsorption process and

if the plot passes through the origin then intraparticle diffusion is the sole rate-limiting step. It has also been suggested that in instances when  $q_t$  versus  $\sqrt{t}$  is multi-linear two or more steps govern the adsorption process.<sup>27–28</sup> Given the non-linearity of this plot for adsorption of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  on polymers particles no. 1, this suggests that intraparticle or pore diffusion adsorption did not occur (Figure 5). While, given the linearity of this plot for adsorption of  $^{210}\text{Po}$  till 120 min and  $^{210}\text{Pb}$  till 300 min on polymers particles no. 2, this suggests that adsorption occurred in two phases (Figure 5). The initial steeper section represents surface or film diffusion. As the plot did not pass through the origin, intraparticle diffusion was not the only rate-limiting step.

## 2.3. Adsorption isotherms

Adsorption of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  by polymers particles was modelled using the Langmuir and Freundlich isotherms with the quality of the fit assessed using the coefficient of determination. The plots of  $C_f/q$  versus  $C_f$  show that the adsorption of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  on the two polymers did not follow Langmuir isotherms.

The results show that the adsorption of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  on the two polymers followed Freundlich isotherms, where  $R^2$  values were more than 0.8. The Freundlich isotherm constants  $K_f$  and  $n$  are determined from the intercept and slope of a plot of  $\log q$  versus  $\log C_f$ . The slope of the isotherm ( $n$ ) varied between 0.42 and 0.97 fulfilling the condition of  $0 < n < 1$  for favorable adsorption (Table 1).<sup>29</sup>

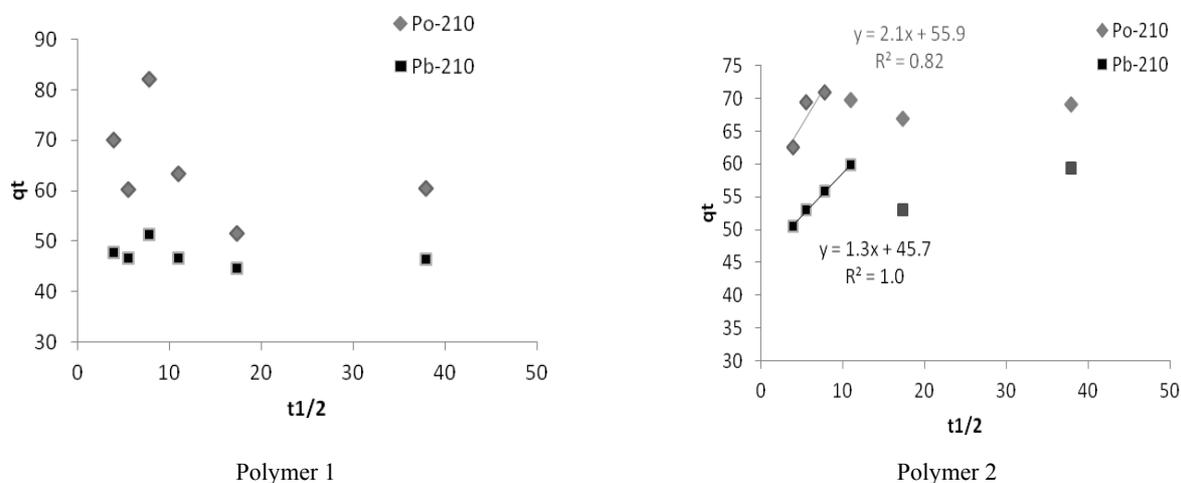


Fig. 5 – Intraparticle diffusion plots for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  sorption onto polymers 1 and 2.

Table 1

Freundlich isotherm parameters, and the kinetics constants for the adsorption of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  onto polymers

Polymer no.	Model	Freundlich			Pseudo-second order		
	Radionuclide	$K_F$	$n$	$R^2$	$K_2$ ( $\text{g Bq}^{-1} \text{min}^{-1}$ )	$q_e$ ( $\text{Bq mg}^{-1}$ )	$R^2$
1	$^{210}\text{Po}$	0.001	0.42	0.95	0.004	62.5	1.00
1	$^{210}\text{Pb}$	1.3	0.97	0.98	0.034	47.6	1.00
2	$^{210}\text{Po}$	1.1	0.79	0.81	0.010	71.4	1.00
2	$^{210}\text{Pb}$	0.6	0.84	0.99	0.002	62.5	1.00

## EXPERIMENTAL PART

### 1. Materials

Expanded polystyrene waste; commercial NaOH (*Niko Chem*, Volgograd, Russia); commercial sulphuric acid obtained from the Syrian Company for Production of Fertilizers.<sup>25</sup>  $\text{HNO}_3$  (65%, EP) and HCl (37%, EP) were obtained from Merck company, Germany.  $\text{H}_2\text{O}_2$  (33%, EP) was obtained from Panreac.  $^{210}\text{Pb}$  was provided by Laboratoire de Metrologie des Rayonnements Ionisants, France.

The polymer has been characterized using differential scanning calorimetry (DSC) {Mettler instrument: type DSC20}, thermogravimetry (TGA) {Mettler instrument: type TG50}, and FTIR {Thermo Scientific Nicolet 6700 FT-IR Spectrometer}.

### 2. Adsorption kinetics

Radioactive solutions were prepared by spiking 100 ml of distilled water with certain activities of  $^{210}\text{Pb}$  ( $^{210}\text{Po}$ ). The mixtures containing 1g of sorbent and 100 ml of radioactive solution were agitated on a shaking incubator at 150 rpm at 25°C. The activity concentrations used for these experiments were 500  $\text{Bq l}^{-1}$  for  $^{210}\text{Pb}$  ( $^{210}\text{Po}$ ). After equilibrium, the sorbent materials were separated from the solution by filtration using 0.45  $\mu\text{m}$  filters and the residual activity concentrations in the solution were analyzed. Radionuclide uptake  $q$  ( $\text{Bq metal ion per g polymer}$ ) was determined.<sup>30</sup>

Parameters from two kinetic models, pseudo first-order<sup>31</sup> and pseudo second-order,<sup>32</sup> were used to fit the experimental data and to examine the adsorption kinetics of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  uptake by the polymer. The pseudo first-order equation (Lagergren's equation) describes adsorption in solid-liquid systems based on the sorption capacity of the solids.<sup>33</sup> It is assumed that one Po or Pb ion is sorbed onto one sorption site on the polymer surface.<sup>28</sup> The pseudo second-order rate expression has been applied for analyzing chemisorption kinetics from liquid solutions.<sup>28, 31, 34</sup>

The intraparticle diffusion equation is expressed as:<sup>28</sup>

$$q_t = K_i \sqrt{t} + C \quad (1)$$

where  $K_i$  is the intraparticle diffusion rate constant ( $\text{Bq g}^{-1} \text{min}^{0.5}$ ) and  $C$  is the intercept.

### 3. Adsorption isotherm models

The equilibrium of a solute between the liquid and solid phases may be described by various models of sorption. In order to investigate the sorption capacity and isotherm, two equilibrium models have been used, namely, Langmuir and Freundlich.<sup>35-36</sup>

The Langmuir model is probably the best known and most widely applied sorption isotherm.<sup>35</sup> This model supposes a monolayer sorption with a homogeneous distribution of sorption sites and sorption energies, without interactions between the sorbed molecules. It has produced good agreement with a wide variety of experimental data.<sup>35</sup>

The Freundlich isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. The Freundlich isotherm is also more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.<sup>29</sup>

### 4. Effect of pH on radionuclide removal

The pH of solution was adjusted at 3, 6 and 9 with (1  $\text{mol l}^{-1}$ )  $\text{NH}_4\text{OH}$  and (1  $\text{mol l}^{-1}$ ) HCl, in 250 ml Erlenmeyer flasks. Each flask initially contained 1 g dry polymer, in 100 ml radionuclide solution and was shaken for 3 h at 25°C. The mixtures were filtered through 0.45  $\mu\text{m}$  membrane filters, and then the residual metal concentration in the solution was analyzed.

### 5. Analytical Methods

The  $^{210}\text{Po}$  was determined using the standard technique (the silver disc technique).<sup>37-38</sup>

## CONCLUSIONS

Functionalized Polymere wastes can be used as an effective adsorbent for removing  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  from contaminated water sources or to separate them from each other. The pseudo second order kinetic model accurately described the adsorption

kinetics. The adsorption mechanism was found to be physicosorption for polymer no 1 and chimicosorption till 120 min for polymer no 2. The experimental data were well explained by Freundlich models.

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