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Comparative study of Pb(II) ions adsorption on pet fibers and flakes: isotherm, kinetic and mechanism considerations

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ABSTRACT

In this study, the adsorption of Pb(II) ions from aqueous media on polyethylene terephthalate (PET) waste (fibers and flakes) was examined as a function of the most important operating parameters, at room temperature (22°C ± 1°C), in batch systems. The effect of initial solution pH, adsorbent dosage, contact time and initial metal ions concentration on Pb(II) ions adsorption efficiency on these two adsorbent materials is compared. It was found that for both PET-based materials (fibers and flakes) the adsorption efficiency depends very little on the initial solution pH (in the range 2.0–6.0), and reaches a maximum at 4.0 g/L adsorbent dose and a contact time of 60 min. However, the adsorption of Pb(II) ions on PET fibers is much more efficient than in the case of PET flakes, over the entire range of initial metal ions concentration (20–420 mg Pb(II)/L). To quantitatively evaluate these adsorption processes, the experimental data were modelled using Langmuir, Freundlich and Temkin isotherm models, and pseudo-first order, pseudo-second order and intra-particle diffusion models. The obtained results indicate that the adsorption process of Pb(II) ions on both PET-based materials (fibers and flakes) follow a pseudo-second order kinetic model ($R^2 > 0.9998$) and Langmuir isotherm model ($R^2 > 0.9857$). In addition, the maximum adsorption capacity for PET fibers (166.66 mg Pb(II)/g) is 13.6 times higher than for PET flakes (12.27 mg Pb(II)/g). To explain this significant difference of maximum adsorption capacities, the structural characteristics of PET fibers and flakes were highlighted using Fourier-transform infrared spectroscopy, scanning electron microscopy and thermogravimetry methods. The results included in this study will provide a clear image of the possibility of functionalization of these materials to obtain high-performance adsorbents for environmental decontamination.

Keywords: Adsorption; Pb(II) ions; PET fibers; PET flakes; Isotherm and kinetic modelling

1. Introduction

In the actual context of rapid industrialization, protection of the environment must become a global priority. Because of this, many studies in the literature have been directed towards the removal, recovery and recycling of various by-products and waste from different industrial activities, in accordance with the principles of circular economy [1,2]. Heavy metals and plastics occupy leading positions.

In most of the cases, heavy metals contribute significantly to environmental pollution, due to discharges

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of incompletely treated industrial effluents [3,4]. Their non-biodegradability and the tendency to accumulate in living organisms cause important negative impacts on the quality of ecosystems [4,5]. Due to its high industrial importance and numerous uses (e.g., electroplating, alloy preparation, batteries, paint and pigments industry, etc.) [6,7], lead is considered to be a toxic heavy metal with greatest potential hazard to human health and environment. Numerous serious health problems (such as cancer, renal and pulmonary diseases, cardiac malformations, etc.) [8] are caused by the presence of lead ions above the maximum permissible limits (0.1 mg/L) [9]. Therefore, the removal of lead ions from industrial wastewater is very important for both environmental protection and economical reasons.

Several methods, such as ion exchange, chemical and electrochemical precipitation, reverse osmosis, membrane separation, coagulation, etc., are now available for the removal of heavy metal ions from wastewater [10–14]. Unfortunately, their poor selectivity, incomplete removal of metal ions, high operating costs and energy consumption, generation of large amounts of waste sludge, etc. [12], led to the examination of other options for decontamination of wastewater containing heavy metal ions.

Adsorption involves the retention of heavy metal ions on solid materials (adsorbents), under certain experimental conditions [15]. Due to the low costs, almost complete recovery of retained metal ions, simplicity of operation and easy to adapt on a large scale [16], adsorption is considered as an effective alternative method for removing heavy metal ions from aqueous media. But all these advantages of adsorption processes largely depend on the nature of solid material used as the adsorbent. In this way various natural materials or industrial and agricultural by-products and waste (such as algae biomass, crop plants residues, clay minerals, zeolites, etc.) [17–20] have been examined as potential adsorbents for the removal of Pb(II) ions from aqueous media, only in the last five years. All these materials have in their structure numerous functional groups that act as binding sites for metal ions in an aqueous solution, so their adsorptive performances can be significantly improved by functionalization [21,22].

The detailed analysis of these studies clearly shows that in the selection of a certain material for the adsorption processes, two aspects must be considered, namely: (i) the availability of the solid material, at least at regional level, and (ii) its possible uses in other industrial and/or agricultural activities. These two aspects are closely linked and highlight the economic efficiency of adsorption processes.

Starting from these observations, the use of PET waste (polyethylene terephthalate) as adsorbent material could be considered as a viable option. This is due to the fact that: (i) PET waste is available in huge quantities worldwide, due to its use as packing material [23], (ii) has high stability, chemical resistance and mechanical strength [24], which allows it to be used for a long time in adsorption processes, and (iii) has only few uses after discharge, most often it is melted and used to obtain PET fibers [25]. In addition, finding of new valorization ways of PET waste (as adsorbent material) could be a more economical solution to control environmental pollution with this waste, which is an actual issue globally.

In this study, PET flakes (obtained by mechanical grinding of PET waste) and PET fibers (obtained by melting of PET flakes) were tested as potential adsorbents for the removal of Pb(II) ions from aqueous media. The selection of Pb(II) ions from this study was made taking into account its toxic potential for the environment (as mentioned above) and its acid-base characteristics, on the basis of which it is considered a model ion, for adsorption studies. The adsorptive performances of PET fibers and flakes was examined as a function of initial solution pH, adsorbent dosage, contact time and initial concentration of Pb(II) ions, in batch systems at room temperature (22°C ± 1°C). The experimental data were analyzed using Langmuir, Freundlich and Temkin isotherm models, and pseudo-first order, pseudo-second order and intra-particle diffusion models. Based on the parameters obtained from the isotherm and kinetics modelling, an adsorption mechanism of Pb(II) ions on PET fibers and flakes was proposed. The results included in this study will be the starting point in designing procedures for functionalization of these materials to obtain high-performance adsorbents for environmental decontamination.

2. Experimental setup

2.1. Adsorbents preparation and characterization

PET flakes and PET fibers, obtained by melting PET flakes (at 260°C–270°C), were purchased from GreenFiber International Company (Iaşi, Romania). Both materials were first washed with 1 N HNO_3 solution to remove the impurities, then several times with distilled water, and dried. The adsorbent materials were then ground to a granulation of 1.0–2.0 mm, and stored in desiccators until use. The superficial functional groups of PET fibers and flakes were identified from Fourier-transform infrared (FTIR) spectra, recorded using a Bio-Rad Spectrometer (Perkin Elmer, Waltham, MA, USA, 400–4,000 cm^{-1} spectral domain, 4 cm^{-1} resolution, blank matrix addition method).

The specific surface area (SSA) of PET fibers and flakes was calculated using the following equation [26]:

$$\text{SSA} = \frac{q_{\max} \cdot N_{\text{AV}} \cdot A_{\text{Pb}}}{M_{\text{Pb}} \cdot 10^{3}} \cdot 10^{-20} \qquad (1)$$

where $q_{\max}$ is the maximum monolayer capacity, calculated from Langmuir isotherm model (mg/g); N_{AV} is the Avogadro number (6.023×10^{23} ions/mol); A_{Pb} is the area of Pb(II) ions, calculated considering that the Pb(II) ions are spherical (m^2); M_{Pb} is the molecular weight of lead (207.19 g/mol).

Scanning electron microscopy (SEM; Hitachi S-3000N, Hitachi, Germany) was used to investigate the surface morphology of PET fibers and flakes samples. A Mettler 851 derivatograph (Mettler-Toledo AG, Greifensee, Switzerland) was used to examine the thermal characteristics of PET fibers and flakes used as adsorbents in this study.

2.2. Adsorption experiments

For the adsorption experiments, a stock solution of Pb(II) ions (2,100 mg/L) was prepared by dissolving lead nitrate (Chemical Company, Iaşi, Romania) in distilled water.

All working solutions were obtained by diluting an exact volume of stock solution with distilled water.

The influence of the most important experimental parameters: initial solution pH (2.0–6.0), adsorbent dosage (4.0–20.0 g/L), initial Pb(II) ions concentration (40–500 mg/L) and contact time (0–180 min) on the adsorption efficiency of Pb(II) ions using PET fibers and flakes as adsorbents was examined in batch systems, at room temperature (22°C ± 1°C). All samples were stirred constantly at 200 rpm for a determined period of time (specific for each experiment). At the end of each adsorption experiment series, the adsorbents were separated by filtration (quantitative filter paper), and the Pb(II) ions in the filtrate was analyzed spectrophotometrically (Digital Spectrophotometer S104D, colour reagent: *p*-amino-resorcinol, λ = 530 nm, ammonia buffer, pH = 10), using a prepared calibration graph.

The adsorption capacity (*q*, mg/g) and percentage of Pb(II) ions removal (*R*, %) were determined using the following equations:

$$q = \frac{\left(c_0 - c\right) \cdot V}{m} \tag{2}$$

$$R = \frac{c_0 - c}{c_0} \cdot 100 \tag{3}$$

where c_0 and c are the initial and residual concentration of Pb(II) ions in aqueous solution (mg/L), V is the volume of solution (L) and m is the mass of adsorbent (g).

The pH of aqueous solutions, before and after adsorption of Pb(II) ions was measured with a pH/ion-meter MM 734, with a combined glass electrode.

2.3. Isotherm and kinetics models

For modelling experimental data, three isotherm models (Langmuir, Freundlich and Temkin) and three kinetic models (pseudo-first order, pseudo-second order and intra-particle diffusion) were used. The mathematical equations of these models are presented in Table 1.

The best isotherm and kinetics model that fit the experimental data were selected using the values of regression coefficients (R^2), obtained from the ANOVA statistical analysis.

3. Results and discussion

3.1. Optimization of experimental parameters

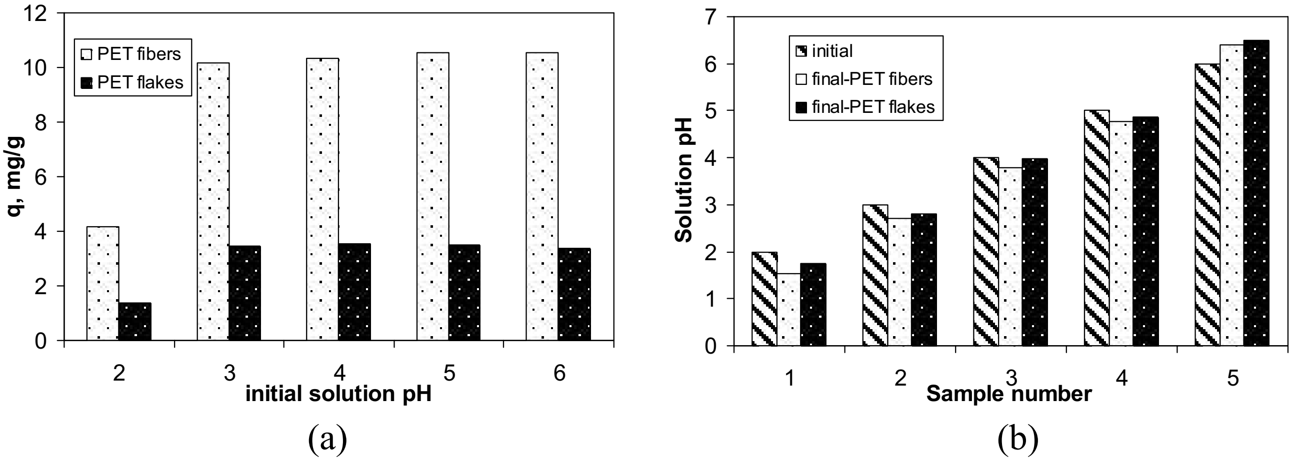
It is well known that the efficiency of adsorption processes depends significantly on the experimental conditions in which they take place [16,30]. Therefore, the selection of optimum solution pH and adsorbent dosage will ensure an adequate chemical state of the metal ions and superficial functional groups of adsorbent, and an adequate ratio between the liquid and solid phases of adsorption system [30].

In this study, the adsorption of Pb(II) ions on PET fibers and flakes was examined in an initial solution pH range between 2.0 and 6.0, and the obtained experimental results are illustrated in Fig. 1. This pH range was selected in order to avoid the precipitation of Pb(II) ions, which is undesirable during adsorption.

The experimental results illustrated in Fig. 1a shows that the adsorption capacity of PET-based adsorbents (fibers and flakes) varies insignificantly (less than 5%) with the increase of the initial solution pH in the range of 3.0–6.0.

Table 1
Mathematical equations of isotherm and kinetics models used in this study [27–29]

Model	Equation	Notations
Isotherm models		
Langmuir	$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c}$	K_F, Freundlich constant; n, a constant which characterizes the surface heterogeneity; $q_{\max}$, the maximum adsorption capacity (mg/g); c, metal ions concentration at equilibrium (mg/L); K_L, Langmuir constant (L/g); b, the constant of Temkin isotherm related to the sorption heat (J/mol); R, the gas constant (8.314 J/mol K); T, the absolute temperature; A and B can be calculated from the linear dependence q vs. ln$c$
Freundlich	$\log q = \log K_F + \frac{1}{n} \log c$	
Temkin	$q = B \cdot \ln A + B \cdot \ln c$ $B = \frac{R \cdot T}{b}$	
Kinetics models		
Pseudo-first order	$\log\left(q_e - q_t\right) = \log q_t - \frac{k_1}{2.303} \cdot t$	q_e, q_t, adsorption capacities at equilibrium and at time t, respectively (mg/g); k_1, rate constant of pseudo-first order kinetics equation (1/min); k_2, pseudo-second order rate constant (g/mg min); k_{diff}, rate constant of intra-particle diffusion model (g/mg min$^{1/2}$); c, concentration (mg/L)
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e}$	
Intra-particle diffusion	$q_t = k_{\text{diff}} \cdot t^{1/2} + c$	



(a) (b)

Fig. 1. (a) Effect of initial solution pH on Pb(II) ions adsorption on PET fibers and flakes. (b) Variation of pH before (initial) and after (final) adsorption of Pb(II) ions (c_0 = 82.20 mg Pb(II)/L; adsorbent dosage = 4.0 g/L; contact time = 24 h).

The only notable difference occurs when the initial solution pH increases from 2.0 to 3.0, when the adsorption capacity of PET fibers increases by 59%, while that of PET flakes by 53% (Fig. 1a). This insignificant variation of the adsorption capacity of PET-based adsorbents with the initial pH of aqueous solution has two important consequences: (i) in the adsorption process of Pb(II) ions on these adsorbents no rigorous control of the solution pH is required, and this is an advantage in terms of industrial applicability, and (ii) in the adsorption process, the superficial functional groups of adsorbents do not dissociate, because the initial pH values and the final pH values are very close, over the entire pH range (Fig. 1b). This means that the binding interactions of Pb(II) ions will be performed predominantly through the electron pairs of the O-donor atoms in the structure of the adsorbents. Therefore, the efficiency of the adsorption process of Pb(II) ions by PET fibers and flakes will largely depend on the surface availability of these types of atoms. Based on the experimental results (Fig. 1), the optimum pH for the adsorption of Pb(II) ions was considered 6.0 (which is natural pH value of aqueous solution), and this value was used in all other experiments.

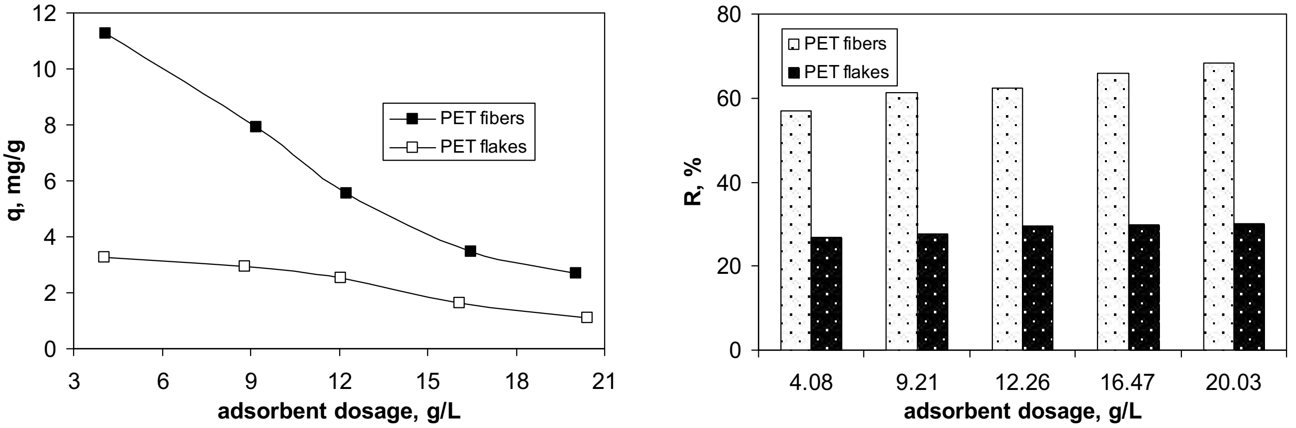
The second experimental parameter to be optimized is the adsorbent dosage. In this case, the adsorption studies of Pb(II) ions on PET fibers and flakes were performed by varying the adsorbent dosage from 4.0 to 20.0 g/L, while the other experimental parameters were kept constant (Fig. 2). This interval of the adsorbent dosage was chosen to clearly highlight the influence of this parameter on the retention efficiency of Pb(II) ions from aqueous solution.

Increasing the adsorbent dosage from 4.0 to 20.0 g/L decreases the adsorption capacity from 11.26 to 2.69 mg/g for PET fibers, and from 3.26 to 1.08 mg/g for PET flakes (Fig. 2a), and slightly improves the removal percents of Pb(II) ions from 56.87% to 68.41% for PET fibers, and from 26.83% to 30.14% for PET flakes (Fig. 2b). These typical variations, reported in many studies in the literature [30–32] show that most Pb(II) ions are retained on the surface of the adsorbent material, due to their interactions with superficial functional groups. Because Pb(II) ions have a large volume and the adsorbent materials (PET fibers and flakes) have a compact structure, the functional groups inside the adsorbent particles remain inaccessible to metal ions, and they do not participate in the adsorption processes. This is probably the main reason why PET fibers have significantly higher performances in the adsorption process of Pb(II) ions compared to PET flakes. Therefore, increasing the adsorbent dosage will not significantly improve the adsorption efficiency of Pb(II) ions on PET fibers and flakes, and consequently, an adsorbent dosage of 4.0 g/L was considered optimal.

3.2. Effect of initial Pb(II) concentration and isotherm modelling

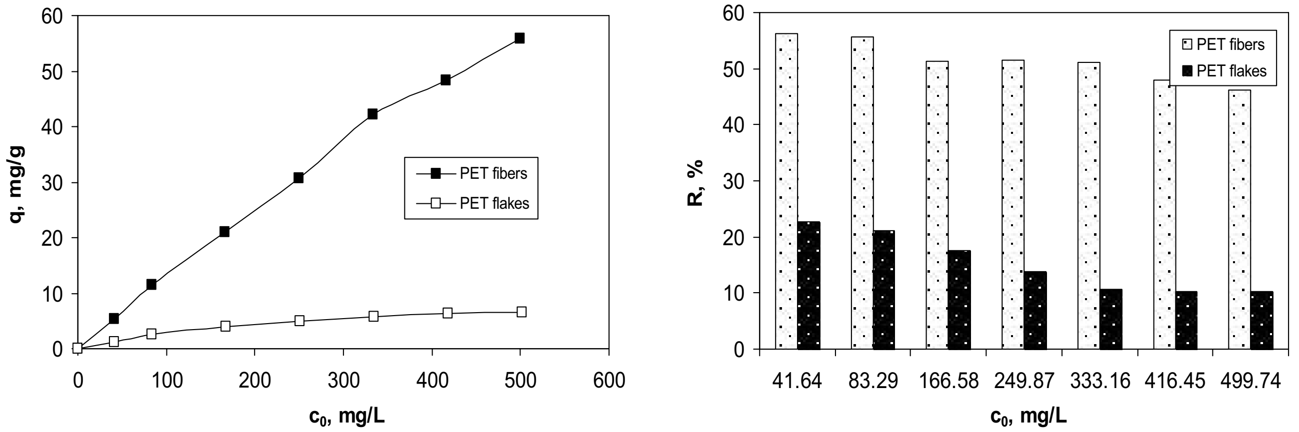
The influence of initial Pb(II) ions concentration on the adsorption efficiency was examined in the concentration range between 40 and 500 mg Pb(II)/L, at constant adsorbent dosage (4.0 g/L), initial solution pH (6.0), contact time (24 h) and temperature (22°C ± 1°C). The experimental data for the adsorption of Pb(II) ions on PET fibers and flakes versus initial metal ions concentration are presented in Fig. 3.

As expected, increasing the initial concentration of Pb(II) ions in aqueous solution increases the values of adsorption capacity (from 5.26 to 55.84 mg/g for PET fibers, and from 1.15 to 6.44 mg/g for PET flakes; Fig. 3a), while the decrease in the removal percents is less pronounced (from 56.20% to 46.19% for PET fibers, and from 22.72% to 10.22% for PET flakes; Fig. 3b). The increase of the adsorption capacities (q, mg/g), and respectively, the decrease of the removal percents (R, %) with the increase of initial metal ions concentration is determined by the increase of the ratio between the number of Pb(II) ions from aqueous solution and the number of active sites on the surface of adsorbent materials [33]. When this ratio has low values (it is the case of low initial Pb(II) concentrations), most Pb(II) ions can bind to the functional groups of adsorbent, which leads to low values of adsorption capacity and high values of removal percent (Eqs. (2) and (3)). If this ratio has high values (as in the case of high initial Pb(II) concentrations), a higher number of Pb(II) ions will have a constant number of active sites on the adsorbent surface,



(a) (b)

Fig. 2. Effect of adsorbent dosage on adsorption capacity (a) and removal percent (b) for Pb(II) ions adsorption on PET fibers and flakes (pH = 6.0; c_0 = 82.20 mg Pb(II)/L; contact time = 24 h).



(a) (b)

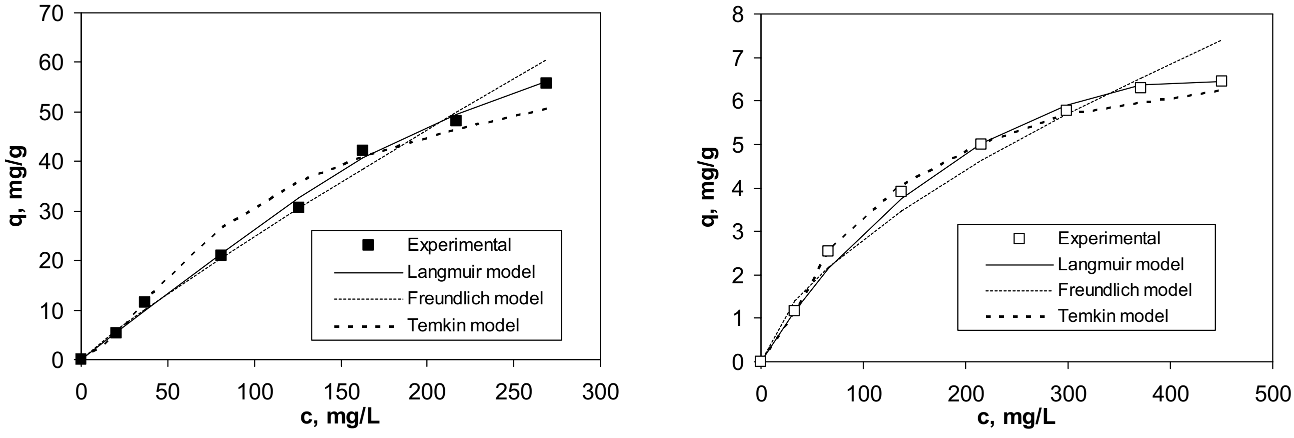
Fig. 3. Effect of initial Pb(II) concentration on adsorption capacity (a) and removal percent (b) for Pb(II) ions adsorption on PET fibers and flakes (pH = 6.0; adsorbent dosage = 4.0 g/L; contact time = 24 h).

for binding. As a result, the values of adsorption capacity will increase, while the values of the removal percent will decrease (Eqs. (2) and (3)).

However, in the adsorption process of Pb(II) ions from aqueous solution, PET fibers are more efficient adsorbents compared to PET flakes, over entire initial metal ions concentration range (Fig. 3). This suggests that there are more functional groups on the surface of PET fibers than in the case of PET flakes, and therefore, the adsorption of Pb(II) ions is more efficient. For example, if at the lowest initial Pb(II) concentration (41.60 mg/L) the adsorption capacity of PET fibers is 4 times higher than that of PET flakes, at the highest initial Pb(II) concentration (500 mg/L), the difference between the adsorption capacity of these two materials is over 9 times higher (Fig. 3). Consequently, a thermal pre-treatment step must be included in the design of the activation method to increase the adsorption capacity of PET waste.

Quantitative evaluation of Pb(II) ions adsorption isotherms on PET fibers and flakes was performed by modelling of the experimental results. Three isotherm models (Langmuir, Freundlich and Temkin) were used for this purpose, and the best fit model was selected based on the values of regression coefficients, obtained from statistical analysis. The theoretical and experimental isotherms are illustrated comparatively in Fig. 4, while the characteristic parameters of each model are summarized in Table 2.

As can be seen from Fig. 4 and Table 2, the adsorption of Pb(II) ions on PET fibers and flakes is best described by the Langmuir isotherm model ($R^2 > 0.98$), compared to Freundlich model ($R^2 > 0.95$) and Temkin model ($R^2 > 0.94$). This indicates that for both adsorbents, the retention of Pb(II) ions takes place at the surface until a complete monolayer is formed, after which the adsorption process reaches equilibrium [34,35]. The maximum adsorption capacity



(a) (b)

Fig. 4. Experimental and theoretical isotherms obtained for Pb(II) ions adsorption on PET fibers (a) and PET flakes (b) (pH = 6.0; adsorbent dosage = 4.0 g/L; contact time = 24 h).

Table 2
Parameters of the isotherm models obtained for Pb(II) ions adsorption on PET fibers and flakes

Isotherm model	Parameter	PET fibers	PET flakes
Langmuir	R^2	0.9986	0.9897
	$q_{\max}$ (mg/g)	166.66	12.27
	K_L (L/g)	0.0041	0.0032
Freundlich	R^2	0.9589	0.9579
	$1/n$	0.79	0.64
	K_F (L/g)	0.3936	0.1495
Temkin	R^2	0.9431	0.9689
	A (L/g)	0.0504	0.0501
	b (J/mol)	125.99	117.38

($q_{\max}$, mg/g) depends on the nature of adsorbent material, being much higher in the case of PET fibers (166.66 mg/g) than in the case of PET flakes (12.27 mg/g). However, the values of Langmuir constants (K_L, L/g), which is a constant related to the affinity of metal ions for binding sites on the adsorbent [35], have the same order of magnitude for both adsorbent materials. This suggests that the same type of functional groups are involved in the adsorption of Pb(II) ions on PET fibers and flakes, and that the difference in the adsorption efficiency of metal ions on PET fibers and PET flakes is probably determined by the number and availability of functional groups to interact with Pb(II) ions. Although the Freundlich and Temkin models do not describe the experimental data as accurately as the Langmuir model, the characteristics parameters calculated for these models support the observations mentioned above. Thus, the parameters of the Freundlich model ($1/n$ and K_F) show that the adsorption process of Pb(II) ions on PET fibers and flakes is favourable [35], which suggests the existence of interactions between metal ions from aqueous solution and the functional groups of the adsorbents, while the parameters of the Temkin model (A and b) indicate that these interactions are predominant electrostatic (physical adsorption) [36], both in the case of PET fibres and in the case of PET flakes.

Therefore, the transformation of PET flakes into fibers, by thermal treatment, improve the availability of functional groups on the surface of adsorbent, but in order to obtain a high-performance adsorbent material, new functional groups must be introduced in its structure.

3.3. *Effect of contact time and kinetics modelling*

The effect of contact time on the adsorption of Pb(II) ions from aqueous solution on PET fibers and flakes is illustrated comparatively in Fig. 5. In both cases, the adsorption process reaches equilibrium after 60 min of contact time, but in this initial stage the retention of Pb(II) ions is more efficient in the case of PET fibers (46%), than in the case of PET flakes (28%). After 60 min of contact time, the values of adsorption capacity vary insignificantly with the increase of the contact time (less than 1% in the case of PET fibers, and by less than 3% in the case of PET flakes; Fig. 5).

Under these conditions, a contact time of 60 min can be considered optimal for the adsorption of Pb(II) ions from aqueous solution both on PET fibers and PET flakes. Therefore, the adsorption of Pb(II) ions on these adsorbents can be considered as a fast process, and this is an advantage from applicative point of view. In addition, the fact that for both materials the time required to reach the equilibrium is same; it is another argument that the same type of interactions (most probable electrostatic) are involved in the adsorption of Pb(II) ion on PET fibers and flakes.

The modelling of the experimental kinetic data was performed using three kinetic models, namely: pseudo-first order model, pseudo-second order model and intra-particle diffusion model (Table 1), and the most suitable kinetic model was selected by considering the values of regression coefficients (R^2) calculated from the statistical analysis. The experimental and theoretical kinetics curves obtained for the adsorption of Pb(II) ions from aqueous media on

PET fibers and flakes are presented in Fig. 6, and the values of the kinetics parameters calculated for each model are summarized in Table 3.

As can be seen from Fig. 6 and Table 3, the highest values of regression coefficients (R^2) and the closest values of the calculated adsorption capacity ($q_{e,\mathrm{calc}}$, mg/g) to the experimental ones ($q_{e,\mathrm{exp}}$, mg/g) are obtained in the case of the pseudo-second order kinetic model, for both PET-based adsorbent materials. Therefore, it can be said that the adsorption of Pb(II) ions on PET fibers and flakes is very well represented by the pseudo-second order kinetic model. This means that in the adsorption processes the rate limiting step is the electrostatic interaction between the superficial functional groups and Pb(II) ions. In addition, the higher value of the rate constant (k_2) obtained in the case of Pb(II) ions adsorption of PET fibers indicates that compared to PET flakes (Table 3), this adsorbent has a higher number of superficial functional groups available to interact with Pb(II) ions from aqueous solution.

The share of elementary diffusion processes in the adsorption of Pb(II) ions on PET fibers and flakes was evaluated using the intra-particle diffusion model. The linear dependencies of the intra-particle diffusion model (Fig. 7) do not pass through the origin, which clearly demonstrates that the elementary diffusion processes do not limit the adsorption of Pb(II) ions on PET fibers and flakes. Two distinct regions can be delimited. The first region corresponds to the movement of Pb(II) ions from the bulk solution to the external surface of adsorbent, while the second region characterizes the diffusion of the metal ions inside the adsorbent particles until equilibrium is reached [37,38].

As can be seen from Table 3, the diffusion rate constant of the first region is much higher than the diffusion rate constant of the second region. This means that the movement of Pb(II) ions from bulk solution to the external surface of adsorbent is much faster than the diffusion of the metal ions inside the adsorbent particles. In addition, for the

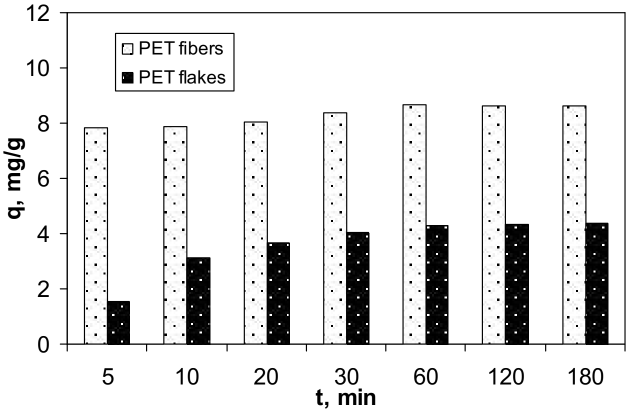
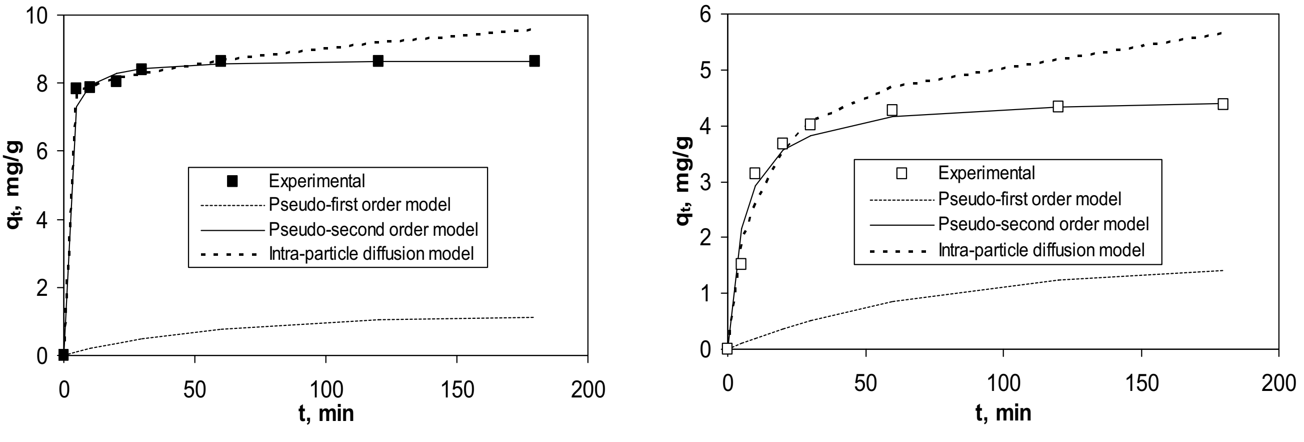


Fig. 5. Effect of contact time on adsorption capacity of Pb(II) ions on PET fibers and flakes (pH = 6.0; adsorbent dosage = 4.0 g/L; c_0 = 82.20 mg Pb(II)/L).

Table 3
Parameters of the kinetic models obtained for Pb(II) ions adsorption on PET fibers and flakes

Kinetic model	Parameter	PET fibers	PET flakes
	$q_{e,\mathrm{exp}}$ (mg/g)	8.6409	4.3837
Pseudo-first order	R^2	0.8773	0.8545
	$q_{e,\mathrm{calc}}$ (mg/g)	1.1487	1.5307
	k_1 (1/min)	0.0191	0.0138
Pseudo-second order	R^2	0.9999	0.9998
	$q_{e,\mathrm{calc}}$ (mg/g)	8.6556	4.4351
	k_2 (g/mg min)	0.1199	0.0401
Intra-particle diffusion	R^2	0.8788	0.8525
	c_1 (mg/L)	7.4005	0.3445
	$k_{\mathrm{diff},1}$ (g/mg min$^{1/2}$)	0.1635	0.0716
	R^2	0.9610	0.9698
	c_2 (mg/L)	8.6544	4.1118
	$k_{\mathrm{diff},2}$ (g/mg min$^{1/2}$)	0.0012	0.0196



(a) (b)

Fig. 6. Experimental and theoretical kinetic curves obtained for Pb(II) ions adsorption on PET fibers (a) and PET flakes (b) (pH = 6.0; adsorbent dosage = 4.0g/L; c_0 = 82.20 mg Pb(II)/L).

first region, both the rate constant and intercept (c, mg/L) are higher in the case of PET fibers than in the case of PET flakes (Table 3). This indicates that after PET fibers are added to the aqueous solution, the Pb(II) ions move rapidly to the external adsorbent surface, where they form a boundary layer with a sufficient large thickness (7.4005 mg/L), to facilitate the adsorption process. Therefore, even if the intra-particle diffusion model does not best describe the experimental kinetic data, the calculated parameters of this model show that: (i) PET fibers have much more active sites on their surface than PET flakes, and (ii) most of these active sites are functional groups that can have electrostatic interaction with Pb(II) ions from aqueous solution (see the diffusion rate constants from Table 3).

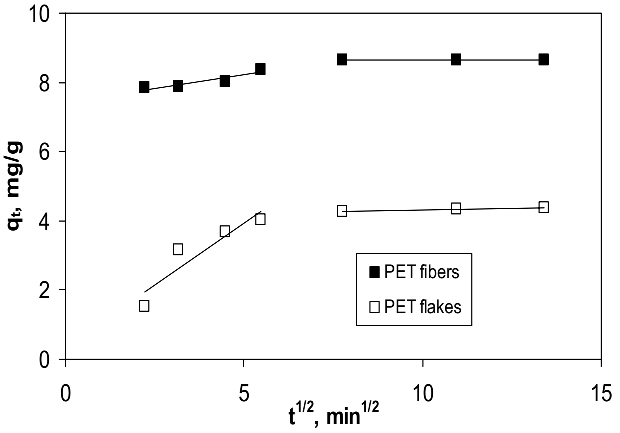


Fig. 7. Linear representation of intra-particle diffusion kinetic model for Pb(II) ions adsorption onto PET fibers and flakes.

3.4. Inside of adsorption mechanism

To explain the significant differences in the adsorption efficiency of Pb(II) ions on PET fibers and flakes, FTIR

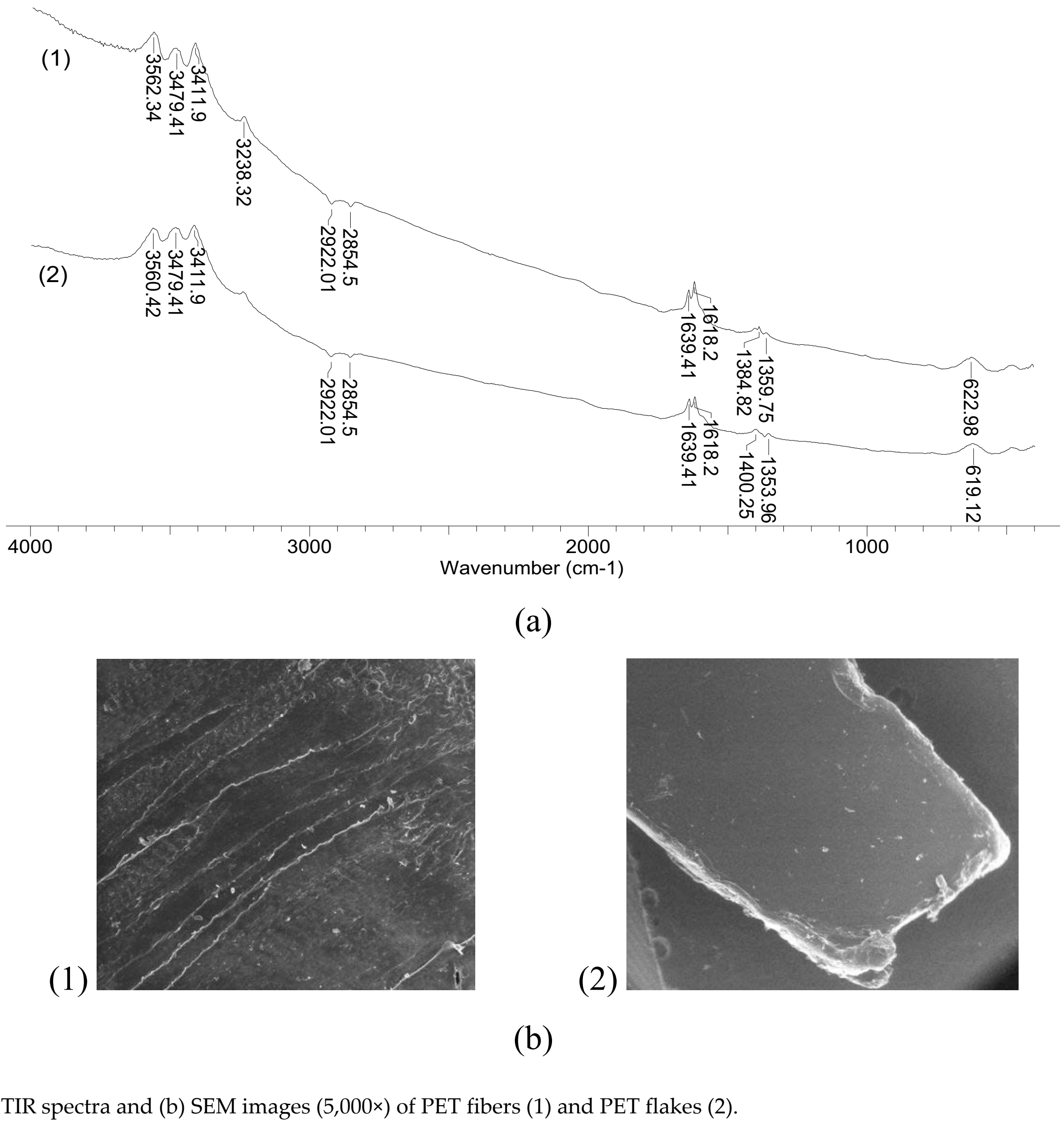


Fig. 8. (a) FTIR spectra and (b) SEM images (5,000×) of PET fibers (1) and PET flakes (2).

spectra and SEM images were recorded for both materials (Fig. 8). FTIR spectra were used to identify the most important functional groups on the surface of PET fibers and flakes, while SEM images were used to observe the morphology of their surface.

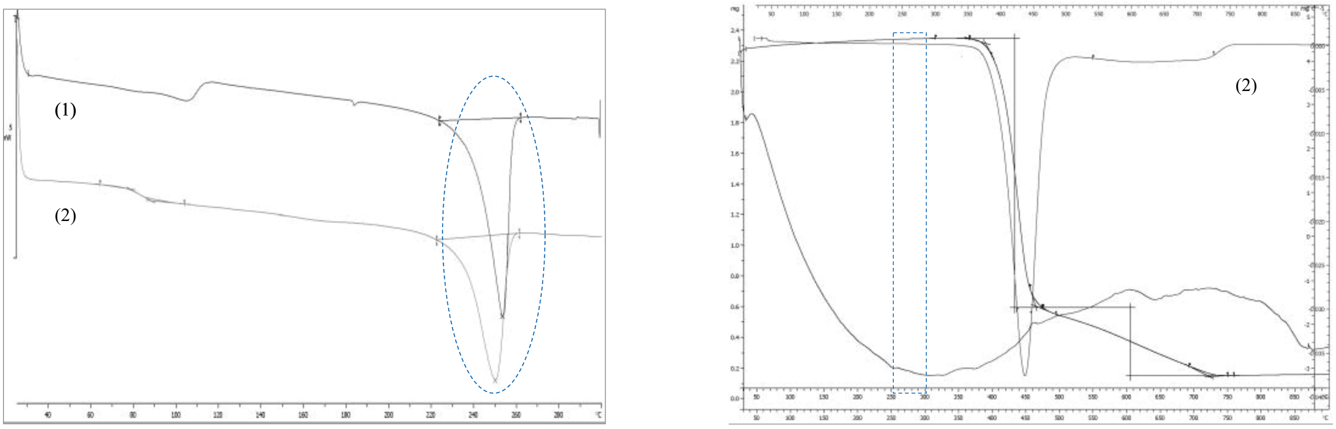
As it is expected, analysis of the FTIR spectra (Fig. 8a) shows that both adsorbent materials (PET fibers and flakes) have on their surface approximately the same types of functional groups, and that most of them have O-donor atoms. The absorption bands at 3,560–3,411 cm^{-1}, 1,639–1,618 cm^{-1} and 1,400–1,350 cm^{-1} indicate the presence of O atoms bonded by single or double bonds of C, O and H atoms. Moreover, significant differences cannot be observed in the morphology of the surfaces of the two adsorbents. As can be observed from Fig. 8b, both adsorbents have a relatively smooth surface, and the few irregularities on the surface of PET fibers cannot explain the significant differences in the adsorption process of Pb(II) ions, compared to PET flakes.

However, the SSA, calculated according with Eq. (1), which represents the accessible area on the surface of adsorbent for Pb(II) ions, per unit mass of material, is much larger in the case of PET fibers (46.32 m^2/g) than in the case of PET flakes (3.41 m^2/g). This significant difference (over 10 times) of the SSA of the two adsorbents can be explained by considering the thermal treatment required for the preparation of PET fibers.

In general, PET fibers are obtained by spinning PET flakes previously heated to temperatures of 260°C–270°C. During this thermal treatment, only the melting of the PET flakes takes places (Fig. 9a), without other processes of decomposition of this material being highlighted (Fig. 9b).

But, the melting of PET flakes leads to a "linearization" of polymer chains, so that in the obtained PET fibers, more functional groups reach the surface and are geometrically favourable to bind Pb(II) ions from aqueous solution. A schematic representation of this possible mechanism is illustrated in Fig. 10.

Consequently, the number of available active sites increases after the melting of PET flakes and the adsorptive performance of obtained PET fibers for Pb(II) ions, is higher. This explains the high value of the maximum adsorption capacity of PET fibers calculated from the Langmuir model (q_{max}, mg/g), which is comparable to the values obtained for other adsorbent materials, reported in the literature (Table 4).



(a) (b)

Fig. 9. Differential scanning calorimetry curves (a) and derivatogram (b) of PET fibers (1) and flakes (2).

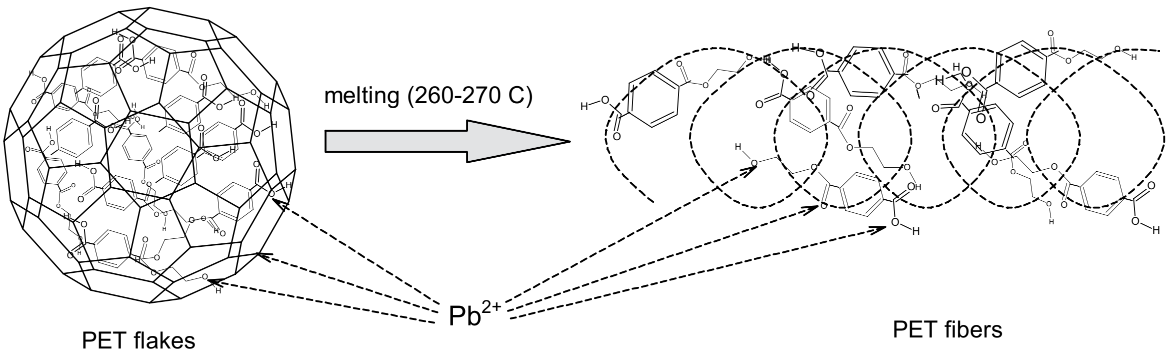


Fig. 10. Schematic illustration of Pb(II) ions adsorption on PET fibers and flakes.

Table 4
A comparison between the values of maximum adsorption capacity (q_{max}, mg/g) of PET fibers and flakes and other adsorbents reported in the literature for Pb(II) ions

Adsorbent	Solution pH	q_{max} (mg/g)	Reference
Chara sp. algae biomass	5.0	8.34	[39]
Chitosan–vanillin polymer	6.0	23.30	[40]
Bacillus subtilis	6.0	7.34	[41]
Granular activated carbon	5.0	29.42	[42]
Pristine biochar	—	177.8	[43]
Hydrochar	5.0	92.80	[44]
Amino-functionalized vermiculite	6.0	219.4	[45]
PET fibers	6.0	166.66	This study
PET flakes	6.0	12.27	This study

Therefore, although PET fibers do not allow the complete removal of Pb(II) ions from aqueous solution, their adsorptive performances clearly superior to PET flakes shows that in designing a functionalization method for these materials, such thermal treatment step must be included.

4. Conclusion

In this study, PET fibers and flakes were used as adsorbents for the removal of Pb(II) ions from aqueous media. The adsorption experiments were performed in batch systems at room temperature (22°C ± 1°C). The efficiency of adsorption processes is influenced by initial solution pH, adsorbent dosage, initial Pb(II) concentration and contact time. All these parameters were examined in turn, and the optimal experimental conditions were established as: initial solution pH of 6.0; 4.0 g adsorbent/L and a contact time of 60 min. The experimental isotherms of Pb(II) ions adsorption on PET fibers and flakes are best described by the Langmuir model, while the experimental kinetic is best fitted by the pseudo-second order kinetic model. In the case of PET fibers, the maximum adsorption capacity (q_{max}, mg/g) is more than 10 times higher (166.66 mg/g) than the value obtained in the case of PET flakes (12.27 mg/g) for Pb(II) ions adsorption from aqueous solution. In addition, the rate constant of the pseudo-second order kinetic model obtained for Pb(II) ions adsorption on PET fibers (0.1199 g/mg min) is one order of magnitude higher than those obtained in the case of Pb(II) ions adsorption on PET flakes (0.0401 g/mg min). These significant differences between the isotherm and kinetics parameters of the two adsorbents can be explained by considering the thermal treatment required for the preparation of PET fibers. The melting of PET flakes (at 260°C–270°C) leads to a "linearization" of polymer chains. The obtained PET fibers on their surface have more functional groups that are geometrically favourable to bind Pb(II) ions from aqueous solution. The results included in this study show that the thermal treatment step is essential for increasing the adsorptive performances of PET-based materials, and this should be taken into account when designing the functionalization methods of these materials.

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