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OBTAINING PET-CLAY ADSORBENT MATERIALS AND THEIR USE FOR THE REMOVAL OF Pb(II) IONS FROM AQUEOUS MEDIA

BY

CODRUŢ-ŞTEFAN CIOBANU[1], DUMITRU BULGARIU[2,3], BIANCA AZAMFIRE[1] and LAURA BULGARIU[1,*]

[1]“Gheorghe Asachi” Technical University of Iași,
“Cristofor Simionescu” Faculty of Chemical Engineering and Environment Protection
[2]“Al. I. Cuza” University of Iaşi, Faculty of Geography and Geology
[3]Romanian Academy, Filial of Iaşi, Branch of Geography

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Abstract. The performance of PET flakes as adsorbents for the removal of harmful pollutants from aqueous solution is quite low and, therefore its use in the decontamination processes of the environment is insignificant. However, increasing quantities of PET waste discharged into the environment require opportunities for valorization. In this study, PET flakes were mixed with clay mineral, and melted under different experimental conditions (temperature, melting time, mixing ratio, addition of phenol, etc.), to obtain new materials with adsorptive potential. The methodology used for the preparation of these materials was detailed discussed, and the experimental conditions were optimized. Also, the adsorptive potential of each obtained material was tested for the removal of Pb(II) ions from aqueous solution. The experimental results have shown that the mixing of PET waste with clay mineral (mixing ration 1: 2) and the melting at 350°C for 25 min, allows to obtain a material (PET-clay(1:2)-350°C-25 min) with an adsorption capacity for Pb(II) ions (18.59 $mg \cdot g^{-1}$) comparable to that of raw clay mineral. Therefore, PET-clay(1:2)-350°C-25 min material has the potential to be used as adsorbent in environmental decontamination processes.

[*]Corresponding author; *e-mail*: lbulg@ch.tuiasi.ro

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1. Introduction

Environmental decontamination is and will remain for a long time one of the most important problems of actual societies worldwide. The accentuated development of industrial activities and consumption determined the generation of waste that ends up being discharged into the environment (Donmez *et al*., 1999; Chojnacka, 2010; Cechinel *et al*., 2018). Therefore, the quality of ecosystems is severely affected, and this has particularly important consequences for people's quality of life (Volesky, 2001).

Although many method of removing contaminants from industrial effluents are known (such as: chemical precipitation, osmosis, coagulation, floculation, ion exchange, etc.) (Oliveira *et al*., 2013; De Gisi *et al*., 2016), they have several disadvantages (high chemicals and energy consumption, high costs, low selectivity, difficult operating conditions, etc.), which limit their practical applicability.

Compared to these, adsorption is considered a much cheaper method, which can be used to remove a wide variety of organic or inorganic contaminants, under different experimental conditions (Farooq *et al*., 2010; Gautam *et al*., 2014; De Gisi *et al*., 2016). But, the applicability of adsorption on an industrial scale depends mainly on the costs of obtaining the adsorbent material (Dabrowski *et al*., 2004; De Gisi *et al*., 2016). Therefore, many studies in the literature have sought to obtain cheap adsorbent materials, starting from natural materials or industrial waste (Babel and Krniavan, 2003; Nguyen *et al*., 2013).

It is well known that PET (polyethylene terephtalate) is common polymer widely used for the manufacture of food and non-food packaging, mainly because is stable for a long time and is resistant to chemical agents (Mendoza-Carrasco *et al*., 2016). Unfortunately, this use of PET has caused very large amounts of such waste to be discharged into the environment, causing serious pollution problems. This is the reason why finding concrete solution for the valorization of PET waste is in attention of researchers around the world. One such solution could be the use of PET waste as adsorbent, as this material is inexpensive and available in large quantities. However, the problem to be solved is related to the very low adsorption capacity of this material (Cojocariu *et al*., 2018; Ciobanu *et al*., 2021).

Clay minerals are natural materials which are easy and inexpensive to obtain in many regions of the world, including in Romania. Moreover, an important deposit of such clay minerals is found in SE part of the city of Iaşi (Azamfire *et al*., 2020) and, therefore, it is easier to procure for us. Although this clay has numerous superficial functional groups and a high adsorption capacity especially for metal ions, after grinding, the size of the obtained granules is small (less than 0.1 mm), which makes it difficult to use for practical applications.

Consequently, the encapsulation of small clay granules in molten PET waste could be a solution that minimizes the main drawbacks of the two materials in the adsorption processes. This results in a new material that is much easier to use from a practical point of view (due to the polymer matrix), and which has enough functional groups (due to clay miners) to be used as an adsorbent.

In this study, new adsorbent materials were prepared by mixing PET waste and clay mineral, in different ratios. The mixtures were heated under different experimental conditions (temperature, melting time, and in presence and absence of phenol) to establish the optimal mixing conditions. The preparation methodology was detailed discusses. The adsorptive potential of each obtained new material was tested in the case of Pb(II) ions adsorption from aqueous media.

2. Materials and Methods

2.1. Materials

PET flakes were obtained from recycling PET bottles (GreenFiber International Company Iaşi, Romania), and used as received. Clay mineral was sampled from Vlădiceni (Iaşi, Romania), from a depth of 10-40 cm. The clay sample was dried in air at 60°C for 6 hours, ground, mortared and sieved before use.

The chemical reagents: lead nitrate and phenol, were purchased form Chemical Company and were used without further purifications. A stock solution of 2100 mg Pb(II)$\cdot L^{-1}$ was prepared by dissolving a certain quantity of lead nitrate in distilled water. This stock solution was then used to prepare all working solutions.

2.2. Preparation of Adsorbent Materials

The adsorbent materials were obtained by mechanically mixing 1.0 g of PET flakes with different amounts of clay mineral (0.1 – 2.0 g), in a metal crucible. The mixtures were then heated (using an electrical hob) at two different temperatures (300 and 350°C) for different time intervals (25 – 50 min) to melt the PET flakes. After cooling, each newly material was removed from the crucible (using a spatula), ground and stored in the desiccators until use. The addition of phenol (0.1 – 1.0 g) before melting was also tested in the experimental studies.

2.3. Adsorption Experiments

The adsorption experiments were performed mixing 25 mL of Pb(II) ions solution (84 mg$\cdot L^{-1}$) with 0.1 g of adsorbent and intermittent stirring. After 24 hour of contact, the two phases were separated by filtration (quantitative filter paper), and Pb(II) ions concentration in filtrate was analyzed spectrophotometrically (VIS Spectrophotometer YA1407020 model) using PAR (4-(2-piridilazo)-resorcinol) as colour reagent (λ = 530 nm; 1 cm glass cells, against blank solution).

The adsorption capacity (q, [mg·g^{-1}]) and removal percent (R, [%]) of each obtained adsorbent material was calculated using the following equations:

$$q = \frac{(c_0 - c)\cdot(V/1000)}{m} \quad (1)$$

$$R = \frac{c_0 - c}{c_0}\cdot 100 \quad (2)$$

where: c_0 is the initial Pb(II) ions concentration in solution, [mg·L^{-1}]; c is the equilibrium concentration of Pb(II) ions in the solution, [mg·L^{-1}]; V is volume of solution, [mL]; and m is the mass of adsorbent used in the experiments, [g].

3. Results and Discussions

The detailed analysis of the derivatograms recorded for PET flakes showed that this material has a high thermal stability (Ciobanu *et al*., 2021). The melting of this material takes place in the temperature range of 260 – 370°C, while its decomposition occurs at temperatures higher than 450°C. Therefore, in order to be able to mix PET flakes with clay mineral, it is necessary that they be melted first. In this study, two different temperatures, namely 300 and 350°C were used for melting of PET flakes. After melting, PET was mixed with clay mineral in a 1:2 mass ratio, and further heated for 25 min. The adsorption performances of obtained materials for Pb(II) ions were compared with those of raw PET flakes and the obtained experimental results are presented in Fig. 1.

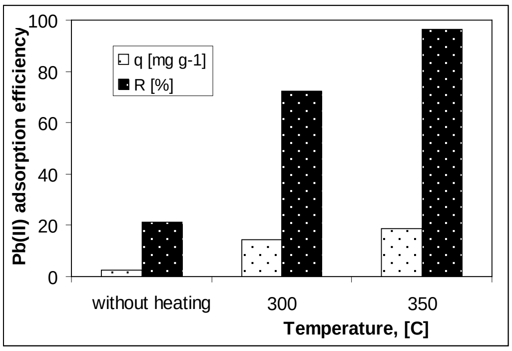

Fig. 1 – Adsorption performances of raw PET flakes and PET-clay (1:2) materials, obtained at 300 and 350°C (c_0 = 84 mg Pb(II)·L^{-1}; pH = 6.0; adsorbent dose = 4.0 g·L^{-1}; contact time = 24 h).

As can be seen from Fig. 1, the addition of clay minerals significantly improves the adsorptive performance of obtained materials compared with raw PET flakes. Thus, in the case of Pb(II) ions retention, the adsorption capacity (q, [mg·g^{-1}]) increases more than 5 times after addition of clay minerals at temperature of 300°C, while the removal percent (R, [%]) increase by more than 50%, compared with raw PET flakes. These results clearly showed that the addition of clay minerals in molten PET flakes increases the number of superficial functional groups of adsorbent materials and their porosity, characteristics that significantly influence their behaviour in adsorption processes.

On the other hand, as can be observed from Fig. 1, the melting temperature of PET flakes also influences the adsorptive performances of the obtained materials. It should be noted that the two temperatures (300 and 350°C) were chosen so as to allow the melting of PET flakes (at temperatures higher than 270°C), without starting the degradation of the polymer (at temperatures higher than 370°C) (Ciobanu *et al*., 2021).

Increasing the melting temperature of PET flakes from 300 to 350°C causes an increase in the adsorption capacity for Pb(II) ion with 30%. At the same time, the removal percent becomes greater than 96%, which means the quantitative retention of these ions from aqueous media. Therefore, to obtain these adsorbent materials, the temperature of 350°C was considered optimal.

In order to reduce heating costs, two other variants of melting PET flakes have bee taken into account, namely: (i) the addition of phenol – which partially dissolves PET flakes and their melting is easier (Ungureanu *et al*., 2018), and (ii) use of microwaves. In each case after PET flakes melting, clay minerals was added (mass ratio = 2:1), and the obtained materials then used to retain Pb(II) ions. The obtained results are summarized in Table 1.

Table 1
Adsorptive Performances of PET-Clay Materials (Mass Ratio = 2:1) Obtained in the Two Variants Mentioned Above, in the Same Experimental Conditions (see Fig. 1)

Procedure	*q*, [mg·g^{-1}]	*R*, [%]
Conventional heating	18.59	96.45
Addition of phenol (1 g)	12.84	66.91
Microwaves heating	14.30	72.31

None of the alternative variants leads to obtaining adsorbents materials that have a higher adsorption capacity for Pb(II) ions than the material obtained by conventional heating. Because of this, conventional heating at 350°C was considered the most suitable for the preparation of these adsorbent materials, and was used in all further experiments.

The second parameter considered in the experimental studies is the heating time of the mixture of PET flakes and clay minerals. In this study, the heating time was varied between 25 and 50 min, and the adsorptive performances obtained for retaining Pb(II) ions from aqueous media on each adsorbent material are illustrated in Fig. 2.

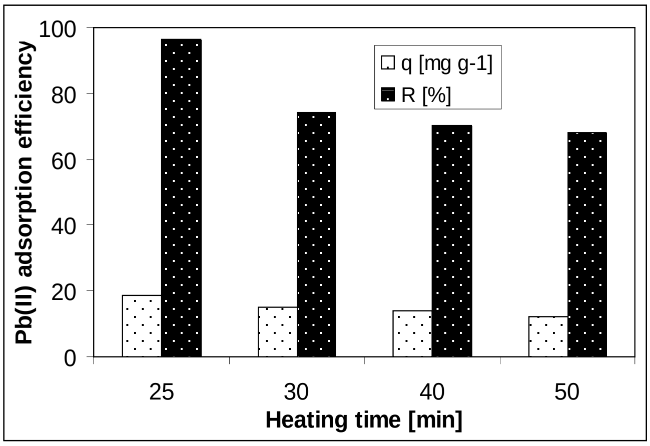

Fig. 2 – Adsorption performances of PET-clay (2:1) materials obtained at 350°C, and different heating time (c_0 = 84 mg Pb(II)·L^{-1}; pH = 6.0; adsorbent dose = 4.0 g·L^{-1}; contact time = 24 h).

Increasing the heating time from 25 to 50 min does not increase the adsorptive performance of the obtained materials, but on the contrary (see Fig. 2). Both the adsorption capacity (q, [mg·g^{-1}]) and the removal percent (R, [%]) decrease with increasing heating time. Thus, for 50 min of heating the decrease of the adsorption capacity is around of 54%, while the decrease with the removal percent is higher than 30%, compared with 25 min of heating. This variation can be explained by taking into account the flow characteristics of molten PET flakes. The higher fluidity of the PET flakes melt (which is obtained at high values of heating time) allows much easier sedimentation of the clay particles, added later. This leads to a material in which the distribution of clay particles is non-uniform, and consequently its adsorptive performance is poorer. Therefore, a heating time of 25 min was considered as optimal.

The influence of the amount of clay mineral added to obtain the adsorbent materials is another important parameter, which was considered in this study. Thus, maintaining a constant melting temperature (350°C) and heating time (25 min), at the optimal values, in experimental studies the amount of clay mineral was varied between 0.1 and 2.0 g (which correspond to a variation of mass ratio between 10:1 to 1:2). After cooling and proper processing, the obtained materials were tested in order to retain Pb(II) ions from aqueous media. The obtained experimental results are presented in Fig. 3, compared to the raw PET flakes.

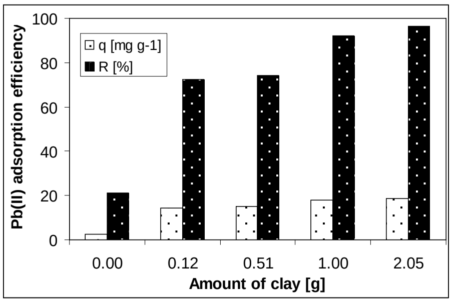

Fig. 3 – Adsorption performances of PET-clay materials obtained at 350°C and 25 min, and different amounts of clay mineral (c_0 = 84 mg Pb(II)·L^{-1}; pH = 6.0; adsorbent dose = 4.0 g·L^{-1}; contact time = 24 h).

The results shown in Fig. 3 indicates that the addition of clay mineral over molten PET flakes, significantly improves the adsorption performance of the obtained materials. Even the smallest amount of clay mineral (0.1 g) increases the adsorption capacity by more than 5 times, compared to raw PET flakes (from 2.53 to 14.30 mg·g^{-1}). On the other hand, increasing the amount of clay mineral causes an increase in adsorption capacity of the obtained materials (Fig. 3). The highest values of the adsorption parameters are reached when adding 2.0 g of clay mineral (Fig. 3), when the removal percent (R [%]) is higher than 96 %, and the retention of Pb(II) can be considered quantitative. Therefore, a mass ratio PET: clay mineral of 1:2 is the best choice, and can be considered optimal for obtaining the adsorbent materials.

Table 2
Adsorptive Performances of PET-Clay Materials (Mass Ratio = 1:2) Obtained in the Two Variants Mentioned Above, in the Same Experimental Conditions

Material	*q*, [mg·g^{-1}]	*R*, [%]
PET flakes	2.53	21.11
Clay mineral	19.79	97.11
PET-clay(1:2)-350°C-25 min	18.59	96.45

In order to highlight the applicative potential of this material (PET-clay(1:2)-350°C-25 min) in the adsorption processes of Pb(II) ions from aqueous media, the values of the adsorption capacity (q, [mg·g^{-1}]) and the removal percent (R, [%]) were compared with those obtained for the component materials (PET flakes and clay mineral). All experimental studies were performed in the same experimental conditions (c_0 = 84 mg Pb(II)·L^{-1}; pH = 6.0; adsorbent dose = 4.0 g·L^{-1}; contact time = 24 h), and the obtained results are summarized in Table 2.

It can be seen from Table 2 that the adsorption capacity and the removal percent of PET-clay(1:2)-350°C-25 min adsorbent is comparable to that of raw clay mineral, even if the amount of clay mineral in the adsorbent composition in much smaller. This means that after mixing the clay mineral with the melt of PET flakes, most of the superficial functional groups remain active and can bind Pb(II) ions from aqueous solution. Moreover, the incorporation of small clay mineral particles in the melt of PET flakes prevent their agglomeration (which is the main disadvantage in the use of clays in adsorption processes), allowing to obtain a materials with large specific surface area. But, these aspects will be detailed discussed in a further study.

3. Conclusions

In this study, PET flakes were mixed with clay mineral and melted under different experimental conditions, to obtain new materials with adsorptive potential. The adsorptive characteristics of these materials were tested for the removal of Pb(II) ions from aqueous solution. The experimental results have indicate that the best adsorptive performance is obtained for the material prepared in the following conditions: PET flakes: clay mineral mass ratio of 1:2, melting temperature of 350°C, heating time of 25 min. In this case the adsorption capacity for Pb(II) ions (18.59 $mg \cdot g^{-1}$) is over 7 times larger than of raw PET flakes (2.53 $mg \cdot g^{-1}$) and comparable to that of raw clay mineral (19.79 $mg \cdot g^{-1}$). The experimental results included in this study clearly shown that by mixing PET flakes with clay mineral, followed by melting under well-defined conditions, a material with good adsorbent properties is obtained. This new adsorbent material has the potential to be used in environmental decontamination processes.

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OBŢINEREA MATERIALELOR ADSORBANTE PET-ARGILĂ ŞI UTILIZAREA LOR PENTRU ÎNDEPĂRTAREA IONILOR DE Pb(II) DIN MEDII APOASE

(Rezumat)

Performanţele fulgilor de PET ca materiale adsorbante pentru îndepărtarea poluanţilor nocivi din soluţii apoase este destul de slabă, și prin urmare utilizarea lor în procesele de decontaminare a mediului este nesemnificativă. Cu toate acestea, creşterea cantităţilor de deşeuri de PET eliminate în mediu necesită găsirea unor oportunităţi de valorificare a acestora. În acest studiu, fulgii de PET au fost amestecaţi cu argilă şi topiţi în diferite condiţii experimentale (temperatură, timp de topire, raport de amestecare, adăugare de fenol, etc.), pentru a obţine materiale noi cu potenţial adsortiv. Metodologia utilizată pentru prepararea acestor materiale a fost discutată în detaliu, iar condiţiile experimentale au fost optimizate. De asemenea, performanțele adsorptive ale fiecărui material obţinut au fost testate pentru îndepărtarea ionilor de Pb(II) din soluţii apoase. Rezultatele experimentale au arătat că amestecarea deşeurilor de PET cu argilă (raport de amestecare 1:2) şi topirea la 350°C timp de 25 min, permite obţinerea unui material (PET-argilă(1:2)-350°C-25 min) cu o capacitate de adsorbţie pentru ionii de Pb(II) de 18,59 $mg \cdot g^{-1}$), comparabilă cu cea a argilei brute. Prin urmare, materialul PET-argilă(1:2)-350°C-25 min are potenţial de a fi utilizat ca adsorbent în procesele de decontaminare a mediului.