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# SIMPLE FUNCTIONALIZATION METHODS OF PET WASTE USING PHENOLIC COMPOUNDS

BY

**OANA IONELA UNGUREANU, ANCA MIHAELA MOCANU and LAURA BULGARIU***

"Gheorghe Asachi" Technical University of Iaşi, Romania,
"Cristofor Simionescu" Faculty of Chemical Engineering and Environmental Protection

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**Abstract.** The adsorptive performances of PET waste are very low, for most of metal ions and dyes from aqueous media, and from this reason their use as adsorbent in the environmental remediation processes, is inefficient. Increasing the adsorption capacity of PET waste involves improving of the number of superficial functional groups, and this can be generally done by the functionalization with certain chemical compounds. But most of functionalization procedure also implies the dissolving of PET waste in a suitable solvent, which is not so easy. In this study, two phenolic compounds (phenol and p-chloride-phenol) have been used for the dissolution and functionalization of PET waste, to obtain new adsorbent materials with applications in the environmental remediation. The preparation of these two adsorbent materials were detailed discusses to highlight the main advantages and disadvantages of each. Also, their adsorptive performances have been tested in case of Cu(II) ions removal from aqueous media. The experimental results have shown that the functionalization of PET waste with these organic compounds increase the adsorption efficiency of obtained materials for Cu(II) ions with more than 200% in case of PET waste functionalized with p-chloride-phenol and with more than 350% in case PET waste functionalized with phenol. This significant increase in adsorption capacity opens up new perspectives in the use of PET

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

waste as adsorbent material for the removal of heavy metal ions from aqueous media.

**Keywords:** PET waste; absorbent material; functionalization; phenolic compounds; Cu(II) ions; aqueous media.

## 1. Introduction

PET (polyethylene terephtalate) is common thermoplastic polyester which is widely used for the manufacture of food and non-food packaging, because it has a high stability over time, high chemical resistance, good transparency, low fragility, low permeability to atmospheric gases, etc., (Parra *et al*., 2004; Mendoza-Carrasco *et al*., 2016). All these characteristics have determined that many of the glass packaging to be replaced with those made of PET. But, the use of PET for the manufacture of packaging made huge amounts of PET waste to be discharged into the environment, causing many pollution problems. In addition, since the degradation of PET waste requires a very long period of time (over 180 years) (Mendoza-Carrasco *et al*., 2016), the environmental pollution can be considered a permanent one. Both, the immense amount of PET used for packaging production and the long-time of degradation have made PET waste the largest components of post-consuming plastic materials in landfills. Therefore, recycling of PET waste is the only viable solution to reduce the environmental pollution, and this alternative could have also some important economic benefits.

In this moment, the most widely used method of PET waste recycling is to convert them into fibers, through simple mechanical operations (Acar and Orbay, 2011). The obtained PET fibers, even if they have a high mechanical resistance and high chemical stability, are usually used only as a filler material, in various industrial sectors. This use does not bring significant economic benefits (the selling price of PET fibers is quite low), which makes recycling of PET waste not very attractive for companies. Therefore, finding new alternatives for the valorification of PET waste by transforming them into high-value added products, will make recycling more attractive, and will contribute to improving the quality of the environment.

It is well known that the pollution of environment with heavy metal ions is another pressing issue of our days (Donmez *et al*., 1999; Chojnacka, 2010; Cechinel *et al*., 2018). Uncontrolled industrial wastewater discharges or incomplete treated wastewater discharges into the environment are considered the main sources of heavy metal pollution worldwide (Cherubini *et al*., 2009; De Gisi *et al*., 2016). Therefore, the development of an appropriate method that can be used to remove heavy metal ions from industrial effluents remains open to research.

Many studies from literature (Farooq *et al*., 2010; Gautam *et al*., 2014; De Gisi *et al*., 2016) have reported that the adsorption of heavy metal ions from aqueous media on various low-cost materials could solve this problem. However, the applicability of the adsorption at large scale depends both on the efficiency of heavy metals removal and on the costs of adsorbent material preparation (Fu and Wang, 2011).

Under these conditions, the possible use of PET waste as an adsorbent material for the removal of heavy metal ions will allow for a new possibility to exploit this waste and will ensure the very low cost of the adsorbent material. The major problem remains its efficiency in the adsorption processes, as our previous studies (Cojocariu *et al*., 2017; Cojocariu *et al*., 2018) have shown that PET waste has a very low affinity for both heavy metal ions and organic dyes in the aqueous solution. In addition, the increase of the number of superficial functional groups of PET waste by functionalization, involve its dissolving in a suitable solvent, which is also not easy to achieve.

In this study, two phenolic compounds (phenol and p-chloride-phenol) have been used for the dissolution and functionalization of PET waste, to obtain new adsorbent materials with applications in the environmental remediation. The preparation of these two adsorbent materials were detailed discusses to highlight the main advantages and disadvantages of each. Also, their adsorptive performances have been tested in case of Cu(II) ions removal from aqueous media.

## 2. Materials and Methods

### 2.1. Materials

PET waste was obtained from recycling PET bottles (purchased from GreenFiber International Company Iaşi, Romania) and was used as received. The organic reagents, phenol and p-chloride-phenol, were purchased form Chemical Company, and were used without further purifications. Stock solution of Cu(II) ions ($10^{-2}$ mol·$L^{-1}$) was obtained by dissolving a certain quantity of copper sulphate (purchased from Chemical Company, Iași) in distilled water. The working solutions were obtained by diluting certain volume of stock solution with distilled water. All reagents used for experiments were of analytical degree.

### 2.2. Preparation of Adsorbent Materials

The dissolution and functionalization of PET waste was performed using two phenolic compounds: phenol and p-chloride-phenol. Thus 3 g of PET waste was mixed with 18 mL of phenol and p-chloride-phenol (previously melted) in a Berzelius glass, at 60-70°C for 1.5 h. The obtained liquid mixtures (PET+phenol and PET+p-chloride-phenol) were spread on a glass plate and allowed to solidify at room temperature. After solidification, the obtained materials were ground in a blender, until uniform granulation, and stored in desiccators for further use.

### 2.3. Adsorption Experiments

The adsorption experiments were performed in batch systems, mixing a constant amount of functionalized PET waste (0.2 g) with volume of 25 mL of known Cu(II) ions concentration, in 150 mL Erlenmeyer flasks, with intermittent stirring. After 24 h, the samples were filtered, and Cu(II) ions concentration was determined spectrophotometricaly (VIS Spectrophotometer YA1407020 model) with rubeanic acid ($\lambda$ = 390 nm; 1 cm glass cells, against blank solution), using a prepared calibration graph (Dean, 1995).

The efficiency of functionalized PET waste adsorbents in the removal of Cu(II) ions from aqueous solution was evaluated using the following parameters: adsorption capacity (q, [$mg \cdot g^{-1}$]) and removal percent (R, [%]):

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

$$R = \frac{c_0 - c}{c_0} \cdot 100 \tag{2}$$

where: $c_0$ is the initial Cu(II) ions concentration in solution, [$mg \cdot L^{-1}$], $c$ is the equilibrium concentration of Cu(II) ions in the solution, [$mg \cdot L^{-1}$], $V$ is volume of solution, [mL], and $m$ is the mass of functionalized PET waste adsorbents, [g].

## 3. Results and Discussions

### 3.1. Preparation of Functionalized PET Waste Adsorbents

As it was mentioned in the previous paragraph, the adsorbents materials were obtained by treating the PET waste with phenolic compounds. Two phenolic compounds were used in this study for the dissolution and functionalization of PET waste, namely phenol and p-chloride-phenol, and the experimental procedure is illustrated in Fig. 1.

As can be observed from Fig. 1, the experimental functionalization procedure of PET waste is simple and requires only few elementary steps, which means that the obtained adsorbent materials can still be included in the low-cost materials category. The phenolic compounds (phenol and p-chloride-phenol) are melting easily at low temperature (50-60°C), and are added to the PET waste. After 1.5 h of heating, the liquids mixtures are solidified at room temperature on glass plates. The obtained solid materials can be easily ground and used as adsorbents. The main experimental advantages and disadvantages of the functionalization of PET waste with these two phenolic compounds are summarized in Table 1.

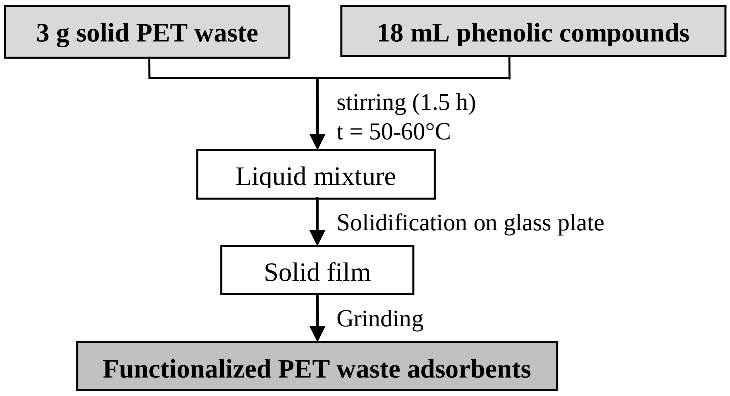



Fig. 1 − Experimental procedure used for dissolution and functionalization of PET waste with phenolic compounds.

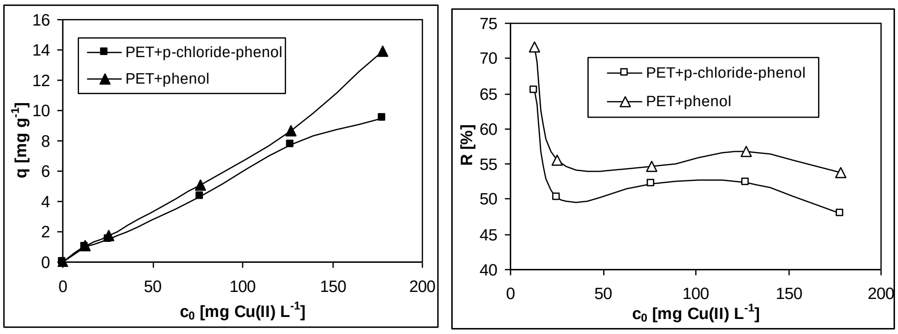
**Table 1**
*Experimental Advantages and Disadvantages of Functionalization Procedures of PET Waste with Phenol and p-Chloride-Phenol*

| | phenol | p-chloride-phenol |
|---|---|---|
| Advantages | - short work time (2 h)<br>- short time of solidification (20-30 min)<br>- easy grinding<br>- high stability over time (at least 4 weeks) | - short work time (2 h)<br>- the obtained material has a weak smell of phenol<br>- easy solubilisation of PET |
| Disadvantages | - the obtained material has a strong smell of phenol<br>- PET dissolution requires a longer heating time | - long-time of solidification (10-15 days)<br>- difficult grinding<br>- lower stability over time |

Considering all the experimental advantages and disadvantages presented in Table 1, it can be said that the functionalization of PET waste with phenol allows the obtaining of an adsorbent materials having better preparation characteristics than the material obtained in case of PET waste functionalization with p-chloride-phenol. However, the strong smell of phenol of this adsorbent represents the main drawback that needs to be minimized before being used in environmental bioremediation processes.

### 3.2. Adsorptive Characteristics of Functionalized PET Waste Materials

The obtained adsorbent materials, PET waste functionalized with phenol and PET functionalized with p-chloride-phenol, have been used for the removal of Cu(II) ions from aqueous solution. In the adsorption experiments, 0.2 g of adsorbent was mixed with 25 mL of Cu(II) ions solution, with different initial concentration (12.71-177.89 mg·L$^{-1}$), for 24 h and at room temperature (26±1.0°C). The adsorption capacities and the values of removal percents, calculated from experimental data, are presented in Fig. 2.




*a* *b*

Fig. 2 − Adsorption capacities (*a*) and removal percents (*b*) obtained in case of Cu(II) ions adsorption on functionalized PET waste with phenolic compounds.

As it can be observed from Fig. 2, the adsorption capacity of both adsorbent materials increases with increasing of initial Cu(II) ions concentration over the whole studied concentration interval. This means that retention of Cu(II) ions on these adsorbent materials takes place through specific interactions, and the absence of a saturation plateau (Fig. 2*a*) shows that even at the highest initial Cu(II) ion concentration, not all the functional groups are occupied. In addition, the adsorbent obtained from PET waste funtionalized with phenol has better adsorption efficiency for Cu(II) ions than the adsorbent obtained from PET waste functionalized with p-chloride-phenol (Fig. 2*b*). For example, at highest initial Cu(II) ions concentration (177.89 mg·L$^{-1}$) the adsorption capacity of PET+phenol adsorbent was of 13.87 mg·g$^{-1}$, in comparison with 9.53 mg·g$^{-1}$ obtained in case of PET+p-chloride-phenol adsorbent.

In order to quantify the performance of the two adsorbents for Cu(II) ions adsorption, the experimental data has been modelled using Langmuir isotherm model. The Langmuir isotherm model assumes that the adsorption process occurs step by step, trough specific interactions, until monolayer coverage is formed, at the surface of adsorbent particles (Rangabhashiyam *et al.*, 2014). The linear equation of the Langmuir isotherm model can be written as:

$$\frac{1}{q} = \frac{1}{q_{\max}} + \frac{1}{q_{\max} \cdot K_L} \cdot \frac{1}{c} \quad (3)$$

where: $q_{max}$ is the maximum adsorption capacity, [mg·g$^{-1}$]; $c$ is Cu(II) ions concentration at equilibrium, [mg·L$^{-1}$] and $K_L$ is the Langmuir constant, related to the energy of adsorption process, [L·g$^{-1}$].

The linear representation of Langmuir isotherm model for the Cu(II) ions adsorption on the two adsorbents obtained by PET functionalization with phenolic compounds are illustrated in Fig. 3, and the isotherm parameters calculated from the slopes and intercepts of these linear representations are summarized in Table 2.

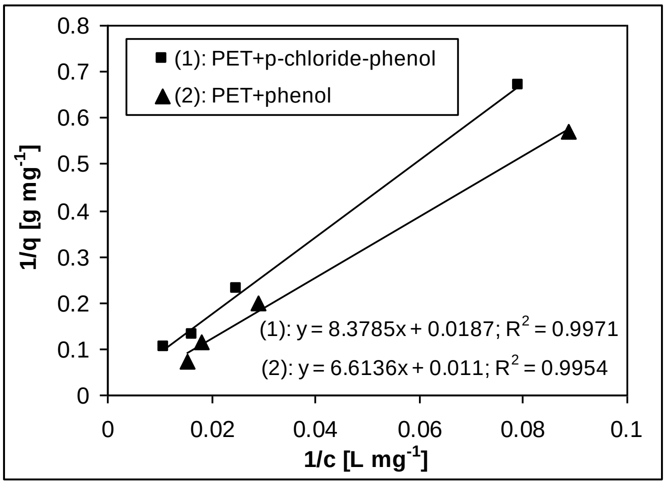



Fig. 3 − Linear representation of the Langmuir isotherm model in case of Cu(II) ions adsorption on functionalized PET waste with phenolic compounds.

**Table 2**
*Langmuir Isotherm Parameters for Cu(II) Ions Adsorption on Functionalized PET Waste with Phenolic Compounds*

| *Parameters* | PET+ phenol | PET+p-chloride-phenol |
|---|---|---|
| $R^2$ | 0.9954 | 0.9971 |
| $q_{max}$, [mg·g$^{-1}$] | 90.91 | 53.48 |
| $K_L$, [L·g$^{-1}$] | 0.07275 | 0.1566 |

As it can be observed from Fig. 3, the Langmuir isotherm model describes very well the experimental results obtained in case of Cu(II) ions adsorption on both adsorbent materials ($R^2$ > 0.99). Therefore, it can be said that the adsorption of Cu(II) ions onto functionalized PET waste with phenolic compounds takes place at the exterior surface of adsorbents, until their particles are completely covered by metal ions. As expected, the amount of Cu(II) ions required for the complete coverage is higher in case of PET waste functionalized with phenol than in case of PET waste functionalized with p-chloride-phenol (Table 2). This parameter can be correlated with the number and availability of adsorption sites, and indicates that the functionalization of PET waste with phenol allows the obtaining of an adsorbent with higher number of superficial functional groups and /or with higher specific surface. In order to prove these hypotheses, additional experiments must be carried out to characterize the adsorbent materials, and these will be discussed in further studies.

On the other hand, the value of Langmuir constant ($K_L$) obtained in case of PET waste functionalization with phenol is over 20 times smaller than that obtained in case of PET waste functionalization with p-chloride-phenol (Table 2). This suggests that for the first adsorbent the energy required in the adsorption process is lower and that the superficial adsorption sites are more available to interact with Cu(II) ions from aqueous media.

### 3.3. Evaluation of Adsorptive Performances Functionalized PET Waste

As we have shown in the first paragraph, the functionalization of PET waste with phenolic compounds requires a simple experimental procedure, and therefore the obtained adsorbent materials can still be considered as low-cost materials. In order to highlight the increasing of adsorption capacity after these simple functionalization procedures, the values of adsorption capacities obtained for Cu(II) ions adsorption on functionalized PET waste with phenolic compounds have been compared with those obtained in case of un-functionalized PET waste, for several initial concentrations of Cu(II) ions (Fig. 4).

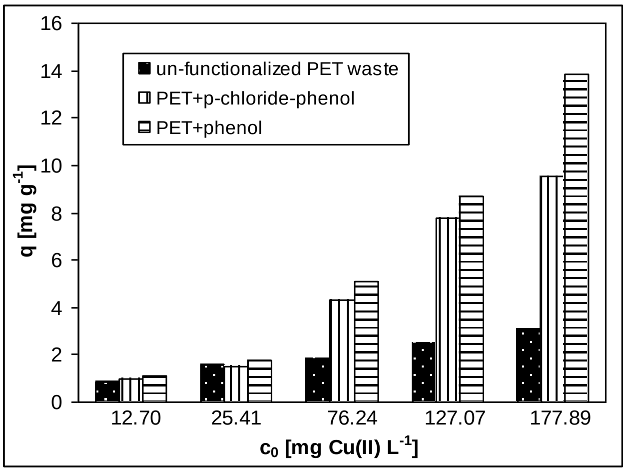



Fig. 4 − Adsorption capacities obtained in case of Cu(II) ions adsorption on un-functionalized PET waste and functionalized PET waste with phenolic compounds.

It can be observed from Fig. 4 that the functionalization of PET waste with phenolic compounds has as result the increasing of adsorption capacity for Cu(II) ions, at all values of initial concentration. Even if at low initial Cu(II) ions concentration (12.71 mg·L$^{-1}$), this increase is not so spectacular (15.66% in case of PET waste functionalized with p-chloride phenol and 34.94% in case of PET waste functionalized with phenol), at high initial Cu(II) ions concentrations, it becomes more significant (217.11% in case of PET waste functionalized with p-chloride phenol and 356.25% in case of PET waste functionalized with phenol). The obtained values of the adsorption capacities open up new perspectives in the use of PET waste as adsorbent material for the removal of heavy metal ions from aqueous media, and some of them will be analyzed in our further research.

## 4. Conclusions

In order to improve the adsorptive performances of PET waste two phenolic compounds (phenol and p-chloride-phenol) have been used for the dissolution and functionalization of PET waste. The experimental procedure is simple and requires only few elementary steps, which makes that the obtained adsorbent materials can still be included in the low-cost materials category. Also, the adsorptive performances of PET waste functionalized with phenol and PET waste functionalized with p-chloride-phenol, have been used for the removal of Cu(II) ions from aqueous solution. The experimental results have shown that the PET waste funtionalized with phenol has better adsorption efficiency for Cu(II) ions than the adsorbent obtained from PET waste functionalized with p-chloride-phenol. For an initial Cu(II) ions concentration of 177.89 mg·L$^{-1}$, the experimental adsorption capacities were 13.87 mg·g$^{-1}$ for PET+phenol adsorbent, and 9.53 mg·g$^{-1}$ PET+p-chloride-phenol adsorbent, respectively. In addition, compared with un-functionalized PET waste, an increase of adsorption capacity with 217.11% in case of PET waste functionalized with p-chloride phenol and 356.25% in case of PET waste functionalized with phenol respectively was obtained. This significant increase in adsorption capacity opens up new perspectives in the use of PET waste as adsorbent material for the removal of heavy metal ions from aqueous media.

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## REFERENCES

Acar I., Orbay M., *Aminoglycolysis of Waste Poly(Ethylene Terephthalate)with Diethanolamine and Evaluation of the Products as Polyurethane Surface Coating Materials*, Polym. Eng. Sci., **51**, 746-754 (2011).

Cechinel M.A.P., Mayer D.A., Mazur L.P., Silva L.G.M., Girardi A., Vilar V.J.P., de Souza A.A.U., de Souza S.M.A.G.U., *Application of Ecofriendly Cation Exchangers (Gracilaria Caudata and Gracilaria Cervicornis) for Metal Ions Separation and Recovery from a Synthetic Petrochemical Wastewater: Batch and Fixed Bed Studies*, J. Clean. Prod., **172**, 1928-1945 (2018).

Cherubini F., Bargigli S., Ulgiati S., *Life Cycle Assessment (LCA) of Waste Management Strategies: Landfilling, Sorting Plant and Incineration*, Energy, **34**, 12, 2116-2123 (2009).

Chojnacka K., *Biosorption and Bioaccumulation – The Prospects for Practical Applications*, Environ. Int., **36**, 299-307 (2010).

Cojocariu B., Mocanu A.M., Bulgariu D., Nacu G., Bulgariu L., *Equilibrium Isotherm Study of Metal Ions Adsorption on PET Recycled Fibers*, Proceeding of the 6th IEEE International Conference on E-Health and Bioengineering - EHB 2017, 85-88 (2017).

Cojocariu B., Mocanu A.M., Nacu G., Bulgariu L., *Possible Utilization of PET Waste as Adsorbent for Orange G Dye Removal from Aqueous Media*, Desalin. Water Treat., **104**, 338-345 (2018).

Dean J.A., *Analytical Chemistry Handbook*, 3rd Ed. New York, USA, McGrow-Hill Inc. (1995).

De Gisi S., Lofrano G., Grassi M., Notarnicola M., *Characteristics and Adsorption Capacities of Low-Cost Sorbents for Wastewater Treatment: A Review*, Sustain. Mater. Technol., **9**, 10-40 (2016).

Donmez G., Aksu Z., Ozturk A., Kutsal T., *A Comparative Study on Heavy Metal Biosorption Characteristics of Some Algae*, Process Biochem., **34**, 885-892 (1999).

Farooq U., Kozinski J.A., Khan M.A., Athat M., *Biosorption of Heavy Metal Ions Using Wheat Based Biosorbents – A Review of the Recent Literature*, Biores. Technol., **101**, 5043-5053 (2010).

Fu F., Wang Q., *Removal of Heavy Metal Ions from Wastewaters: A Review*, J. Environ. Manag., **92**, 407-418 (2011).

Gautam R.K., Mudhoo A., Lofrano G., Chattopadhyay M.C., *Biomass-Derived Biosorbents for Metal Ions Sequestration: Adsorbent Modification and Activation Methods and Adsorbent Regeneration*, J. Environ. Chem. Eng., **2**, 239-259 (2014).

Mendoza-Carrasco R., Cuerda-Correa E.M., Alexandre-Franco M.F., Fernandez-Gonzalez C., Gomez-Serrano V., *Preparation of High-Quality Activated Carbon from Polyethyleneterephthalate (PET) Bottle Waste. Its Use in the Removal of Pollutants in Aqueous Solution*, J. Environ. Manag., **181**, 522-535 (2016).

Parra J., Ania C., Arenillas A., Rubiera F., Palacios J., Pis J., *Textural Development and Hydrogen Adsorption of Carbon Materials from PET Waste*, J. Alloys Compoun., **379**, 280-289 (2004).

Rangabhashiyam S., Anu N., Nandagopal Giri M.S., Selvaraju N., *Relevance of Isotherm Models in Biosorption of Pollutants by Agricultural Byproducts*, J. Environ. Chem. Eng., **2**, 398-414 (2014).

# METODE SIMPLE DE FUNCŢIONALIZARE A DEŞEURILOR DE PET UTILIZÂND COMPUŞI FENOLICI

(Rezumat)

Performanțele adsorbtive ale deșeurilor PET sunt foarte scăzute, pentru majoritatea ionilor metalici și coloranților din medii apoase și din acest motiv utilizarea lor ca material adsorbant în procesele de remediere a mediului este ineficientă. Creșterea capacității de adsorbție a deșeurilor PET implică creșterea numărului de grupări funcționale superficiale, iar acest lucru se poate face în general prin funcționalizarea cu anumiți compuși chimici. Dar majoritatea procedurilor de funcționalizare implică și dizolvarea deșeurilor de PET într-un solvent adecvat, ceea ce nu este foarte ușor. În acest studiu, pentru dizolvarea și funcționalizarea deșeurilor PET s-au utilizat doi compuși fenolici (fenol și p-clor-fenol) pentru a obține noi materiale adsorbante cu aplicații în remedierea mediului. Prepararea acestor două materiale adsorbante este discutată în detaliu pentru a evidenția principalele avantaje și dezavantaje pentru fiecare caz în parte. De asemenea, performanțele adsorbante ale materialelor obținute au fost testate în cazul reținerii ionilor de Cu (II) din medii apoase. Rezultatele experimentale au arătat că funcționalizarea deșeurilor PET cu acești compuși organici mărește eficiența adsorbției a materialelor obținute pentru ionii Cu (II) cu peste 200% în cazul deșeurilor PET funcționalizate cu p-clor-fenol și cu peste 350% în cazul deșeurilor PET funcționalizate cu fenol. Această creștere semnificativă a capacității de adsorbție deschide noi perspective în utilizarea deșeurilor PET ca materiale adsorbante pentru îndepărtarea ionilor de metale grele din medii apoase.