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FUNCTIONALIZATION OF PET WASTE USING PHENOLIC COMPOUNDS

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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. 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 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*

Keywords: PET waste, absorbent material, functionalization, phenolic compounds, aqueous media

1. Introduction

Polymers are substances with very large molecular masses derived from a large number of repeated units. There are both natural polymers and synthetic polymers. Synthetic polymers are commercially available in a wide variety and have a wide range of properties and uses. Such a synthetic polymer is polyethylene terephthalate (PET) having multiple utilities due to its excellent properties [1]. It is well known that plastic products are extremelly difficult to be degraded naturally, although their applicability, stability and durability have made them so popular. There are, however, four ways in which plastics can naturally degrade (photodegradation, thermo-oxidative degradation, hydrolytic degradation and biodegradation by microorganisms), but the processes take a long time. Polymers are widely used materials in various fields because of their valuable properties such as good mechanical properties, low density, low cost and easeness of processing. Total production of plastics is over 230 million tonnes per year,

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which will reach 400 million tonnes in 2020 on the basis of a more conservative anual growth of about 5% [2].

PET is a 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. [3, 4]. All these characteristics have determined that 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) [3], 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.

2. Use of recycled PET

It is well known that PET is a non-degradable plastic under normal conditions, so that complicated and costly procedures are required for PET to biodegrade. The postconsumer-PET (POSTC-PET) recycling industry started as a result of environmental pressure to improve waste management. Recycling processes are the best way to economically reduce PET waste. First effort to recycle POSTC-PET bottles in the world was in 1977 [5]. The recycling process can be divided into two categories: physical and chemical. The first is achieved by thermal extrusion and pelletisation, and then the pellets obtained can be remodeled. The second category includes many chemical treatments, e.g. glycolysis, hydrolysis, methanolysis, alcoholysis, aminolysis and ammonolysis; these techniques are established based on the decomposition of PET into depolymerized oligomers [6].

Petcore, the European trade association that promotes the collection and recycling of post-consumer PET, reported that 1.68 million tons of PET bottles were collected in Europe in 2012, of which about 1.18 million tonnes of PET flakes, used in several applications, as shown in Fig. 1. Various applications also include the use of PET flakes for the production of concrete and other building materials. In this respect, high-quality technical assessments have been developed over the years. For example, Frigione (2010) has developed a study in which a 5% substitution test in the concrete of a fine aggregate (natural sand) with equal weight of PET aggregates made from waste from unwrapped PET bottles was evaluated [7].

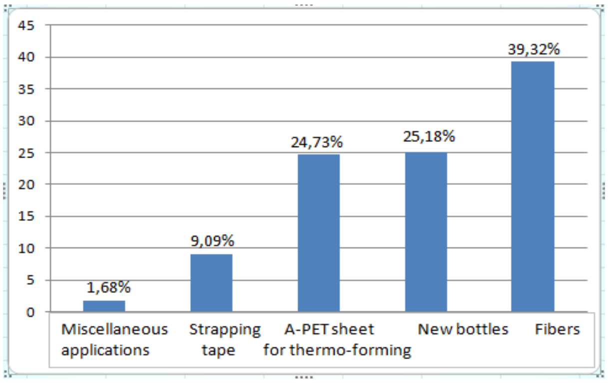


Fig. 1. The most common applications of R-PET flakes [8]

2.1. PET into fibers

Polyethylene terephthalate (PET), known in the textile industry as "polyester", is considered one of the most important thermoplastic polyesters. PET fiber originally patented by DuPont, dominates over 50% of the world's synthetic fiber market. In 2008, the total world production size of PET was estimated at 64 400 kt. PET fibres and PET bottles represented 63.5% and 30.3% respectively of the bulk of total world production, while the production of polyester film and engineering resin was about 6.2%. Since PET fibers and bottles became very important for daily lifespan, their production and consumption were developed continuously. PET recycling was mentioned first in 1977, and then many studies were devoted to the development of PET recycling methods. Most of the recycled PET was transformed into fiber as shown in Fig. 2 and based on the Noone report [9].

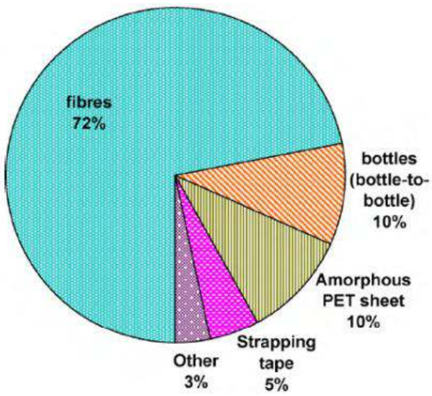


Fig. 2. Applications of recycled PET flakes based on Noone 2008 data [9].

2.2. Reinforced composites

An important application of the recycled PET to be considered is the production of reinforced composites. The use of polymer fiber reinforcement through short fibers has increased rapidly. The first polymeric composites using chopped glass fibers are based on unsaturated polyesters and epoxy resins, but also thermoplastic materials have obtained acceptance. In the literature, there are numerous studies on short fiber reinforced plastics such as polyethylene terephthalate (PET), polycarbonate and polyamides [10].

Based on the consumption of R-PET fibers and flakes, a study reported the use of R-PET fibers for panel manufacturing, which led to the consumption of recycled PET fibers without compromising the durability of the final product [8]. Most research shows that plastic adhesion affects workability, compressive strength, modulus of elasticity, tensile strength, thermal conductivity, and slightly increases resistance to abrasion and bending.

2.3. PET wastes as adsorbent materials

The absorption term refers to the accumulation of a substance at the interface between two phases. Adsorption can be classified into two types: chemical and physical adsorption. Chemical adsorption or chemosorption occurs by the formation of strong chemical associations between molecules or ions on the adsorbent surface. Physical adsorption is characterized by van der Waals weak bonds between adsorbent and sorbat and thus are reversible in most cases [11]. This process provides an attractive alternative for treating polluted water, especially if the sorbent is inexpensive and does not require an additional pretreatment before it is applied. With regard to the purpose of environmental rehabilitation, adsorption techniques are widely used to remove certain classes of chemical contaminants from water.

It is well known that the pollution of environment with heavy metal ions is another pressing issue of this days [12, 13]. Uncontrolled industrial wastewater discharges or incomplete treated wastewater discharges into the environment are considered the main sources of heavy metal pollution worldwide [14, 15]. Therefore, the development of an appropriate method that can be used to remove heavy metal ions from industrial effluents remains open to research.

There are many factors that affect the adsorption of heavy metal ions and dyes. These factors include the pH of the solution, the adsorbent dose, the contact time, the concentration of the heavy metal / dye initial and the temperature [16]. Optimization of these conditions can significantly help the removal of heavy metal ions / dyes.

Acar et al. [17] investigated the use of the PET waste depolymerization products obtained by the aminoglycolysis process with diethylamine and ethylene glycol to remove the cationic dyes (Brilliant Green and Safranin T) from aqueous solutions [17]. They concluded that the four PET depolymerization products obtained due to the different functional groups they possess may be preferred as an alternative adsorbent. El Essawy prepared graphene from PET bottles by simple, reproducible and accessible methods, involving the thermal decomposition of PET waste in a closed system under autogenous pressure [18].

Therefore, searching for new ways to capitalize PET waste and avoiding hazardous materials have become interesting both theoretically and practically. For example, Wang reported the possibility to obtain chelate fibers prepared with PET fiber for the rapid removal of heavy metal ions from water [19]. 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 have shown [20, 21], since 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.

3. Preparation of adsorbent materials

PET wastes were obtained from recycling PET bottles (purchased from GreenFiber International Company Iasi, Romania) and were used as such. The organic reagents, phenol and p-chloride-phenol were purchased form Chemical Company, and were used without further purifications.

The dissolution and functionalization of PET waste was accomplished using two phenolic compounds: phenol and p- chloride-phenol. Therefore, 3 g of PET waste was mixed with 18 mL of phenol and p- chloride-phenol (previously melted) in a Berzelius at 60-70 °C for 1.5 hours. 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 materials obtained were ground in a blender until uniform granulation.

The main experimental advantages and disadvantages of the functionalization of PET waste with these two phenolic compounds are summarized in Table 1.

Table 1. Experimental advantages and disadvantages of functionalization procedures of PET waste with phenol and p-chloride-phenol

	Advantages	*Disadvantages*
1. phenol	- short working time (2 hours) - short time of solidification (20-30 min) - high stability over time (at least 4 weeks)	- the obtained material has a strong smell of phenol - PET dissolution requires a longer heating time
2. p-chloride-phenol	- short working time (2 hours) - easy solubilisation of PET	- long time of solidification (10-15 days) - lower stability over time - the obtained material has a weak smell of phenol

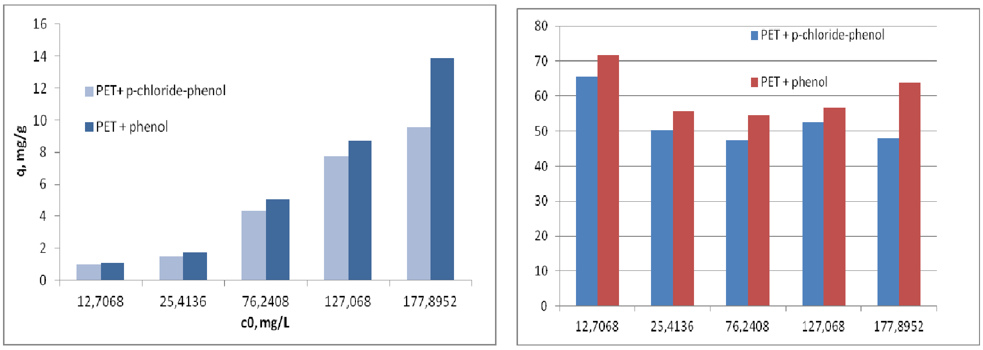
Adsorption experiments were carried out by mixing a constant amount of functional PET waste (0.2 g) with a known volume of 25 mL of known Cu (II) concentration in Erlenmeyer glass with intermittent agitation. After 24 hours, the samples were filtered and the concentration of Cu (II) ions was determined spectrophotometrically. The efficiency of PET waste adsorbents functionalized to remove Cu (II) ions from the aqueous solution was evaluated using the following parameters: adsorption capacity (q, [mg / g]) and removal percentage (R, [%]):

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

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

where: c_0 is the initial concentration of Cu (II) ions in solution [mg / l], c is (mL) and m is the mass of adsorbents of functionalized PET waste, [g].

The obtained adsorbent materials, PET waste functionalized with phenol and p-chloride-phenol were used to remove Cu (II) ions from the aqueous solution. In the adsorption experiments, 0.2 g of adsorbent was mixed with 25 mL of Cu (II) ion solution with a different initial concentration (12.71 - 177.89 mg / L) for 24 hours and at room temperature (26 ± 1.0 °C). Absorption capacities and percent removal rates, calculated from experimental data, are shown in Fig. 3.



(a) (b)

Fig. 3. Adsorption capacities (a) and removal percents (b) obtained in case of Cu(II) ions adsorption on functionalized PET waste with phenolic compounds

As can be seen from Fig. 3, the adsorption capacity of both adsorbents increases, as the initial concentration of Cu (II) ions increases over the entire concentration range studied. In addition, the adsorbent obtained from PET functionalized with phenol was effectively better for the adsorption of Cu (II) ions than the adsorbent obtained from PET waste functionalized with p- chloride-phenol (Fig. 3b) [22].

Table 2. Removal percents obtained in case of Cu(II) ions adsorption on functionalized PET waste with phenolic compounds and untreated PET waste

c_{Cu}, *mg/L*	*% R PET*	*% R PET + Phenol / % R PET + p-chloride-phenol*	*% ΔR*
25.42	13.63	55.63 / 50.25	75.51 / 72.88
76.24	10.11	54.64 / 47.26	81.45 / 78.6
127.07	10.11	56.72 / 52.45	82.22 / 80.72

As can be seen from Table 2, the removal percent increases with the increase of the concentration of Cu (II) in the solution. Also, the removal percentage is higher for the adsorbent obtained from PET + phenol than for the adsorbent obtained from PET + p-chloride – phenol.

The obtained values open new perspectives on the use of PET waste as adsorbent materials for removing heavy metal ions from aqueous media.

Conclusions

Due to the large-scale use of PET for packaging, huge amounts of PET waste are discharged into the environment, causing many pollution problems. In addition, because the degradation of PET waste requires a very long period of time, environmental pollution can be considered a permanent one. The immense amount of PET used for packaging production and long degradation made PET waste the largest components of post-consuming plastic materials in landfills.

At this time, the most widespread method of recycling PET was their transformation into fibers through simple mechanical operations. PET fibers obtained, even if they have high mechanical strength and high chemical stability, are usually only used as filler in different industrial sectors. Therefore, finding new alternatives for recycling PET waste by turning them into high added-value products will make recycling more attractive and will help improve the quality of the environment.

It is well known that environmental pollution with heavy metal ions is another serious problem of our day. Under these circumstances, the possible use of PET waste as an adsorbent material to remove heavy metal ions will allow a new possibility to exploit this waste and will ensure the very low cost of the adsorbent material.

To improve the adsorptive performance of PET waste, two phenolic compounds (phenol and p- chloride-phenol) were used to dissolve and function PET waste. The experimental procedure is simple and requires only a few elementary steps, making the adsorbent materials available as low-cost materials.

Adsorbent performances of PET waste functionalized with phenol waste and p-chloride-phenol functionalized PET were used to remove Cu (II) ions from aqueous solution. Experimental results have shown that phenol-functionalized PET waste has a better adsorption efficiency for Cu (II) ions than adsorbent obtained from p-chloride-phenol functionalized PET waste.

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