DEGRADED PET FOR THE REMOVAL OF METAL IONS FROM AQUEOUS SOLUTION

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ABSTRACT

Poly(ethylene terephthalate) waste was degraded by glycolysis in order to obtain low molecular weight molecules for the batch removal of Cd(II), Cr(III), Cu(II), Ni(II), and Pb(II) from aqueous solution. The degradation product was characterized by IR, ¹H-NMR, DSC, and GPC, being identified as bis(2-hydroxy ethyl) terephthalate (BHET). The results show that metal absorption follows the order Pb(II)>Cd(II)>Ni(II)>Cu(II)>Cr(III). Degraded PET presented an affinity to remove over 75% of lead in solution at pH 4 and 5 and cadmium over 70% at pH 6. IR spectroscopy and DSC evidenced the presence of metal ions in the structure of the material.

Keywords: adsorption, metal ions, PET degradation, removal.

INTRODUCTION

Pollution caused by the presence of heavy metal ions is of great importance because some of these species have high toxicity at low concentrations. Toxic metals as lead, chromium, copper, nickel, cadmium, and zinc are released into the water mainly through industrial activities¹.

Different materials such as homopolymers and modified polymers² including polypropylene³, polyacrylic acid⁴, polyacrylamide⁵, polyurethane⁶, polyethylene terephthalate^{7,8} among others, have been studied to reduce the amount of heavy metals in aqueous solution.

PET, principally as fibers, has been used as a stripping agent for metal ions. It has also been grafted with different molecules like itaconic acid/acrylamide⁷, acrylic acid⁹, methacrylic acid¹⁰, acrylic acid/acrylamide¹¹, acrylonitrile¹², hydroxylamine and vinyl pyridine¹³ in order to increase its adsorption capacity towards metal ions. Nevertheless, if virgin PET is used for this purpose new waste is generated and does not contribute to solve the global plastic accumulation problem.

In view of the fact that high amounts of PET bottles become waste, different recycling and chemical degrading processes have been studied in order to control this situation. Chemical degradation of PET produces low molecular weight compounds with functional groups taken from the nucleophilic agent used in the chemical process, for example, hydroxyl group in glycolysis or amine group in aminolysis¹⁴. These degradation products have been used as precursors of new products such as fatty amide derivate in textile processes¹⁵, unsaturated polyester resins¹⁶, epoxy resin hardeners¹⁷, and polyurethanes¹⁸. Due to the nature of the generated functional groups, products of PET chemical recycling can be considered as an alternative for the removal of metal ions from water and consequently help resolve many problems caused by plastic accumulation^{19,20}.

The aim of this manuscript is to study the removal of Cd(II), Cr(III), Cu(II), Ni(II), and Pb(II) from aqueous solution, at various pH values and metal ion concentration using water-insoluble products of PET glycolysis.

Materials and equipment

Zinc acetate, copper, nickel, cadmium, chromium and lead nitrates, ethyleneglycol, nitric acid and NaOH were purchased from Sigma Aldrich and used without further purification. Bottle grade PET was rinsed with detergent solution at room temperature for 1 h and then washed with water. Washed PET was filtered and dried at 70 °C for 24 h.

Infrared analysis was performed using a Magna Nicolet IR-550 spectrometer coupled with ATR. The Nuclear Magnetic Resonance spectrum of the samples was obtained using a Bruker Advance III 500 Plus spectrometer, operating at 500 MHz in deuterated chloroform. A Perkin Elmer Sapphire Differential Scanning Calorimeter was used to determine the thermal behavior of the samples at a heating rate of 20 °C/min from 10 to 350 °C under nitrogen atmosphere. The molecular weight was determined through Gel Permeation Chromatography (GPC) in an Agilent HP 1100 chromatograph, using THF

as mobile phase; PET and degradation product samples were dissolved in a mixture of 1,1,1,3,3,3-hexafluoroisopropanol and CHCl₃. The not retained metal ion concentration was determined using a Unicam Solaar5 MS Series Absorption Atomic Spectrophotometer.

EXPERIMENTAL

To carry out the degradation reaction, 5 g of PET were mixed with 27 mL (30 g) of ethyleneglycol and 250 mg of zinc acetate as a catalyst. The reaction mixture was heated at 180°C, under magnetic stirring for 6 h, then 50 mL of distilled water were added and the mixture was left to cool down in an ice bath to precipitate water-insoluble product. The product was filtered, dried and then characterized by IR, ¹H-NMR, DSC, and GPC. The degradation reaction is presented in Scheme 1.

Scheme 1. Chemical degradation of PET using ethyleneglycol.

Removal of metal ions was investigated under batch equilibrium conditions. To determine the effect of pH, 20 mL of 25 mg/L aqueous solution of the different metal ions were treated with 50 mg of degraded PET at different pH values (3-7) adjusted with dilute HNO₃ or NaOH. To analyze the effect of the initial concentration at pH 5, 20 mL of the metal ion solutions at different concentrations (5-100 mg/L) were placed in a tube with 50 mg of degraded PET. All the experiments were shaken at 140 rpm at 25 °C during 2h. The solutions were filtered in order to separate degraded PET from the solution and the metal ion concentration in the aqueous phase was determined using AAS. The metal uptake ratio was calculated according to Eq. 1:

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \quad \text{Equation (1)}$$

Where % R is the percentage of the uptake metal ion, C_i is the initial concentration of the metal ion solution and C_f is the residual concentration of metal ions in solution after a certain contact time with degraded PET. After retention studies, degraded PET (loaded with lead and virgin) was characterized in order to determine the possible interactions between metal ions and functional groups from the degraded polymer.

RESULTS AND DISCUSSION

PET degradation

PET was degraded using zinc acetate as catalyst, obtaining a white

precipitate in 92% yield, which is higher than yields reported in other manuscripts when acetic acid, lithium hydroxide, sodium sulfate, and potassium sulfate are used as catalysts (54-60%)²¹. Moreover, the excess of ethyleneglycol in the reaction mixture allows a complete degradation after 3 h of reaction, as shown in Figure 1, which is faster compared to a lower molar ratio studied previously^{15, 22-23}. The maximum yield was obtained after 4 hours.

Figure 1. Effect of time on PET by ethylene glycol (▲) and on the yield (■).

FTIR spectrum of degraded PET presents principally the absorption signals corresponding to the OH stretching tension bond at 3439 cm^{-1} , the C=O stretching bond of the ester group at 1714 cm^{-1} and the C-OH peak at 1126 cm^{-1} . The ^1H NMR spectrum shows the signals of the expected functional groups. The corresponding signals to the methylene group located next to the hydroxyl and ester group were found at $\delta = 3.4$ and 3.7 ppm, the signal that corresponds to the proton of the hydroxyl group was found at $\delta = 4.5$ ppm and the signals that represent the protons of the aromatic ring can be seen at $\delta = 8.2$ ppm.

The DSC thermogram of the degradation product shows an endothermic process at 106 °C which is attributed to its melting point. At 260 °C there is no sign of any transition that could correspond to the original polymer's melting point, which proves a complete degradation.

The molecular weight determined by GPC was 383 g/mol and is thought to be bis(2-hydroxy ethyl) terephthalate (BHET) dimer. Conjointly, the determined molecular weight, the endothermic process that represents the sample's melting temperature in the thermogram and the absorption signals in the IR and ^1H NMR spectrum are attributed to the formation of BHET, as it was proposed in Scheme 1, when $m = 1.5$ -2.

Removal of metal ions

Effect of pH values in metal ions removal from an aqueous solution by degraded PET is shown in Figure 2. At lower pH values due to high concentration of hydronium ions (H_3O^+) there is a competition between these and metal ions (M^{n+}) for the functional groups in degraded PET (hydroxyl and ester groups). In these conditions, the heteroatoms (X) with lone pairs are preferentially bonded with protons, which decrease the degraded polymer's removal capacity towards metal ions. When solution pH increased, metal uptake was enhanced as a result of the decreasing proton concentration which made the heteroatoms more available to interact with metal ions, increasing its retention onto degraded PET.

The variation of metal ion retention when modifying pH values has a similar effect on Pb(II) and Cd(II); the higher metal ion uptake for Pb(II) was achieved at pH 4-5 and Cd(II) at pH 6. The results show lower removal concentrations for Ni(II), Cu(II), and Cr(III), since these ions are easily complexed with hydroxyl ions (OH^-) this species decrease their retention onto degraded PET. Additionally, charge and size of each formed species play an important role due to the competence for heteroatoms between all the metal species in solution²⁻⁵.

Degraded PET preferentially removes Pb(II) and Cd(II) showing the following order of retention at pH 4 and 5: Pb(II) > Cd(II) > Ni(II) > Cu(II) > Cr(III), these results coincide with other reports, attributing this order to factors like complexation abilities, which can be explained by hard and soft acids and bases

(HASB) theory²⁴⁻²⁶, trends of hydrated radius, polarizability, and electronic configuration²⁷⁻²⁹.

Figure 2. Retention of metal ions by degraded PET at different pH. (25 mg/L, 25°C)

The effect of initial concentration at pH 5 is shown in Figure 3. There is a greater retention at lower initial concentrations of each studied metal, this retention decreases as the metal concentration increases due to saturation of the available functional groups in the degraded polymer.

Figure 3. Retention of metal ions by degraded PET at different initial concentrations. (pH 5, 25°C).

The retention values obtained are comparable with other studies when PET was used to remove metal ions like Cu(II), Co(II), Fe(II), Pb(II), and Ni(II) among others. The PET fibers without modification, remove between 22 and 46% and when PET fibers are grafted the retention increases significantly (35-95%) at similar conditions that the experiments carried out in this study. The process of functionalization sometimes requires Soxhlet extraction, use of dissolvent, radical initiator, or vacuum. Meanwhile, the chemical degradation of PET allows by precipitation with water to obtain an insoluble product for retention experiments^{7-13,30}.

FTIR spectra of degraded PET and degraded PET-Pb(II) are shown in Figure 4. The comparison of both IR spectra reveal the interaction between the metal ion and degraded PET, which was evidenced by a shift in the positions of the absorption peaks, principally by disappearing of O-H signal at 3439 cm^{-1} , a splitting of the C-OH signal at 1265 cm^{-1} , and the change of the ester group C=O peak's intensity at 1714 cm^{-1} as a result of the coordinate bond between oxygen and metal atoms². In scheme 2 the proposed interaction between degraded PET and metal ions through hydroxyl groups is shown.

Degraded PET's DSC thermogram before and after contact with lead is presented in Figure 6, where an endothermic absorption is shown at approximately in 106 °C. There was a decrease in the intensity through the packing of the molecules, therefore the energy required to melt the material is lower.

CONCLUSIONS

BHET obtained from PET glycolysis removes preferentially Pb(II) and Cd(II) from aqueous solution. The order of metal ion retention at pH 4 and 5 was Pb(II) > Cd(II) > Ni(II) > Cu(II) > Cr(III). These results are attributed to complexation abilities, charge and size of each formed species. The metal speciation of Ni(II), Cu(II), and Cr(III) decrease the uptake of these metals. The presence of metal ions in BHET's structure was evidenced principally by FTIR spectroscopy, through the observed shifting of characteristic signals of functional groups.

Figure 4. IR spectra of degraded PET before and after contact with Pb(II).

Scheme 2. Proposed metal ion interaction between degraded PET and metal ions.

Figure 5. DSC thermogram of degraded PET before and after contact with Pb(II). (10°C/min, N₂).

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