

# Surface Hydrolysis of Postconsumer Polyethylene Terephthalate to Produce Adsorbents for Cationic Contaminants

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**ABSTRACT:** In this work, the surface hydrolysis of post-consumer polyethylene terephthalate (PET) was used to produce an ion exchange material to adsorb cationic contaminants from water. The PET surface hydrolyses were carried out in neutral, alkaline, and acid media (NaOH or HNO<sub>3</sub> at 7, 10, and 15 mol L<sup>-1</sup>) under reflux producing surface carboxylic acid sites (–COOH) characterized by ATR-IR, pyridine adsorption, titration, TG, and DSC analyses. Acid hydrolysis produced high concentrations of –COOH (up to 0.5 mmol g<sub>PET</sub><sup>-1</sup>), whereas no significant concentration of carboxylic acid sites was obtained by neutral and alkaline hydrolysis. SEM analyses suggest that the acid sites are likely located at the

cracks and defects produced on the PET surface by acid hydrolysis. Neutral or alkaline hydrolysis produced a very regular and smooth PET surface with very low acid site concentrations. The adsorption isotherms of Cd<sup>+2</sup> as a model of heavy metal and the dye methylene blue as a model of large organic cationic molecules showed high adsorption capacities for the HNO<sub>3</sub>-hydrolyzed PET, whereas no adsorption takes place on the neutral- or alkaline-hydrolyzed polymer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5284–5291, 2006

**Key words:** PET; recycling; adsorption; hydrolysis

## INTRODUCTION

The development of new processes for polymer recycling is currently a relevant area of academic and technological research due to two main aspects: (i) to reduce the increasing volumes of polymer waste coming from different sources and (ii) to convert low cost sources such as plastic wastes into value-added materials with technological applications.<sup>1</sup>

Polyethylene terephthalate (PET) is considered one of the most important engineering polymers in the past two decades due to rapid growth in its use. For this reason, recycling PET waste is increasingly demanded for both ecological and economical motivations.<sup>2</sup>

There are three distinct approaches to the recycling of postconsumer PET: (i) direct reuse, (ii) physical reprocessing, e.g., grinding, melting, and reforming, and (iii) chemical recycling whereby its components are isolated and reprocessed for use in manufacture.

Because of the economical attractiveness, the chemical recycling of PET has been attracting much more attention due to a large variety of processes resulting in a great number of different products. For example, PET can be recycled by catalytic hydrolysis,<sup>3</sup> aminoly-

sis,<sup>4</sup> alcoholysis,<sup>5</sup> glycolysis,<sup>6</sup> and even the production of copolymers by reaction with other polymers.<sup>7</sup>

The hydrolysis of PET catalyzed by acid and by base has been extensively studied<sup>1–3</sup> as a means to produce terephthalic acid (TA) and ethylene glycol (EG) for recycling.

In this work, the catalytic hydrolysis process was investigated to recycle PET in a completely novel approach, i.e., the production of a material with cation exchange properties for industrial and environmental applications (Fig. 1).

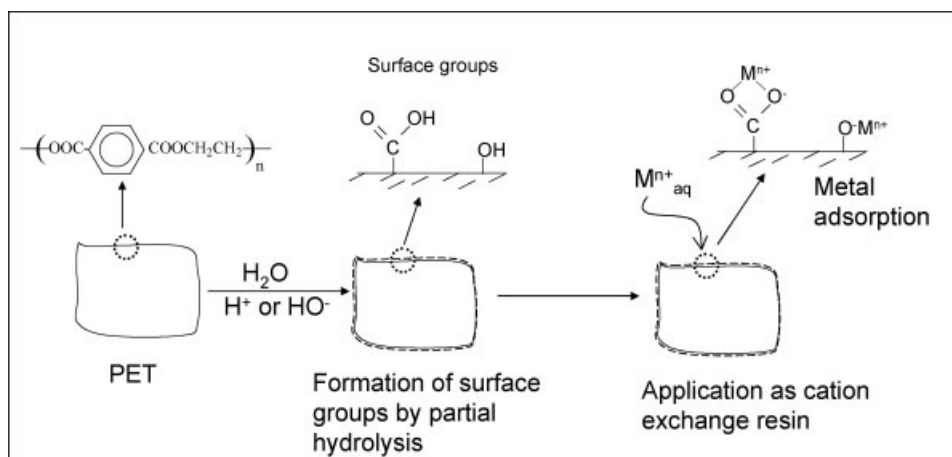
## EXPERIMENTAL

Postconsumer PET was obtained from noncolored soft drink bottles in square pieces of 5 mm. The hydrolyses were carried out with 1 g of PET and 5 mL of pure water, HNO<sub>3</sub>, or NaOH under reflux in a 20-mL round bottom flask connected to a condenser in a silicone oil bath at about 120°C.

The purification of PET after hydrolysis is a very important step, since all the results are dependent on the purity of the partially hydrolyzed PET. After the acid hydrolysis, the PET pieces were washed with NaOH solution (15 mL, 1 mol L<sup>-1</sup>, stirring for 30 min) to solubilize and remove solid terephthalic acid from the surface. The PET was then washed with distilled water (30 mL, stirring for 5 min) to remove the NaOH excess followed by a HCl wash-

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**Figure 1** PET surface hydrolysis producing  $-\text{COOH}$  and  $-\text{OH}$  groups and the adsorption process of cationic species in these groups.

ing (15 mL,  $1 \text{ mol L}^{-1}$ , stirring for 5 min) to recover the surface carboxylic acid groups. Finally, the PET is washed again with distilled water (3 times with 30 mL portions for 5 min each) to rinse the HCl excess. In this step, it is important to verify a neutral pH of the water after washing the PET to make sure that all HCl was removed. The PET pieces are dried in oven at  $100^\circ\text{C}$  for 12 h.

For the acid sites determination, 30 mg of the partially hydrolyzed PET is reacted with NaOH ( $0.0500 \text{ mol L}^{-1}$ ) and the excess titrated with a solution of potassium biphthalate ( $0.00150 \text{ mol L}^{-1}$ ) using phenolphthalein as indicator.

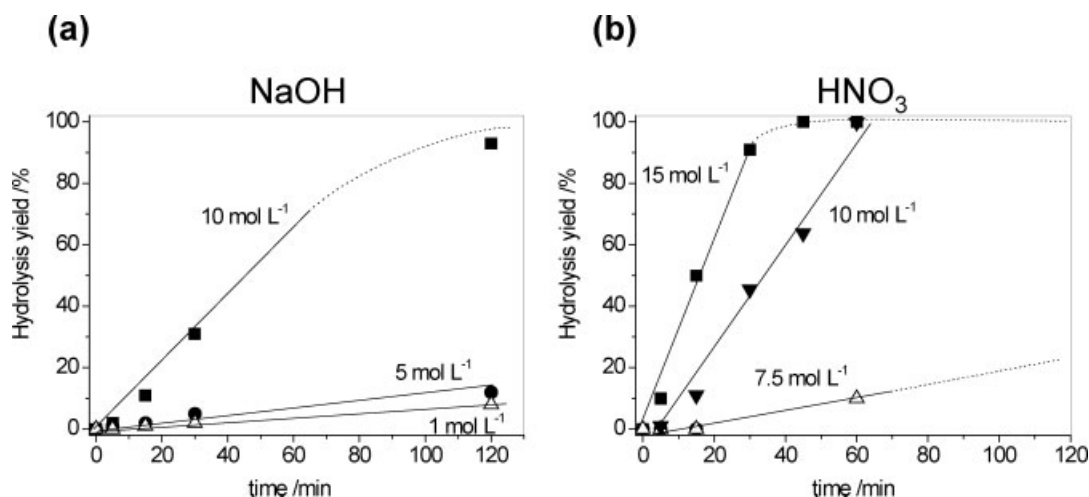
TG analyses were carried out in a TG50 Mettler STAR ( $10^\circ\text{C min}^{-1}$ ,  $\text{N}_2$   $200 \text{ mL min}^{-1}$ ) and DSC in a Shimadzu DSC50 ( $10^\circ\text{C min}^{-1}$ ,  $\text{N}_2$   $50 \text{ mL min}^{-1}$ ). The FTIR spectra were recorded in ATR mode in a Perkin-Elmer Spectrum GX instrument using 300 mg sample. The pyridine adsorption experiments were carried out

by exposing the PET pieces to pyridine vapor at  $25^\circ\text{C}$  for 24 h in a closed glass system. The SEM images were obtained in a Jeol JKA 8900RL microscope after gold metallization of the PET samples.

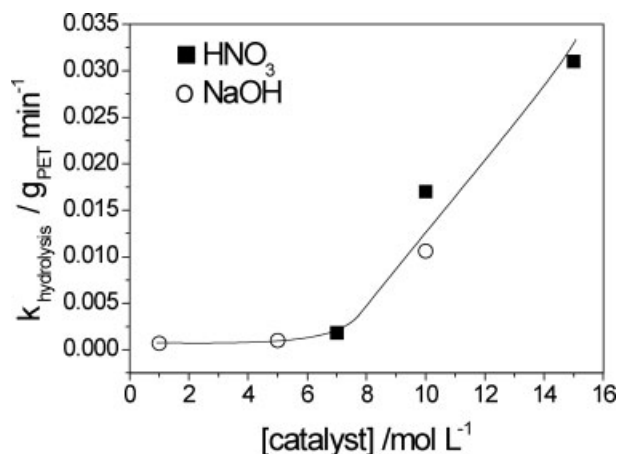
The adsorption experiments<sup>8</sup> were carried out with aqueous solutions prepared with Millipore MilliQ water of the dye methylene blue ( $25^\circ\text{C}$ , pH 6.0) or  $\text{CdCl}_2$  ( $25^\circ\text{C}$ , pH 6.0, 20 mL at 5 up to  $400 \text{ mg L}^{-1}$ ) with 30 mg of the partially hydrolyzed PET in a closed flask for 12 h. The amount of methylene blue adsorbed was obtained by spectrophotometric measurements at  $\lambda_{\text{max}}$  627 nm (UV/Vis Varian Cary 50 Conc), and the  $\text{Cd}^{2+}$  concentration after adsorption was measured by atomic absorption (Carls Zeiss Jena AASA).

## RESULTS

To control the PET surface hydrolysis,  $\text{HNO}_3$  and NaOH were used as catalysts at different concentra-



**Figure 2** PET hydrolysis yields in the presence of different concentrations of (a) NaOH and (b)  $\text{HNO}_3$  (reflux, 1 g PET in 5 mL solution).



**Figure 3** Pseudo zero order reaction rate constants for the hydrolysis with HNO<sub>3</sub> and NaOH catalysts at different concentrations.

tions and reaction time. The obtained results are shown in Figure 2.

The hydrolysis yields were obtained by weighting the hydrolyzed PET after reaction. It can be observed that for both catalysts, HO<sup>-</sup> and H<sup>+</sup>, at concentration lower than 7 mol L<sup>-1</sup>, very low hydrolysis yields were obtained even after 120 min. On the other hand, for higher catalyst concentration, e.g., 10 and 15 mol L<sup>-1</sup>, total hydrolysis of PET can be produced. It is interesting to observe a linear behavior of the hydrolysis plots, especially in the first 60 min, suggesting a pseudo zero order dependence. A simple expression of the reaction rate can be written as:

$$V_{\text{hydrolysis}} = k_{\text{hydrolysis}}[\text{H}_2\text{O}]^0[\text{PET}]^0[\text{catalyst}]^0 \quad (1)$$

The rate constants  $k_{\text{hydrolysis}}$  calculated by the slope of the hydrolysis plots are shown in Figure 3.

### Characterization of the surface hydrolyzed PET

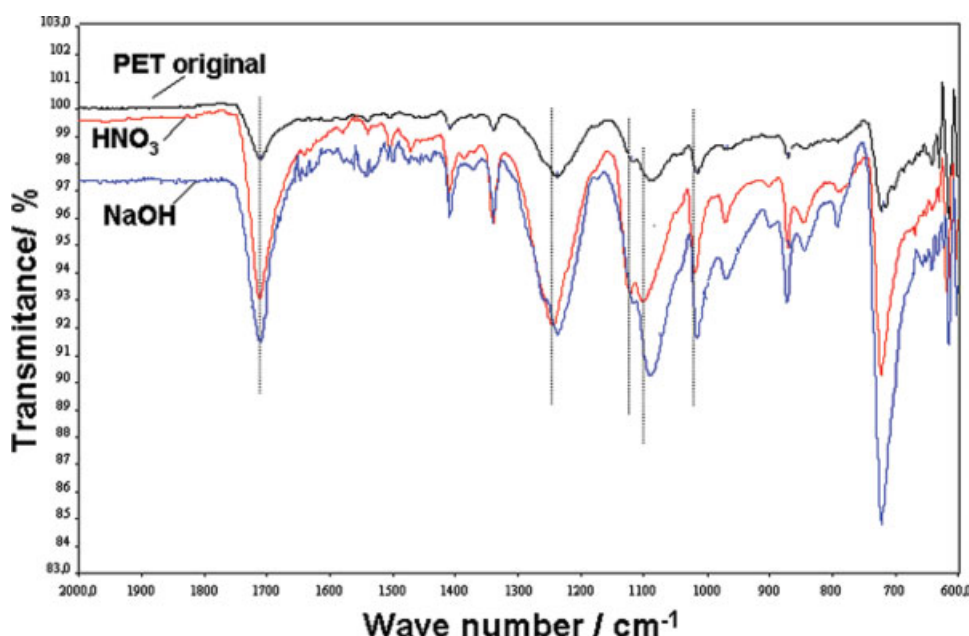
The partial hydrolysis of the polyester chain should produce carboxylic acid (—COOH) and alcohol (—OH) groups bound to the polymer chains on the PET surface. After reaction, the hydrolyzed PET pieces were treated by a careful procedure, i.e., extensive washing with NaOH, water, HCl, water, followed by drying at 100°C overnight under vacuum.

The PET surface was analyzed by infra-red spectroscopy using attenuated total reflectance (ATR) to investigate the more superficial groups. The spectra obtained for the nonhydrolyzed PET and the PET after hydrolysis with NaOH and HNO<sub>3</sub> (10 mol L<sup>-1</sup>) for 30 min are shown in Figure 4.

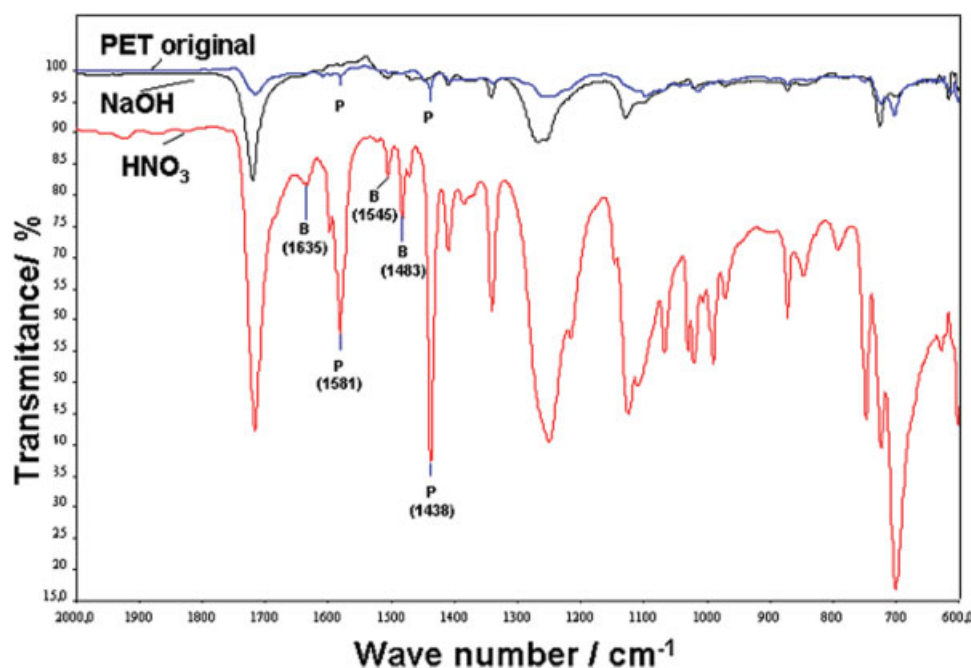
It can be observed for the nonhydrolyzed PET bands at 1014 cm<sup>-1</sup>, 1089 cm<sup>-1</sup>, 1237 cm<sup>-1</sup> (C—O), 1710 cm<sup>-1</sup> (C=O) all related to the terephthalic ester. Upon hydrolysis these bands are intensified and small shift to higher wavenumbers is observed, e.g., 1017 cm<sup>-1</sup>, 1100 cm<sup>-1</sup>, 1245 cm<sup>-1</sup>, 1713 cm<sup>-1</sup>, especially for the acid-hydrolyzed PET.

To confirm the presence of acid groups the IR of pyridine adsorbed on hydrolyzed PET was studied (Fig. 5).

The physically adsorbed pyridine showed bands at 1581 and 1438 cm<sup>-1</sup> (P bands). On the other hand,



**Figure 4** ATR-IR spectra for the nonhydrolyzed PET and PET after hydrolysis with HNO<sub>3</sub> and NaOH (10 mol L<sup>-1</sup>) for 30 min under reflux. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 5** ATR-IR spectra for the PET hydrolyzed with  $\text{HNO}_3$  and  $\text{NaOH}$  ( $10 \text{ mol L}^{-1}$ ) for 30 min under reflux, after adsorption of pyridine. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

new bands at  $1635$ ,  $1545$ , and  $1483 \text{ cm}^{-1}$  can be clearly observed for the acid-hydrolyzed PET. These bands are related to the adsorption of pyridine at Brønsted acid sites (B bands), e.g.  $-\text{COOH}$ .<sup>9–13</sup> It is interesting to observe that the  $\text{NaOH}$ -hydrolyzed polymer did not show the pyridine bands.

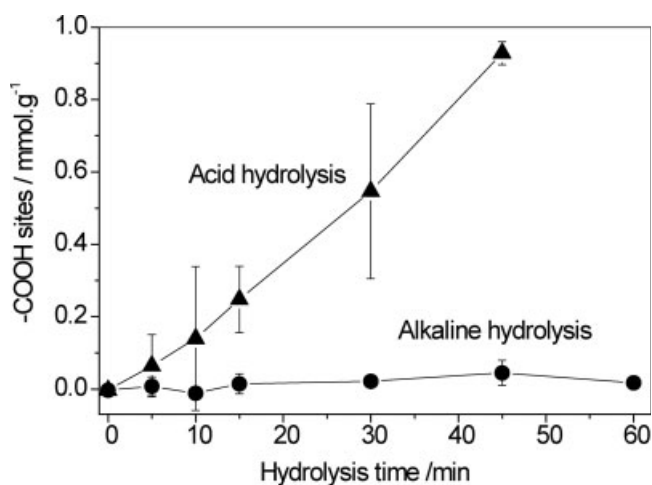
The number of carboxylic acid groups formed on the PET-hydrolyzed surface was determined by simple acid–base titration. The obtained results are shown in Figure 6.

It can be observed that the PET hydrolyzed by  $\text{HNO}_3$  showed a concentration of acidic sites, which

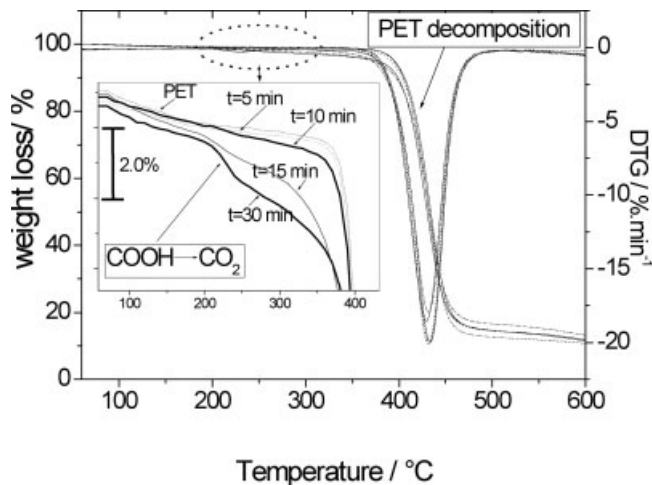
increased almost linearly with the hydrolysis time reaching about  $0.9 \text{ mmol g}_{\text{PET}}^{-1}$  with 45 min reaction. However, after 45 min hydrolysis,  $\sim 95\%$  of the original PET was destroyed and obtained material was extremely fragile and brittle. On the other hand, the  $\text{NaOH}$ -hydrolyzed PET did not show any significant increase on the number of acidic sites after hydrolysis.

The hydrolyzed-PET was also analyzed by thermogravimetry and the obtained results are shown in Figure 7.

It can be observed that the different hydrolyzed-PET samples showed similar TG decomposition pro-



**Figure 6** Surface acidic carboxylic sites for the PET hydrolyzed with  $\text{HNO}_3$  and  $\text{NaOH}$  ( $120^\circ\text{C}$ , catalyst  $10 \text{ mol L}^{-1}$ ).

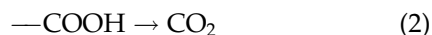


**Figure 7** TG analyses ( $\text{N}_2$ ) of the PET hydrolyzed with  $\text{HNO}_3$  ( $10 \text{ mol L}^{-1}$ , under reflux) for different times.

**TABLE I**  
**Comparison of the Number of Acid Sites Determined by Titration and by TG (reflux, 120°C, Catalyst 10 mol L<sup>-1</sup>)**

Hydrolysis	Acid sites by TG (mmol g <sup>-1</sup> )	Acid sites by titration (mmol g <sup>-1</sup> )
Nonhydrolyzed	0.00	0.00
HNO <sub>3</sub> /5 min	0.01	0.02
HNO <sub>3</sub> /30 min	0.47	0.55
NaOH/30 min	0.01	0.02

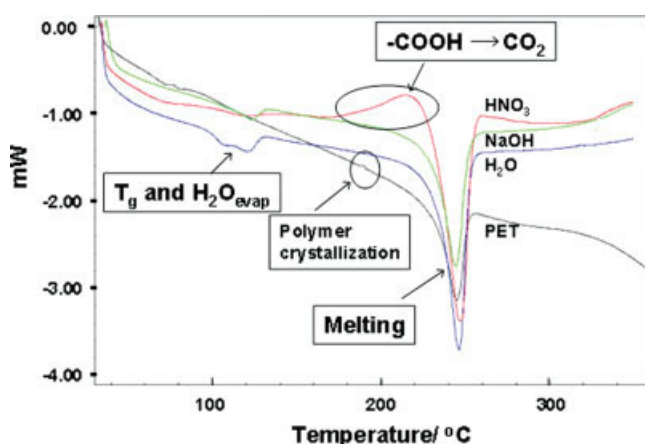
file with a main weight loss near 90% between 380 and 470°C related to decomposition of the polyester to volatile products. On the other hand, significant differences can be observed between 200 and 300°C. The nonhydrolyzed PET does not show any significant weight loss in this temperature range. The PET hydrolyzed for 5 and 10 min with HNO<sub>3</sub> showed similar results with very small weight changes below 300°C. On the other hand, the PET hydrolyzed for 15 and 30 min showed significant weight losses between 200 and 300°C. In this temperature range, it is well known that carboxylic acid groups in polymers thermally decompose according to the process<sup>14</sup>:



From the weight losses in this temperature range it is also possible to estimate the number of acid sites. Table I shows that the number of acid sites determined by titration and by TG are very similar.

The PET nonhydrolyzed, PET after neutral (H<sub>2</sub>O), acid (HNO<sub>3</sub> 10 mol L<sup>-1</sup>), and alkaline (NaOH 10 mol L<sup>-1</sup>) hydrolysis for 30 min under reflux were also analyzed by DSC (differential scanning calorimetry) (Fig. 8).

The DSC of the nonhydrolyzed PET shows mainly three events: the  $T_g$  (glass transition) near 80°C, the



**Figure 8** DSC of the PET nonhydrolyzed, PET after neutral (H<sub>2</sub>O), acid (HNO<sub>3</sub> 10 mol L<sup>-1</sup>), alkaline (NaOH 10 mol L<sup>-1</sup>) for 30 min under reflux. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

crystallization near 185°C, and melting at about 245°C. After hydrolysis in pure water and also with NaOH, two endothermic events appear between 100 and 140°C likely related to elimination of H<sub>2</sub>O adsorbed or trapped in the polymer. On the other hand, for the HNO<sub>3</sub>-hydrolyzed PET, a pronounced exothermic event at 200–250°C is observed, which could be related to the decomposition of COOH groups as suggested by TG.

The PET hydrolyzed by NaOH and HNO<sub>3</sub> were also analyzed by scanning electron microscopy (SEM) and the results can be seen in Figure 9.

It can be observed that the nonhydrolyzed PET shows very regular surface and lateral walls. After NaOH hydrolysis, the PET surface and laterals are still fairly regular, showing some voids produced by the hydrolysis. On the other hand, the HNO<sub>3</sub> hydrolysis strongly modifies the polymer texture, producing a large concentration of defects and cracks on the surface and side wall.

### Adsorption studies

The presence of the carboxylic and hydroxyl groups makes the hydrolyzed PET very interesting to be used as a cation exchange material. Figure 10 shows the adsorption isotherms obtained for Cd<sup>2+</sup> onto nonhydrolyzed PET and the PET hydrolyzed with HNO<sub>3</sub> and NaOH (10 mol L<sup>-1</sup>, 30 min, 120°C).

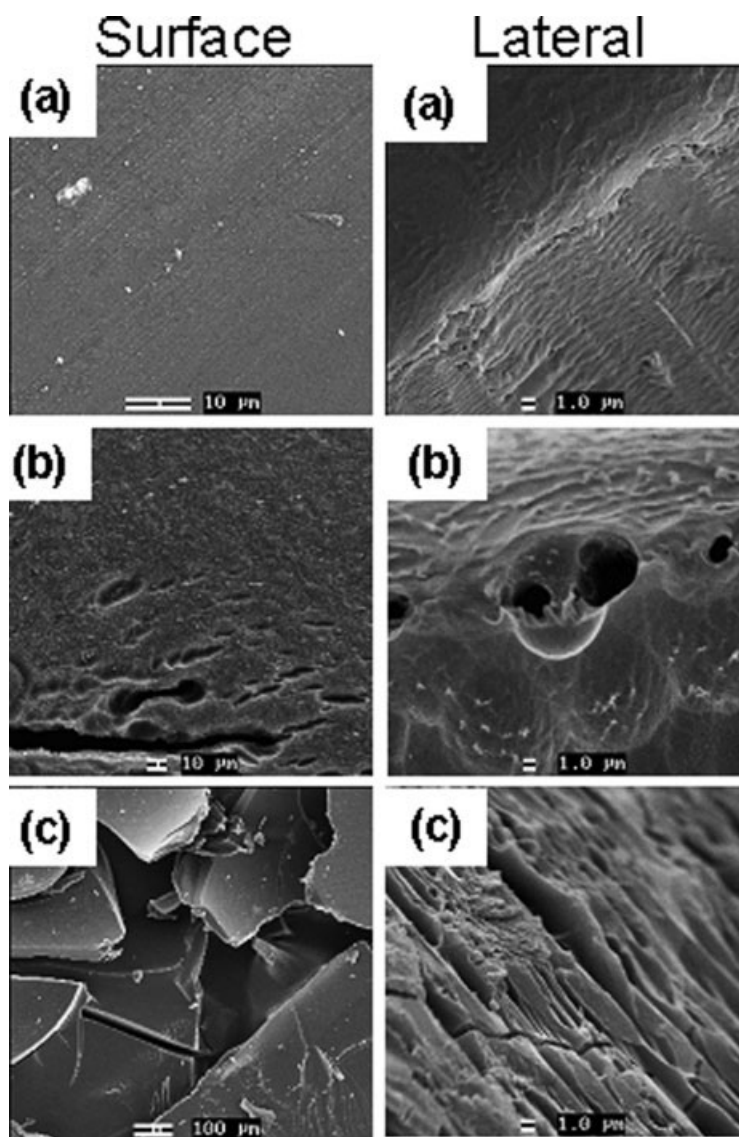
It can be observed that the nonhydrolyzed and the NaOH-hydrolyzed PET do not adsorb any Cd<sup>2+</sup> from solution, whereas the HNO<sub>3</sub>-hydrolyzed material shows an adsorption capacity of about 0.18 mmol Cd<sup>2+</sup> per gram. From the results shown in Table I it can be estimated that ~40% of the –COOH sites are used for adsorption under the experimental conditions employed (considering the total acid site concentration of 0.5 mmol g<sup>-1</sup><sub>PET</sub>).

The adsorption isotherms were also obtained using the dye methylene blue as a large cationic organic species (Fig. 11).

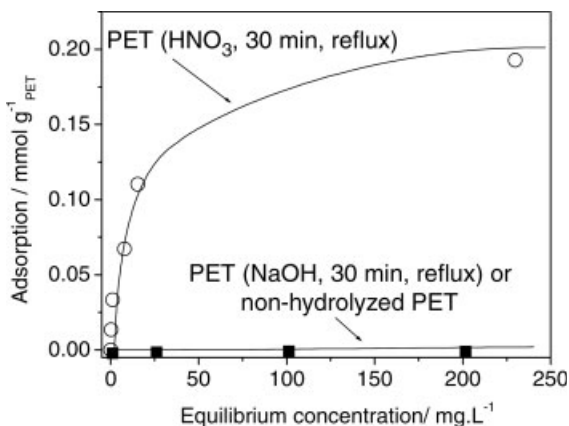
It can be observed that the nonhydrolyzed PET adsorbs only a very low amount of the dye methylene blue. Also, hydrolysis for 5 and 10 min with HNO<sub>3</sub> did not cause a significant change on the adsorption properties of the PET. On the other hand, upon hydrolysis for 15 min, the adsorption capacity reaches ~3 mg g<sup>-1</sup>, whereas the 30 min-hydrolyzed PET strongly increases its adsorption capacity to almost 10 mg g<sup>-1</sup>.

### DISCUSSION

The results obtained in this work clearly showed that, under controlled conditions, the PET can be partially hydrolyzed to produce surface –COOH sites, which can act as cation exchange sites. Alkaline or neutral hydrolysis did not produce significant con-



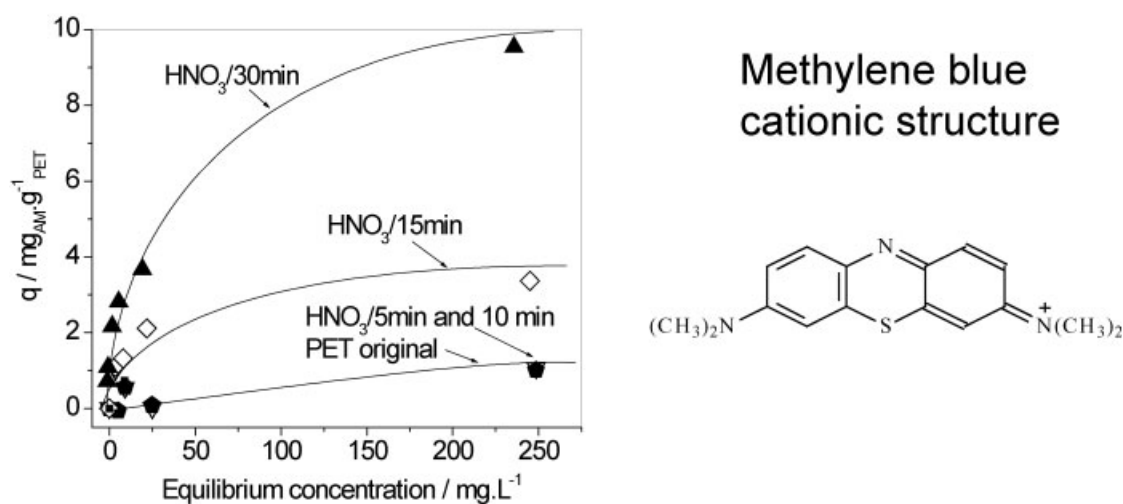
**Figure 9** SEM of the PET (a) nonhydrolyzed and after hydrolysis with (b) NaOH and (c) HNO<sub>3</sub> (10 mol L<sup>-1</sup>, 30 min, reflux).



**Figure 10** Adsorption isotherms of Cd<sup>2+</sup> on PET hydrolyzed with HNO<sub>3</sub> (10 mol L<sup>-1</sup>, 30 min, reflux), with NaOH (10 mol L<sup>-1</sup>, 30 min, reflux) and PET nonhydrolyzed (25°C, pH = 6.0).

centrations of —COOH sites as shown by titration, TG, DSC, and IR measurements. On the other hand, high concentrations of acid sites were produced by HNO<sub>3</sub> hydrolysis. To explain this result one has to consider the “shrinking-core model” used to explain the PET hydrolysis kinetics. According to this model, the hydrolysis takes place on the polymer surface removing the more superficial layers leading to a decrease in the size of polymer particles. This model works well for alkaline hydrolysis where the terephthalic acid formed is completely soluble in the NaOH solution. On the other hand, for the acid-catalyzed hydrolysis a modified shrinking core model has been proposed where the insoluble terephthalic acid and other insoluble products remain on the PET surface during hydrolysis producing two effects: a decrease on the hydrolysis rate and the formation of cracks and defects on the PET surface.<sup>15,16</sup>





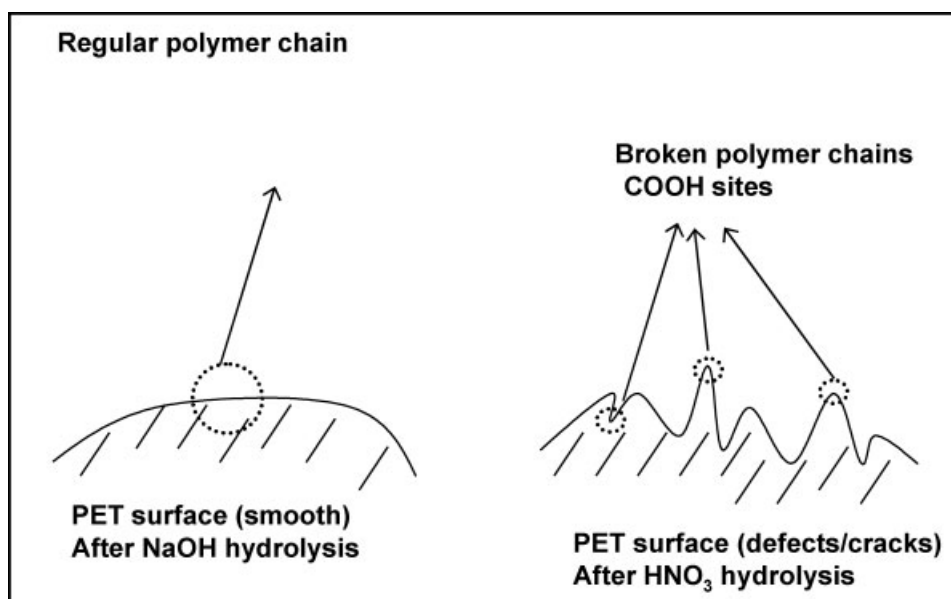
**Figure 11** Adsorption isotherms of methylene blue on hydrolyzed PET and the dye chemical structure (25°C, pH = 6.0).

A large amount of cracks and defects were clearly observed by SEM analyses of the HNO<sub>3</sub>-hydrolyzed samples. These defects likely contain a large concentration of polymer chain ends, i.e. —COOH and —CH<sub>2</sub>CH<sub>2</sub>OH (Fig. 12). On the other hand, the alkaline hydrolysis proceeds in a regular fashion producing mainly terephthalate acid and ethylene glycol. It is known in the literature that alkaline hydrolysis attacks preferentially amorphous region leaving a more crystalline PET.<sup>17</sup> As a result of this regular hydrolysis, a very smooth surface is produced with low concentration of defects. These results might explain the low concentration of acid sites produced by alka-

line hydrolysis in contrast of the high amounts of acid sites for the HNO<sub>3</sub> hydrolysis.

### CONCLUSIONS

PET waste can be transformed in cation exchange materials by a simple hydrolysis procedure. The controlled hydrolysis of PET using HNO<sub>3</sub> as catalyst can produce cation exchange sites based on acidic groups, i.e. —COOH, with up to about 0.5 mmol g<sub>PET</sub><sup>-1</sup>. These acid sites can adsorb heavy metal cations, e.g. Cd<sup>2+</sup>, and large cationic organic molecules, such as the dye methylene blue.



**Figure 12** Schematic representation of the PET surface after acid and alkaline hydrolysis, and the defects produced responsible for the creation of —COOH sites.

The acid hydrolysis is much more efficient to generate acid sites compared to the neutral and alkaline hydrolysis. Apparently, the surface acid sites are located at the cracks and defects produced on the PET surface during hydrolysis. Alkaline hydrolysis does not produce defects on the PET surface leading to a very low acid site concentration.

The process disclosed in this work is technically simple, has a low cost, and tailor PET waste producing a material with potential technological and environmental applications.

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