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Electrochemical Regeneration of Activated Carbon Saturated with Toluene

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Abstract

The electrochemical regeneration of an activated carbon, previously saturated with toluene by gas phase adsorption, was studied. Cathodic and anodic regeneration methods were analyzed using a small batch electrochemical cell. In both cases, a stripping efficiency close to 100% was obtained under appropriate conditions of potential, current, and time of electrolysis. Successive loading and regeneration cycles of the activated carbon were performed under cathodic conditions without loss of the adsorption properties of the activated carbon, thus achieving a high regeneration efficiency (close to 99%). This electrochemical method is very effective for regeneration of activated carbon compared to conventional thermal regeneration as it does not modify the porous texture of the material.

1. Introduction

Activated carbon (AC) has been widely used for the purification of drinking water, the tertiary treatment of sewage water and, in general, to remove pollutants from process streams containing organic materials which are not easily biodegraded. Nowadays, pollutant removal from gaseous streams is a subject of great study. The removal of volatile organic compounds (VOC) implies very often the treatment of high flow rate gaseous streams with low concentration of VOC, which is carried out by activated carbon adsorption processes [1].

In order to make the use of activated carbons economically feasible on a large scale, the exhausted AC must be regenerated and reused. This regeneration stage remains an important problem from an economic standpoint.

Regeneration may be performed by several methods: thermal treatment in oxidizing atmosphere, thermal treatment in steam or water at high temperature and high pressure, solvent extraction, electrochemical regeneration, etc. [2–8]. The first method consists in the treatment of the saturated activated carbon at high temperature in oxidizing atmosphere. This thermal treatment can produce changes in both the surface chemistry and porous texture of the AC, thus modifying the adsorption properties of the starting material. With this method, a percentage of activated carbon, from 10 to 20% in weight, is burnt off [2–4]. Another possibility is the regeneration using steam or water at high temperature; this method reduces the change in both surface chemistry and weight loss of carbon [5]. During solvent extraction, the organic pollutant is also removed but about 10–15% of the pores of the activated carbon are blocked by the extraction solvent [5, 6].

An alternative, not so widely studied, is the electrochemical regeneration of activated carbon. Narbaitz and Cen [8] used the electrochemical method for the regeneration of AC loaded with phenol. They observed that this regeneration slightly depends on the loading of phenol. The desorption of phenol takes place due to the increase of the OH^- concentration near the electrode during the cathodic treatment, which results in an increase in pH of the solution near the electrode surface. Cathodic regeneration is about 5–10% more effective than anodic regeneration. The regeneration efficiency in the cathodic process obtained in this case is around 95%.

Zhang [9] also studied the regeneration of activated carbon loaded with phenol. This author concluded that electrochemical regeneration depends on several operating variables such as electrolyte concentration (NaCl), current intensity and regeneration time. A regeneration efficiency of 85.2% was obtained.

Bonnecaze et al. [10, 11] studied the adsorption and electrosorption of organic compounds on the activated carbon taking into account the applied potential. They concluded that the attractive forces between non-polar molecules like benzene and the granular activated carbon, depend on the polarizability of the molecule.

This parameter is influenced by the adsorbate orientation and the loading of benzene depends on the potential applied [10]. In the case of a polar molecule like chloroform, a negative potential increases its adsorption whereas a positive potential has the opposite effect [11].

The potential of electroadsorption/desorption on activated carbon for wastewater treatment of industrial effluents was studied by Bán et al. [12]. The adsorption isotherms of different reference substances were measured. These authors concluded that, in all cases, the adsorption equilibrium is dependent on the applied potential in the electrolyte.

The combined adsorption and oxidation of phenol on granular activated carbon has been studied by Cañizares et al. [13]. Electrochemical regeneration of the activated carbon was performed in a cylindrical cell with stainless steel electrodes. The regeneration efficiency obtained in this case was around 80%, but this efficiency decreases linearly with the number of regeneration cycles, possibly due to damage in the carbon structure during the electrochemical process. In addition, the steel anode is not stable in the operating conditions and it is consumed during electrolysis, producing Fe^{3+} ions. These metal ions react with the phenol in solution producing insoluble iron–phenol complexes.

As can be observed in the previous references, the literature is beginning to pay attention to the electrochemical removal of organic pollutants. Among the various organic compounds, the removal of phenol and benzene is often studied. However, little information exists regarding other organic pollutants such as toluene. One of the reasons for such lack of information is related to the difficulty in maintaining constant toluene concentration in solution, due to the volatility of this compound.

In this paper, the electrochemical regeneration of a commercial granular activated carbon saturated with toluene has been studied. Anodic and cathodic treatments have been analysed in order to remove the toluene and to reuse the activated carbon. The obtained results can be compared with those previously shown in the literature for pollutants other than toluene.

2. Experimental

The activated carbon selected was provided by Westvaco (WV-A1100 10 × 25) and Table 1 summarizes the characterization of this adsorbent. Table 1a includes the BET surface area and the micropore volumes measured by N_2 and CO_2 adsorption at 77 and 273 K, respectively. Micropore volumes were calculated using the Dubinin–Radushkevich equation. Table 1b contains additional characterization data provided by the company.

Table 1a. Porosity characterization of the activated carbon used in the regeneration experiments (Westvaco A-1100, 10 × 25)

BET surface area ($m^2\ g^{-1}$)	V-DR N_2 ($cm^3\ g^{-1}$)	V-DR CO_2 ($cm^3\ g^{-1}$)
1757	0.67	0.36

Table 1b. Typical properties of the activated carbon used in the regeneration experiments (Westvaco A-1100, 10 × 25)

Mesh size	Mean particle diameter/mm	Nominal butane capacity (g/100 ml)	Apparent density ($g\ l^{-1}$)
10 × 25	1.3	11.3	275

Before electrochemical regeneration, the AC samples were exhausted with toluene by using a toluene–helium cylinder containing 200 ppm-toluene in a fixed-bed reactor, BTRS-Jr from Autoclave Engineers (10 mm inner diameter) coupled to a mass spectrometer (Thermocube, Balzers). A gas flow of 90 ml min^{-1} was used, and the temperature was kept at 25 ± 1 °C. The adsorption capacity for toluene on this AC is 30 g of toluene for 100 g of carbon at these experimental conditions, as has been reported before [14, 15]. 0.2 g of AC were used in each adsorption experiment.

The regeneration experiments were performed in a conventional electrochemical glass cell (100 ml capacity). For the preparation of the solutions, ultra pure water (Millipore Milli Q 18.2 Mohm cm) was employed. The reagents employed were Sodium Hydroxide pellets p.a. (Merck), Sodium Sulphate Decahydrate p.a. (Merck) and Anhydrous Sodium Carbonate p.a. (Merck).

Once each sample was exhausted in the described conditions, it was transferred into a basket made of nickel gauze (0.114 mm diameter wire, Alfa Aesar) that acted as working electrode (Ni–AC set). The nickel basket had a cylindrical shape, with a diameter of 7 mm and 40 mm in height. This nickel basket with the activated carbon inside acted as cathode or anode depending on the cathodic or anodic electrochemical treatment, respectively. Inside this basket a platinum wire was placed in order to achieve better electrical contact with the activated carbon.

The Ni–AC set was immersed in a standard three-electrode electrochemical cell made of Pyrex glass containing the supporting electrolyte. A reversible hydrogen electrode (RHE) was employed as reference electrode and a spiral of platinum wire was used as counterelectrode.

Solution analysis during the electrochemical treatment were measured by HPLC (Lichrospher 100 RP-18). The electrochemical treatments were made under constant current (galvanostatic) or at constant potential (potentiostatic) conditions. The electrochemical treatment was performed for 3 h and Total Organic Carbon (TOC) was determined using a MICRO N/C Analytic Jena analyser.

The amount of toluene remaining in the activated carbon after regeneration was evaluated by temperature programmed desorption (TPD) experiments using TG-DSC equipment coupled to a mass spectrometer

(TA instruments-Balzers). Before these experiments, the samples were washed several times with distilled water and dried in an oven using very mild conditions (80 °C for 3 h).

The TPD experiments were performed using a helium flow of 60 ml min^{-1}, heating up to 400 °C, with a heating rate of 5 °C min^{-1}. The quantity of AC used for these experiments was around 0.075 g. Under these conditions, the amounts of toluene adsorbed and desorbed in a gas phase adsorption experiment coincide. Thus, this heat treatment ensures complete regeneration of the activated carbon and an accurate quantification of the retained toluene once the carbon has been electrochemically regenerated.

The regenerated activated carbons were used for the adsorption of toluene at low concentrations (i.e., 200 ppm) to check the efficiency of the electrochemical regeneration from the point of view of modification of the adsorption properties of the sample.

The surface chemistry of some used samples and of the electrochemically-treated samples with no contact with toluene, were studied to determine the change in surface functional groups with electrochemical regeneration. Thus, the oxygen groups that evolve as CO and CO_2 were quantified by TPD experiments in helium (60 ml min^{-1}) using a heating rate of 20 °C min^{-1} up to 900 °C.

3. Results and discussion

The electrochemical regeneration of activated carbon was evaluated by means of the Stripping Efficiency (SE). This coefficient is defined as follows:

$$\text{SE} = \frac{T_i - T_r}{T_i} \times 100$$

T_i being the amount of toluene adsorbed by the AC before the regeneration and T_r the amount of toluene remaining in the AC after the regeneration treatment (both expressed in grams).

The Regeneration Efficiency (RE) is defined as follows:

$$\text{RE} = \frac{\text{adsorptive capacity of regenerated activated carbon}}{\text{adsorptive capacity of fresh activated carbon}} \times 100$$

This parameter has been calculated for samples subjected to multiple regeneration treatments.

3.1. *Potentiostatic anodic regeneration*

The AC saturated with toluene was introduced into the electrochemical cell and was subjected to a constant anodic potential of +3V/RHE for 3 h in 0.5 M NaOH, using platinum wire as cathode. The current was initially 1.3 A and during electrolysis increased continuously up to 2.4 A.

Figure 1 shows the toluene desorption from a saturated AC sample not subjected to electrochemical treatment (curve a) and from a sample exhausted and regenerated in anodic conditions (curve b). Anodic treatment strongly reduces the amount of toluene adsorbed on the activated carbon. From the TPD experiments (Figure 1, curve b), the stripping efficiency obtained was 99% using anodic regeneration treatment. Using HPLC, toluene was measured in the solution and methyl-*p*-benzoquinone was detected as oxidation product.

Figure 2 includes the CO and CO_2 evolution from the original AC and from an exhausted sample regenerated in anodic conditions. Table 2 shows data of the CO and CO_2 evolved and the total amount of oxygen desorbed calculated as CO + $2CO_2$. Anodic regeneration produces a significant increase in the amount of oxygen surface groups, which is not favourable to the retention of toluene as it is a hydrophobic compound. This result is also relevant because the surface chemistry strongly affects the adsorption capacity of an AC towards toluene [7, 15]. It is interesting to note that anodic regeneration does not produce an increase in either the

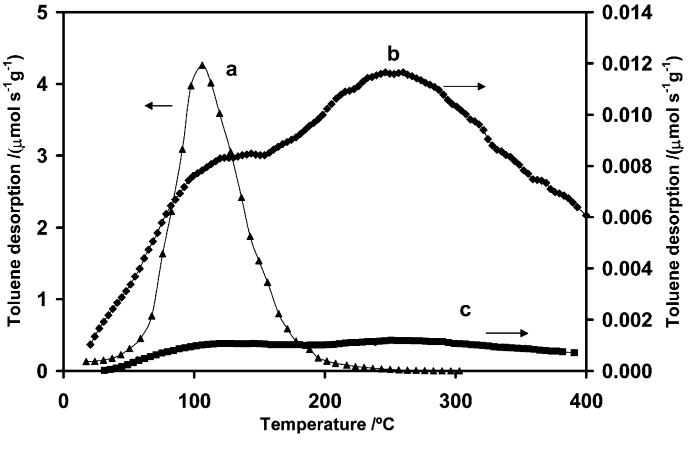

Fig. 1. TPD experiment for the activated carbon saturated with toluene (a), for the AC saturated and anodically-regenerated (b) and for the AC saturated and cathodically-regenerated (c).

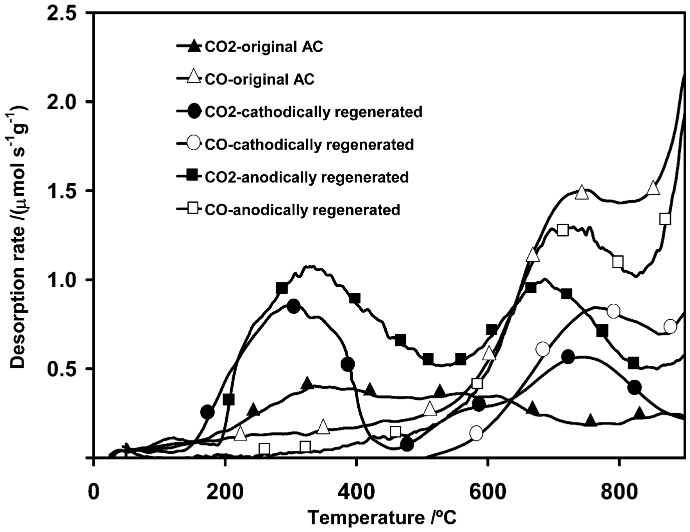

Fig. 2. CO and CO_2 evolution from TPD experiments for the original AC (—▲—), saturated and anodically-regenerated (—■—) and saturated and cathodically-regenerated (—●—) in potentiostatic conditions.

Table 2. CO and CO_2 evolved and the total amount of oxygen from TPD experiments of the original activated carbon (AC) and the anodically-and cathodically-regenerated after toluene adsorption and the anodic and cathodic blanks

Sample	CO (μmol g^{-1})	CO_2 (μmol g^{-1})	CO + $2CO_2$ (μmol g^{-1})
Original AC	1764	471	2706
AC anodically-regenerated	1210	1606	4422
AC cathodically-regenerated	613	950	2513
Anodic blank	1425	1278	3981
Cathodic blank	1210	1030	3269

CO or the CO_2 type surface oxygen groups. However, a decrease in the CO evolution and a significant increase in the CO_2 desorption can be clearly observed, both at low and at high temperatures, compared to the original activated carbon.

In order to further explore the changes in surface chemistry of the AC upon electrochemical treatment, a blank experiment was carried out by treating the AC at the same potential but in the absence of toluene. Figure 3 contains the TPD from the original AC and after the anodic treatment. Table 2 shows the data for the TPD. The anodic treatment produces a significant increase in the CO_2 desorption, whereas the CO evolution remains nearly unchanged. As expected, some oxidation of the AC surface takes place during the anodic treatment.

From the TPD in Figures 2 and 3 and the data of Table 2, it can be concluded that anodic treatment produces, in general, an increase in the oxygen content compared to the original AC. However, important differences in the shape of the TPD can be observed between the anodically-treated AC in the presence and in the absence of toluene. The presence of toluene during the electrochemical regeneration seems to favour strong oxidation of the CO-type groups into CO_2-type groups, whereas in the absence of toluene, the CO profile remains almost unchanged (see TPD in Figures 2 and 3). The presence of a small amount of oxidized species formed by toluene oxidation cannot be disregarded and may affect the TPD profile, especially the CO_2 curve. However, the strong decrease in CO observed in Figure 2 shows that the existence of toluene in the solvent during the anodic treatment modifies the carbon surface oxidation.

3.2. *Potentiostatic cathodic regeneration*

AC regeneration was achieved by applying a constant cathodic potential of -2 V/RHE for 3 h in 0.5 M. NaOH. The current was initially 1.1 A and during the electrolysis increased continuously up to 1.7 A. During cathodic treatment, evolution of gases was observed from the Ni–AC electrode, due to the decomposition of the solvent, and the temperature of the solution increased from 25 to 75 °C. The increase in temperature is related to an increase in the ohmic resistance in the cell. These facts could distort the results of the regeneration because toluene could be thermally desorbed from the activated carbons. However, TPD experiments show that toluene only desorbs slightly in the range of temperatures reached during the electrochemical regeneration (see Figure 1).

During these experiments toluene, benzyl alcohol, benzoic acid and benzaldehyde were detected in the solution at trace levels by HPLC. Because the experiments were performed in a non-divided electrochemical cell, these compounds are produced on the platinum spiral which acts as anode in these conditions. This indicates that toluene desorbed from the AC is oxidized at the anode of the cell. The same experiments were performed using a gold electrode as anode, because toluene is not oxidized by this metal [16], and only

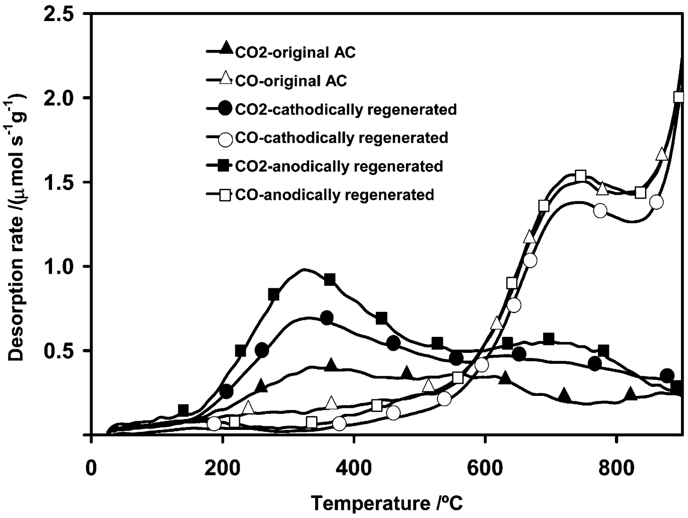

Fig. 3. CO and CO_2 evolution from TPD experiments obtained in blank experiments for AC (—▲—) after an anodic treatment (—■—) and after a cathodic treatment (—●—) in potentiostatic conditions.

toluene was detected in the solution during the electrolysis. Figure 1 shows the toluene evolution from a sample exhausted and regenerated at these cathodic conditions (see curve c in Figure 1). The amount of toluene desorbed is very small compared to the saturated AC (Figure 1, curve a) and even lower than that obtained from the anodically-regenerated AC described in Section 3.1 (Figure 1, curve b). The stripping efficiency obtained from TPD experiments for several cathodically-regenerated samples is very high and complete desorption of toluene from the activated carbon can be achieved.

Figure 2 and Table 2 show the CO and CO_2 evolution from the exhausted sample after cathodic regeneration measured by TPD. From the comparison between the oxygen surface groups in the original AC and in the sample after cathodic regeneration, it can be concluded that the electrochemical treatment results in a decrease in the total oxygen content. This is beneficial and improves the selectivity towards the adsorption of these compounds, with regard to other polar molecules like H_2O [7, 15]. The TPD profile shows that cathodic treatment produces a large decrease in the CO-type surface oxygen groups (as expected from a cathodic treatment), whereas some increase in the CO_2 evolution occurs. This again indicates that the electrochemical cathodic treatment produces a significant change in the surface chemistry of the activated carbon.

A blank experiment was carried out consisting in a cathodic treatment of the AC without any contact with toluene. Figure 3 and Table 2 contain the TPD profile and data for CO and CO_2 evolved. The TPD shows that the cathodic treatment results in a decrease in the CO-type groups and, unexpectedly, an increase in CO_2 desorption. The presence of toluene during the cathodic treatment (see Figures 2 and 3), produces significant changes in the TPD profile, especially a change in CO desorption, which is much greater when toluene is present.

The changes in the surface chemistry of the AC during both anodic and cathodic treatment and as a function of the electrolyte composition are interesting and should be analysed in detail.

3.3. *Galvanostatic cathodic regeneration*

The cathodic regeneration was performed at a constant current of 500 mA for 3 h and in different supporting electrolytes (NaOH, Na_2CO_3 and Na_2SO_4). The potential of the cathode was around 1.10–1.20 V during the electrolysis. In all cases, the evolution of gases from the decomposition of the solvent was avoided. Under these conditions, the temperature remains lower than in the potentiostatic conditions and almost constant at about 31 °C. Table 3 shows the values of stripping efficiency obtained with this method. The values reached are very high. As a general trend, the stripping efficiency increases with the pH of the solution. The same compounds as in the potentiostatic conditions and using platinum electrode as anode were detected (benzyl alcohol, benzoic acid and benzaldehyde) using HPLC. These results are significant in order to remove the pollutant (toluene) by this method. That is, the toluene desorbed from the cathode (Ni–AC set) is oxidized on the anode to less pollutant compounds.

Table 3. Stripping Efficiency (SE) obtained in the cathodic regeneration by galvanostatic conditions of different samples of AC saturated with toluene using different electrolytes

SE (%)	Electrolyte
98	0.5 M NaOH
96	2 M Na_2CO_3
92	0.5 M Na_2CO_3
94	0.5 M Na_2SO_4

3.4. *Multiple regeneration of the activated carbon in cathodic conditions*

An AC sample was subjected to adsorption of toluene and electrochemical regeneration cycles to follow the changes occurring in the adsorption capacity of the regenerated samples. The adsorption procedure was described in the experimental section. After each electrochemical regeneration, the AC was washed and dried under very mild conditions (70 °C) to evaporate most of the water before the adsorption step. The regeneration efficiency is about 99% after eight cycles in galvanostatic conditions at 500 mA in 0.5 M NaOH solution. Figure 4 contains the breakthrough curves for the fresh activated carbon and after three and eight electrochemical regeneration cycles, respectively, in cathodic conditions. The adsorption capacity of the activated carbon did not decrease with the adsorption/desorption cycles. This indicates that electrochemical regeneration in cathodic conditions does not modify the narrow microporosity of the AC, which determines the adsorption capacity of toluene at low concentrations [14, 15].

3.5. *Regeneration in a filter-press cell*

An electrochemical filter-press cell with a single compartment was used for the regeneration treatment in order to increase the weight of activated carbon sample used in the electrochemical treatment and to test the use of a flow system. About 5.7 g of activated carbon were saturated with toluene and were placed inside the filter-press cell. The electrolytic solution was continuously stirred and forced to pass through the cell containing the AC by means of centrifugal pumps. A diagram of the cell is shown in Figure 5. The size of the electrodes was 40 × 50 mm and the gap between electrodes was 10 mm. The activated carbon was placed in the area between both electrodes.

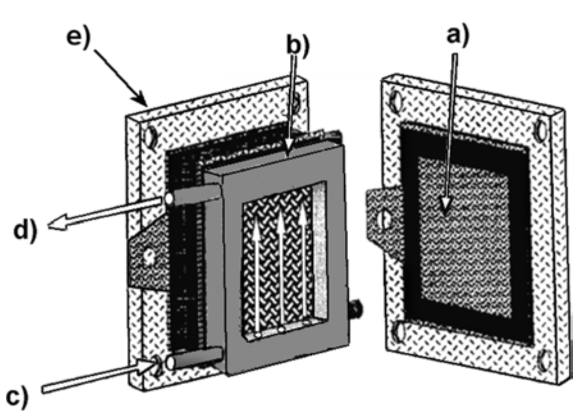

Fig. 5. Diagram of the filter press cell: (a) anode, (b) flow distributor, (c) electrolyte inlet and (d) electrolyte outlet. The cathode is placed just behind the flow distributor.

The regeneration was performed in a non-divided filter-press cell at a constant current of 1 A for 3 h in 0.5 M NaOH using a graphite electrode as cathode and a Ti/SnO_2–Sb electrode as anode. In this cell, the AC was placed close to the cathode. The preparation of the doped tin dioxide electrode has been previously described [16, 17], being adequate for the anodic oxidation of organic compounds [16]. Then, in this treatment the possibility was checked of the simultaneous oxidation of the toluene desorbed from the AC. The volume of electrolyte was 300 ml, and the temperature was maintained at 30 °C. The stripping efficiency obtained was 95%. This result is similar to that obtained with the electrochemical batch cell.

During electrolysis, the amount of toluene in the solution was analysed and it increased at the beginning of the electrolysis indicating that it is being desorbed from the activated carbon. After some time, it decreased as a consequence of its oxidation at the anode. The permanent TOC was determined after total evaporation of the volatile organic compound in order to analyse the soluble products formed. This value remained practically invariable during electrolysis indicating that a small amount of toluene was oxidized to soluble

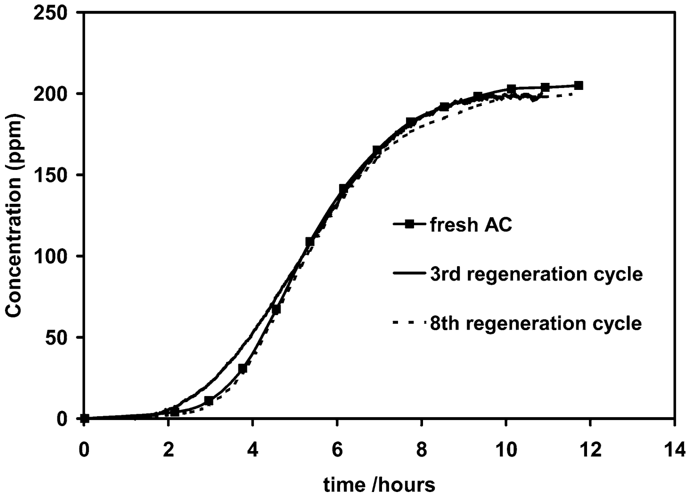

Fig. 4. Breakthrough adsorption curves for toluene at 200-ppm in the fresh AC and after three and eight cathodic regeneration cycles.

products. This electrochemical method has not only the advantage of the regeneration of the exhausted activated carbon, but it also allows removal of the pollutant from the solution by its oxidation in the anode of the cell to less harmful compounds.

4. Conclusions

The electrochemical regeneration of activated carbon saturated with toluene was carried out with high efficiency. The stripping efficiency obtained was higher than 90% in all cases. This method permits not only the regeneration of the activated carbon but also the removal of the organic pollutants by oxidation in solution. Several adsorption and electrochemical desorption cycles were performed without loss of the adsorption capacity of the activated carbon (in cathodic conditions) and obtaining a regeneration efficiency close to 99%.

The stripping efficiency obtained using a filter-press cell was very similar to that obtained with an electrochemical batch cell. The use of a filter-press cell shows that the method could be scaled up.

Both the surface chemistry and the porosity have a great effect on the adsorption of toluene. Cathodic regeneration produced some decrease in the content of oxygen surface groups of the AC, which is favourable for the adsorption of toluene. However, the anodic treatment created higher oxygen content on the carbon surface. Significant differences on the AC surface chemistry have been detected depending on the presence of toluene in the solvent during the electrochemical treatment, which merit further research.

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