EFFECT OF THE ANODE ON THE ELECTROCHEMICAL REGENERATION AND POROSITY RECOVERY OF PHENOL-SATURATED ACTICVATED CARBON

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Introduction

Nowadays, activated carbons (ACs) are being widely used for the treatment of industrial water effluents to meet environmental legislations. In the particular case of high toxic, refractory and non-biodegradable phenolic compounds, the unique properties of ACs make the adsorption technology the most frequently used method for their removal from aqueous solutions.

During the use of the AC, the porosity becomes progressively saturated and the economics of the adsorption process greatly depends on the reuse of the spent activated carbon. For this reason, the regeneration of spent activated carbon is an important issue in order to increase the efficiency and feasibility of the overall process on an industrial scale [1].

In spite of the several advantages compared with the more traditional methods (thermal, chemical, etc.), less attention has been paid to the electrochemical regeneration. In this sense, we have recently demonstrated [2] that the electrochemical regeneration process under appropriate conditions can produce similar regeneration efficiency (RE) values and higher porosity recovery than those obtained by thermal treatment.

The influence of different electrochemical parameters on the RE and porosity recovery achieved by the electrochemical regeneration method has been recently reported and an overall electrochemical regeneration mechanism has been proposed. The best results were obtained in alkaline medium by cathodic regeneration in an undivided cell, at moderate current intensities and for regeneration times of 3 h [3].

It was also found that although the electrooxidation of desorbed phenol during the electrochemical regeneration of AC, favours phenol desorption it can also hinder the regeneration process due to the AC blockage of porosity by the electrooxidation products (quinones, polymers, etc.). These results suggested that the nature of the anode should play a key role on the electrochemical regeneration performance [3]. Thus, the objective of this work is to analyze the influence of the anode material, current and electrolysis time on the RE and the recovery of the textural properties of a commercial phenol-saturated granular AC.

Experimental

A commercial granular activated carbon, from Waterlink Sutcliffe Co. (207A; 12 × 20), was selected for this work. Adsorption experiments for the saturation of the ACs (0.254 g PhOH/g AC) were obtained from closed batch experiments. The detailed adsorption conditions have been previously reported [2,3].

The electrochemical regeneration of AC has been carried out in a filter-press electrochemical cell [2,3] with the most efficient undivided cell configuration and in 0.5 M NaOH [3].

Essentially, 2 g of the phenol-saturated original AC (W) were placed in the cell, like a granular AC fluidized bed, just in contact with the cathode. A stainless steel electrode was used as the cathode in all the experiments. For the study of the effect of the anode material, four different electrodes were employed: Ti/SnO_2-Sb(13%)-Pt(3%), Ti/SnO_2-Sb(9.75%)-Ru(3.25%)-Pt(3%), Ti/RuO_2 and Ti/Co_3O_4. The area of all electrodes was 20 cm^2. Electrochemical regeneration was carried out at constant current conditions (0.2, 0.5 and 1.0 A) and the effect of the regeneration time was studied within the range of 0-72 h.

The change in electrode potential, solution pH, chemical oxygen demand (COD) and phenol and p-benzoquinone (as a main oxidation intermediate product) concentrations were monitored throughout the regeneration experiments. The amount of phenol and p-benzoquinone were measured by UV-Vis Absorption Spectroscopy.

The regenerated AC samples were used for the readsorption of phenol, under the same initial conditions, to determine the percentage of regeneration efficiency (RE):

$$RE = \frac{\text{adsorption capacity of regenerated activated carbon}}{\text{adsorption capacity of fresh activated carbon}} \text{x} 100$$

The textural properties of all regenerated samples were analyzed by means of N_2 (at 77K) and CO_2 (at 273K) adsorption isotherms.

Results and Discussion

As seen in Table 1, the electrochemical regeneration with the different tested anodes produces RE values as high as 70%, which are, at least, a 10% higher than those obtained with the same solution in the absence of current (chemical regeneration) [2]. An increase in the applied current between 0.2-1.0 A slightly rises the RE values, mainly in the case of SnO_2-Sb-Pt, whereas the performance of the Co_3O_4 electrode seems to be independent of this parameter.

The RuO_2 anode shows the highest REs (80-85%) at the different currents, whereas the SnO_2-Sb-Pt presents a similar performance only at 1.0 A. These REs values for both electrodes are achieved after 3h-experiments, and are not further improved by increasing the regeneration time. The introduction of Ru in the SnO_2 anode slightly decreases the RE values. However, this anode achieves higher REs when the regeneration time is increased (close to 80% after 7 h) (figure not shown).

The better performance of the SnO_2-Sb-Pt and RuO_2 anodes is attributed to their higher phenol and COD elimination rates and efficiencies (data not shown). The introduction of Ru in the doped-SnO_2 anode decreases the efficiency and slows down the kinetics of phenol oxidation.

However, it increases the electrochemical stability. The poor catalytic performance towards phenol oxidation shown by the Co_3O_4 anode seems to indicate that electrodesorption would be the main process, from the overall regeneration mechanism [3], acting during the electrochemical regeneration of AC with this electrode.

Table 1. Effect of the anode and the applied current on the RE and porosity recovery (%S_{BET}) of the electrochemically-treated AC samples (t = 3 h).

	Current (A)					
	0.2		0.5		1.0	
Anode	RE	%S_{BET}	RE	%S_{BET}	RE	%S_{BET}
SnO_2-Sb-Pt	73	65	76	75	81	85
SnO_2-Sb-Ru-Pt	72	43	73	45	74	47
RuO_2	82	58	84	58	85	65
Co_3O_4	69	55	70	57	68	52

The UV-Vis spectrum evolution of the electrolyte during electrochemical regeneration experiments indicated that desorbed phenol (PhOH) is electrooxidized to p-benzoquinone (BQ). Fig. 1 shows that initial Ph desorption is higher with the SnO_2-Sb-Pt anode. The higher COD and similar BQ concentration achieved after 3h-experiments indicates that a lower proportion of BQ is produced with the SnO_2-Sb-Pt anode. Moreover, both the Ph and the BQ concentrations and the COD decrease with the SnO_2-Sb-Pt anode faster than those observed with the RuO_2 one.

Table 1 also shows the porosity recovery (%S_{BET}) of the different regenerated samples. As it can be seen, the low porosity recoveries obtained by the anodes with Ru do not agree with their corresponding REs. As shown in Fig. 1, these discrepancies between RE and %S_{BET} values could be attributed to the higher proportion and/or lower elimination activity of BQ blocking oxidation product obtained with these anodes. On the contrary, faster BQ elimination and/or a lesser favoured BQ generation seem to be responsible for the highest porosity recovery obtained with the SnO_2-Sb-Pt anode, which agrees with RE values. The highest REs achieved with the RuO_2 anode suggest that BQ blocking the porosity does not hinder the phenol re-adsorption after regeneration.

Conclusions

Results presented in this work show that the nature of the anode material strongly influences the performance of electrochemical regeneration of AC. Thus, both the RE values and the porosity recovery achieved by the electrochemical method can be properly optimized by the right choice of a suitable anode material, as well as other electrochemical parameters [3].

Considering the previously proposed mechanism of electrochemical regeneration of AC [3], this anode influence can be explained by the different electrocatalytic activity towards phenol oxidation of each anode and its favored phenol electrooxidation pathway, which determines the degree of phenol elimination and the amount and nature of blocking electrooxidation products, respectively.

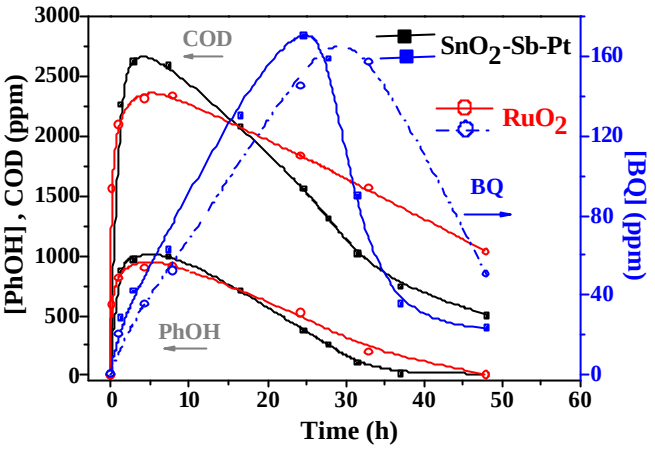

Fig. 1 Evolution of phenol (PhOH), COD and p-benzoquinone (BQ) in the NaOH electrolyte during regeneration experiments performed with different anodes (I = 0.5 A; Total time = 48 h).

The highest REs are achieved with the most active RuO_2 and SnO_2-Sb-Pt anodes. Lower porosities can be recovered with the Ru-containing anodes because of the favored benzoquinone generation. On the contrary, the better performance towards p-benzoquinone elimination and/or its unfavoured formation may account for the highest porosity recovery obtained with the Ru-free SnO_2 electrode. Although less efficient, for real applications, the SnO_2-Sb-Ru-Pt anode appears as a good alternative to the much more expensive RuO_2 electrode and the less stable SnO_2-Sb-Pt one.

Acknowledgments. The authors thank the Ministerio de Ciencia e Innovación and FEDER (MAT2007-60621) and GV (PROMETEO/2009/047) for financial support.

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