CATALYZED REGENERATION OF ACTIVATED CARBONS USED FOR NONYLPHENOL ADSORPTION FROM AQUEOUS SOLUTIONS

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Introduction

Polyethoxylated alkylphenols (PEAP) have been applied nonionic surfactants since the mid-1940s. Actually more than 200.000 tons per annum of these compound are produced in Europe per year. They have a wide variety of applications, i.e. agricultural and industrial applications, cosmetic preparations, detergents, industrial cleaners, emulsifying agents and biochemical research [1-3]. The PEAP's biodegrade to alquilphenols in aqueous environment [4] and then bio-accumulate in aquatic organisms. It has been demonstrated that these kind of substances have estrogen properties (e.g. feminizing plants, fish and animals) [5]. The aim of this work is to study: the use of activated carbons as adsorbents of nonylphenol from aqueous solutions, and to try a catalyzed thermal regeneration of spend carbon-adsorbents.

Experimental

Materials. Two commercial microporous activated carbons were used. A carbon R 0.8 from Norit N. V. (The Netherlands) (N) and a carbon prepared from olive stones ICASA (Spain) (S). These carbons were sieved between 0.5 and 1 mm. Supported metal oxide samples were prepared by the incipient-wetness impregnation method using aqueous solutions of ammonium metavanadate (ratio V/carbon 10%) and zirconyl nitrate hydrate (ratio Zr/carbon 8%). After the impregnation step, the samples were heated up 400°C in N_2 flow of 100 ml/min during 5 hours.

Specific surface areas. The specific surface areas were determined by nitrogen adsorption at 77 K by B.E.T. method. An automatic Micromeritics ASAP 2000 volumetric system was used to obtain the corresponding gas adsorption isotherms. The accuracy of this measurements is at least of 5%.

Nonylphenol adsorption isotherms. The nonylphenol adsorption isotherms from water solutions were obtained by the immersion method [6]. The adsorbed amount was calculated on basis of the concentration change, determined by UV (Varian Cary 1 Spectrophotometer) at 225.4 nm before and after nonylphenol adsorption on active carbons.

Temperature programmed desorption (TPD). In order to understand the desorption and decomposition of nonylphenol adsorbed on carbons, TPD experiments were performed in an oven under a flow (50 ml/min) of nitrogen or air. The heating rate was 10°C/min to 500°C. The gases evolved were analyzed by a mass spectrometer (Balzers Thermostar).

Results and Discussion

On Table 1, surface areas and adsorbed amount at the "plateau" (Γ) are given. The impregnation of carbon N with zirconium and of carbon S with vanadium produces a slight decrease of surface areas. Whereas the adsorbed amount of nonylphenol, in presence of zirconium, increases.

Table 1. Specific surface areas and adsorbed amount (Γ)

Sample	$S_{BET}(m^2/g)$	$\Gamma(\mu mol/m^2)$
N	1291	1.03
NZr	1183	1.28
S	1530	1.63
SV	1173	-

A regeneration based on thermal desorption with liquid water of activated carbons has been tried. However, as it can be seen in the Figure 1, the nonylphenol behaves like a typical nonionic surfactant. When the adsorption temperature increases, the amount of adsorbed nonylphenol rises also.

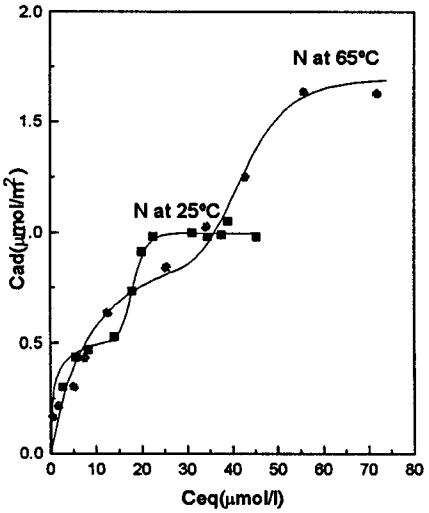

Figure 1. Nonylphenol adsorption isotherms on carbon N

The thermal desorption of nonylphenol is followed by mass 41 (Figure 2). The thermal regeneration under N_2 gas shows that, zirconium do not have any catalytic effect on nonylphenol desorption. However, the air shifts the nonylphenol desorption peak to lower temperatures probably by displacement of nonylphenol from carbon samples (oxygen is chemisorbed on carbons at around 300°C).

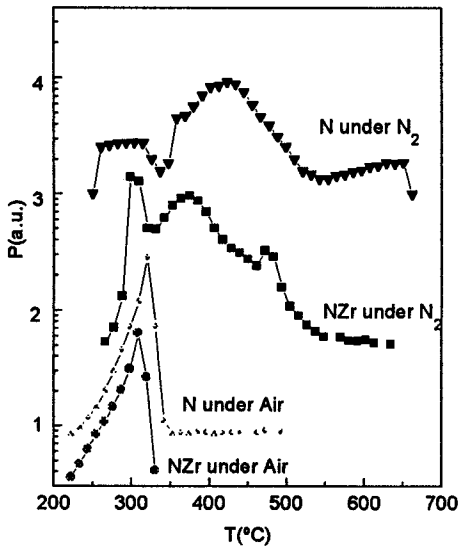

Figure 2. Desorption of nonylphenol during thermal regeneration of carbon N with and without

When the carbon S is impregnated with V, a clear catalytic effect on thermal desorption of nonylphenol (under air) is observed (Figure 3). Two peaks of nonylphenol desorption are present on S sample, at 300 and 450°C. When vanadium is added, only one peak is detected at 250 °C.

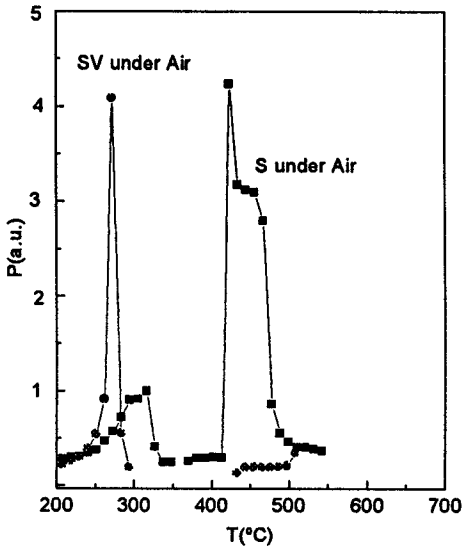

Figure 3. Desorption of nonylpenol during thermal regeneration of carbon S with and without V

Conclusions

It is not possible to regenerate active carbons with nonylphenol adsorbed by thermal desorption with liquid water. The zirconium do not have catalytic effect on thermal regeneration of carbons after nonylphenol adsorption. The air shifts the nonylphenol desorption peak to lower temperatures. The vanadium has a catalytic effect on thermal regeneration of carbons after nonylphenol adsorption.

Acknowledgments

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