



Aqueous thermal desorption as an effective way to regenerate spent activated carbons



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ABSTRACT

This work deals with the regeneration of p-Nitrophenol (PNP) loaded Activated Carbons by means of aqueous thermal desorption.

Continuous desorption experiments were performed under different temperature (140–200 °C) and stirring (100–600 rpm) conditions. The study was made with a double point of view; firstly, desorption kinetics was analyzed by applying non-linear Lagergren model. Secondly, the improvements on the textural parameters of the regenerated adsorbents as well as the regeneration efficiency were evaluated.

The results obtained revealed that the final amount of PNP desorbed was temperature dependent in the range 140–180 °C, while no improvement was found for higher temperatures, independently of the stirring speed. Likewise, temperature did not exert a marked effect on desorption kinetics.

The irreversibility of the adsorption processes was confirmed from N₂ and PNP adsorption analyses, although some differences were found. It is worth mentioning that increasing temperature did have a relevant influence on the adsorption regain of the adsorbents, being maximum for 200 °C (N₂ and PNP adsorption efficiency values up to 61% and 80%, respectively). This might be attributed to the occurrence of some activating effect induced by water under these conditions. The study of the prevalence of desorption over adsorption for enhanced temperature was complemented by the development of an Arrhenius-based model.

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1. Introduction

As it is well known, activated carbons (ACs) are widely used in water purification processes because of their versatility and ease to be tailored to meet specific applications. Nowadays, global consumption of ACs is raising significant growth, almost 10% per year, with a current AC consumption of 1.36×10^6 annual tons [1].

Once an AC has been used, their adsorption properties are damaged, due to the permanence of adsorbate or secondary products on the carbon porosity. In most cases, the spent AC is burnt, which entails some disadvantages, including the impossibility to reuse the adsorbent and the generation of highly toxic compounds, among others.

Thus, the regeneration of ACs allows a significant reduction in the costs associated with their production, and also ensures the use of a residue that would otherwise be discarded. In this sense, efficiency and regeneration cost have a relevant role in the adsorption process feasibility [2–4].

In most cases, regeneration consists in removing the compounds adsorbed from the saturated carbon in order to recover the adsorptive properties. In general, regeneration is carried out by subjecting

the spent carbon to conditions under which the adsorption equilibrium is altered in favor of desorption [5]. The ideal treatment would involve the desorption of the contaminant retained in the porous AC without producing any change in its porosity, neither on its surface chemistry characteristics. However, this is rarely possible, given the existence of irreversible adsorbent–adsorbate interactions, pore destruction, chemical interactions between the adsorbent surface and the products evolved during regeneration, and other effects such as erosion, which can influence the adsorbent properties of AC.

In general, the most interesting conditions to carry out a regeneration process will be those which allow a greater regeneration efficiency; that is the ratio between the adsorptive capacity of regenerated and fresh ACs. However, the regeneration efficiency is not the only parameter that governs the greater or lesser suitability of a process as economic cost factors. The generation of toxic products, ease of use, the possibility of cyclability or energy costs are crucial parameters when evaluating a regeneration method.

In this sense, various regeneration techniques have been proposed. Among them, desorption from AC in aqueous warm phase stands out due to its simplicity. Moreover, aqueous desorption comprises the first step in order to evaluate the potential of an adsorbate–adsorbent system to be regenerated via wet oxidation methods. The few works devoted to the study of desorption from

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ACs in aqueous warm solutions show a wide variety of results. While some of them state that the temperature driving force is not sufficient to regenerate the carbons, other studies report complete regeneration of adsorbents. For instance, Shende et al. [6] found regeneration efficiency values lower than 2% during regeneration of activated carbons exhausted with dyes. Also, Charzopoulos found irreversible adsorption of toluene when subjecting spent ACs to aqueous regeneration processes [7]. Dissimilarly, Pelech et al. [8] reported regeneration efficiency values up to 100% for ACs exhausted with toluene and benzene.

In the same line, Tamon et al. [9] have reported that the type of substituent groups in aromatic compounds affects the subsequent regeneration, as irreversible adsorption processes are involved. Moreover, these authors found that an increase on surface acidity weakens the adsorption irreversibility. Rivera-Utrilla et al. [10] studied the aqueous desorption of chlorophenol exhausted ACs and achieved regeneration efficiency values close to 100%, although their porosity analyses showed that a fraction of the adsorbent remained chemisorbed on the carbon. Salvador and Sánchez Jiménez [5] proposed this procedure for regenerating ACs with liquid water under subcritical conditions (300 °C), achieving a total recovery of adsorption capacity.

The variety of results concerning aqueous desorption processes motivates the need of studying each particular adsorption system. In this context, and provided that our research group has previously investigated the adsorption of p-Nitrophenol (PNP) onto ACs as well as the subsequent inert thermal regeneration [11], this work is aimed to get insights on the aqueous regeneration of this system. It is worth mentioning that p-Nitrophenol and phenols in general have been listed as top priority pollutants, and are widely used in the textile, paint, varnish, paper and plastic industries [12]. Since AC adsorption has been established as a suitable technology to remove these compounds [13], great amounts of phenol-spent AC are expected to be generated.

Desorption processes were made with liquid water at low temperature (140–200 °C) and different stirring speed (100 and 600 rpm). Previous spectrophotometric scanning tests showed the thermal stability of PNP solutions in the experimental range used.

It is worth noticing that our experimental conditions are less drastic than those reported in previous works on thermal desorption processes [14]. This is very interesting in order to provide a lower cost and simplicity to the process.

The desorption results were studied regarding the desorption equilibrium and kinetics using a model based on Arrhenius approach. The analysis of the desorption process irreversibility was complemented by the textural characterization of the adsorbents.

2. Materials and methods

p-Nitrophenol (Sigma, spectrophotometric grade, denoted as PNP) was selected as the model pollutant.

The adsorbent employed was a commercial activated carbon, Carbsorb from Chemviron, denoted as CB. Prior to use, the AC was repeatedly washed with boiling distilled water, oven-dried at 110 °C for 2 days and stored in a desiccator at room temperature.

The analysis of the fresh adsorbent, described in a previous work [15], showed that this adsorbent is a granular activated carbon ($\phi = 1.0\text{--}2.0\text{ mm}$), with a value of apparent surface (S_{BET}) equal to $930\text{ m}^2\text{ g}^{-1}$, and a very microporous nature.

2.1. Saturation of activated carbon

The saturation of the adsorbent was made by adding 5 g of CB carbon to a PNP solution (1 L, 3 g L^{-1}). The system was then left to

equilibrium under a thermostated temperature of 298 K for 72 h, as previous works showed that these conditions guarantee the complete saturation of the carbon and the adsorption equilibrium, respectively [16].

2.2. Regeneration of activated carbons

A diagram of the experimental installation used for regeneration processes is shown in Fig. 1. Experiments were performed in a 500 mL stainless steel autoclave equipped with a mechanically driven stirrer working at different velocities (100 and 600 rpm). Temperature was maintained constant at 140, 160 180 and 200 °C, depending on the experiment, using an electric jacket.

The procedure for PNP desorption experiments was as follows: a mass of 0.5 g of spent activated carbon was added to the reactor with 433 mL of distilled water; these conditions were defined based on previous calculations, with ensure the coexistence of two phases (water and steam), in order to favor mass transference processes, under the experimental conditions used. Subsequently, heating was switched on, under the corresponding stirring conditions, up to the defined value of temperature.

The solution sample collection (0.5 mL) was done by slightly opening the valve named as “Sample out” in Fig. 1. This process was performed at various intervals of time, up to 430 min.

After filtering, the concentration of PNP in the supernatant solutions was analyzed by UV/Vis spectrophotometry at a wavelength of 225 nm (spectrophotometer UNICAM Heλios- α). This wavelength was selected after previous spectral scanning tests, which showed the stability of this signal (λ_{max}), along the whole pH range. Then, the absorbances of a series of standard solutions of different concentrations were measured and the suitability of Beer's law was confirmed. The regression coefficients were very close to one under the range of concentrations used in this study; the corresponding calibration curve has been included as Supplementary material (S1).

Subsequent to regeneration, the ACs were oven-dried at 80 °C for 2 days, weighed and stored in a desiccator at room temperature.

The regenerated adsorbents were denoted as Des/T/S, where T stands for the temperature of each desorption process and S denotes the stirring speed.

2.3. Characterization of activated carbons

The porosity of pristine, saturated and regenerated ACs was studied by N_2 adsorption at 77 K (AUTOSORB-1, Quantachrome). Previous to analyses, the samples were outgassed at 100 °C during 12 h.

Adsorption data were used to calculate typical textural parameters by means of suitable models [17]. In particular, the following parameters were calculated: (a) the value of the BET specific surface (S_{BET}), (b) the external surface (S_{EXT}) by the α_s -method using the reference non-porous solid proposed by Carrott et al. [18], (c) the volume of micropores through the Dubinin–Radushkevich equation (V_{DR}), and (d) the volume of mesopores (V_{me}), as the difference between the pore volume at $P/P_0 = 0.95$ and $P/P_0 = 0.10$.

Moreover, the predominance of acid or basic functionalities in the adsorbents' surface was estimated by calculating the point of zero charge (pzc) by mass titrations at different pH following the procedure described elsewhere [19].

The regeneration efficiency (R.E. %) was determined according to Eq. (1), which was used with two adsorbates: N_2 at 77 K (taking the adsorbed quantity as that corresponding to a partial pressure of 0.95), and PNP in aqueous solution at 25 °C (taking the adsorption

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