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A key parameter on the adsorption of diluted aniline solutions with activated carbons: The surface oxygen content

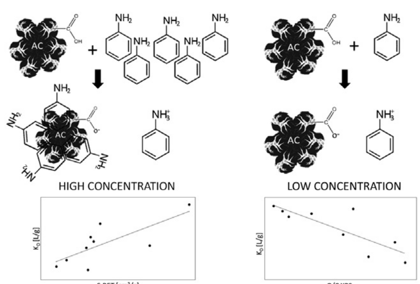
Beatrice Pardo [a, b], Nabí Ferrer [a], Julià Sempere [a], Rafael Gonzalez-Olmos [a, *]

[a] IQS School of Engineering, Universitat Ramon Llull, Via Augusta 390, 08017, Barcelona, Spain
[b] Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Piazza L. da Vinci, 32, Milan 20133, Italy

HIGHLIGHTS

- Physical properties of AC determines the maximum aniline adsorption capacity.
- Oxygen content of AC drives the adsorption at low aniline concentration.
- AC with low oxygen content and basic character are the best adsorbents for aniline.

GRAPHICAL ABSTRACT



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ABSTRACT

A total of 11 different commercial activated carbons (AC) with well characterized textural properties and oxygen surface content were tested as adsorbents for the removal of aniline as a target water pollutant. The maximum adsorption capacity of aniline for the studied AC was from 138.9 to 257.9 mg g^{-1} at 296.15 K and it was observed to be strongly related to the textural properties of the AC, mainly with the BET surface area and the micropore volume. It was not observed any influence of the oxygen surface content of the AC on the maximum adsorption capacity. However, it was found that at low aniline aqueous concentration, the presence of oxygen surface groups plays a dominant role during the adsorption. A high concentration of oxygen surface groups, mainly carboxylic and phenolic groups, decreases the aniline adsorption regardless of the surface area of the AC.

1. Introduction

Aniline is an important compound in the petrochemical industry, used primarily for the synthesis of isocyanate, an intermediate in the polyurethane manufacture. Aniline derivatives are also key precursors for the production of accelerators and antioxidants in the rubber industry, herbicides and pharmaceuticals (Chen and Huang, 2015). It is estimated that the world emission of aniline into the environment is 30,000 tons per year caused by accidental spills, illegal release of industrial and municipal wastewater, and excessive use of pesticides (Xiao et al., 2015). Due to the high toxicity of aniline for humans and aquatic life it is necessary to remove it from wastewaters.

Previous works have studied the removal of aniline from

* Corresponding author.
E-mail address: rafael.gonzalez@iqs.url.edu (R. Gonzalez-Olmos).

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aqueous solution using different treatments such as oxidation (Chen and Huang, 2015; Faria et al., 2007), extraction (Li, 2010), biodegradation (Orshansky and Narkis, 1997) and adsorption (Fazylova et al., 2015; Hu et al., 2014; László, 2005; Li et al., 2010; Valderrama et al., 2010; Wu et al., 2012; Xiao et al., 2015; Xie et al., 2007; Yao et al., 2008). Among all these methods, adsorption has been widely used in industry due to its easy operation and wide adaptability. Many investigations have analysed different adsorbents for the removal of aniline such as polymers (Hu et al., 2014; Yao et al., 2008), activated carbon (Han et al., 2006; László, 2005; László et al., 2007; Li et al., 2010; Nevskaia et al., 2004; Orshansky and Narkis, 1997; Podkościelny and László, 2007; Villacañas et al., 2006), inorganic layered materials (Xiao et al., 2015), nanotubes (Al-Johani and Salam, 2011) and minerals (Guan et al., 2015). Activated carbon (AC) has been the most studied and used adsorbent in industrial wastewater treatments, especially for those wastewaters with low organic pollutants concentrations (below 50 mg L^{-1}).

Although the use of AC in adsorption processes is a widely used technology, there are still some problems related with its use: high cost, the requirement of complex agents to improve the adsorption capacity, non-selectivity, problems with hydrophilic substances (Hu et al., 2014) and the regeneration of the saturated adsorbents (Cabrera-Codony et al., 2015). Another challenging problem is the selection of the best AC for each adsorption process. This selection must be based on the knowledge of the optimal physical and chemical properties of the AC. The knowledge of the optimal properties of AC is critical for those operators working with adsorption units.

Few works have barely studied the influence of textural properties (surface area and porosity) and chemical properties of AC in the adsorption of aniline (László, 2005; Li et al., 2010; Nevskaia et al., 2004). Li et al. proposed that aniline adsorption increases with micropore volume and that oxygen surface groups could affect negatively the aniline uptake. Nevskaia et al. concluded that aniline adsorption is governed by the presence of micropores and mesopores and also mentioned that the presence of oxygen on the AC surface affects the aniline adsorption. These works do not say anything about which properties, oxygen content or textural properties, are more relevant during the adsorption of aniline. Also, it has not been studied which type of oxygen surface groups could play a dominant role during the adsorption. For that reason, the objective of this work was to assess the combined effect of five textural properties and the oxygen surface content of AC on the aniline adsorption from water. The contribution of different 6 oxygenated groups was studied.

2. Materials and methods

2.1. Activated carbons

For the isotherms adsorption tests, 11 commercial granular AC supplied by MeadWestvaco (MWV) (U.S.A.), Desotec (DST) (Belgium), Chemviron Carbon (CMV) (Belgium), Calgon (CLG) (U.S.A.), and Norit (NRT) (U.S.A.) were tested. This materials were the same used in our previous work (Cabrera-Codony et al., 2014). Pellets were grounded and sieved, using molecular sieves, to obtain a particle size between 200 and 400 μm.

2.2. Physical and chemical characterization

The surface areas and pore volumes were calculated from the N_2 and CO_2 adsorption/desorption isotherms performed at −196 °C in a Micromeritics ASAP 2420 volumetric adsorption system and at 0 °C in a Quantachrome Nova Station A, respectively, following the same methodology of previous work (Cabrera-Codony et al., 2014). From the isotherms were calculated five textural properties: the specific surface area (S_{BET}), the total micropore volume (VDR_{N2}), the total pore volume (V_t), the mesopore volume (V_{meso}) and the volume of the narrow (<0.7 nm) micropore volume (VDR_{CO2}).

The oxygen content groups of the AC were analysed by Temperature Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS) and Elemental Analysis, using the methodology explained in previous work (Cabrera-Codony et al., 2014). TPD was measured with an Autochem II apparatus (Micromeritics). The XPS spectra of C and O were obtained with a VG ESCALAB 220i-XL spectrometer. Elemental analysis was carried out with a 2400 series II CHNS/O system (PerkinElmer). Oxygen surface groups (carboxylic, lactone, anhydride, phenolic, carbonyl and ether) content of AC was determined by the deconvolution of the TPD curves following the methodology explained in previous work (Cabrera-Codony et al., 2014).

2.3. Isotherm experiments procedure

Batch adsorption experiments were carried out in Erlenmeyer flasks with 100 mL of aniline solution. Aniline was purchased from Sigma-Aldrich and its purity was 99.5%. Seven different aqueous samples were prepared with an initial aniline concentration ranging between 10 and 1000 mg L^{-1}. The pH was adjusted using NaOH or HCl. Then, the adsorbent (0.1 g) was added into each flask and placed in a thermostatic mixer at 350 rpm, at three different temperatures ranging among 290–313 K, for 1 day to assure that the equilibrium was reached. The samples were filtered with a 0.45 μm regenerated cellulose filter in order to separate the AC particles. The concentration of aniline in the aqueous solution was measured using an UV-Vis Thermo Scientific Evolution 60 spectrophotometer at a wavelength of 280 nm. The experiments were carried out by triplicate.

The equilibrium data were fitted using the Langmuir and Freundlich adsorption isotherm models. The Langmuir isotherm (Eq. (1)) assumes monolayer adsorption onto a surface containing a finite number of adsorption sites.

$$q_e = q_{\max}\frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \tag{1}$$

The linear form of Langmuir equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{1}{q_{\max}} \cdot C_e \tag{2}$$

where C_e (mg L^{-1}) is the equilibrium concentration of aniline in solution; q_e (mg g^{-1}) is the amount of aniline adsorbed at equilibrium; q_{max} (mg g^{-1}) is the maximum adsorption capacity of the adsorbent which is calculated from the slope, and K_L (L mg^{-1}) is the Langmuir isotherm constant, which is calculated from the intercept.

The Freundlich isotherm (Eq. (3)) is an empirical equation, which suggests that adsorption energy exponentially decreases upon completion of the active centres of the AC.

$$q_e = K_F \cdot C_e^{1/n} \tag{3}$$

The linear form of Freundlich equation is expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{4}$$

where K_F (mg $g^{-1}\cdot$(L $mg^{-1})^{1/n}$) is the Freundlich constant, which is calculated from the intercept; and 1/n is the heterogeneity factor,