Dyes and Pigments 96 (2013) 459–466

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Role of acid blue 25 dye as active site for the adsorption of Cd^{2+} and Zn^{2+} using activated carbons

I.A. Aguayo-Villarreal [b], V. Hernández-Montoya [a,*], A. Bonilla-Petriciolet [a], R. Tovar-Gómez [a], E.M. Ramírez-López [b], M.A. Montes-Morán [c]

[a] Instituto Tecnológico de Aguascalientes, Av. Adolfo López Mateos No. 1801 Ote. C.P. 20256, Aguascalientes, Ags., Mexico
[b] Universidad Autónoma de Aguascalientes, Av. Universidad No. 940, Ciudad Universitaria, C.P. 20131, Aguascalientes, Ags., Mexico
[c] Instituto Nacional del Carbón, INCAR-CSIC, Apartado 73 E-33080, Oviedo, Spain

ARTICLE INFO

Article history:
Received 13 July 2012
Received in revised form
26 August 2012
Accepted 29 August 2012
Available online 7 September 2012

Keywords:
Adsorption
Dyes
Heavy metals
Activated carbon
Synergic effect
Binary solutions

ABSTRACT

The adsorption of acid blue 25, Cd^{2+} and Zn^{2+} on a physically activated bituminous carbon and a phosphoric activated carbon from wood was studied using single and binary (dye/metal) solutions, at 30 °C and pH 5. Results showed a synergic effect of acid blue 25 in the adsorption of Cd^{+2} and Zn^{+2}. Thus, the amount of metal ions adsorbed on both activated carbons increased with the initial concentration of acid blue 25. The effect was especially remarkable in the case of the adsorption of Zn^{2+} ions on the wood-based carbon. For this particular system, the metal uptake increased up to 60 times in presence of acid blue 25, when compared to the results obtained for the mono-component (Zn^{2+}-only) solutions. Modeling of the adsorption results showed that a surface response methodology approach was required to attain an adequate description of the multi-component adsorption.

1. Introduction

Activated carbon (AC) is the universal adsorbent used in the purification of gases and in the adsorption of organic and inorganic pollutants from drinking water and wastewater. The adsorption properties of ACs are determined by their textural characteristics and surface chemistry. The porous structure of ACs is attained via physical activation using steam or carbon dioxide, or by chemical activation using appropriate chemical agents (e.g., KOH, $ZnCl_2$, H_3PO_4) that are mixed with the AC precursor prior to its thermal treatment [1]. On the other hand, the surface chemistry of ACs is strongly determined by the presence of heteroatoms such as oxygen or nitrogen. Oxygen functional groups are the most common ones and they are reported to exhibit both basic (i.e., pyrone groups) and acidic character (i.e., anhydrides, lactones, carboxyls, phenols). Mineral impurities, if present, also have an influence on the surface chemistry of ACs [2].

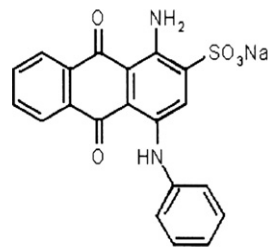
ACs are widely used for the removal of dyes from wastewater. Effluents from textile, paper and printing factories are highly colored and their disposal into receiving waters causes damage to the environment. Specifically, dyes may significantly affect the photosynthetic activity in aquatic life by reducing the penetration of light [3]. The efficiency and economy of the adsorption process depend on the physical and chemical characteristics of the adsorbent and the adsorption operating conditions (pH, temperature, mass to volume ratio). Accordingly, there is extensive literature covering multiple aspects of the adsorption of a number of different dyes on carbons. However, most of these studies concentrate in mono-component systems (aqueous solutions containing a single dye), i.e. [4–6], only few investigations report the adsorption of binary or ternary dye solutions [7,8]. This multi-component approach is obviously required in order to understand and predict the performance of the ACs in the treatment of real wastewater, which normally contain complex admixtures of dyes and/or other pollutants.

Indeed, industries are also compelled to minimize the release of heavy metals to the environment. Heavy metals are priority pollutants according to the US Environmental Protection Agency (EPA) classification because they are not biodegradable (hence tending to accumulate in living organisms) and many of them are toxic and carcinogenic [9]. They constitute a family of contaminants that may be found coexisting with dyes in wastewater. The

* Corresponding author. Tel.: +52 449 9105002x137.
E-mail address: virginia.hernandez@yahoo.com.mx (V. Hernández-Montoya).

0143-7208/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.dyepig.2012.08.027

Table 1
Structure and selected physicochemical characteristics of Acid Blue 25 (AB25).

Parameter	Description or value
Structure	
λ_{max} (nm)	600
Molecular weight (g mol^{-1})	416.38
Molecular volume (Å^3)	316.558
Length (Å)	5.413
Width (Å)	15.518
Depth (Å)	12.573

treatment of water containing both dye and metal ions is quite challenging and the simultaneous adsorption of such mixtures has been scarcely reported. To the best of our knowledge, only two studies investigate the adsorption of dye/heavy metal binary mixtures, in which fly ash and zeolites were used as adsorbents [10,11]. In those works, the adsorption of binary systems consisting of methylene blue and Cd^{2+}, Ni^{2+} and Cu^{2+} salts and aqueous solutions containing malachite green-Pb^{2+} were considered, respectively. The authors of both studies agreed in concluding that the adsorbed amount of heavy metals strongly decrease when the cationic dyes are present in the aqueous solution. However, we have recently reported that an important increase of heavy metal adsorption on a carbon adsorbent modified with a calcium solution was observed in the presence of the acid blue 25 (AB25) dye [12].

In the present paper, we shall demonstrate that such a synergistic effect is mainly due to the specific character of the dye selected (AB25), rather than the particular surface properties of the ACs used.

2. Experimental

2.1. Materials

Two commercial activated carbons from Clarimex (Mexico) were selected: CW is a wood-based AC prepared by chemical activation with H_3PO_4; and CB is a water vapor activated carbon from bituminous coal. CW and CB were milled and sieved in the lab and the 18–20 mesh fractions were selected to perform the adsorption experiments. Prior to this, the carbon particles were washed with deionized water until constant pH and, finally, they were dried at 110 °C for 24 h.

AB25 (C.I. 62055) was purchased from Aldrich and used without any additional purification. Its structure and some selected properties are shown in Table 1. The dimensions of the AB25 molecule were calculated using the Physical Properties Pro software (ChemSW, USA).

Standards of HCl and NaOH 1 M (Aldrich) were used for the titration analyses and nitrates of zinc (II) and cadmium (II) (J.T. Baker, purity of 100 and 99.9%, respectively) were used to prepare the heavy metal solutions.

2.2. Methods

2.2.1. Characterization of the ACs

The content of carbon, hydrogen, nitrogen and sulfur of the ACs were obtained in a LECO CHNS-932 elemental analyzer. The oxygen content of the ACs was measured directly in a LECO VTF-900 analyzer. FT-IR spectrometry at room temperature was used to ascertain the occurrence of functional groups on CW and CB surfaces. A Nicolet-8700 (Thermo Electron Co.) spectrometer equipped with a Smart Orbit accessory, which is a horizontal single-reflection attenuated total reflectance (ATR) accessory (HATR) with a Type IIA diamond crystal, was used for such purpose. The spectrometer was equipped with a deuterated triglycine sulfate (DTGS) detector that allowed us to collect the IR spectra in the 4000–500 cm^{-1} spectral range. The acidity and basicity of the carbon surfaces were quantified by potentiometric titrations following the reported methodology [13]. An Oakton pH meter was used for the titrations and special care was taken to minimize CO_2 interference, by continuous deaeration of the solutions/suspensions with nitrogen. The textural parameters of the ACs were calculated from the adsorption isotherms of nitrogen at −196 °C using an automated adsorption apparatus (Micromeritics ASAP2020). The experimental points of the nitrogen isotherms were analyzed using suitable models for microporous and mesoporous materials.

Table 2
Experimental design used for the simultaneous adsorption of AB25 dye and heavy metals on activated carbons.

	Factor A Concentration of AB25 (mg/L)					
Factor B	Levels	0	20	125	250	500
Concentration	0		$q_{e,[20,0]}$	$q_{e,[125,0]}$	$q_{e,[250,0]}$	$q_{e,[500,0]}$
of heavy	25	$q_{e,[0,25]}$	$q_{e,[20,25]}$	$q_{e,[125,25]}$	$q_{e,[250,25]}$	$q_{e,[500,25]}$
metal (mg/L)	50	$q_{e,[0,50]}$	$q_{e,[20,50]}$	$q_{e,[125,50]}$	$q_{e,[250,50]}$	$q_{e,[500,50]}$
	75	$q_{e,[0,75]}$	$q_{e,[20,75]}$	$q_{e,[125,75]}$	$q_{e,[250,75]}$	$q_{e,[500,75]}$
	100	$q_{e,[0,100]}$	$q_{e,[20,100]}$	$q_{e,[125,100]}$	$q_{e,[250,100]}$	$q_{e,[500,100]}$

2.2.2. Multi-component adsorption studies of AB25 and heavy metals

Adsorption tests were performed in batch systems using polycarbonate cylindrical cells with a lid, at constant temperature (30 °C) and pH (5). Specifically, 20 mg of adsorbent were suspended in 10 mL of the dye, metal or binary aqueous solutions. The concentration of the active species in solution was followed until the adsorption equilibrium was reached. Initial concentrations ranged from 20 to 500 mg/L for AB25 and from 25 to 100 mg/L for heavy metals. For these adsorption tests, a full factorial experimental design was used (see Table 2), the selected factors of the adsorption process being the initial concentration of both AB25 and heavy metal ion (i.e., Cd^{2+} or Zn^{2+}) in the metal–dye binary solution. The amounts of AB25, Zn^{2+} and Cd^{2+} adsorbed on CW and CB at equilibrium were selected as response variables in this factorial design. For comparison, the capacities of the adsorbents when using mono-component solutions of dye and each metal ion were also measured, at the same operating conditions (i.e., pH, temperature and adsorbent dosage).

Dye concentration was determined by UV–Vis spectrophotometry at the maximum absorbance of AB25 (i.e., 600 nm) using a UV–Vis HACH DR-5000 spectrometer. Concentrations of Zn^{2+} and Cd^{2+} were determined with a Perkin Elmer AAnalist 100 atomic absorption spectrometer equipped with an air–acetylene burner. All the experiments were conducted in triplicate, and average results are reported. Reproducibility of the experiments was within 6% of the mean values.

The retention capacities of the ACs for the different pollutants tested (q_i, mg/g) were calculated as follows:

$$q_i = \frac{(C_{0,i} - C_{e,i})V}{m} \tag{1}$$

where $C_{0,i}$ and $C_{e,i}$ is the initial and final (equilibrium) concentration (mg/L) of pollutant i (i.e., dye or heavy metal) in the binary solution,