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Relevance of anionic dye properties on water decolorization performance using bone char: Adsorption kinetics, isotherms and breakthrough curves

H.E. Reynel-Avila [a,b], D.I. Mendoza-Castillo [a,b], A. Bonilla-Petriciolet [a,*]

[a] Tecnológico Nacional de México, Instituto Tecnológico de Aguascalientes, Aguascalientes 20256, México
[b] CONACYT, Cátedras Jóvenes Investigadores, México, D.F., 03940, México

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ABSTRACT

This manuscript reports the performance of bone char for decolorization of aqueous solutions containing anionic dyes with different molecular properties. Kinetics, isotherms and breakthrough curves for the adsorption of acid blue 25 (AB25), acid blue 74 (AB74) and reactive blue 4 (RB4) on bone char have been determined and used for the assessment of the process performance where the impact and relevance of dye properties have been studied. An artificial neural network-based analysis was used to understand the relevance and impact of dye molecule properties on the adsorption behavior of bone char. Dye adsorption and intra-particle diffusion rates, adsorption capacities, equilibrium constants, enthalpies and breakthrough-curve parameters were calculated and correlated with the dye molecular properties. Results showed that these adsorption parameters were highly dependent on the properties of anionic dye molecules where the dimension of dye molecules is relevant during kinetics and breakthrough curves, while dye molecular weight has more impact on adsorption isotherms. These findings suggested that steric factors may govern the dye removal mainly in dynamic adsorption experiments. Experimental findings and FTIR characterization of bone char supported an anionic dye removal mechanism based on electrostatic interactions. In summary, the results of this study highlight the impact of anionic dye properties on the efficacy of batch and dynamic adsorption processes using bone char and provide new insights in water decolorization using this adsorbent.

1. Introduction

Dye adsorption from aqueous solutions is of considerable practical interest in the context of wastewater treatment and purification because these compounds are considered as priority pollutants due to their stability, low biodegradability and toxicological profile [1–4]. Performance of water decolorization processes can vary significantly depending on the adsorbent, dye chemical structure and operating conditions [2,5]. In particular, physico-chemical properties of dyes play an important role in the type of molecular interactions involved in aqueous phase adsorption [1]. Adsorbent surfaces and dyes molecules can interact via a variety of mechanisms such as Van der Waals forces, hydrogen bonding and electrostatic attraction [6,7]. The dye–adsorbent interactions depend on the dye molecule, solution properties (temperature, pH, ionic strength) and adsorbent properties (surface chemistry, textural properties, point of zero charge). These parameters determine the efficacy of dye removal, which are also impacted by the operating configuration of water treatment system (i.e., batch or dynamic mode). A limited number of studies have analyzed the importance of dye properties on the adsorption performance. Available studies have focused on assessing the influence of adsorbent properties on the removal efficacy of different dyes in aqueous solution [1,3,4]. Therefore, there is few information concerning the relevance and effect of properties of this type of pollutant molecules on the behavior of adsorbents. Note that the understanding of removal mechanisms involved in water decolorization and its relationship with pollutant properties can be employed for the synthesis of tailored adsorbents with outstanding removal capacity.

To date, several adsorbents have been reported for dye removal from aqueous solutions and they include different materials obtained from inorganic and organic sources [1,2,8]. They can be synthesized using different routes where the activated carbons obtained from lignocellulosic precursors have been widely used for water decolorization [1,3,4]. However, alternative dye adsorbents can be obtained from other precursors such as animal wastes [9–11]. Specifically, bone char can be synthesized from the pyrolysis of bovine bone wastes and its adsorption behavior can be tailored for a specific pollutant [12]. This mesoporous adsorbent is mainly composed of hydroxyapatite (70–76%), calcium carbonate (7–9%) and an amorphous carbon phase (9–11%) [12–14]. It shows attractive properties for water treatment and purification and several authors have reported its application in the removal of both organic and inorganic compounds [12,13,15–18]. Unfortunately, few studies have

* Corresponding author.
E-mail address: petriciolet@hotmail.com (A. Bonilla-Petriciolet).

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reported the water decolorization using bone char [9,10,19,20]. For example, Walker and Weatherley [19] analyzed the adsorption of acid dyes tectilon blue 4R, tectilon red 2B and tectilon orange 3G on this adsorbent where the adsorption capacities varied up to 500 mg/g. In another set of studies, Iq et al. [9,10] compared the removal of reactive black 5 using bone char and other adsorbents including activated carbons, where bone char showed a dye uptake of ~143 mg/g; while Ghanizadeh and Asgari [20] reported kinetics and isotherms for methylene blue adsorption on bone char. These studies have highlighted the potential application of this adsorbent for dye removal from aqueous solutions where it is clear that its adsorption capacities may vary significantly depending on the pollutant chemical structure and operating conditions of removal process.

This study reports the performance of bone char for decolorization of aqueous solutions containing anionic dyes with different molecular properties. These dyes are the acid blue 25 (AB25), acid blue 74 (AB74) and reactive blue 4 (RB4). These water-soluble anionic dyes are relevant as priority pollutants but, to the best of authors knowledge, there is no studies on its liquid-phase adsorption using bone char. Kinetics, isotherms and breakthrough curves have been used for the assessment of the removal performance of bone char where the impact and relevance of dye properties were studied at batch and dynamic operating conditions. An artificial neural network–based analysis was done in order to understand how the dye molecule properties impact the adsorption behavior of bone char. FTIR spectroscopy characterization was used for studying the surface chemistry of the adsorbent after dye adsorption and the possible removal mechanism of these anionic dyes has been discussed. In summary, the results of the present manuscript highlight the impact of anionic dye properties on the efficacy of batch and dynamic adsorption processes using bone char and results provide new insights in water decolorization using alternative mesoporous materials.

2. Methodology

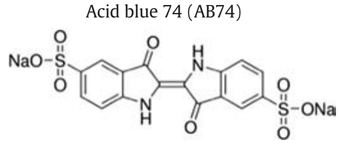
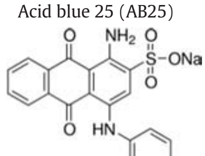
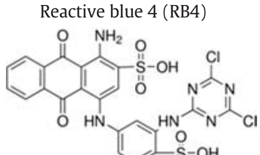
2.1. Bone char used for dye removal and its FTIR characterization

A commercial bone char supplied by Bonechar Carvão Ativado do Brazil Ltda. company was used in this study. This material has been applied in other adsorption experiments reported in the literature, e.g., [14]. It can be considered as a mesoporous adsorbent with the next physicochemical properties [14]: specific surface area = 113.3 m^2/g, total volume = 0.29 cm^3/g, mean pore diameters = 32.5 and 100.8 Å; and $pH_{pzc} = 7.5$. Bone char was washed using boiling deionized water, until obtaining a constant pH in the washing solution, prior to its use in dye adsorption experiments. Adsorbent particles were dried at 110 °C and sieved to obtain a mean size of 0.30–0.42 mm. These adsorbent particles were used in the decolorization experiments with no additional treatment. Surface chemistry of bone char has been analyzed, with and without loaded dyes, using FTIR spectroscopy. FTIR analysis of the adsorbent samples was performed using a Thermo Scientific Nicolet iS10 FTIR spectrophotometer. All spectra were collected in the range of 400–4000 cm^{-1} with 32 scans and a resolution of 4 cm^{-1} using the KBr pellets technique.

2.2. Adsorption of anionic dyes on bone char at batch and dynamic operating conditions

Kinetic, equilibrium and breakthrough curve studies were performed for analyzing the impact of anionic dye properties on the adsorption with bone char. As stated, these dyes are AB25, AB74 and RB4 where Table 1 shows the properties of their molecules. In the first stage, dye adsorption was done in batch reactors using an adsorbent-solution ratio of 2 g/L at 150 rpm. These decolorization studies involved different operating conditions (i.e., pH, dye concentration and temperature). In particular, adsorption rates were calculated at pH 4–6 and 30 °C using initial dye concentrations of 100 and 500 mg/L. These experimental data were used to obtain kinetic parameters such as dye intraparticle diffusion and uptake rates. On the other hand, the adsorption isotherms were obtained at 25, 30 and 40 °C and pH 4–6 using initial dye concentrations from 100 to 1000 mg/L where an equilibrium time of 24 h was used in these experiments. Mono-layer adsorption capacities and enthalpies were calculated from these experimental isotherms. Water decolorization experiments at dynamic conditions were performed in packed-bed micro-columns. The experimental setup consisted of polyethylene cylindrical micro-columns with an inner diameter of 1.07 cm where 2.6 g of bone char (i.e., bed length of 3.2 cm)

Table 1
Properties of anionic dyes used for water decolorization studies using bone char.

Dye molecule[a]	*Molecular dimensions*, Å			*Volume*, $Å^3$	*Molecular weight*, g/mol
	Length *X*	Width *Y*	Depth *Z*		
Acid blue 74 (AB74)  $C_{16}H_8N_2Na_2O_8S_2$	19.93	10.69	6.41	315.75	466.36
Acid blue 25 (AB25)  $C_{20}H_{13}N_2NaO_5S$	16.13	14.02	6.12	305.48	416.38
Reactive blue 4 (RB4)  $C_{23}H_{14}Cl_2N_6O_8S_2$	17.21	16.03	5.94	370.79	637.43

[a] Properties of dye molecules were taken from Aguayo-Villarreal et al. [36].