Journal of Hazardous Materials 161 (2009) 148–156

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Equilibrium and kinetic adsorption study of Basic Yellow 28 and Basic Red 46 by a boron industry waste

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ARTICLE INFO

Article history:
Received 4 July 2007
Received in revised form 8 January 2008
Accepted 13 March 2008
Available online 21 March 2008

Keywords:
Adsorption
Basic dyes
Kinetics
Isotherms
Waste material

ABSTRACT

In this study, the adsorption characteristics of Basic Yellow 28 (BY 28) and Basic Red 46 (BR 46) onto boron waste (BW), a waste produced from boron processing plant were investigated. The equilibrium adsorption isotherms and kinetics were investigated. The adsorption equilibrium data were analyzed by using various adsorption isotherm models and the results have shown that adsorption behavior of two dyes could be described reasonably well by a generalized isotherm. Kinetic studies indicated that the kinetics of the adsorption of BY 28 and BR 46 onto BW follows a pseudo-second-order model. The result showed that the BW exhibited high-adsorption capacity for basic dyes and the capacity slightly decreased with increasing temperature. The maximum adsorption capacities of BY 28 and BR 46 are reported at 75.00 and 74.73 mg g^{-1}, respectively. The dye adsorption depended on the initial pH of the solution with maximum uptake occurring at about pH 9 and electrokinetic behavior of BW. Activation energy of 15.23 kJ/mol for BY 28 and 18.15 kJ/mol for BR 46 were determined confirming the nature of the physisorption onto BW. These results indicate that BW could be employed as low-cost material for the removal of the textile dyes from effluents.

1. Introduction

In our century, waste disposal has become an issue of increasing worldwide concern. The use of waste materials for different purposes can play a significant role in helping to solve disposal problems. In addition, utilization of waste materials can contribute to the wise and efficient use of materials, to protect environment, and to improve the balance of trade by reducing the dependence on imported materials.

Amongst the various wastes, removal of hazardous industrial effluents is one of the growing needs of the present time. Various techniques like precipitation, ion exchange, chemical oxidation, and adsorption have been used for the removal of toxic pollutant from, wastewater [1–3]. Amongst these, adsorption has by far the highest potential because of its high efficiency and ability to separate a wide range of chemical compounds [4]. Over the years, a number of workers have used different waste materials such as coal fly ash [5,6], coal bottom ash [7–9], bagasse fly ash [10], blast furnace slag [11], deoiled soya [9,12], red mud [13], and sawdust [14] from industrial and agricultural products, as adsorbent for the removal of different pollutants. Recently, apart from these commonly used waste materials the authors have been trying to utilize waste materials from the boron industry to remove hazardous dyes [15].

Boron waste (BW) is a waste material originated in great amounts in enrichment process in boron plant. The amount of waste material has been progressively increasing. Therefore, its disposal currently poses a serious problem. Research is needed to find out a new application that reduces the amount of waste discharged. BW primarily contains ulexite ($NaCaB_5O_9 \cdot 8H_2O$), calcite, dolomite, and some clay. The combination of these materials to form a new type of adsorbent may produce somehow optimal properties. The key materials in BW are zeolite and ulexite. Zeolite is a silicate mineral with H^+ and OH^- ions being the potential-determining ions. The surface of zeolite is negatively charged in the entire pH region of practical interest. The basic structure of ulexite contains chains of sodium, water, and hydroxide octahedrons linked in endless chains. The chains are linked together by calcium, water, hydroxide, and oxygen polyhedra and massive boron units. The basic boron unit has a formula of $B_5O_6(OH)_6$ and a negative charge of three (−3). It is composed of three borate tetrahedrons and two borate triangular groups. The potential-determining ions for ulexite are Ca^{2+}, $B_4O_7{}^{2-}$, H^+, and OH^- ions [16].

Adsorption of dyes is mainly dependent on the dye's properties and structure and to an equal extent on the surface chemistry of the adsorbent [3]. It has been reported that ulexite carries negative charges at all practical pH values [16]. Since opposite charges attract, the negatively charged surface of BW may have an affinity

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0304-3894/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2008.03.064

Table 1
Properties of Basic Yellow 28 and Basic Red 46

Dye properties	Basic Yellow 28	Basic Red 46
Commercial name	Maxilon Golden Yellow GL 200%	Maxilon Red (GRL)
λ_{max} (nm)	438	530
Type	Cationic	Cationic
M_w (g mol^{-1})	433	322
Azo group	1	1

for cationic dye. Thus, it could be assumed that BW has a greater capacity to adsorb cationic dye.

In this study, we investigated the adsorption property of BW for cationic dye removal from aqueous solutions. The adsorption properties in terms of adsorption capacity were described. The influence of several parameters (kinetics, contact time, sorbent amount, dye concentration, and pH) on the adsorption capacity was evaluated and discussed. The equilibrium data have been analyzed using various adsorption isotherms.

2. Materials and methods

2.1. Dye stuff

The Basic Red 46 (BR 46) and Basic Yellow 28 (BY 28) are from a textile factory in Istanbul and were of commercial quality. They are particularly suitable for dying of paper, leather, and textile. The structure of the dyes and their properties are given in Fig. 1 and Table 1. All dye materials were used as supplied and without further purification.

2.2. Adsorbent material

The BW used in this study was supplied from Etibor (Bigadiç Balıkesir, Turkey). It was received without any treatment. X-ray diffraction patterns of BW and calcinated BW were obtained with a Rikagu Miniflex X-ray diffractometer using monochromatic Cu Kα radiation operating at 30 kV and 15 mA over the range (2θ) of scanning 5–60°. Chemical compositions of raw BW and calcinated BW samples were determined by using XRF spectrometer (Spectro X-Lab). Major chemical constituents of BW are given in Table 2.

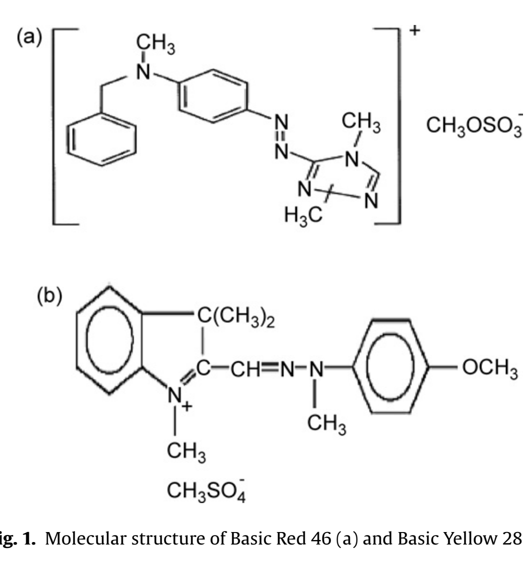

Fig. 1. Molecular structure of Basic Red 46 (a) and Basic Yellow 28 (b).

Table 2
Chemical composition of BW

Constituents	Chemical analysis (wt.%)
SiO_2	14.68
Al_2O_3	0.334
Fe_2O_3	0.136
CaO	12.551
MgO	9.57
SO_3	15.135
Na_2O	8.135
K_2O	0.031
B_2O_3	17.60
Loss on ignition	21.828

2.3. Adsorption procedure

In order to calculate the concentration from each experiment two calibration curves of BY 28 and BR 46 were first prepared. Different concentrations were prepared and absorbance values were recorded at λ_{max} = 530 nm and λ_{max} = 438 nm for BR 46 and BY 28, respectively. The adsorption of the two dyes at a fixed concentration on BW adsorbent was studied as a function of contact time. Nearly, 60 and 90 min are required for the equilibrium adsorption for BR 46 and BY 28, respectively. Equilibrium data were obtained by agitating various dye concentrations (50, 100,150, 200, 250, and 300 mg l^{-1}) for BR 46 and BY 28 separately with a fixed BW dose until equilibrium was established. The solution pH was adjusted to 9 by adding a small amount of HCl or NaOH (1 M). A fixed dose of 2 g l^{-1} was chosen after performing several trial studies to achieve maximum equilibrium sorption capacity for the dye concentrations in the range of (50–300 mg l^{-1}). After equilibrium or defined time intervals, the samples were taken from the magnetic stirrer, filtered off using Filtrak Filter Discs (number 391) and the filtrate was analyzed for residual dye concentration at the wavelength corresponding to maximum absorbance, λ_{max}, using a spectrophotometer (Shimadzu UV-1700 Double Beam). The effects of BW doses on the amount of dye adsorbed were investigated by agitating different amounts of BW (1–16 g l^{-1}) with BR 46 and BY 28 solutions (150 mg l^{-1}). The change of the absorbance of dye was determined at a certain time intervals (10, 20, 30, 45, 60, 90, 120, 150, and 180 min) during the adsorption process. The influence of pH on dye removal was studied over a wide range of pH (1–11) by adjusting dye solutions (150 mg l^{-1}). In order to study the adsorption kinetics 0.1 g of BW was kept in contact with 50 ml of dye solution for 60 min for BR 46, and 90 min for BY 28 to allow attainment of equilibrium at constant temperatures of 25, 35, 45, and 55 °C.

Zeta potential measurements were conducted using a Zeta-Meter System 3.0+ over a broad range of pH (2–11). One gram of BW in 100 ml of solution was conditioned for 10 min. The suspension was kept still for 5 min. to let larger particles settle. Each data point is an average of 10 measurements. All measurements were made at 20 ± 1 °C.

3. Results and discussion

3.1. Characteristics of adsorbent

Chemical composition of BW is given in Table 2. It contains SiO_2 and B_2O_3 with some calcium oxide, magnesium oxide, sodium oxide, and other oxides present in trace amounts. The XRD patterns of BW and calcinated BW are given in Fig. 2. The major phases of BW are ulexite, calcite, and colemanite, with minor dolomite, and zeolite. After heating, the peak intensities for ulexite significantly decrease.

To study the electrokinetic behavior of BW, zeta potential measurements were made. Fig. 3 shows the zeta potential of BW in