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Chemical Engineering Journal 124 (2006) 89–101

Chemical Engineering Journal

www.elsevier.com/locate/cej

Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions

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Received 11 January 2006; received in revised form 16 July 2006; accepted 6 August 2006

Abstract

Adsorption isotherm of maxilon blue GRL on sepiolite was determined and correlated with common isotherm equations such as Langmuir and Freundlich models. It was found that the Langmuir model appears to fit the isotherm data better than the Freundlich model. Furthermore, adsorption kinetics experiments were carried out to remove the maxilon blue GRL from its aqueous solutions using sepiolite as an adsorbent. The remove rate of maxilon blue GRL by sepiolite was studied by varying parameters such as the contact time, stirring speed, initial dye concentration, ionic strength, pH and temperature. The kinetics experiments indicated that initial dye concentration, ionic strength, pH and temperature could affect the adsorption rate of maxilon blue GRL. Sorption data were fitted to pseudo-first-order, the Elvoich equation, pseudo-second-order, mass transfer and intra-particle diffusion models, and found that adsorption kinetics can be described according to the pseudo-second-order model, from which the rate constant and the adsorption capacity were determined. Rate constants under different conditions were also estimated. In addition, we found that the rate-limiting step was intra-particle diffusion. According to the change of intra-particle diffusion parameter, the adsorption processes could be divided into different stages. Thermodynamic activation parameters such as activation energy E_a, enthalpy ΔH^*, entropy ΔS^* and free energy ΔG^* were determined. These parameters indicate that the adsorption has a low potential barrier corresponding to a physisorption; the adsorption reaction is not a spontaneous one; and the adsorption is physical in nature involving weak forces of attraction and is also endothermic.

Keywords: Sepiolite; Dye; Adsorption; Adsorption isotherms; Adsorption kinetics; Diffusion; Activation parameters

1. Introduction

(Ad)sorption at a solid–liquid interface is a complex process playing a crucial role in numerous industrial applications as well as in the fate and migration of chemical pollutants in the environment. In industry, the sorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are hardly destroyed in conventional wastewater treatment plants [1]. Dyes and pigments represent one of the problematic groups because they are toxic in nature with suspected carcinogenic and mutagenic effects [2] that affect aquatic biota and humans [3]. They are emitted into wastewaters from various industrial branches, mainly from the dye manufacturing and textile finishing [4] and also from food coloring, cosmetics, paper and carpet industries. Synthetic dyes have complex aromatic structures which provide them physicochemical, thermal and optical stability [5,6]. The sorption process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pretreatment step (such as activation) before its application [1].

Over the last few decades, adsorption has gained importance as a purification and separation process on an industrial scale and become an attractive option for industrial water treatment, especially the removal of organic compounds that are chemically and biologically stable [7,8]. The first step to an efficient adsorption process is the search for an adsorbent with high selectivity, high capacity, long life and if possible, it has to be available in tonnage quantities and at economical cost. Granular activated carbon is the most popular adsorbent that has been used with great success for the removal of dye from water [9–11]. However, adsorbent-grade activated carbon is cost-prohibitive and

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1385-8947/$ – see front matter
doi:10.1016/j.cej.2006.08.016

Nomenclature

C_t	dye concentration in solution at any time t (mol/L)
C_0	initial dye concentration in aqueous solution (mol/L)
D	diffusion coefficient (cm^2/s)
E_a	activation energy (kJ/mol)
ΔG^*	free energy of activation (kJ/mol)
h	Planck's constant
ΔH^*	enthalpy of activation (kJ/mol)
k_b	Boltzmann's constant
k_i	intra-particle diffusion rate constant (mol/$s^{1/2}$ g)
k_0	Arrhenius factor (g/mol s)
k_1	adsorption rate constant for pseudo-first-order kinetic equation (1 s^{-1})
k_2	adsorption rate constant for pseudo-second-order kinetic equation (g/mol min)
K	adsorption constant (L/mol)
K_F	a constant which is a measure of adsorption capacity (mol/g)
m	mass of adsorbent (g)
m_s	mass of adsorbent per unit volume (g/L)
$1/n$	a measure of adsorption intensity (L/mol)
q_e	equilibrium dye concentration on adsorbent (mol/g)
q_m	the adsorption capacity of adsorbent (mol/g)
q_t	the amount of dye adsorbed per unit mass of the adsorbent at time, t (mol/g)
r_0	the radius of the adsorbent particle (cm)
R_g	gas constant (J/K mol)
R^2	linear regression coefficient
S_s	the surface area of adsorbent (m^2/g)
ΔS^*	entropy of activation (kJ/mol)
t	time (s)
$t_{1/2}$	the half-adsorption time of dye (s)
T	temperature (K)

Greek symbols

α	the initial sorption rate (mol/g min)
β	the desorption constant (g/mol)
β_L	mass transfer coefficient (m/s)

both regeneration and disposal of the used carbon are often very difficult. Therefore, a number of nonconventional sorbents have been tried for the treatment of wastewaters. Natural materials, biosorbents, and waste materials from industry and agriculture represent potentially more economical alternative sorbents. For example, Vijayaraghavan et al. [12] investigated the use of six species of green, brown and red sea weeds as adsorbents. Again, the same authors [13] tested for its ability to remove copper(II) from aqueous solution using a brown marine alga *Turbinaria ornate* as an adsorbent. Moreover, they also reported the pH profiles during both sorption and desorption process.

Sepiolite, ($Mg_4Si_6O_{15}(OH)_2 6H_2O$), is a natural clay mineral with formula of magnesium hydro-silicate that occurs as a fibrous chain-structure mineral in clays in several areas of the world, although the major commercial deposits of sepiolite are in Spain and Turkey. Its structure, consisting of ribbons alternating with open channels along the fibre axes, has provided sepiolite with good adsorption properties [14,15]. It has been reported that sepiolite has a high adsorptive capacity for many gases and vapours, especially when the dimensions of their molecules allow them to penetrate into the channels of the adsorbent [16,17]. It has been also used as adsorbent of pesticides [18], as a catalyst support [19,20], in the anaerobic digestion of wastewater and solid wastes [21] and also as a support material on the methanogenesis from sewage sludge, reducing the toxic effect of some heavy metals [22]. In the present study, sepiolite has been used as a low-cost adsorbent for the removal of maxilon blue GRL dye. The effects of various factors such as contact time, stirring speed, initial dye concentration, ionic strength, pH and temperature on the adsorption rate of maxilon blue GRL dye on sepiolite from aqueous solutions were investigated. The experimental data was analyzed using various kinetic models such as pseudo-first-order, the Elvoich equation, pseudo-second-order, mass transfer and intra-particle transfer models. In addition, diffusion coefficient and thermodynamic activation parameters for removal of maxilon blue GRL on sepiolite from aqueous solutions were also determined.

2. Materials and methods

2.1. Materials

Sepiolite sample used in this study was obtained from Aktaş Lületaşı Co. (Eskişehir, Turkey). Some physical and physicochemical properties, and the chemical composition of the sepiolite found in Eskişehir, Turkey are given in Tables 1 and 2.

Table 1
Some physical and physicochemical properties of sepiolite

Parameters	Value	References
Surface area (m^2 g^{-1})	342	[23]
Density (g cm^{-3})	2.5	[23]
Cation exchange capacity (mg 100 g^{-1})	25	[23]
pH of solution	7.8–8.3	[23]
Porosity	50.8%	[24]
Color	White	[23]
Melting temperature	1400–1450 °C	[23]
Drying temperature	40 °C	[23]
Reflective index	1.5	[23]

Table 2
The chemical composition of sepiolite [20]

Compounds	Weight (%)
SiO_2	53.47
MgO	23.55
CaO	0.71
Al_2O_3	0.19
Fe_2O_3	0.16
NiO	0.43
Weight losing	21.49