Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Colloid and Interface Science 287 (2005) 6–13

Journal of Colloid and Interface Science
www.elsevier.com/locate/jcis

Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: A kinetic study

M. Al-Ghouti [a], M.A.M. Khraisheh [b,*], M.N.M. Ahmad [a], S. Allen [a]

[a] School of Chemical Engineering, Queen's University Belfast, Stranmillis Road, Belfast, BT9 5AG, UK
[b] Department of Civil and Environmental Engineering, University College London, Gower Street, London WC1E 6BT, UK

Received 17 August 2004; accepted 1 February 2005

Abstract

The effect of solution temperature and the determination of the thermodynamic parameters of adsorption of methylene blue (MB), Cibacron Reactive black C-NN (RB) and Cibacron Reactive golden yellow MI-2RN (RY) onto manganese-oxides-modified diatomite (MOMD), such as activation energy, E, enthalpy of activation, ΔH^*, entropy of activation, ΔS^*, and free energy of activation, ΔG^*, on the adsorption rates is important in understanding the adsorption mechanism. The rate and the transport/kinetic processes of dye adsorption onto the adsorbents were described by applying various kinetic adsorption models. This would lead to a better understanding of the mechanisms controlling the adsorption rate. The pseudo-second-order model was the best choice among all the kinetic models to describe the adsorption behaviour of RB onto MOMD, suggesting that the adsorption mechanism might be a chemisorption process. The activation energies, E, for RB, RY and MB were -6.74, 56.65 and 99.80 kJ/mol, respectively. The negative value of the activation energy suggested that the rise in the solution temperature did not favour RB adsorption onto MOMD. Moreover, the activation energy of the diffusion process, E', for RB, RY and MB increased as MB $>$ RY $\gg$ RB. It means that the RB molecules are much faster moving and a lower energy is needed to diffuse into MOMD than RY and MB molecules. E', the activation energy for adsorption into pores, of RY is higher than E, indicating that the rate-limiting step of RY adsorption onto MOMD might be diffusion controlled, while the activation energy of the diffusion process, E', of MB is slightly lower than E, suggesting that the rate-limiting step is a combination of chemical and diffusion adsorption.

Keywords: Adsorption; Diatomite; Modified adsorbents; Thermodynamic parameters; Kinetic studies; Reactive dyes; Methylene blue

---

1. Introduction

The removal of coloured and colourless organic pollutants from industrial wastewater is considered an important application of adsorption processes using a suitable adsorbent [1]. There is growing interest in using low cost, commercially available materials for the adsorption of dyes. Diatomite, a siliceous sedimentary rock available in abundance in various locations around the world, has received attention for its unique combination of physical and chemical properties (such as high permeability, high porosity, small particle size, large surface area, low thermal conductivity and chemical inertness) and as low cost material for the removal of pollutants from wastewater [2]. Previous studies by the authors established that chemical modification of diatomite, especially with manganese oxides, enhanced its dye removal capacity and its feasibility for large-scale application to the treatment of textile effluents containing reactive dyes; a difficult class of dyes to treat in traditional methods. Detailed information about the effect of this chemical modification can be found in Ref. [3]. For a successful scale-up of such a process, kinetic studies are essential since they describe the adsorbate uptake rate, which in turn controls the residence time in the adsorbent–solution interface. A number of experimental parameters are usually considered in these studies, including the effect of agitation speed, particle size, adsorbent mass, initial adsorbate concentration, as well as

---

[*] Corresponding author. Fax: +44-20-7380-0986.
E-mail address: m.khraisheh@ucl.ac.uk (M.A.M. Khraisheh).

0021-9797/$ – see front matter
doi:10.1016/j.jcis.2005.02.002

solution temperature. This paper focuses on the effect of solution temperature on the kinetics of dye removal from solution using manganese-oxides-modified diatomite (MOMD). The effect of the other variables is subject to pending publications by the authors.

Adsorption reactions are normally exothermic; thus the extent of adsorption generally increases with decreasing temperature. The change in the heat content of a system in which adsorption occurs, the total amount of heat evolved in the adsorption of a defined quantity of adsorbate on an adsorbent, is termed the heat of adsorption [4]. When any spontaneous process occurs, there is a decrease in the Gibbs free energy. Further, there must also be a decrease in entropy because the molecules lose at least one degree of freedom when adsorbed [5].

Various kinetic models have been reported in the literature to describe the adsorption process [6,7]. Each model has its own limitations and is derived according to certain conditions. However, the simplest way to describe the kinetics of dye removal from an aqueous solution could be represented by using a pseudo-second-order equation

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t, \quad h = k_2 q_e^2$$
$$\Rightarrow \quad q_t = q_e \frac{q_e k_2 t}{1 + q_e k_2 t}, \tag{1}$$

where q_t is the amount of solute adsorbed on the surface of adsorbent (mg/g) at any time t (min), q_e is the amount of solute adsorbed at equilibrium (mg/g), k_2 is the rate constant of a pseudo-second-order equation (g/mg min) and h is the initial adsorption rate (mg/g min).

In the intraparticle diffusion model, the relationship between the adsorption capacity at time t, q_t, and $t^{1/2}$ could be written as [8]

$$q_t = x_i + k_p t^{1/2}, \tag{2}$$

where k_p is the intraparticle diffusion constant (mg/g min$^{1/2}$) and x_i is the intercept of the line which is proportional to the boundary layer thickness.

The intraparticle diffusion coefficient, D, was determined by using the following equations, which are derived from Fick's law [9,10],

$$F(t) = \frac{C_0 - C_t}{C_0 - C_e} = \frac{q_t}{q_e} = \left[1 - \exp\left(-\frac{\pi^2 D t}{r^2}\right)\right]^{1/2} \tag{3}$$

or

$$\ln\left[1 - F(t)^2\right] = -\frac{\pi^2 D}{r^2} t, \tag{4}$$

where C_0 is the initial dye concentration (mg/dm^3), C_t is the dye concentration (mg/dm^3) at time t (min), C_e is the dye equilibrium concentration (mg/dm^3), D is the intraparticle diffusion coefficient (m^2/s) and r is the particle radius assuming spherical geometry (m).

A plot of $\ln[1 - F(t)]$ versus time, t, should be linear with a slop of $-\pi^2 D/r^2$, which is commonly known as the diffusional rate constant.

The activation energy of dye adsorption onto the adsorbent can be calculated by the relationships [5,11]

$$k_2 = k_0 \exp\left(\frac{-E}{RT}\right) \quad \Rightarrow \quad \ln(k_2) = \ln(k_0) - \frac{E}{R}\left(\frac{1}{T}\right), \tag{5}$$

$$k_p = k' \exp\left(\frac{-E}{RT}\right) \quad \Rightarrow \quad \ln(k_p) = \ln(k') - \frac{E}{R}\left(\frac{1}{T}\right), \tag{6}$$

$$D = D_0 \exp\left(\frac{-E'}{RT}\right) \quad \Rightarrow$$
$$\ln(D) = \ln(D_0) - \frac{E'}{R}\left(\frac{1}{T}\right), \tag{7}$$

where k_2 is the pseudo-second-order constant (g/mg min), k_0 is the rate constant of adsorption (g/mg min), k_p is the intraparticle diffusion coefficient (mg/g min$^{1/2}$), k' is the pre-exponential constant, D is the intraparticle diffusion coefficient (cm^2/s), D_0 is the pre-exponential factor, E is activation energy of adsorption (kJ/mol) (i.e., activation energy for adsorption to an external surface of the adsorbent), R is the gas constant (8.314 J/mol K), T is the solution temperature (K) and E' is the activation energy for adsorption into pores (kJ/mol). Plotting the rate of the adsorption against the reciprocal temperature gives a reasonably straight line, the gradient of which is $-E/R$.

To calculate the thermodynamic activation parameters such as enthalpy of activation, ΔH^*, entropy of activation, ΔS^*, and free energy of activation, ΔG^*, the Eyring equation was applied [12],

$$\ln\left(\frac{k}{T}\right) = \left[\ln\left(\frac{k_B}{h_P}\right) + \frac{\Delta S^*}{R}\right] - \frac{\Delta H^*}{R}\left(\frac{1}{T}\right), \tag{8}$$

where k_B is the Boltzmann constant (1.3807×10^{-23} J/K), h_P is the Planck constant (6.6261×10^{-34} J s), k is the pseudo-second-order constant (k_2) for RB adsorption or the intraparticle diffusion constant for adsorption of MB or RY (k_p).

The aim of this paper is therefore to consider the effect of solution temperature on the transport/kinetic process of reactive and basic dyes adsorption. The thermodynamic parameters of the process, such as activation energy, enthalpy and entropy and the free energy of activation, were determined.

2. Experimental materials and methods

Jordanian diatomite consisting mainly of SiO_2 (72%), 11.42% Al_2O_3, 5.81% Fe_2O_3, 7.21% Na_2O and 1.48% CaO was used. The composition was obtained by X-ray florescence (XRF) technique. Manganese chloride and sodium hydroxide were mainly used in the modification of raw diatomite to enhance the adsorption capacity of diatomite [3,13,14]. 15 g of the diatomite were immersed in sufficient 6 M sodium hydroxide and the temperature of the reaction mixture was maintained between 80 and 90 °C for 2 h. The diatomite was then placed in 100 cm^3 of 2.5 M manganese