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ScienceDirect
Journal of Hazardous Materials 146 (2007) 316–327
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Microcolumn studies of dye adsorption onto manganese oxides modified diatomite

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Received 6 August 2006; received in revised form 10 December 2006; accepted 12 December 2006
Available online 15 December 2006

Abstract

The method described here cannot fully replace the analysis of large columns by small test columns (microcolumns). The procedure, however, is suitable for speeding up the determination of adsorption parameters of dye onto the adsorbent and for speeding up the initial screening of a large adsorbent collection that can be tedious if a several adsorbents and adsorption conditions must be tested. The performance of methylene blue (MB), a basic dye, Cibacron reactive black (RB) and Cibacron reactive yellow (RY) was predicted in this way and the influence of initial dye concentration and other adsorption conditions on the adsorption behaviour were demonstrated.

On the basis of the experimental results, it can be concluded that the adsorption of RY onto manganese oxides modified diatomite (MOMD) exhibited a characteristic "S" shape and can be simulated effectively by the Thomas model. It is shown that the adsorption capacity increased as the initial dye concentration increased. The increase in the dye uptake capacity with the increase of the adsorbent mass in the column was due to the increase in the surface area of adsorbent, which provided more binding sites for the adsorption. It is shown that the use of high flow rates reduced the time that RY in the solution is in contact with the MOMD, thus allowing less time for adsorption to occur, leading to an early breakthrough of RY. A rapid decrease in the column adsorption capacity with an increase in particle size with an average 56% reduction in capacity resulting from an increase in the particle size from 106–250 μm to 250–500 μm.

The experimental data correlated well with calculated data using the Thomas equation and the bed depth–service time (BDST) equation. Therefore, it might be concluded that the Thomas equation and the BDST equations can produce accurate predication for variation of dye concentration, mass of the adsorbent, flow rate and particle size. In general, the values of adsorption isotherm capacity obtained in a batch system show the maximum values and are considerably higher than those obtained in a fixed-bed.

Keywords: Diatomite; Modified diatomite; Microcolumn; Reactive dyes; Textile effluent; Adsorption

1. Introduction

The disposal of textile wastewater effluents has become an important factor in running factories in many industries, and attention has to be given to methods of dealing with wastewaters in order to select the most economical methods [1,2]. 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 [3]. Previous studies by the authors established that chemical modification of diatomite, especially with manganese oxides (manganese oxides modified diatomite (MOMD)), 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 reference [4]. Other modifications have also been done by the authors such as microemulsion modified diatomite. This modification was not highly effective in reactive dye removing. But it was an excellent

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doi:10.1016/j.jhazmat.2006.12.024

Nomenclature

a	the slope
b	the intercept of the equation
C	the initial dye concentration (mg/L)
C_b	the breakthrough dye concentration (mg/L)
C_t	the equilibrium concentration (mg/L) at time t (min)
F	the flow rate (L/min)
k_T	the Thomas constant (L/min mg)
K	the adsorption rate constant (L/g min)
m	the mass of adsorbent (g)
N_0	the column adsorption capacity in BDST model (g/L)
q	the maximum column adsorption capacity (mg/g)
V	the throughput volume (L)
Z	the bed depth (dm)

one for methylene blue removing. Moore and Reid [5] showed that manganese-impregnated acrylic fibres were effective for removing radium from natural waters. Khraisheh et al. [6] also showed the effectiveness of removal of Pb^{2+}, Cu^{2+} and Cd^{2+} ions from wastewater using manganese modified diatomite. De Castro Dantas et al. [7] studied the removal of cadmium from aqueous solutions by diatomite with microemulsion.

Here, column studies are carried out to investigate the adsorption behaviour of dye adsorption onto the adsorbent. Batch type process is usually limited to the treatment of small volumes of effluents, whereas the bed column system has the advantage of operating continuous. For application of activated carbon adsorption in advanced water and wastewater treatment, the fixed-bed adsorber is considered most efficient [1]. Column studies could be conducted using large and small-scale columns. In this paper, it also has been decided to use a microcolumn to investigate the adsorption parameters and compare the results with those of large column. Furthermore, studying the adsorption process of a material using the microcolumn gives quick results. It is worthwhile mentioning here that large column studies give accurate results of the adsorption systems [8]. However, it has been suggested that the microcolumn technique could satisfactorily simulate the bed performance for large column runs [1].

Diatomite, as an adsorbent, can effectively remove the basic dye from solution and is inexpensive [4]. The capability of diatomite to remove reactive dyes from aqueous solution is less efficient compared to activated carbon [4]. In addition, when diatomite is directly used in wastewater treatment, there are some limitations, especially in column studies, especially in relation to low filtration rate. Al-Ghouti et al. [3] and Khraisheh et al. [4] showed that MOMD is a much more effective adsorbent for the removal of basic and reactive dyes from aqueous solutions. As a result, in this paper, MOMD was used as the main adsorbent. It has also been shown that MOMD has a high selectivity for dye removal.

Once the adsorbent has been chosen, the next important step is to conduct adsorption column tests and to investigate the column performance subject to different experimental conditions. In investigation of the column adsorption for removing the dye, two types of column experiments were conducted, small (microcolumn) and large (macrocolumn) columns. To our knowledge there is no research in the literature related to the use of microcolumns connected to a detector (spectrophotometer) in the study of the adsorption behaviour of dye onto adsorbent. Therefore, a rapid method for determining the adsorption parameters of dye onto MOMD for microcolumn application is proposed here.

Two simple mathematical models have been applied for the experimental data to predict the dynamic behaviour of the column and the following models characterising fixed-bed performance are discussed in detail here.

1.1. Thomas model

Thomas derived the mathematical expression for a column with a typical breakthrough curve [9]

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\ [k_T(q_0 m - C_0 V)/F]} \tag{1}$$

$$\Rightarrow \ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_T q_0 m}{F} - \frac{k_T C_0}{F} V \tag{2}$$

where C_0 is the initial dye concentration (mg/L), C_t is the equilibrium concentration (mg/L) at time t (min), k_T is the Thomas constant (L/min mg), F is the volumetric flow rate (L/min), q_0 is the maximum column adsorption capacity (mg/g), m is the mass of adsorbent (g) and V is the throughput volume (L).

Hence, a plot of $\ln(C_0/C_t - 1)$ versus V gives a straight line with a slope of $(-k_T C_0/F)$ and an intercept of $(k_T q_0 m/F)$. Therefore, k_T and q_0 can be obtained.

1.2. Bed depth–service time model (BDST)

The linear relationship between bed depth, Z, and service time, t, is [10]:

$$\ln\left(\frac{C_0}{C_b} - 1\right) = \ln(e^{K_a N_0 Z/F} - 1) - K_a C_0 t \tag{3}$$

Because the exponential term,$e^{K_a N_0 Z/F}$, is usually much higher than unity, the unity term within the brackets on the left-hand side of equation is often neglected [10]. Therefore, the linear relationship between the bed depth, Z, and the service time at breakthrough, t_B, is:

$$t_B = \left(\frac{N_0}{C_0 F}\right) Z - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \Rightarrow t_B = aZ + b \tag{4}$$

where C_0 is the initial dye concentration (mg/L), C_b is the breakthrough dye concentration (mg/L), Z is the bed depth (dm), N_0 is the column adsorption capacity in BDST model (g/L), F is the flow rate (L/min), K_a is the adsorption rate constant (L/g min), a is the slope and b is the intercept of the equation.