Available online at www.sciencedirect.com
ScienceDirect
Bioresource Technology 99 (2008) 2009–2017
BIORESOURCE TECHNOLOGY

Kinetics and thermodynamics of the adsorption of some dyestuffs from aqueous solution by poplar sawdust

Hüseyin Pekkuz, İlhan Uzun *, Fuat Güzel

Department of Chemistry, Faculty of Education, Dicle University, 21280 Diyarbakir, Turkey

Received 12 July 2006; received in revised form 8 March 2007; accepted 11 March 2007
Available online 30 April 2007

Abstract

The effect of temperature on the adsorption of metanil yellow (MY) (acidic) and methylene blue (MB) (basic) by poplar sawdust was investigated. In addition, the amounts of $NaHCO_3$, Na_2CO_3, NaOH and C_2H_5ONa adsorbed by 1 g of poplar sawdust to determine its surface acidity were also determined. Kinetical data obtained at different temperatures (293 K, 313 K and 333 K) for the adsorption of each dyestuff by poplar sawdust were applied to the pseudo first-order, the pseudo second-order and the intraparticle diffusion equations, and the rate constants of first-order adsorption (k_1), the rate constants of second-order adsorption (k_2) and intraparticle diffusion rate constants (k_p) at these temperatures were calculated, respectively. In addition, isothermal data obtained at different temperatures (293 K, 313 K and 333 K) for the adsorption of each dyestuff by poplar sawdust were applied to thermodynamical equations, and thermodynamical parameters (ΔG, ΔH and ΔS) were also calculated.

Keywords: Adsorption; Poplar sawdust; Dyestuff; Kinetics; Thermodynamics; Surface acidity; Diffusion

1. Introduction

Synthetic dyes are widely used for textile dyeing, paper printing, leather dyeing, colour photography and as additives in petroleum products (Radha et al., 2005). Unlike pigments, these dyes are absorbed to a certain extent by the material to which they are applied (Pilyugin et al., 1967). They exhibit a wide range of different chemical structures, primarily based on substituted aromatic and heterocyclic groups (Raymound and Dunald, 1984). Many synthetic dyes are toxic to some organisms and may cause direct destruction of creatures in water (Papic et al., 2004). Due to these reasons, these dyes must be removed from effluent. But synthetic dyes are highly soluble in water, and their removal from effluent is difficult by conventional physicochemical and biological treatment methods (Chern and Huang, 1998; Ozacar and Sengil, 2003).

In general, there are five main methods used for the treatment of dye-containing effluent: oxidation–ozonation; biological treatment; coagulation–flocculation; membrane; adsorption processes (Walker et al., 2003). However, these processes are costly and cannot effectively be used to treat the wide range of dye wastewater. For this purpose, to remove synthetic dyes from effluent new methods are still under development. The advantages and disadvantages of methods used are given in Table 1. The adsorption process is one of the most efficient methods of removing pollutants from wastewater. Also, the adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available (Namasivayam et al., 2001). Many studies have been made on the possibility of adsorbents using activated carbon (McKay, 1983; Uzun and Guzel, 2000), peat (Allen and McKay, 1987), chitosan (Uzun, 2006), chitin (Akkaya et al., 2007), silica (McKay et al., 1991), fly ash (Gupta et al., 1990), clay (Sethuraman and Raymahashay, 1975) and others (Frei and Zeitlin, 1965; Macchi et al., 1986; Maranon and Sastre, 1991; Balk-

* Corresponding author. Tel.: +90 533 5269110; fax: +90 412 2488257.
E-mail address: iuzun21@yahoo.com (İ. Uzun).

0960-8524/$ - see front matter
doi:10.1016/j.biortech.2007.03.014

Nomenclature

A	constant	q	amount of adsorbate adsorbed at time t (mmol g^{-1})
b	Langmuir constant related to adsorption energy (L $mmol^{-1}$)	q_e	amount of adsorbate adsorbed at equilibrium (mmol g^{-1})
C	concentration of adsorbate at time t (mmol L^{-1})	q_m	Langmuir constant related to the adsorption capacity of adsorbent (mmol g^{-1})
C_e	equilibrium concentration of adsorbate (mmol L^{-1})	R	universal gas constant (J mol^{-1} k^{-1})
C_o	initial concentration of adsorbate (mmol L^{-1})	r	correlation coefficient
E_a	activation energy (J mol^{-1})	S	the BET surface area (m^2 g^{-1})
k_1	the rate constant of first-order adsorption (min^{-1})	t	time (min)
k_2	the rate constant of second-order adsorption (g $mmol^{-1}$ min^{-1})	T	absolute temperature (K)
k_p	intraparticle diffusion rate constant (mmol g^{-1} $min^{-1/2}$)	ΔG	free energy change (J mol^{-1})
		ΔH	enthalpy change (J mol^{-1})
		ΔS	entropy change (J mol^{-1} k^{-1})

Table 1
The advantages and disadvantages of the methods used for the treatment of dye-containing effluents

Methods	Advantages	Disadvantages
Oxidation–Ozonation	The greatest advantages of oxidation are the rapid treatment time and the ability to treat dye-containing effluents at high concentrations	Oxidation is nonselective. Capital costs are typically high. Operating costs can also be high
Biological treatment	Some materials, such as amines and dyes, can also be biologically treated, whereas they cannot be treated by either chemical or ultrafiltration methods	Some chemical compounds do not readily degrade by biological treatment. Biocides used in the manufacturing environment greatly inhibit biological reactions
Coagulation–Flocculation	Coagulation and flocculation are very effective at removing fine suspended particles such as dyes	Some coagulants and flocculants are effective over a limited pH range. In addition, some coagulants and flocculants also add dissolved solids to water
Membrane filtration	Membrane filtration consistently separates a wide variety of dyes, surfactants, and chelating chemicals and various mixtures	Membranes are expensive. Synthetics are not effectively treated by this method
Adsorption	Adsorption process is one of the most effective methods to remove dyes from wastewater. It can achieve high recovery efficiencies	Some adsorbents are costly, and they adsorb dyes only chemically. It may result in the generation of a wastewater stream

ose and Baltacioglu, 1992; Roy et al., 1993). The advantages and disadvantages of some important adsorbents are given in Table 2. However, new adsorbents like new methods are also still under development to remove better the synthetic dyes from effluent.

Sawdust is a waste by-product of the timber industry that is either used as cooking fuel or a packing material (Garg et al., 2004). It is composed of three important constituents: cellulose, lignin, and hemicellulose. Cellulose is a long chain of glucose molecules, linked to one another primarily with β-(1-4) glycosidic bonds. Lignin is a complex polymer of phenylpropane units, which are cross-linked to each other with a variety of different chemical bonds. Hemicelluloses are branched polymers of xylose, arabinose, galactose, mannose, and glucose. Hemicelluloses bind the bundles of cellulose fibrils to form microfibrils, which enhance the stability of the cell wall. They also cross-link with lignin, creating a complex web of bonds which provide structural strength, but also challenge microbial degradation (Raji and Anirudhan, 1998; Ladisch et al., 1983; Kirk and Farrell, 1987). Numerous studies on the adsorption properties of naturally occurring and low-cost adsorbents, such as agricultural by-products or natural fibers, have been documented. Namely, barley straw, tree bark, peanut skins, human hair, waste tire rubber, moss peat, etc. have been reported in recent years. Studies have shown that sawdust, among the low-cost adsorbents mentioned, is the most promising adsorbent for removing heavy metals, acidic and basic dyes, and some other unwanted materials from waste water. Sawdust is not only abundant, but also it is actually an efficient adsorbent that is effective to many types of pollutants, such as dyes, oil, salts, heavy metals, etc. Many agricultural by-products are little or no economic value, and some, such as sawdust, which are available in large quantities in lumber mills, are often present a disposal problem. The use of sawdust for removing pollutants would benefit both the environment and wood agriculture: contaminated streams would be cleaned, and a new market would be opened for the sawdust (Shukla et al., 2002).