Journal of Saudi Chemical Society (2016) **20**, S241–S249

King Saud University

Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Alkaline treatment of timber sawdust: A straightforward route toward effective low-cost adsorbent for the enhanced removal of basic dyes from aqueous solutions

Yamina Djilali [a], El Hadj Elandaloussi [a,*], Abdallah Aziz [a], Louis-Charles de Ménorval [b]

[a] *Equipe Déchets Solides, Biomatériaux et Matériaux Polymériques, Laboratoire de Valorisation des Matériaux, Université Abdelhamid Ibn Badis, B.P. 227, 27000 Mostaganem, Algeria*
[b] *ICG–AIME–UMR 5253, Université Montpellier 2, Place Eugène Bataillon CC 1502, 34095 Montpellier Cedex 05, France*

Received 27 March 2012; accepted 13 October 2012
Available online 15 November 2012

KEYWORDS

Color removal;
Lignocellulosics;
Alkaline treatment;
Sorption;
Isotherms;
Regeneration

Abstract The present study assesses the ability of two low-cost adsorbents – timber sawdust (TS–OH) and its alkaline treated analog (TS–ONa) – to remove two basic dyes, namely, Methylene Blue and Methyl Green, from aqueous solutions. The presence of new functional groups on the surface of TS–ONa resulted in a dramatic increase of surface polarity and the density of sorption sites, thereby improving the sorption efficiency of the cationic dyes. The results obtained from the sorption characteristics have revealed that the sorption process for TS–ONa was uniform and rapid. The adsorption of cationic dyes reached equilibrium within the first 10 min of contact time and the treated material acts efficiently in a wide pH range of dye solutions. The extent of adsorption was measured through equilibrium sorption isotherms and analyzed using the Langmuir model. The monolayer saturation capacities for Methylene Blue are 694.44 and 1928.31 mg g^{-1} and for Methyl Green are 892.86 and 1821.33 mg g^{-1} for TS–OH and TS–ONa, respectively. Therefore, the chemically treated sawdust proved two- to threefold higher adsorption capacities of these dyes than those of the untreated analog. The exothermic nature of adsorption is demonstrated by a decrease of adsorption capacity with increasing temperature, and the negative value of free energy change indicated the spontaneity of adsorption. Desorption experiments with 1 M aqueous NaCl put into evidence that cationic dyes were completely desorbed from the matrices and the reusability of the TS–ONa matrix after three repeated cycles led to just a slight attenuation in its performance. These results show that alkaline treatment of a low value by-product of the timber industry leads to a

* Corresponding author. Tel.: +213 778118404.
E-mail address: andalou777@yahoo.com (E.H. Elandaloussi).

Peer review under responsibility of King Saud University.

ELSEVIER | Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jscs.2012.10.013

powerful and efficient low-cost adsorbent, which may be used for the treatment of colored wastewaters.

1. Introduction

Dyes are an important class of pollutants that are of environmental concern because of their known toxicity and tendency to accumulate in the natural environment (Bae and Freeman, 2007; Hai et al., 2007; Husain, 2006). Effluents originating from textile, dyeing, paper and pulp, tannery and paint industries and other plants manufacturing dyes tend to contain dyes in sufficient quantities. Wastewaters containing residual color are visible to the human eye and are therefore obnoxious on esthetic grounds. The non-biodegradable nature of the residual dye may also interfere with light penetration, and thereby can potentially affect the aquatic life in the ecosystem (Rai et al., 2005; Forgacs et al., 2004; Kuo, 1992; Walsh et al., 1980).

During the past three decades, several wastewater treatment methods have been developed for the removal of dyes from industrial effluents. Comprehensive studies dealing with the treatment of dyeing effluents by these techniques have been thoroughly reviewed in the literature (Gupta and Suhas, 2009; Crini, 2006; Aksu, 2005; Forgacs et al., 2004; Pokhrel and Viraraghavan, 2004; Thompson et al., 2001; Robinson et al., 2001; Banat et al., 1996). Hence, a great deal of published papers have established and proved their feasibility with regard to wastewater treatment. Among these methods, adsorption is one of the processes which has been frequently applied in wastewater treatment and especially for dye removal.

In the past decade, researchers have endeavored to develop alternative adsorbents deriving from renewable resources or less expensive natural materials. Recently, Gupta and Suhas have published an excellent review which provides further insight into this growing and important field of research (Gupta and Suhas, 2009). The availability of agricultural wastes or byproducts in large quantities and at low price has driven a growing interest in dye wastewater treatment. Accordingly, numerous studies have been conducted to investigate the efficiencies and mechanism of removal of dyes by various types of low-cost adsorbents (Ferrero, 2007; Hamdaoui, 2006; Ozacar and Sengil, 2005; Batzias and Sidiras, 2004; Aygun et al., 2003; Bouzaida and Rammah, 2002; Ho and McKay, 1998).

Sawdust is one of the most attractive materials used for removing pollutants from water/wastewater (Shukla et al., 2002). The lignocellulosic material is a by-product of the timber industry which is available in large quantities in lumber mills and this waste often represents a disposal problem. The material consists of cellulose, lignin and hemicellulose. Cellulose is composed of a long chain of glucose molecules, linked to one another primarily with β-(1–4) glycosidic bonds. Lignin is a complex polymer composed of phenylpropane units, which are cross-linked to each other by a variety of different chemical bonds. Hemicelluloses are branched polymers composed 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, and also challenge microbial degradation (Pekkuz et al., 2008; Raji and Anirudhan, 1998; Kirk and Farrell, 1987; Ladisch et al., 1983).

In addition to its complex chemical structure, the lignocellulosic matrix of sawdust embodies a wide variety of functional groups that play a major role for binding dyes through different mechanisms. The adsorption generally takes place by complexation, ion exchange and hydrogen bonding. Consequently, the use of lignocellulosic wastes in their raw state will ultimately lead to fair adsorption capacities of contaminants due to the antagonism of different mechanisms evolving throughout the removal process. Of course, one cannot argue with the success of these low-cost adsorbents, however, different studies illustrated the efficiency of the chemical treatment of raw lignocellulosic wastes. For instance, Batzias and Sidiras examined the adsorption of Methylene Blue and basic red 22 by beech sawdust and noticed that the chemical treatment of the raw adsorbent whether with calcium chloride (Batzias and Sidiras, 2004) or by subjecting the beech sawdust to mild acid hydrolysis (Batzias and Sidiras, 2007) did improve the adsorption capacity of the treated material.

As a contribution to this matter, we postulate that alkaline treatment of timber sawdust will lead to a modified material that ensures enhanced adsorption capacities for basic dyes. As a matter of fact, the treatment of timber sawdust with aqueous NaOH will not only permit the extraction of hemicelluloses and most part of lignin but will also allow the conversion of the polyol structure into a negatively charged cellulose-based material. The newly designed material will bear a large number of negatively charged sites on its surface favoring the adsorption of cationic dyes via electrostatic attraction. In fact, the adsorption capacity is a particularly important consideration when evaluating candidates for use in low-cost sorbents. However, the regeneration capacity of these materials often poses a serious drawback, which considerably limits their practical application. Therefore, when any given sorbent is efficiently regenerated without any essential loss in the sorption capacity in repeated sorption–desorption cycles, the material could then offer a cost-effective solution to the removal process, yet a better approach to the waste disposal problem. To meet these objectives, our work was set to prepare an appropriate low-cost sorbent material by a cost-effective chemical modification, namely, by treating a low value by-product of the timber industry with aqueous NaOH. The raw timber sawdust (TS–OH) and the chemically treated sawdust (TS–ONa) were subjected to batch experiments in order to evaluate and compare their removal capacities for Methylene Blue (MB) and Methyl Green (MG) from aqueous solutions and eventually to check the performance of the TS–ONa material after regeneration to ascertain its stability and reusability.

2. Materials and methods

2.1. Materials

Timber sawdust (TS–OH) was kindly provided by a local carpenter. The material as obtained was sieved for a particle size