Journal of Cleaner Production xxx (2016) 1–10

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Bentonitic clay as adsorbent for the decolourisation of dyehouse effluents

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ARTICLE INFO

Article history:
Received 26 October 2015
Received in revised form
10 February 2016
Accepted 11 March 2016
Available online xxx

Keywords:
Textile dyeing
Adsorption
Clay
Bentonite
Equilibrium
Kinetics

ABSTRACT

Textile dyehouses generate high volumes of coloured wastewaters, which require convenient treatment in order to avoid water bodies' contamination, adverse effects to aquatic life and risks to human health. The complete decolourisation of such contaminated waters in a cost-effective manner is still a challenge nowadays. This work focuses on the use of a clayey material as a low-cost adsorbent for a basic textile dye (Red 46), commonly used in acrylic fibres dyeing. The bentonitic clay (49% of montmorillonite) presents a considerable (50 $cmol_c/kg$) cationic exchange capacity and a porosity of 10%. Dye adsorption kinetics was successfully described by a pseudo-second order model, resulting an average kinetic constant of 0.23 $g_{dye}\ g_{clay}^{-1}\ min^{-1}$. Adsorption equilibrium was reached in 12–24 h and data were successfully fitted to Freundlich and Langmuir equations. The maximum adsorption capacity predicted by the Langmuir model depends on the pH, varying between 217 mg/g at pH 8 and 584 mg/g at pH 9 (25 °C). Increasing the temperature from 25 to 35 °C also led to an increase in adsorbed amounts. In addition to the excellent adsorption performance, the clay showed a great affinity to the dye, indicating high propensity to complete decoulorization of textile dyeing wastewaters. The results obtained in the present work show that a natural, readily-available and cheap material i.e. a bentonitic clay can be used as an effective and environmentally-friendly adsorbent for basic dyes.

1. Introduction

Industries have been facing more strict regulations in terms of environmental protection and are subject to pressures to include greener approaches in their processes. Textile industries are known to generate high volumes of wastewaters, with considerable biological (BOD) and chemical (COD) oxygen demands and persistent colour (Pereira and Alves, 2012; Santos and Boaventura, 2009). Research efforts have been dedicated to preventive measures in order to reduce the amount and toxicity of the wastewaters and increase the degree of fixation of the dyes onto the fibres. These measures have included the development of improved reactive dyes structures, modification of dyeing machinery and techniques, chemical modification of the fibres and use of greener compounds in dyebaths formulations (Bechtold and Turcanu, 2009; Khatri et al., 2015; Shahid-ul-Islam et al., 2013).

In spite of the progress achieved, attaining 0% of dye loss to the wastewater is not usually possible. In the particular case of acrylics dyeing with basic dyes, the typical dye loss is up to 5% (Easton, 1995). The residual colour is easily visible considering the high tinctorial strength of basic dyes and the high concentrations used. The introduction of dyes into water bodies harms their aesthetic condition, compromising many water uses (water supply, irrigation and recreational use). It also affects aquatic life, by reducing the sunlight penetration, decreasing photosynthetic activity and the dissolved oxygen (Saratale et al., 2011; Waters, 1995). The presence of dyes in water bodies, especially from the azo chemical class, poses serious health risks to humans and to aquatic life. The biodegradation of azo dyes under reductive conditions can result in potentially dangerous aromatic amines (Pereira and Alves, 2012). Textile effluents, being highly polluted, require a suitable treatment and, desirably, complete decoulorization.

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http://dx.doi.org/10.1016/j.jclepro.2016.03.092
0959-6526/

Conventional biological and coagulation/flocculation treatments, per se, are not effective and consistent on colour removal (Santos and Boaventura, 2015; Verma et al., 2012). In fact, the chemical stability of the dyes, their non-biodegradable nature and the enormous variety of colours and types, make colour removal even nowadays a problematic issue. Other methods such as electrocoagulation (Asghar et al., 2015), advanced oxidation processes (Asghar et al., 2015; Turhan and Turgut, 2009) and membrane separation (Dasgupta et al., 2015) have achieved good results but are not economically attractive to the industry. Adsorption is an interesting option, especially if applied as a tertiary refining step, after a conventional treatment method. Activated carbon is usually the adsorbent of choice in commercial systems, but its use is limited by the high costs of acquisition and regeneration (Santos and Boaventura, 2009). Many natural and waste materials have been investigated as non-conventional precursors for activated carbons preparation, with good results on the removal of different types of dyes (Kaouah et al., 2013; Sathishkumar et al., 2012; Saygili et al., 2015). In spite of the advantage of the use or reuse of these natural materials, chars and activated carbon production requires high temperatures and activation times and then high energy consumption (Gupta and Suhas, 2009; Sathishkumar et al., 2012).

Clay materials are inexpensive and present high specific surface area and reactivity. High-grade clays, such as montmorillonite, sepiolite, stevensite and kaolin have showed great adsorption capacities for basic dyes (Abidi et al., 2015; Bilgic, 2005; Turabik, 2008). In spite of competitive prices when compared to activated carbon, the worldwide production of pure clays is located in specific countries. Chemical modified clays, such as pillared clays, acid-activated and organoclays have been also explored (Anirudhan and Ramachandran, 2015; Eren et al., 2010; Fan et al., 2014), but with an additional cost related to the further treatment required. Literature is relatively silent about the use of non-pure clays as adsorbents. However, if these materials present enough efficiency, their use would be advantageous, due to the higher abundance, and especially if no or little processing is required. The inclusion of this kind of adsorbent in the water treatment technology contributes to a more efficient use of resources and energy and provides a cleaner production of textile fabrics.

In the present work, a Portuguese low-grade bentonitic clay (49% of montmorillonite) was employed as adsorbent. The aim was to study a readily-available and cheap material and compare its adsorption performance with conventional adsorbents and higher-grade clays. It is intended to show that, even without any purification or chemical treatment, an excellent adsorptive performance could be achieved. A textile dye commonly used in industry (C. I. Basic Red 46) was selected as adsorbate. It is from the azo chemical class, which is of special concern due to the mutagenic and carcinogenic effects of its derivatives (Chung and Cerniglia, 1992; Garg et al., 2002). The bentonitic clay was characterized and dye adsorption studied in terms of equilibrium, kinetics and influence of several factors.

2. Materials and methods

2.1. Materials

C. I. Basic Red 46 dye (designated hereafter as BR) was used as adsorbate. It is a basic dye, from the azo chemical class and commonly used for the acrylic fibres dyeing. The structure of BR dye is illustrated in Fig. 1. BR was supplied in the commercial form, with no purification. Aqueous solutions (BR concentration 200 mg/L) were prepared, by dissolving the required mass of dye in distilled water.

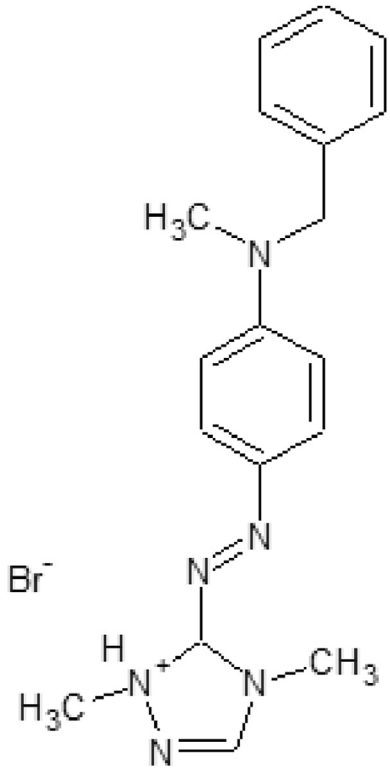

Fig. 1. Molecular structure of BR 46 dye.

Bentonitic clay was collected from soil deposits in Benavila, Avis, Portugal. After grain size separation, using a motorized sieve shaker, the fraction 0.150–0.300 mm was selected for use. The clay material was dried at 105 °C, stored in a desiccator and used with no further treatment.

2.2. Adsorbent characterization

2.2.1. Chemical and mineralogical characterization

The mineralogy of bulk sample was determined by X-ray diffraction carried out on a Philips diffractometer, PW1820 goniometer with a cobalt 2700W bulb (PW2256/20). The data were processed with the PW1877 Automatic Powder Diffraction program version 3.6 h (operating conditions: potential 40 kV, current intensity 40 mA).

For the chemical analysis, bulk samples milled to 200 mesh were analysed for their major elements by X-ray fluorescence spectrometry on fused discs using a Philips PW 2404 equipped with Rh tube and monochromator. Tube voltage and current were 40 kV and 60 mA, respectively. The accuracy and precision were respectively, 1% and 5%, for all major elements in general. Loss on ignition (LOI) was determined by heating at 1050 °C for 1 h.

Organic content of the bentonitic clay was determined using the solid sample analyser *SSM-5000A Shimadzu* and the European standard method EN 13137 (CEN, 2001).

Cation exchange capacity (CEC) was determined by method no. 9081 – EPA (1986), which is based on sodium adsorption followed by exchange with ammonium ion. The procedure was performed in triplicate.

The surface charge of the bentonitic clay was evaluated by the pH-drift method, reported by Lazarevic et al. (2007). A dose of 150 mg of clay was stirred with 50.0 mL of NaCl solutions (0.1, 0.01 and 0.001 mol/L, to provide three different ionic strengths), at different initial pH values (range 2–12), for 48 h and under orbital

Please cite this article in press as: Santos, S.C.R., et al., Bentonitic clay as adsorbent for the decolourisation of dyehouse effluents, Journal of Cleaner Production (2016), http://dx.doi.org/10.1016/j.jclepro.2016.03.092