Water Resources and Industry 9 (2015) 16–29

Contents lists available at ScienceDirect

Water Resources and Industry

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

Adsorption of textile dyes on raw and decanted Moroccan clays: Kinetics, equilibrium and thermodynamics

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ARTICLE INFO

Article history:
Received 13 August 2014
Received in revised form
28 September 2014
Accepted 3 November 2014

Keywords:
Clays
Adsorption
Textile dyes
Equilibrium
Thermodynamics

ABSTRACT

Inexpensive and easily available Moroccan natural clays were investigated for the removal availability of textile dyes from aqueous solution. For this purpose, the adsorption of methylene blue (MB) as reference molecule, malachite green (MG) representative of cationic dyes and methyl orange (MO) representative of anionic dyes, was studied in batch mode under various parameters. The clays were characterized by means of XRD, cationic exchange capacity and BET surface area analysis. The experimental results show that, the adsorption was pH dependent with a high adsorption capacity of MB and MG in basic range and high adsorption of MO in acidic range. The pseudo-second-order kinetic model provided the best fit to the experimental data for the adsorption of MB and MG by the clays. However, the adsorption of MO was more suitable to be controlled by an intra-particle diffusion mechanism. The equilibrium adsorption data were analyzed by Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. The adsorption process was found to be exothermic in nature in the case of MB and MO. However, the adsorption of MG was endothermic.

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http://dx.doi.org/10.1016/j.wri.2014.11.001

1. Introduction

Organic dyes constitute one of the larger groups of pollutants in wastewater released from textile and other industries. Among 7×10^5 t and approximately 10,000 different types of dyes and pigments produced world wide annually, it is estimated that 1–15% of the dye is lost in the effluents during the dyeing process [1]. This massive influx of untreated organic chemicals into the waterways not only introduces aesthetic concerns, but far more importantly it promotes eutrophication and adversely affects the environmental health of the region. It also represents an increasing environmental danger due to their refractory carcinogenic nature [2]. From an environmental point of view, the removal of synthetic dyes is of great concern. Among several chemical and physical methods, adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater.

Many adsorbents have been tested to reduce dye concentrations from aqueous solutions. Activated carbon is regarded as an effective but expensive adsorbent due to its high costs of manufacturing and regeneration [3]. In addition to activated carbon, some adsorbents including agricultural wastes [4,5], lignite [6], natural phosphate [7], chitosan [8], silica [9], kaolinite [10], hydroxyapatite [11,12], perlite [13], sepiolite [14], montmorillonite [15] and some natural biosorbents have also been reported [16,17]. However, studies in this field have not produced materials which meet all demands of adsorption activity. The use of natural materials is a promising alternative due to their relative abundance and their low commercial value.

Clays have a high adsorption capacity due to their lamellar structure which provides high specific surface areas [18], which may even exceed that of activated carbon under the same conditions of temperature and pH [19]. Adsorption and desorption of organic molecules in the clays are primarily controlled by surface properties of the clay and the chemical properties of the molecules [20].

The focus of the present study was to assess the potentiality of Moroccan natural clays as a low-cost adsorbent for the removal of methylene blue, malachite green and methyl orange from aqueous solution as an ideal alternative to the current expensive methods of removing dyes from wastewater.

Adsorption studies were carried out under various parameters such as pH, contact time, initial dye concentration and temperature. The adsorption kinetic data was tested by pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models. The equilibrium data were analyzed using Langmuir, Freundlich and Dubinin–Radushkevich isotherm models. The thermodynamics of the adsorption was also evaluated.

2. Experimental

2.1. Materials

All the necessary chemicals used in the study were of analytical grade. Methylene bleu (MB), malachite green (MG) and methyl orange (MO) were provided by the Sigma-Aldrich chemicals and used without further purification. The chemical formula and some other specific characteristics of these dyes are summarized in Table 1.

2.2. Preparation and characterization of the adsorbents

The raw clays used in this work were collected from Safi and Berrechid regions in Morocco. The raw clays were purified according to the following procedure: clay dispersion was placed in a graduated cylinder for allowing particles >2 μm in size to settle down and the fine fraction, whose size was <2 μm was extracted at the time of the static sedimentation of the particles in suspension based on Stokes equation [21]:

$$t = 191.5 \times \frac{X}{d^2} \quad (1)$$