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Interactive effect of garlic straw on the sorption and desorption of Direct Red 80 from aqueous solution

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ABSTRACT

The present research describes the sorption potential of low cost and easily available garlic straw for the removal of an azo textile dye, Direct Red 80 (DR 80), which is frequently used in the textile industry, from aqueous phase. The adsorbent was first subjected to several structural and chemical characterizations by FTIR, ^{13}C NMR, TGA, XRD and SEM. The influence of variables including pH, concentration of the dye and amount of adsorbent, particle size, contact time and temperature on the dye removal has been investigated. Three kinetic models were used to describe the sorption process. Three isotherm models were applied to evaluate the sorption equilibrium, and its thermodynamic parameters were calculated. More than 85% removal efficiency was obtained within 100 min at adsorbent dose of 0.2 g per 10 mL for initial dye concentration of 100 mg mL^{-1}. The maximum capacity of the garlic straw for sorption of DR 80 was 107.53 mg g^{-1} at pH 4 and 323 K. The sorption kinetic data were found to be in accordance with pseudo-second order kinetics. The sorption process and equilibrium of DR 80 were well fitted by Langmuir model. Calculation of various thermodynamic parameters such as free energy change, ΔG° enthalpy change, ΔH°; and entropy change, ΔS° indicate feasibility and endothermic nature of DR80 sorption. Desorption experiments were conducted for regenerating garlic straw which exhibited higher desorption capacity after sorption DR 80 using NaOH at pH 11. Overall, the relatively low cost and high capabilities of raw garlic straw make him a potentially attractive sorbent for the removal of DR 80 from the aqueous solution.

1. Introduction

Contamination of surface and ground water with synthetic dyes is a serious environmental problem and is a threat to human being and aquatic life (Gupta et al., 2006, 2007, 2013). Till date, more than 100,000 commercial dyes are known with an annual production of >7 × 10^5 tonnes/year (McMullan et al., 2001; Pearce et al., 2003). The total dye consumption in textile industry worldwide is more than 10,000 tonnes/year and approximately 100 tonnes/year of dyes are discharged into waste streams (Iqbal and Ashiq, 2007; Dizge et al., 2008). Azo dyes are synthetic colored compounds which consist of a diazotized amine coupled to an amine or a phenol, and characterized by the presence of one or more azo bonds (N=N). These dyes dominate the worldwide market of dyestuffs with a share of about 70% (Carliell et al., 1995), making them the

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largest group of synthetic colorants and the most common dyes released into the environment (Saratale et al., 2009; Zhao and Hardin, 2007). Azo dyes accounts for the majority (more than 3000 different varieties) of all textile dyestuffs produced because of the ease and cost effectiveness of their synthesis, their stability and the variety of colors available compared to natural dyes (Elbanna et al., 2010). They are extensively used in the textile, paper, food, leather, cosmetics and pharmaceutical industries (Telke et al., 2008). They possess toxicity like lethal effect, genotoxicity, mutagenicity, and carcinogenicity to plants and animals (Puvaneswari et al., 2006). Direct Dyes such as direct red are water-soluble anionic dyes, and, when dyed from aqueous solution in the presence of electrolytes have high affinity for cellulosic fibers. Generally the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines (Gupta and Suhas, 2009). Their discharge into the hydrosphere possess a significant source of pollution due to their visibility even at very low concentrations and due to their recalcitrance nature, giving undesirable color to the water, reducing sunlight penetration, resisting photochemical and biological attack, and their degradation products being toxic or even mutagenic, carcinogenic and increased COD and BOD levels of aquatic sources (Saleh and Gupta, 2014a; Van der Zee and Villaverde, 2005).

The wastewater including azo dyes is very difficult to treat because they contain one or more azo groups with aromatic ring and sulfonate groups which induce that they are resistant, stabile at aerobic digestion and oxidizing agent conditions (Dakiky and Nemcova, 2000; Saleh and Gupta, 2011; Shokoohi et al., 2010). Nowadays great attention has been focused on elimination of the effluents bearing dyes due to their potential toxicity and visibility problems. Various methods of treatment for dye/color removal are adopted in order to decrease their impact on the environment (Gupta et al., 2012a; Mahmoodian et al., 2015). These methods include coagulation, filtration, ion exchange, biological treatment, advanced oxidation processes, electrolysis, activated sludge, adsorption and solvent extraction (Bhaskar et al., 2003; Neumann, 2002). Among various methods of dye removal, adsorption is regarded as the simplest, the impactful and the most economical method for dyes treatment in wastewater (Gupta et al., 2011a,b; Abussaud et al., 2016). Adsorption is a surface phenomenon and defined as the increase in the concentration of a particular component at the surface or interface between two phases (Saleh and Gupta, 2014b). It is used for source reduction, wastewater treatment and reclamation for potable, industrial and other purposes (Saleh, 2015a). The basic problems associated with adsorption are the regeneration of columns. Moreover, the management of the exhausted adsorbent is also a challenging issue for scientists (Gupta and Saleh, 2013). The cost of the treated water ranges 50–150 US$ per million liters (Gupta et al., 2012a,b).

Highly functional porous materials with high surface area are generally used as suitable adsorbents to investigate adsorption efficiency for removing of dyes (Gupta et al., 2007; Saleh et al., 2011). In the last few years the by-products from the agricultural and food industry could be assumed to be low-cost adsorbents since they are abundant in nature, inexpensive, require little processing and are effective materials. The agricultural solid wastes from cheap and readily available resources such as almond gum (Bouaziz et al., 2015), corncob (Robinson et al., 2002a), barley husk (Robinson et al., 2002a), wheat straw (Robinson et al., 2002b; Nigam et al., 2000), mustard cake (Gupta et al., 2013) and orange peel (Rajeshwarisivaraj et al., 2001; Namasivayam et al., 1996) have also been successfully employed for the removal of dyes from aqueous solution. Some by-products are used for the adsorption of anionic dyes such as mango seed (Alencar et al., 2012), bagasse (Tsai et al., 2001; Valix et al., 2004), bamboo (Mui et al., 2010) and garlic peel (Asfaram et al., 2014).

In fact, during harvesting period garlic bulb yields a considerable amount of straw which is simply thrown or disposed causing a severe problem in the community. To the authors' knowledge, the use of garlic straw adsorbent for removal of Direct Red 80 (DR 80) has not been investigated. The present study aims to evaluate the potentiality of GARLIC STRAW for the removal of DR 80 from aqueous solution. X-ray diffraction (XRD), Fourier transform infrared (FTIR), solid-state ^{13}C CP/MAS NMR spectra, thermogravimetric analysis and scanning electron microscopy (SEM) were used to characterize the adsorbent. The effects of initial dye concentration, contact time, solution pH, particle size and temperature on DR 80 has been discussed. The equilibrium, kinetic and thermodynamic data of the adsorption process was analyzed to elucidate the mechanism of adsorption of DR 80 molecules onto garlic straw.

2. Materials and methods

2.1. *Preparation and characterization of the adsorbent*

2.1.1. *Preparation of garlic straw*

Garlic straw used in this study, was discharged from the manufacturing process of conservation of garlic. It was first cleaned, dried in sunlight and then cut into small pieces (1–3 cm). The cut straw was ground to pass a 0.1–2-mm size screen and stored at 4 °C (Kallel et al., 2015). The diameter and surface of garlic straw was measured automatically with the MorFi v7 fiber analyzer (Techpap, France) by a computer analysis of images of the suspension flowing through a flat cell observed by a digital CCD video camera. The sample was washed with distilled water, boiled with water for 30 min, filtered out and dried in an oven at 313 K for 24 h. The dried materials were crushed and sieved to obtain a particle size between >100, 110–250 and 260–350 μm.

2.1.2. *Chemical composition*

The chemical composition of garlic straw was determined according the methods showed in the sequence.

2.1.2.1. *Determination of extractives.* This method is based on standard T207 cm-08, using ethanol–toluene instead ethanol-benzene as extraction media. The extractives (E %) removed from lignocellulosic matter mainly consist on low molecular weight carbohydrates, salts, waxes, fats, resins and non-volatile hydrocarbons. For their determination, 4.0 ± 0.1 g of sample (m_0) were placed in a tarred extraction thimble (m_1) and positioned in the Soxhlet apparatus. The extraction was conducted for 6–8 h using 150 mL of mixture ethanol–toluene 2:1 under reflux. Afterwards, the extraction thimble was oven-dried at 105 ± 3 °C for 24 h, cooled and finally weighed (m_2), keeping the extractives-free sample in a desiccator for further analyses.

2.1.2.2. *Determination of acid insoluble lignin.* On the basis of the standard T222 om-11, 1.0 ± 0.1 g of moisture and extractives free sample (m_0), were placed in a 1 L flask with 15.0 mL of 72% sulphuric acid and kept at 20 ± 1 °C for 1 h in a thermostatic water-bath. After this, 575 mL of distilled water were