Ecotoxicology and Environmental Safety 135 (2017) 68–74

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

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

Zinc peroxide nanomaterial as an adsorbent for removal of Congo red dye from waste water

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ARTICLE INFO

Article history:
Received 17 June 2016
Received in revised form
10 September 2016
Accepted 19 September 2016

Keywords:
Adsorption
Congo red dye
Isotherm
Kinetics
Zinc peroxide

ABSTRACT

In the past decade, various natural byproducts, advanced metal oxide composites and photocatalysts have been reported for removal of dyes from water. Although these materials are useful for select applications, they have some limitations such as use at fixed temperature, ultra violet (UV) light and the need for sophisticated experimental set up. These materials can remove dyes up to a certain extent but require long time. To overcome these limitations, a promising adsorbent zinc peroxide (ZnO_2) nanomaterial has been developed for the removal of Congo red (CR) dye from contaminated water. ZnO_2 is highly efficient even in the absence of sunlight to remove CR from contaminated water upto the permissible limits set by the World Health Organization (WHO) and the United States- Environmental Protection Agency (US-EPA). The adsorbent has a specific property to adjust the pH of the test solution within 6.5–7.5 range irrespective of acidic or basic nature of water. The adsorption capacity of the material for CR dye was 208 mg g^{-1} within 10 min at 2–10 pH range. The proposed material could be useful for the industries involved in water purification. The removal of CR has been confirmed by spectroscopic and microscopic techniques. The adsorption data followed a second order kinetics and Freundlich isotherm.

1. Introduction

Contamination of water by dyes is one of the major threats to human health as well as environment. Dyes are the aromatic organic compounds having delocalization of electrons in a conjugated system (Zollinger, 2003). Dyes have wide range of utilization in paper, pulp, paints and textile industries, which requires large amount of water for washing and cleaning purposes. The resulting processed solutions from these industries are discharged without proper treatment into surface water which deteriorates the quality of water. Synthetic dyes including azo dyes are considered to be more toxic, mutagenic and carcinogenic in nature. Such dyes are difficult to remove from water as most of them are stable and non-biodegradable due to their complex aromatic molecular structure (Patel and Vashi, 2012).

Congo red (CR) is one of the highly water soluble secondary diazo dye. It is a sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulphonic acid with a molecular formula ($C_{32}H_{22}N_6Na_2O_6S_2$). The chemical structure of CR dye is shown in Fig. 1(a). The strong affinity of CR dye towards cellulose fibers makes it utilitarian in textile industries (Han et al., 2008). CR dye is considered as a metabolizer to carcinogenic products and causes serious irritation to eyes, skin, gastrointestinal gland, reproductive system and respiratory system (Mittal et al., 2009). In order to cope up with the problems caused by the CR and other dyes in the environment, several conventional chemical, physical and biological techniques like ozonation (Koch et al., 2002), advanced oxidation (Malik and Saha, 2003), electrochemical oxidation (Fan et al., 2008), reverse osmosis (Gupta et al., 2007), coagulation/flocculation (Pollock, 1973), precipitation (Liu et al., 2002), membrane filtration (Sachdeva and Kumar, 2009) etc. have been used for purification of water. However individual techniques have their own limitations. Out of these techniques some are very costly, time consuming and generate highly toxic sludge. So an economical and ecofriendly process is required for the removal of dyes from contaminated water. In recent years adsorption has gathered a lot of attention and proves to be more effective and efficient technique because of its simplicity, economic viability, ease of operation and availability of wide range of adsorbents.

Activated carbon (Namasivayam and Kavitha, 2002) is most commonly used due to its better adsorption capacity but it is very expensive and difficult to regenerate. So research has been focused towards development of low cost and effective adsorbents. In this

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http://dx.doi.org/10.1016/j.ecoenv.2016.09.017
0147-6513/

regard several natural and agricultural by products such as aerobic gram positive bacillus (Sawhney and Kumar, 2011), marble powder (Roy and Mondal, 2015), hazel nutshells (Carletto et al., 2008), Chitosan and cetyl trimethyl ammonium bromide (CTAB) modified chitosan (Chatterjee et al., 2009), phosphomolybdic acid (Jeyabalan and Peter, 2014), Raphanus sativus peels (Abbas et al., 2011), orange peels (Namasivayam et al., 1996), banana peels (Namasivayam and Kanchana, 1992), activated red mud (Tor and Cengeloglu, 2006), untreated sawdust (Alam et al., 2015), sugarcane bagasse (Saiful Azhar et al., 2005), boiler fly ash (Okoronkwo and Igwe, Uruakpa), rice husk (Abbas, 2013), barnacle shell (Salman et al., 2015), eggshell (Arami et al., 2006), neem leaves (Bhattacharyya and Sharma, 2004) and clay materials (Bulut et al., 2008) etc. have been utilized as adsorbents for removal of CR from contaminated water. Earlier studies have also reported the use of different materials with diverse properties and functionalities like nickel oxide (Cheng et al., 2011), mixed iron oxide-alumina nanocomposite (Mahapatra et al., 2013), iron oxide-graphene nanocomposite (Yao et al., 2012), ZnO nanorods loaded activated carbon (Ghaedi et al., 2012), functionalized carbon nanotubes (Hu et al., 2006) etc. have used for removal of dyes. However some of these adsorbents have low adsorption capacity and some involves complex synthesis process, which consumes a lot of time and expensive chemicals and equipments. In addition to these various semiconductors like ZnO, TiO_2, SnO_2, ZrO_2, CeO_2, Fe_2O_3, Bi_2O_3, Al_2O_3, Sb_2O_3, NiS, ZnS, CdS (Pradhan and Parida, 2010) etc. are used as photocatalysts for degradation of dyes which require exposure of UV light to surface of water at fixed distance and temperature. In the present work functionalized ZnO_2 nanomaterial has been tested for purification of water contaminated by highly loaded CR dye and it has been observed that proposed material efficiently and effectively purifies water and makes its suitable for reusability in the same process. The proposed adsorbent is easy to synthesize, does not require complex experimental set up and serves as a promising adsorbent for removal of CR dye. The adsorption experiments were studied as a function of pH, adsorbent dose, contact time and concentration for maximum adsorption. The experimental adsorption data for varying time and concentration was fitted to kinetics and isotherm models to analyze adsorption process.

2. Experimental

2.1. Materials and methods

For the synthesis of ZnO_2, analytical grade chemicals like zinc acetate dihydrate, methanol, ammonia, polyvinylpyrrolidone (PVP), hydrogen peroxide, CR dye etc. were procured from Merck India. High purity de-ionized (DI) water (18.2 MΩ-cm resistivity; 0.22 μm filtered, metallic impurities at ng kg^{-1} level) obtained from Millipore milli-Q element water purification system, USA was used for all experimental work. A 1000 mg L^{-1} stock solution of CR dye was prepared by dissolving 1 g of CR dye in 1000 mL of DI water. This solution was further diluted to the desired concentrations for the experimental work. The pH of the solution was adjusted by adding 0.1 M solution of NaOH and HCl using Orion make benchtop pH meter. The concentration of the dye in the solutions was measured at optimized wavelength (495 nm) using Hitachi make UV–VIS spectrophotometer (U-3900H).

2.2. Synthesis of ZnO_2 nanomaterial

ZnO_2 was synthesized by earlier reported method (Singh Nahar et al., 2014) in which zinc acetate dihydrate (10 g) was dissolved in 10% ammonia solution (200 mL). The solution was diluted to 400 mL with methanol-water mixture (water: solvent:: 4:1). To this solution, PVP (1 g) was added and mixed thoroughly on a magnetic stirrer at constant temperature (50–55 °C). Further 30% hydrogen peroxide solution (50 mL) was added to the solution, white precipitate formed, which was further centrifuged at 10,000 rpm. Further the precipitate was washed several times with DI water and finally dried in an oven at 105 °C.

2.3. Batch adsorption experiment

Batch adsorption experiments were performed to optimize several adsorption parameters like pH, adsorbent (ZnO_2) dose, contact time and adsorbate (CR dye) dose. Initially known amount of ZnO_2 was added to fixed volume of CR dye solution to optimize

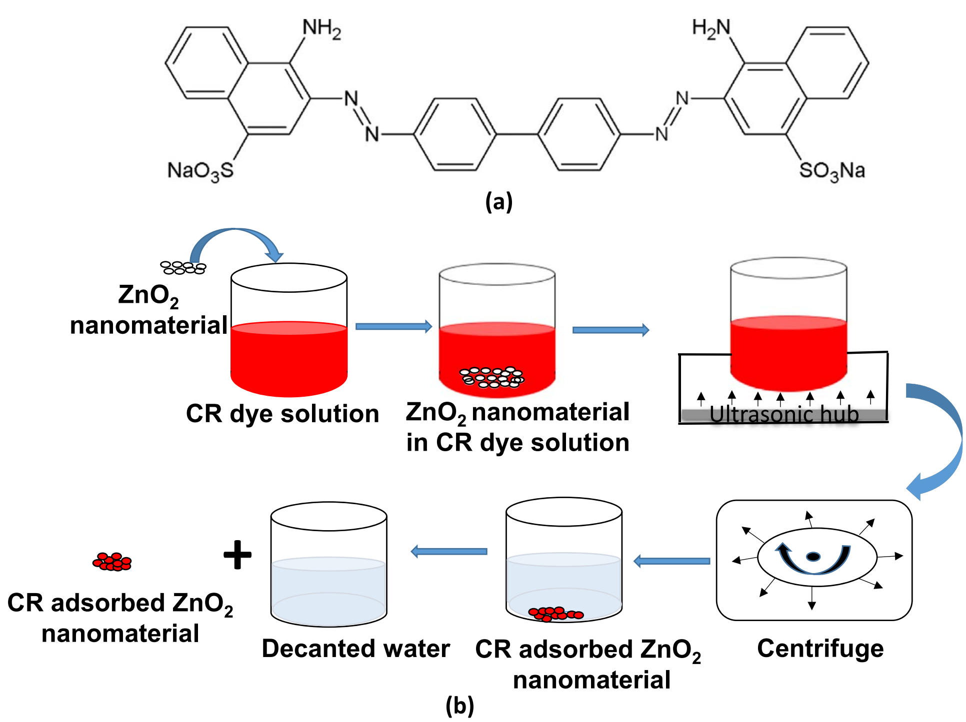

Fig. 1. (a) Chemical structure of CR and (b) Schematic representation for adsorption of CR dye over ZnO_2.