Advanced Powder Technology 27 (2016) 223–231

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Textile dye removal from aqueous solutions using cheap MgO nanomaterials: Adsorption kinetics, isotherm studies and thermodynamics

Hala R. Mahmoud *, Shaimaa M. Ibrahim [1], Sahar A. El-Molla

Department of Chemistry, Faculty of Education, Ain Shams University, Roxy 11757, Cairo, Egypt

ARTICLE INFO

Article history:
Received 30 March 2015
Received in revised form 7 October 2015
Accepted 18 December 2015
Available online 29 December 2015

Keywords:
Sol–gel
Nanomaterials
Adsorption isotherms
Thermodynamics

ABSTRACT

In the present study, three MgO nanomaterials (MgO_S, MgO_N and MgO_U) were synthesized by sol–gel and two different precipitation methods, respectively, and used for the sorption of Remazol Red RB-133 from aqueous solution. The effect of parameters like contact time, initial dye concentration and temperature on the adsorption capacity was studied. The adsorption isotherm studies were carried out using Langmuir, Freundlich and Temkin models. Langmuir was the most suitable model to describe the adsorption isotherm. Pseudo- first -order model fitted well with good agreement with the experimental values of q_e (equilibrium adsorption capacity). The complete removal efficiency of the dye on MgO_S, MgO_N and MgO_U adsorbents was attained when the contacting time was continued to 11, 40 and 60 min, respectively. Hence, the MgO_S adsorbent was found to possess the highest removal efficiency of the dye from aqueous solutions. In addition, the thermodynamic parameters, $\Delta H°$, $\Delta S°$, $\Delta G°$, and E_a were also calculated for Remazol Red RB-133 adsorption onto MgO_S adsorbent. In order to reveal the adsorptive characteristic of MgO nanomaterials, XRD, HR-TEM, FT-IR and N_2 adsorption/desorption isotherms were carried out. The results showed that MgO_S nanomaterial had potentially lowering capital and operational costs for practical applications.

1. Introduction

Synthetic dyes are widely used in textile, paper, printing, plastic, leather and cosmetic industries. Dyeing effluent has a serious environmental impact because its disposal into water causes carcinogenic effects. Furthermore, colored effluent can affect photosynthetic processes of aquatic plants, reducing oxygen levels in water and in severe cases, resulting in the suffocation of aquatic flora and fauna [1]. Various pollutants such as dyes, degradable organics, surfactants, heavy metals, and pH adjusting chemicals can be found in textile wastewater [2]. Conventional treatment methods for removal of pollutants from aqueous solution, like photochemical degradation, biological degradation, coagulation, chemical oxidation and adsorption have been investigated with varying degree of success [3–5]. Among available wastewaters treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. The most widely used adsorbent is activated carbon, but its initial cost and the need for a costly regeneration system make it less economically viable as an adsorbent. This has led many researchers to search for cost effective and efficient alternative materials such as clays including bentonite [6], sepiolite [7], zeolite [8], and periodic mesoporous titanium phosphonate [9]. Recently, nanocrystalline metal oxides have gained considerable interest among researchers as potential adsorbents for decontamination of wastewater [10]. Due to their high surface area, large numbers of highly reactive edges, corner defect sites, unusual lattice planes and high surface to volume ratio.

Magnesium oxide (MgO) is a versatile metal oxide having numerous applications in many fields. It has been used as a catalyst and catalyst support for various organic reactions [11,12], as an adsorbent for removing dyes and heavy metals from wastewater [13,14], antimicrobial material [15], and electrochemical biosensor [16]. Obtaining MgO via thermal decomposition of various magnesium salts give large crystallite size with low surface area-to-volume ratio that limits its applications for nanotechnology especially in

* Corresponding author. Tel.: +20 1003739822; fax: +20 2 22581243.
E-mail addresses: halamahmoud2@yahoo.com, halarashaad@edu.asu.edu.eg (H.R. Mahmoud).
[1] Present address: Department of Chemistry, Faculty of Science, Qassim University, P.O. Box 6666, Al-Qassim, Buraidah 51452, Saudi Arabia.

http://dx.doi.org/10.1016/j.apt.2015.12.006
0921-8831/

adsorption and catalysis [17,18]. Formation of MgO nanostructures with a small crystallite size of less than 100 nm and homogeneous morphology has attracted much attention due to their unique physicochemical properties including high surface area-to-volume ratio. It is widely accepted that the properties of MgO nanostructures depend strongly on the synthesis methods and the processing conditions. MgO nanostructure was synthesized using precipitation [19], solvothermal [20], chemical vapour deposition [21], sonochemical [22], microwave [23], combustion [24] and template [25] methods. Each method has its own advantages and disadvantages. An important issue regarding synthesis and preparation of nanostructured MgO is controlling the parameters in order to obtain a more uniform size as well as morphology of the nanoparticles.

A sol–gel method is a promising technique for the formation of magnesium oxalate di-hydrate followed by annealing at a suitable temperature to form MgO. The advantages are its simplicity, low cost, low reaction temperature, high surface area-to-volume ratio and high purity of the final product. The present study is focused on the effect of preparing MgO nanomaterials by different methods for removal of Remazol Red RB-133 from aqueous solution. The as-prepared adsorbents were characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Fourier transform infrared (FT-IR) spectroscopy and N_2 adsorption/desorption isotherms. The removal studies of the dye by MgO nanomaterials have been carried out using batch adsorption experiments. The influence of various important parameters, such as contact time, initial dye concentration and temperature was investigated. The isotherm studies were carried out using Langmuir, Freundlich and Temkin models. Pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models were used to evaluate the mechanism of adsorption. The thermodynamic parameters, such as ΔG°, ΔH°, and ΔS° were calculated.

2. Experimental

2.1. Materials

Remazol Red RB-133 (RR RB-133) was purchased from DyStar and was used as received without further purification. The UV–visible absorption spectrum of Remazol Red RB-133 shows characteristic absorption both in UV and visible regions. The concentration of Remazol Red RB-133 was measured at λ_{max} 520 nm throughout the work. Magnesium nitrate, ($Mg(NO_3)_2{\cdot}6H_2O$, BDH), oxalic acid dihydrate, ($C_2H_2O_4{\cdot}2H_2O$, Adwic), urea, [$(NH_2)_2CO$, Adwic], absolute ethanol, C_2H_5OH (Adwic, 99.9% purity) and ammonia solution, (NH_4OH, Alpha). Bi-distilled water was used to prepare all the solutions. An accurate weighed quantity of the dye was dissolved in bi-distilled water to prepare a stock and the diluted dye solutions.

2.2. Preparation of MgO nanomaterials

2.2.1. Sol–gel method

The MgO nanomaterial was prepared by sol–gel method. Initially, Magnesium nitrate and oxalic acid precursors in 1:1 M ratio were first dissolved separately in ethanol and stirred magnetically to obtain two clear solutions, then mixed together to yield a thick white gel. The gel product was digested for 12 h and dried subsequently at 100 °C for 24 h and then calcined at 500 °C for 3 h. The nominated formula of the prepared adsorbent is MgO_S, where *S* indicates the sol–gel method.

2.2.2. Precipitation method

The MgO nanomaterials were synthesized using two different precipitation methods – one used ammonium hydroxide as the precipitating agent and the other urea.

For the ammonia precipitated adsorbent, 0.2 M NH_4OH was added drop-wise to 200 mL of 1 M $Mg(NO_3)_2{\cdot}6H_2O$ at 50 °C till aqueous solution pH reached 10 under vigorous stirring. The so-formed white precipitate was washed several times with bi-distilled water, dried overnight in an oven at 110 °C and finally calcined at 500 °C for 3 h in a muffle furnace to get MgO nanomaterial.

For the urea precipitated adsorbent, urea (40 g) and 200 mL of 1 M $Mg(NO_3)_2.6H_2O$ were aged under reflux conditions with stirring in a round-bottomed flask for 4 h at 100 °C in the pH reached 10.5. The resulting slurry was filtered, washed with bi-distilled water and dried at 70 °C overnight. This was followed by calcination in a muffle furnace at 500 °C for 3 h. The nominated formula for the adsorbents is MgO_N and MgO_U, which denotes precipitation using ammonia and urea respectively.

2.3. Characterization

Powder X-ray diffraction (XRD) study was carried out using Bruker Axs D8 Advance X-ray diffractometer (Germany). CuKα1 irradiation (λ = 0.15404 Å) was used with a scan rate of 2° in 2θ/min. The crystallite size of the sample was calculated using the Scherrer equation [26]. Fourier transform infrared spectroscopy (FT-IR) was recorded on Nicolit IR 6700 spectrometer (USA) using KBr pellets. The morphology of the adsorbents was analyzed using high-resolution transmission electron microscope (HR-TEM) (JEM-2100CX (JEOL). The textural properties of the samples were determined by physically adsorbing nitrogen (N_2) at 77 K using a Quantochrome AS1Win™-automated gas-sorption apparatus (USA). Before each N_2 sorption measurement, samples were degassed at 200 °C for 2 h. The N_2 adsorption on the samples was used to calculate the specific surface area by means of the Brunauer–Emmett–Teller (BET) equation. The total pore volume, V_p was estimated to be the liquid volume of the nitrogen at a relative pressure of about 0.99. The pore size distribution was calculated from desorption branch of the isotherm by the Barrett, Joyner and Halenda (BJH) method.

2.4. Adsorption experiments

Batch adsorption study of water-soluble reactive dye Remazol Red RB-133 (RR RB-133) onto MgO nanomaterials was carried out in 250 mL beakers which contained 100 mg MgO and 100 mL dye solution of desired concentration. The solution in the beakers was kept stirred at the desired temperature and pH = 7. At various time intervals, the solutions were centrifuged at 7000 rpm for 5 min and the absorbance of supernatant solution was recorded using UV–vis spectrophotometer (Jasco V-550, Japan). The corresponding concentration in the supernatant solution was obtained using a previously constructed calibration graph. The equilibrium adsorption capacities (q_e) were then obtained by using the following mass balance equation.

$$q_e = (C_o - C_e) \times V/M \quad (1)$$

where C_o and C_e are the initial and equilibrium dye concentrations in solution (mg/L), *V* is the solution volume (L) and *M* is the weight (g) of dry adsorbent used.

2.4.1. Effect of contact time

The effect of contact time was investigated by taking 100 mL of 75 mg L^{-1} Remazol Red RB-133 solution (pH 7.0). MgO nanomaterials (100 mg) were added and then the whole solution was stirred at 35 °C. An aliquot (3 mL) of dye sample was withdrawn from the beaker at regular time intervals and centrifuged. The concentration of dye in the supernatant solution was analyzed and the percentage removal (%R) of dye is calculated using the following relation:

$$\%\,\text{Removal} = 100 \times (C_o - C_t)/C_o \quad (2)$$