Chemical Engineering Journal 223 (2013) 76–83

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Adsorption behavior of methyl orange onto nanoporous core–shell $Cu@Cu_2O$ nanocomposite

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HIGHLIGHTS

- MO onto $Cu@Cu_2O$ nanocomposite follows pseudo-first-order and IPD model.
- MO adsorption onto $Cu@Cu_2O$ nanocomposite is spontaneous and exothermic process.
- Activation energy of 12.4 kJ/mol indicates physisorption nature of MO adsorption.

ARTICLE INFO

Article history:
Received 7 December 2012
Received in revised form 1 March 2013
Accepted 5 March 2013
Available online 13 March 2013

Keywords:
Nanoporous metal
Nanocomposite
Methyl orange
Adsorption behavior
UV–vis spectrophotometry

ABSTRACT

In this work, the adsorption behavior of methyl orange onto nanoporous core–shell $Cu@Cu_2O$ nanocomposite has been investigated using an UV–vis spectrophotometer, considering the influence of pH value, temperature, additive amount of nanocomposite and initial methyl orange (MO) concentration. The adsorption kinetics of MO on the $Cu@Cu_2O$ nanocomposite has been discussed based upon the pseudo-first-order model, intraparticle diffusion model and Langmuir adsorption model. Thermodynamic parameters such as change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have also been evaluated. The negative changes in Gibbs free energy (-18.4 to -15.1 kJ mol^{-1}) and enthalpy (-51.5 kJ mol^{-1}) indicate the spontaneous and exothermic nature of the adsorption process of MO. The activation energy (E_a) of 12.4 kJ mol^{-1} reveals the physisorption nature of MO adsorption onto the nanoporous $Cu@Cu_2O$ nanocomposite.

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1. Introduction

Synthetic azo dyes constitute about a half of global dye-stuff production (700,000 ton annually), and about 15% of them are directly discharged into water without proper treatment [1]. Extensive use of these chemicals poses a potential threat to aquatic creatures and human beings since most of the azo dyes are carcinogenic [2]. Therefore, removal of dyes from water has received increasing attention. A wide range of conventional methods have been developed to treat wastewater including coagulation–flocculation [3], membrane separation [4], and adsorption [5,6]. Among the traditional wastewater process techniques, adsorption has been found to be a convenient and effective treatment methodology due to its simplicity of design, ease of operation and insensitivity to toxic substances [7], but the high price of current adsorbents such as activated carbon, and mesoporous carbon has limited their applications since coals are considered as non-renewable and expensive starting materials [8,9]. Besides, adsorption merely transfers dye molecules from liquid to solid and cannot radically eliminate the water pollutant.

Photocatalysis has attracted much attention as a new and efficient method to treat wastewater containing azo dyes in the past few years [10–18]. Semiconductor-based photocatalysts have been extensively studied, such as TiO_2, ZnO, and Cu_2O [11–15]. Among those photocatalysts, Cu_2O has been considered as a promising photocatalyst due to its narrower band gap (2.0–2.2 eV) than that of TiO_2 and ZnO (3.0–3.2 eV) [11,16]. It should be noted that adsorption as an important precondition has a significant impact on the whole photocatalysis process since photodegradation includes reactions between adsorbed species (substrates, reducers and oxidants) on the surface of the photocatalyst [17]. Moreover, adsorption capacity is a key factor in photocatalysis because it determines the degradation rate and in most cases, the enhanced photoactivity of semiconductors is also attributed to superior adsorption capacity [7,18].

Recently, nanoporous metals with high specific surface areas and unique bicontinuous ligament–channel structures have attracted much attention because of their novel optical, catalytic,

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http://dx.doi.org/10.1016/j.cej.2013.03.013

and sensing properties [19–29]. For example, it has been reported that nanoporous gold (NPG) could be used in ultra-capacitors and heterogeneous catalysis, such as CO oxidation and NO_x reduction [20,21]. Dealloying has been proved to be an effective method to generate new types of nanoporous metals via selective dissolution of one or more active elements out of suitable precursor alloys [22,23]. During the dealloying process, diffusion and reorganization of more noble element(s) lead to a 3-D bicontinuous interpenetrating ligament–channel structure [24–26]. Cu is much cheaper than Au, and nanoporous Cu has been synthesized from different precursor alloys. Qi et al. [27] reported the fabrication of nanoporous Cu through dealloying of Al–Cu (33–50 at%) in acid and alkaline media. Hayes et al. [28] synthesized monolithic nanoporous Cu by dealloying of Mn–Cu solid solution. Surface modification is regarded as an effective way to produce efficient catalysts [30]. For instance, Ding et al. [29] reported that Pt-modified NPG has high electrocatalytic performance. In addition, the heterojunction of Cu and Cu_2O can enhance the photocatalytic property of Cu_2O-based semiconductors since Cu can transfer photoelectrons avoiding the combination of electron–hole pairs [31].

In our previous study, we have successfully synthesized a novel nanoporous core–shell $Cu@Cu_2O$ nanocomposite photocatalyst with superior photocatalytic activity through a facile two-step strategy involving dealloying and surface oxidation [10]. But the adsorption capacity of the as-synthesized photocatalyst under various conditions has not been studied systematically. The aim of this work is to find the optimum condition for adsorption and photocatalysis of our synthesized photocatalyst by tuning a series of parameters such as pH value, temperature, additive amount of catalyst, and dye concentration. Methyl orange (MO) was used as a model pollutant mainly because it is a common azo dye and widely used in textile, printing, paper manufacturing, pharmaceutical, and food industries [32]. In order to investigate the adsorption mechanism, the pseudo-first-order model and intraparticle diffusion (IPD) model have been applied to analyze the experiment data.

2. Experimental section

The nanoporous core–shell $Cu@Cu_2O$ nanocomposite was fabricated by dealloying the ball-milled $Al_{66.7}Cu_{33.3}$ precursor powders in a 2 mol L^{-1} NaOH aqueous solution, followed by surface oxidation of the as-dealloyed samples in air at room temperature. The detailed fabrication procedure can be found in our previous work [10]. The morphology and nanoporous structure of the as-prepared nanocomposite were studied by employing a field-emission scanning electron microscope (FESEM, Quanta FEG 250) and transmission electron microscope (TEM, Hitachi H 9500). Energy dispersive X-ray (EDX) analysis was used to determine chemical compositions of the nanocomposite after adsorption.

To investigate the effect of parameters such as pH value, temperature, additive amount of nanocomposite and MO concentration on adsorption capacity, we designed nine systems as follows: (I) nanocomposite (2 mg) + MO (20 mg L^{-1}), 20 °C; (II) nanocomposite (4 mg) + MO (20 mg L^{-1}), 20 °C; (III) nanocomposite (4 mg) + MO (20 mg L^{-1}), 35 °C; (IV) nanocomposite (4 mg) + MO (20 mg L^{-1}), 50 °C; (V) nanocomposite (4 mg) + MO (20 mg L^{-1}), 65 °C; (VI) nanocomposite (6 mg) + MO (20 mg L^{-1}), 20 °C; (VII) nanocomposite (8 mg) + MO (20 mg L^{-1}), 20 °C; (VIII) nanocomposite (8 mg) + MO (30 mg L^{-1}), 20 °C; (IX) nanocomposite (8 mg) + MO (40 mg L^{-1}), 20 °C. All batch adsorption experiments were performed under dark conditions. Nanocomposites were dispersed in a 100 mL beaker containing 50 mL MO dye solution with different initial concentrations, being stirred in a constant temperature magnetic heating stirrer. The optimum pH value for adsorption (carried out in system II) was investigated firstly by adjusting the MO solution to the required pH values through adding HCl (5 wt%) or NaOH (2 mol L^{-1}) solutions at 20 °C before mixing with the nanocomposite. During adsorption experiments, a small amount of MO solution (5 mL) was extracted at predetermined time intervals until the adsorption equilibrium was achieved. The analysis of MO concentration was done by using an UV–vis spectrophotometer (Mapada) at 465 nm which is the maximum absorbance wavelength of MO. The kinetic experiments were carried out by varying the solution temperature (20, 35, 50 and 65 °C), additive amount of nanocomposite (2, 4, 6, and 8 mg) and the initial MO dye concentration (20, 30, and 40 mg L^{-1}) at the identical pH value. Concentration (C) of MO dye can be obtained through Beer–Lambert law in which the absorbance value for MO versus concentration obeys a linear relationship. The adsorbed MO dye amount per unit mass of nanocomposite (q_t, mg g^{-1}) at any time was calculated by Eq. (1) as follows,

$$q_t = \frac{C_0 - C_t}{m} \times V \tag{1}$$

where C_0 is the initial MO concentration (mg L^{-1}), C_t is the MO concentration at the time t (mg L^{-1}), V is the solution volume (L) and m is the nanocomposite mass (g). The computing program used for fitting experimental data is Origin® 8.0 in this work.

3. Results and discussion

Fig. 1 shows the morphology and nanoporous structure of the nanoporous $Cu@Cu_2O$ nanocomposite. As we can see from Fig. 1a, the particle size roughly ranges from several hundred nanometers (ca. 300 nm) to several micrometers (ca. 4 μm) and the bicontinuous interpenetrating ligament (ca. 30 nm)-channel (ca. 15 nm) structure can be clearly seen in the inset. It is worth mentioning that although the size of particle exceeds nanoscale, each particle actually owns a nanoporous structure with three-dimensional interpenetrating ligament–channel distribution. In addition, it is the nanosized ligaments that possess the composite structure of Cu and Cu_2O. The TEM results further confirm the nanoporous structure of the as-prepared nanocomposite. As shown in Fig. 1b, the typical TEM bright-field image clearly shows that the nanocomposite exhibits an open bicontinuous ligament–channel structure, which is consistent with the FESEM observation. The detailed confirmation of core–shell structure of the nanocomposite can be found in our previous work [10]. The adsorption mechanism of anionic dyes on Cu_2O has been mainly attributed to electrostatic adsorption [33]. The pH value of the solution not only affects the amount of adsorbed species through changing the surface charge of the adsorbent but also has an impact on the stability of Cu_2O [34,35]. At a strongly acidic pH value of 2.00, protons can be picked up on one of the nitrogens in nitrogen–nitrogen double bond, which can generate a reddish color of MO dye solution before the mixture with our nanocomposite [36]. As shown in Fig. S1a (Supplementary material), the maximum absorbance wavelength of MO at 512 nm at the strongly acidic pH (2.00) is the contribution of hydrazone structure to the resonance [37]. After being stirred in dark for 40 min, the reddish color of the solution and the nanocomposite disappeared. UV spectra show the agreement with the experimental phenomena, and the absorbance peak of hydrazone disappears after 40 min (Fig. S1a). Although bulk Cu is inert to dissolve in dilute strong acids except nitric acid, Cu in nanoscale can become more chemically active to be dissolved due to the intensive surface effect of nanomaterials, especially under stirring conditions [38,39]. Finally, the released Cu ions from the dissolved Cu and Cu_2O in the solution interacted with MO ions, resulting in the formation of a colorless complex. When the pH value was tuned to 11.4, MO existed in a basic form but the concentration

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