Journal of the Taiwan Institute of Chemical Engineers 64 (2016) 279–284

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Remarkable adsorption capacity of Ni-doped magnolia-leaf-derived bioadsorbent for congo red

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ARTICLE INFO

Article history:
Received 11 November 2015
Revised 1 April 2016
Accepted 7 April 2016
Available online 25 April 2016

Keywords:
Adsorption
Magnolia leaf
Ni-doped
Anionic dyes

ABSTRACT

A novel high-performance porous carbon material, nickel-doped magnolia-leaf-derived porous carbon (Ni/MPC), is synthesized by a KOH activation process and nickel-doping strategy. The morphology, microstructure, and element composition of Ni/MPC are characterized by scanning electron microscopy, nitrogen adsorption and desorption, and X-ray photoelectron spectroscopy, respectively. Removal of anionic dye congo red (CR) from contaminated water was performed in a batch reactor system to obtain adsorption kinetics and isotherms. The results showed that pseudo-second-order kinetic model and Langmuir adsorption isotherm matched well for the adsorption of CR onto Ni-doped MPCs. Compared with previously reported adsorbents, Ni/MPCs demonstrated a superior CR dye adsorption capability. The results of the present study substantiate that Ni/MPC is a promising adsorbent for the removal of the anionic dyes from wastewater.

1. Introduction

As one of the typical anionic dyes, congo red (1-napthalenesulfonic acid, 3,3′-(4,4′-biphenylene bis (azo)) bis (4-amino-) disodium salt) is a benzidine-based anionic disazo dye (Scheme S.I.1), which is acknowledged to metabolize to benzidine, a known human carcinogen [1]. The discharge of CR into the aquatic ecosystem has generated much concern due to its reported genotoxic, mutagenic, teratogenic and carcinogenic effects [1,2]. Therefore, hazardous anionic dyes such as CR containing effluents have to be adequately treated before they are discharged into the environment. Among several chemical and physical methods, adsorption has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation [3,4]. For example, a simple, rapid and sensitive solid phase extraction procedure based on separation and preconcentration of trace levels of allura red in water samples via adsorption column system has been established by Soylak et al. [5] Because adsorbent is one of the most important factors determining the effectiveness of any adsorption processes, much effort has been dedicated to development of alternative adsorbents suitable for a particular purpose. Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as alumina [6], clay [7], polymer [8] and zeolite molecular sieves [9]. However, the above adsorbents only display limit dye removal efficiency. Thanks to their high surface areas, large pore sizes, narrow pore-size distributions, good thermal and mechanical stabilities, porous carbons have indeed attracted a great deal of attention for purification dyeing wastewater. For example, separation and enrichment of tartrazine on multiwalled carbon nanotubes was performed by Soylak et al. [10]. Ghaedi et al. investigated adsorptive removal of arsenazo(III) and methyl red from waste water with activated carbon and multiwalled carbon nanotubes [11]. However, porous carbon poses several disadvantages, such as non-selective and ineffective against disperse and vat dyes, relatively low dyes uptake capacities, some adsorbents have the capacities between 200 and 1000 mg/g and others show lower than 50 mg/g uptake [2,12]. The use of porous carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [13]. This has led many research workers to search for alternative low cost adsorbents. The precursor should be freely available, cheap and non-hazardous in nature. In recent years, a number of inexpensive and abundant biosorbents especially agro-waste materials such as rice husk [14], groundnut shell [15], orange peel [16], sawdust [17], rice straw [18], soybean hull [19], waste apricot [20], degreased coffee beans [21], lemon peel [22], de-oiled soya [23], and different natural products [24,25] have been reported to remove anionic dyes from waste water. The advantage of using the waste resource is that it saves disposal costs while alleviating potential environmental problems.

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http://dx.doi.org/10.1016/j.jtice.2016.04.008
1876-1070/

Recent research works have focused on enhancing the effectiveness of porous carbon by modifying their specific properties to develop its affinity for certain dyes. Suárez-García et al. [26] investigated the positive effect of the *N*-containing functional groups of ordered mesoporous carbons on removal of three dyes with different molecular sizes and containing acidic or basic functional groups. Dong et al. [27] concluded that the surface chemical groups played a key role in dye adsorption. The presence of oxygen-containing (acid) groups on the surface of CMK-3 also enhanced the adsorption capacity of anionic dyes. The authors attributed this to the increase of the surface hydrophilicity and the improved dispersion of the adsorbent in an aqueous medium. Other works about the effect of the surface chemistry of porous carbons modified by oxidation and/or thermal treatments on dye adsorption can be also found in the literature [28,29]. The surface modification of porous carbons can be easily carried out by means of metal ions impregnation method to improve its adsorptive capacity [2,30]. However this method still constitutes a major challenge for certain dye adsorption, such as low selectively, low uptake capacity, difficult to recycle, *etc.* [2,30] To our knowledge, the study of influence of metal ions doping on dye adsorption for porous carbons is relatively scarce. Therefore, a suitable selection of both the precursor and the experimental conditions has to be done in order to achieve high selectivity and capacity.

Given the porous texture and chemical composition, magnolia leave is an optional precursor for preparing of porous carbon material [3]. The aim of this work was to synthesize and characterize the magnolia-leaf-derived porous carbons (MPCs), which is further modified with nickel ions for removal of CR dye from aqueous solutions. The adsorption kinetics was tested under various conditions and the adsorption equilibria were investigated to find out the best isotherm model fitting to the experimental data. The effect of the adsorbate concentration and contact time on adsorption capacity was examined to determine the optimal adsorption conditions. The possible mechanism of the adsorption process is also discussed in this study.

2. Materials and methods

2.1. Materials

Magnolia leaves (MLs) were collected from the local campus of Zhejiang Normal University, Jinhua, China. The procedure used to prepare the MPCs was referred to our recent work [3]. Potassium hydroxide (KOH) and nickel nitrate ($Ni(NO_3)_2$) were purchased from Sigma Chemical Company (St. Louis, Mo., USA). High purified nitrogen (99.995%) was provided by Gas Supplier Center of Datong Co., Ltd., Jinhua, China. All the other reagents were of analytical reagent grade.

2.2. Preparation of porous carbons from biomass precursors

The magnolia leaves were first washed with deionized water to remove dirt from their surface and were then dried overnight in an oven at 378 K. The dried husk was cut and sieved to desired mesh size (~150 μm) and mixed with KOH (the mass ratio of KOH and MLs precursor was 4:1). Then the resulting mixture was placed into a horizontal pipe reactor (50 mm o.d.). The temperature of the reactor was raised to the activation temperature (1073 K) at a heating rate of 1 K/min. During the carbonization process, high purified nitrogen (99.995%) flows through the reactor at flow rate of 40 mL/min. Finally, it was cooled down to room temperature. The obtained samples were washed with deionized water until the filtrate reached neutral. The final samples (MPCs) were obtained by heating these samples at 423 K under vacuum for 24 h.

2.3. Modification of biomass porous carbons

Incipient wetness technique was applied to impregnate MPCs with an aqueous solution of nickel nitrate. The amounts of $Ni(NO_3)_2$ used for modification were pre-calculated to achieve the loading of nickel equal to 1, 5 or 7 wt.%. After impregnation the adsorbents were successively dried at 373 K for 5 h and heated nitrogen atmosphere for 3 h at 973 K. The samples obtained were denoted as: Ni10/MPC, Ni-50/MPC and Ni70/MPC, respectively.

2.4. Sample characterization

Pore structure of samples obtained in this work was characterized by low-temperature nitrogen adsorption–desorption isotherms measured on an automated adsorption apparatus (Micromeritics, ASAP 2020). The specific surface areas were calculated by the BET method (the relative pressure p/p_0 range taken into account in the BET calculations was 0.005–0.2). The *t*-plot method was applied to calculate the volume and micropore surface area. The total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of $P/P_0 = 0.99$. The pore size distribution was calculated by density functional theory (DFT). For TEM measurements, powdered samples were deposited on a grid with a perforated carbon film and transferred to a JEOL 2100F electron microscope operating at 80 kV. The influence of Ni(II)-related defects on the electronic structure of Ni/MPC surfaces is studied by means of X-ray photoelectron spectrometer (XPS, ESCALAB 250Xi).

2.5. Batch equilibrium studies

A series of CR solutions with concentrations ranging from 50 to 1200 mg/L were prepared by dissolving different amounts of the dye in deionized water. In each batch experiment, 20 mg of adsorbents were suspended in 50 mL of the dye solution. At first the time dependence of CR adsorption onto all adsorbents was investigated to determine the time required for adsorption equilibrium. After certain contact time, the resulting mixture was continuously shaken in a shaking bath at a constant temperature (25 ± 1 °C). Finally, the samples were filtered and the residual concentrations of CR in the filtrate were analyzed by a UV–visible spectrophotometer (Thermo Fisher Evolution 300 PC) at maximum wave lengths of 497 nm. It was found that the calibration curves were very reproducible and linear relation between the concentration and absorbance over the concentration range were found in this work. The adsorbed amount of CR at equilibrium, q_e (mg/g) was calculated by the following expression:

$$q_e = \frac{(C_o - C_e) \cdot V}{W} \tag{1}$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations of CR solution, respectively; V (L) is the volume of solution, and W (g) is the weight of adsorbents used. Duplicate experiments were carried out and the average values were taken into consideration. The average deviation of duplicate results in the units of concentration was found to vary between ±1%.

3. Results and discussion

3.1. Material characterization

Nitrogen adsorption–desorption isotherms and the pore size distributions of the MPCs samples before and after doping Ni(II) are recorded in Fig. 1(a) and (b) with the related parameters listed in Table S.I.1. MPC exhibits type-I adsorption isotherm without apparent hysteresis loop between adsorption and desorption curves, which is quite typical for the microporous materials. However,