Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Carbon-doped graphitic carbon nitride as environment-benign adsorbent for methylene blue adsorption: Kinetics, isotherm and thermodynamics study

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ARTICLE INFO

Article history:
Received 26 December 2017
Revised 1 March 2018
Accepted 21 March 2018
Available online xxx

Keyword:
C_3N_4
Methylene blue
Adsorption
Electrostatic attraction
$\pi-\pi$ interactions

ABSTRACT

A novel, carbon-doped graphitic carbon nitride (C–C_3N_4-20) was used for methylene blue (MB) removal from an aqueous solution. In dye adsorption experiments, C–C_3N_4-20 showed a high MB adsorption efficiency due to its extended π-conjugation system and porous structure, the maximum adsorption capacity of C–C_3N_4-20 for MB was 57.87 mg g^{-1}, when the initial concentrations of MB were 20 mg L^{-1}. A Langmuir model fit the MB adsorption isotherm of C–C_3N_4-20, and a pseudo-second-order kinetic model fit the adsorption kinetics. The MB adsorption process on C–C_3N_4-20 is physical and mainly via electrostatic attraction and $\pi-\pi$ interactions.

1. Introduction

In recent years, the rapid development of industrialization has resulted in organic pollution in water, which has been deemed a global environmental issue due to serious threats to the environment and human health [1]. A representative organic pollutant, methylene blue (MB), which mainly comes from dye synthesis, printing and papermaking, has already been detected in many rivers. Many symptoms are considered to be the result of MB pollution, such as mental disorders and eye injuries [2]. In addition, MB pollution can cause water body contamination and serious environmental issues. Many efforts, such as photo-catalytic decomposition [3,4] and chemical oxidation–reduction [5,6], have been used for MB removal. However, the high energy requirements and high operational costs are the main drawbacks of these methods, which seriously restrict their large-scale application for MB treatment. Therefore, a low cost, simple and easily adaptable method for MB treatment is desired. An effective and environmentally benign method, adsorption [7–11], has been used for many wastewater treatment applications. In recent years, chitosan [12], zeolite [13,14] and active carbon [15] have been explored as adsorbents for MB removal in water. However, the removal of methylene blue in a safe and effective method is still consider as a technical challenge. Therefore, it is urgent to develop a novel adsorbents prepared via simple, green and effective method for the methylene blue wastewater treatment. Recently, graphitic carbon nitride (g-C_3N_4) [16,17], a novel 2D material, which can be synthesized via simple and green pyrolysis of melamine, has been used in many applications, such as energy conversion [18], biomedical applications [19], and hydrogen production [20], due to its excellent chemical and thermal stabilities and lack of toxicity [21]. Because of its highly ordered tri-s-triazine (C_6N_7) units, g-C_3N_4 can stack via a hydrophobic effect and $\pi-\pi$ interaction. According to the literature, g-C_3N_4 can absorb aromatic pollutants via the conjugated π region [22], which makes g-C_3N_4 a potential effective adsorbent. Although g-C_3N_4 works as an adsorbent for removing pollutants, such as aromatic compounds, its adsorption capacity for aromatic compounds is insufficient. Therefore, further enhancement in the adsorption performance of g-C_3N_4 materials is desirable. Recently, Dong and Zhao [23] theoretically and experimentally demonstrated that carbon doping C_3N_4 can enlarge the π-conjugation system in g-C_3N_4, which is favorable for aromatic compound (such as MB) adsorption, and enlarge the g-C_3N_4 surface area, which is another important factor in the adsorption performance. However, to the best of our knowledge, the adsorption of aromatic compound pollutants (such as MB) on carbon-doped g-C_3N_4 has not been extensively studied.

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https://doi.org/10.1016/j.jtice.2018.03.041
1876-1070/

Therefore, in this work, carbon-doped g-C_3N_4 (denoted C–C_3N_4) composites were prepared via a simple doping method using glucose as the carbon dopant and melamine as the g-C_3N_4 precursor. We investigated the effects of different amounts of glucose on the structure and properties of g-C_3N_4. The as-prepared C–C_3N_4 materials were used as adsorbents for MB removal from aqueous solutions. The influence of some important parameters (such as the initial MB concentration and equilibration time) on the adsorption process were systematically studied. In addition, adsorption thermodynamic and kinetic analyses were conducted to clarify the possible adsorption mechanism.

2. Experimental

2.1. Synthesis of g-C_3N_4

g-C_3N_4 was synthesized via heating melamine (Shanghai Aladdin Bio-Chem Technology Co., LTD) (2 g) at 600 °C for 4 h at a rate of 2.5 °C min^{-1} in a N_2 atmosphere. After the heat treatment, a light yellow solid was obtained.

2.2. Synthesis of C–C_3N_4

Typically, 2 g of melamine and different amounts of glucose (Shanghai Aladdin Bio-Chem Technology Co., LTD) (0.1 g, 0.2 g, and 0.3 g) were dispersed in water (50 mL), and the water was evaporated at 70 °C with stirring. The white mixture was thermally treated at 600 °C for 4 h at a rate of 2.5 °C min^{-1} under N_2 protection. Finally, a dark beige powders were obtained. The products were denoted C–C_3N_4-10, C–C_3N_4-20, and C–C_3N_4-30, respectively.

2.3. Dye adsorption experiments

MB (Shanghai Aladdin Bio-Chem Technology Co., LTD) was chosen as the organic contaminant in this work. In the adsorption measurements, 20 mL of 5 mg L^{-1} −30 mg L^{-1} MB ($C_{16}H_{24}ClN_3O_3S$) aqueous solutions containing 6 mg of the C–C_3N_4-20 adsorbent were stirred at different temperatures (298.15 K−318.15 K) and different pH (2.0–10.0) for the dye adsorption. After 10–300 min of adsorption, the C–C_3N_4-20 was collected via centrifugation. A UV–vis spectrophotometer (TU-1900, Beijing Persee Instruments Co. Ltd., China) was used to measure the MB concentration, and the characteristic adsorption of MB at 665 nm [24] was used to monitor the adsorption process. In comparison, similar experiments were conducted with g-C_3N_4, C–C_3N_4-10 and C–C_3N_4-30. In addition, to test the usability after recycling, C–C_3N_4-20 was collected. The MB-adsorbed C–C_3N_4-20 was placed into an eluent containing 0.1 M HCl and 0.1 M HNO_3, shaken for 20 h, separated by centrifugation and washed with water, and dried at 60 °C overnight. The re-activated adsorbent was used in the dye absorption test under the same conditions mentioned above. The adsorption amount (mg g^{-1}) was determined using the equation:

$$Q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

Where C_0 is the initial concentration of MB (mg L^{-1}), C_t is the concentration of MB at contact time t (mg L^{-1}), V is the volume of the solution used (L), and W is the weight of the adsorbents (g).

2.4. Characterization

The crystallographic structures of the solid samples were determined using X-ray diffraction (XRD, Ultima IV, Rigaku). The morphologies of the samples were characterized by scanning electron microscopy (SEM, Hitachi S-4800, Japan). N_2 adsorption–desorption measurements were conducted on a ASAP2420 surface area analyzer at 77 K. Before the measurements, the samples were degassed at 200 °C for 6 h. The Brunauer–Emmett–Teller (BET, Micromeritics ASAP 2420) specific surface areas were determined using the desorption data. The pore size distribution was determined using the Barrett–Joyner–Halenda (BJH) method. The surface compositions of the C_3N_4 materials were examined by X-ray photoelectron spectroscopy (XPS, PHI5600 Physical Electronics). A zeta potential analyzer (Malvern, Model Nano ZS) was used to determine the corresponding zeta potential of the C_3N_4 materials.

2.5. Kinetic and adsorption isotherm models

The solute uptake rate can be described by the adsorption kinetics and is considered an important characteristic that defines the adsorption efficiency. In this work, kinetic models were used to fit the experimental data and determine the adsorption process kinetics. The pseudo-first-order model [25] can be express as:

$$\ln\,(Q_e - Q_t) = \ln\,Q_e - k_1 t \tag{2}$$

The pseudo-second-order kinetic model [25] is:

$$\frac{t}{Q_t} = \frac{1}{k_2 {Q_e}^2} + \frac{t}{Q_e} \tag{3}$$

In the equations, the amounts of dye adsorbed at equilibrium and at time t (min) are represented by Q_e and Q_t (mg g^{-1}), respectively. k_1(min^{-1}) and k_2(g m g^{-1} min^{-1}) stand for the rate constants of pseudo-first-order and pseudo-second-order adsorption, respectively. The linear plots of ln $(Q_e - Q_t)$ versus t and $(\frac{t}{Q_t})$ versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively, by which the rate constants k_1 and k_2 can be derived.

Information on the surface properties, adsorbate affinity, and adsorption capacity of an adsorbent can be obtained from an adsorption isotherm. The Langmuir and Freundlich isotherm models are two extensively used mathematical models. The Langmuir model assumes a monolayer coverage and that all the adsorbent sorption sites are the same. While the Freundlich isotherm model assumes that the coverage is multilayer and that all the adsorption sites are heterogeneous. The Langmuir and Freundlich models are presented as Eq. (4) [26] and Eq. (5) [27], respectively, as follows:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \tag{4}$$

$$\ln\,Q_e = \frac{1}{n} ln\,C_e + ln\,K_F \tag{5}$$

where Q_e and Q_m (mg g^{-1}) are stand for the equilibrium adsorption capacity and the maximum adsorption capacity (corresponding to complete monolayer coverage), respectively, C_e (mg L^{-1}) represent the adsorbate concentration at adsorption equilibrium, b (L mg^{-1}), K_F and n are all constants. The Q_m and b can be calculated according to the slope and intercept of the linear plot of $\frac{C_e}{Q_e}$ against C_e. The n and K_F can be calculated from the slope and intercept of the linear plot of ln Q_e versus ln C_e.

2.6. Thermodynamic evaluation

The thermodynamic parameters such as ΔG^0 (standard Gibbs free energy change), ΔH^0 (standard enthalpy change) and ΔS^0 (standard entropy change) were calculated from following equations:

$$K_c = \frac{Q_e}{C_e} \tag{7}$$

$$\Delta G^0 = -RT\,lnK_c \tag{8}$$

Please cite this article as: B. Ren et al., Carbon-doped graphitic carbon nitride as environment-benign adsorbent for methylene blue adsorption: Kinetics, isotherm and thermodynamics study, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.03.041