Journal of the Taiwan Institute of Chemical Engineers xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Adsorption of Cr(VI) from aqueous solution on mesoporous carbon nitride

Huan Chen, Tingting Yan, Fang Jiang [*]

Key Laboratory of Jiangsu Province for Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

ARTICLE INFO

Article history:
Received 13 November 2013
Received in revised form 5 March 2014
Accepted 9 March 2014
Available online xxx

Keywords:
Mesoporous carbon nitride
Cr(VI)
Adsorption
Electrostatic interaction

ABSTRACT

Mesoporous carbon nitride (MCN) was synthesized using mesoporous silica SBA-15 as the template and employed for the adsorption of Cr(VI) from aqueous solutions. Cr(VI) adsorption over MCN followed pseudo-second-order kinetic model and the Langmuir adsorption model. The maximum sorption capacity of MCN for Cr(VI) was 48.31 mg/g at pH 5.7, higher than activated carbon (AC) and ordered mesoporous carbon (CMK-3). An electrostatic interaction mechanism between Cr(VI) and surface pyridine groups on MCN was proposed by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analysis. The coexisting anions, especially the carbonate, influenced the adsorption amount due to the competitive adsorption of Cr(VI) on the surface of MCN. The adsorbed Cr(VI) could be effectively desorbed by 0.5 mol/L NaOH solution, suggesting that MCN could be a promising adsorbent for Cr(VI) removal from waste effluents.

1. Introduction

Hexavalent chromium (Cr(VI)) is a primary contaminant in the effluents of many industries, such as plating, leather tanning and mining operation [1]. Cr(VI) is a known carcinogen causing severe environmental and public health problems. Because of its high toxicity, Cr(VI) is recorded on the top-priority list of toxic pollutants defined by the US Environmental Protection Agency (EPA), and the tolerance limit for Cr(VI) discharge in potable water is 0.05 mg/L [2,3]. Thus, it is necessary to develop techniques to remove Cr(VI) from water and prevent further Cr(VI) discharge.

Adsorption is one of the most common approaches for Cr(VI) removal from wastewater [4,5]. Activated carbon and some low cost adsorbents including industrial wastes, agricultural waste products and various solid substances have been used as Cr(VI) adsorbents recently [6–9]. As electrostatic attraction, ion exchange and surface complexation are the main adsorption mechanisms of Cr(VI), surface modification of adsorbents can enhance Cr(VI) adsorption by invoking the interaction of Cr(VI) and adsorbents. In particular, Cr(VI) adsorption is favored by grafting functional groups onto the adsorbent surface, such as amine and amino. Deng et al. studied the Cr(VI) adsorption over polyethylenimine-modified fungal biomass and observed substantially higher Cr(VI) adsorption compared to pristine biomass [10]. Similarly, modification of polyacrylamide-grafted coconut coir pith with amine groups also resulted in the enhanced Cr(VI) adsorption [11].

Compared with conventional porous adsorbents, mesoporous materials with high specific area, high pore volume and controllable morphology are considered to be promising adsorbents for heavy metal ions removal [12]. To improve Cr(VI) adsorption, some amino modified mesoporous materials have been used as adsorbents. Yoshitake et al. prepared amino-functionalized ordered mesoporous silica, MCM-41 and SBA-1, they observed these functioned materials presented high Cr(VI) adsorption [13]. Similar observation of enhanced Cr(VI) adsorption was also found in amino-functionalized SBA-15 [14,15]. Besides amine and amino functional groups, other N-containing groups have also been proved to be beneficial to Cr(VI) adsorption. Li et al. synthesized aminopropyl, imidazole and triazole modified SBA-15, it was discovered that N-containing functional groups could act as adsorption sites and electrostatic interaction between the N-containing groups and Cr(VI) facilitated the adsorption [16].

Mesoporous carbon nitride (MCN) is known as a fascinating material which has attracted worldwide attention [17–20]. As reported, the MCN material could be considered as mesoporous carbon incorporated with nitrogen [21]. Since N-containing functional groups are beneficial to Cr(VI) adsorption, MCN with

---

[*] Corresponding author. Tel.: +86 25 84311819; fax: +86 25 84315352.
E-mail address: fjiang@njust.edu.cn (F. Jiang).

http://dx.doi.org/10.1016/j.jtice.2014.03.005
1876-1070/© 2014 Published by Elsevier B.V. on behalf of Taiwan Institute of Chemical Engineers.

Please cite this article in press as: Chen H, et al. Adsorption of Cr(VI) from aqueous solution on mesoporous carbon nitride. J Taiwan Inst Chem Eng (2014), http://dx.doi.org/10.1016/j.jtice.2014.03.005

many pyridine groups is reasonably expected to present high adsorption capacity for Cr(VI). In addition, so far few studies have been conducted to investigate the adsorption properties of Cr(VI) using such adsorbent containing surface pyridine functional groups.

In the present study, an ordered MCN was developed for efficient Cr(VI) adsorption from aqueous solutions, and the adsorption behavior of MCN was compared with activated carbon (AC) and ordered mesoporous carbon (CMK-3) through batch experiments. The characteristic parameters for the kinetics and adsorption model were determined. The mechanism of Cr(VI) adsorption onto MCN was identified by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS) analysis. The effects of contact time, pH, temperature, coexisting anion on the adsorption capacity and the regeneration of MCN were also investigated.

2. Materials and methods

All reagents used in the experiments were purchased in analytical purity and used without further purification.

2.1. Synthesis of MCN

MCN was prepared using SBA-15 as the template [22,23]. Briefly, 1.0 g of calcined SBA-15 was added into the mixture of ethylenediamine (4.4 g) and carbon tetrachloride (10.8 g). The resultant mixture was stirred at 90 °C until a brown solid material was obtained, and then the solid was transferred to a drying oven at 60 °C for 12 h. Subsequently, the resulting sample was calcined at 600 °C for 5 h under N_2 flow of 40 mL/min. Finally, the calcined sample was treated with 5 wt% Hydrofluoric acid (HF) to remove silica template, and washed with ethanol and distilled water for several times. The dried sample in a vacuum oven at 60 °C was denoted as MCN.

AC and CMK-3 were used for comparison. AC was a coconut shell based powdered activated carbon obtained from Nanjing Ningshi Chemical Reagents Ltd. (Jiangsu, China). CMK-3 was synthesized by the reported procedure using SBA-15 as template and sucrose as carbon source [24].

2.2. Characterization

The crystalline phases of the samples were analyzed by X-ray diffraction (XRD) using a Rigaku D/max-RA powder diffractionmeter. The morphologies of the MCN before and after Cr(VI) adsorption were observed on a transmission electron microscope (TEM) using JEM-200CX microscopy. Brunauer-Emmett-Teller (BET) surface areas of the samples were measured by N_2 adsorption/desorption isotherms on Micromeritics ASAP 2200. Prior to measurement, the samples were pre-treated at 300 °C under vacuum (1.33 Pa) for 1 h.

FT-IR spectra of MCN before and after Cr(VI) adsorption were collected in 1000-4000 cm^{-1} using a Nexus 870 FT-IR spectrophotometer. XPS measurements of MCN before and after Cr(VI) adsorption were performed on an RBD upgraded PHI-5000C ESCA system equipped with a monochromatized Mg Kα excitation source ($h\nu$ = 1253.6 eV). The MCN after Cr(VI) adsorption was obtained through contact with 20 mg/L Cr(VI) at pH 5.7 for 48 h. The MCN sample was washed with deionized water and dried at 60 °C before TEM, FT-IR and XPS measurement.

2.3. Batch adsorption experiments

Cr(VI) adsorption kinetics were performed by batch adsorption experiments in a flask on a shaker at 150 rpm. Typically, 0.5 g of AC, CMK-3 or MCN was added into a 500 mL flask containing 500 mL of 20 mg/L Cr(VI) concentration and the flask was shaken at 25 °C. Samples were withdrawn from the flask at the desired contact time and filtered with a 0.45 μm membrane. Cr(VI) concentration in the filtrate was determined spectrophotometrically using diphenylcarbazide as color agent. Adsorption capacity of Cr(VI) at time of t was calculated by conducting a mass balance of Cr(VI) using Eq. (1):

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

where q_t is the adsorption amount at time t (mg/g), C_0 is the initial concentration of Cr(VI) (mg/L), C_t is the concentration of Cr(VI) at time of t (mg/L). W is the mass of the adsorbent (g), and V is the volume of the solution (L).

The adsorption isotherms of Cr(VI) were conducted in a 40 mL beaker on a shaker at 150 rpm. In a typical run, 30 mg of adsorbent was introduced into 30 mL of aqueous Cr(VI) solution with initial concentration ranging from 0 to 700 mg/L. AC, CMK-3 and MCN were used as the adsorbents. The initial pHs of Cr(VI) solution were 5.5-6.1 before adsorption and the pHs changed to 3.5-3.9 after adsorption. The mixture was taken out and filtered with a 0.45 μm membrane after adsorption for 48 h. Adsorption capacity of Cr(VI) at equilibrium time was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where q_e is the equilibrium adsorption amount (mg/g), C_e is the concentration of Cr(VI) at equilibrium adsorption time (mg/L).

The effects of aqueous pH, solution temperature and coexisting anion on Cr(VI) adsorption by MCN were also investigated. Briefly, a series of tubes containing 30 mg of MCN and 30 mL of 20 mg/L Cr(VI) solution were shaken at 25 °C for 48 h. The pH values of the Cr(VI) solution varying from 2 to 11 were adjusted by 0.1 mol/L H_2SO_4 or 0.1 mol/L NaOH, respectively. The adsorption studies were carried out at different temperatures (15, 20 and 25 °C) to determine the effect of temperature. The coexisting anion with different concentrations, such as carbonate, chloride, sulfate or nitrate was added before adsorption.

2.4. Regeneration of adsorbent

The Cr(VI)-adsorbed MCN was collected and washed with distilled water to remove unadsorbed chromium ions. Hereafter, a series of NaOH solution with various concentrations were used for the desorption of Cr(VI). The desorption efficiency could be obtained from the ratio of the desorbed Cr(VI) concentration to the adsorbed Cr(VI) concentration.

3. Result and discussion

3.1. Material characterization

The SBA-15 template and CMK-3 were characterized by low-angle XRD and MCN was characterized by both of low-angle and wide-angle XRD (as shown in Fig. 1). The CMK-3 sample with three typical diffraction peaks indexed as (100), (110) and (200) was similar to the SBA-15 template, reflecting the two-dimensional hexagonal structure. The low-angle XRD pattern of the MCN material was also similar to that of SBA-15, indicating MCN possessed two-dimensional hexagonal structure. The peak intensities of (110) and (200) in CMK-3 slightly decreased comparing to SBA-15, and the peak intensities in MCN decreased more dramatically than CMK-3. The phenomenon showed that there is a more obvious decrease in the structural order of MCN during carbonization step than that of CMK-3.

Please cite this article in press as: Chen H, et al. Adsorption of Cr(VI) from aqueous solution on mesoporous carbon nitride. J Taiwan Inst Chem Eng (2014), http://dx.doi.org/10.1016/j.jtice.2014.03.005