Chemical Engineering Journal 281 (2015) 491–501

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Efficient simultaneous removal of Cu(II) and $Cr_2O_7^{2-}$ from aqueous solution by a renewable amphoteric functionalized mesoporous silica

Qiuping Wu [a,b], Ruirong You [a,b], Qiufeng Lv [b], Yali Xu [a,b], Weijie You [a,b], Yan Yu [a,b,*]

[a] Key Laboratory of Eco-materials Advanced Technology (Fuzhou University), Fujian Province University, China
[b] College of Materials Science and Engineering, Fuzhou University, New Campus, Minhou, Fujian Province 350108, China

HIGHLIGHTS

- A renewable amphoteric functionalized mesoporous silica (AG-SBA-15) was synthesized and characterized.
- AG-SBA-15 was effective to remove Cu(II) and $Cr_2O_7^{2-}$ from aqueous solution simultaneously.
- AG-SBA-15 could immobilize Cr(VI) by reduction.
- AG-SBA-15 showed good regeneration and reusability.

ARTICLE INFO

Article history:
Received 6 May 2015
Received in revised form 1 July 2015
Accepted 4 July 2015
Available online 9 July 2015

Keywords:
Amphoteric
Mesoporous silica
Copper(II)
Chromium(VI)
Reusability

ABSTRACT

A renewable, amphoteric functionalized mesoporous silica (AG-SBA-15) was synthesized with a two-steps process: firstly, aluminum atoms was incorporated into the framework of SBA-15 and then melamine-based dendrimers groups were anchored onto the Al-substituted SBA-15. The amphoteric AG-SBA-15 kept an ordered hexagonal mesostructure after the functionalization and regeneration processes and exhibited an excellent performance for simultaneous removal of Cu(II) cations and $Cr_2O_7^{2-}$ metalloid anions from aqueous solution, with the maximum adsorption capacity of 2.216 mmol/g Cu(II) and 3.305 mmol/g $Cr_2O_7^{2-}$, respectively. Batch adsorption experiments results indicated that the optimized pH value for simultaneous removal of Cu(II) and $Cr_2O_7^{2-}$ was 5.0. The adsorption rate was extremely fast and the equilibrium reached within 30 min. The adsorption of Cu(II) and $Cr_2O_7^{2-}$ by AG-SBA-15 were fitted better to Langmuir than Freundlich Model and thermodynamic parameters revealed the spontaneous and exothermic nature of the adsorption. Reusability studies of AG-SBA-15 were carried out by 5 repeated adsorption–desorption cycles and the results confirmed that AG-SBA-15 could be easily reused with little loss in removal efficiency. Furthermore, simultaneous removal mechanism of Cu(II) and $Cr_2O_7^{2-}$ by AG-SBA-15 was proposed by X-ray photoelectron spectroscope analysis (XPS), which revealed that Cu(II) was adsorbed by a combination of electrostatic interaction, while Cr(VI) could be immobilized by reduction.

1. Introduction

Copper (Cu(II)) and hexavalent chromium (i.e., $Cr_2O_7^{2-}$ and CrO_4^{2-}) are two heavy metal ions which existed in the aqueous solution with the forms of metal cations and metalloid anions, respectively [1–3]. Due to the widespread presence of copper and chromium in industrial applications such as electroplating, metal finishing, metal polishing, smelting and refining etc., Cu(II) and $Cr_2O_7^{2-}$ are becoming the abundant harmful ions in the liquid effluents [4–6]. Their levels in the aqueous solution are much higher than the maximum acceptable level of 0.05 mg/L for Cu(II) and 0.1 mg/L for $Cr_2O_7^{2-}$, which are set by the US Environmental Protection Agency (EPA) [7,8]. The excessive Cu(II) and $Cr_2O_7^{2-}$ existed in aqueous solution will seriously destroy ecological systems and human bodies through accumulation and circulation in the environment and food chain [9,10]. Therefore, in order to keep control of water quality and human health, removal of Cu(II) and $Cr_2O_7^{2-}$ from liquid effluents must be implemented to meet the emission standard before being discharged into the environment.

Many methods have been used to remove Cu(II) and $Cr_2O_7^{2-}$ from wastewater, such as precipitation, ion exchange, adsorption, membrane process, etc. [11,12]. Among them, adsorption

* Corresponding author at: Key Laboratory of Eco-materials Advanced Technology (Fuzhou University), Fujian Province University, China. Fax: +86 591 22866534.
E-mail address: yuyan@fzu.edu.cn (Y. Yu).

http://dx.doi.org/10.1016/j.cej.2015.07.019
1385-8947/

techniques are the most economical and widely used method for removal of metal cations and metalloid anions [13–15]. Recent works have shown that many materials such as functionalized nanomaterials, magnetic particles, functionalized silica, nanotubes, etc. [1–8,16–23] have been used as effective adsorbents for the removal of Cu(II) or $Cr_2O_7^{2-}$ from wastewater. However, to the best of our knowledge, most of published works on these adsorbents only focus on the excellent selectivity of Cu(II) cations [1,5,6,20–22] or the perfect extraction of $Cr_2O_7^{2-}$ metalloid anions [2–4,16–19]. Thus, to achieve the aim of simultaneous removal of Cu(II) and $Cr_2O_7^{2-}$, an unavoidable method of two-steps treatment with different adsorbents was applied, which was certainly time consuming and tedious [24]. Hence, it is significant to develop an adsorbent with the ability of simultaneous removal of Cu(II) and $Cr_2O_7^{2-}$ from wastewater.

In recent decades, the development of functionalized mesoporous adsorbents for heavy metal ions using incorporated ligands with appropriate functional groups has generated considerable interest [25–27]. As reported in the literature [28,29], the functional groups with acidic or basic properties on the surface of mesoporous silica is responsible for the preferential interaction with cations or anions, respectively. Therefore, simultaneous removal of Cu(II) and $Cr_2O_7^{2-}$ from wastewater with a single adsorbent is attainable through anchoring of both acidic and basic functional groups onto the mesoporous silica. Furthermore, it is worth mentioned that a series of amphoteric mesoporous silica with acidic and basic functional groups on the surface had been synthesized in the catalyst area, such as Al-SBA-15-NH_2, benzyl-APS-S-SBA-15 [30], etc, and there were no reports involved in the removal of Cu(II) and $Cr_2O_7^{2-}$ about these amphoteric materials.

Thus, in this work, the amphoteric functionalized mesoporous silica (AG-SBA-15) was applied to simultaneously remove Cu(II) cations and $Cr_2O_7^{2-}$ metalloid anions from aqueous solution, which was synthesized with a two-steps method shown as follows: firstly, aluminum atoms was incorporated into the framework of SBA-15 by direct-synthesis generating acidic aluminum hydroxyl groups, and then melamine-based dendrimers groups containing abundant basic amine groups (—NH_2, —NH—, —N<), were anchored onto the surface of the Al-substituted SBA-15. The aluminum hydroxyl groups and amine groups of AG-SBA-15 are responsible for the capturing of Cu(II) and $Cr_2O_7^{2-}$, respectively. Owing to the stereo-hindrance effect generated by the aromatic triazine rings of the melamine-based dendrimers groups [27,31], the neutralization reactions which referred in the literature [23] between the aluminum hydroxyl groups and amine groups on surface of AG-SBA-15 were avoided, hence, the amphoteric material was able to simultaneously remove Cu(II) and $Cr_2O_7^{2-}$ species from aqueous solution with a high adsorption capacity. The physical and chemical properties of the obtained materials were characterized by XRD, SEM, TEM, N_2 adsorption and desorption, FTIR, TGA, NH_3-TPD, elemental analysis and XPS. The adsorption isotherms, thermodynamic, effects of pH value, contact time, temperature on simultaneous removal of Cu(II) and $Cr_2O_7^{2-}$ by AG-SBA-15 were investigated in this study through batch experiments. In order to test the reusability and stability of AG-SBA-15, the adsorption–desorption experiments of AG-SBA-15 were repeated 5 times using the same absorbent. In addition, the simultaneous removal mechanisms of Cu(II) and $Cr_2O_7^{2-}$ by AG-SBA-15 were also proposed.

2. Experimental

2.1. Chemicals and reagents

All materials and chemicals were of analytical grade and used as purchased without further purification. Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800) and tetraethylorthosilicate (TEOS 98%) were obtained from Sigma Aldrich Co., Ltd. (St Louis, MO, USA). Aluminum isopropoxide (Mw = 204.24, $C_9H_{21}AlO_3$), 3-aminopropyltrimethoxysilane (APTES 99%), N,N-diisopropylethylamine (DIPEA), 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride), ethylenediamine (EDA), hydrochloric acid (HCl, 37%), sodium hydroxide, copper sulfate ($CuSO_4.5H_2O$) and potassium dichromate (K_2Cr_2O7) were provided by Sinopharm Chemical Reagents Co., Ltd. China. Methanol, dichloromethane, tetrahydrofuran (THF) and toluene were purchased from Fuzhou United Experimental Instrument Co., Ltd. (Fujian, China).

2.2. Synthesis of AG-SBA-15

The synthesis steps of AG-SBA-15 contained two main procedure: firstly, aluminum atoms was incorporated into the framework of SBA-15 by direct-synthesis to obtain the Al-substituted SBA-15 (A-SBA-15) and then melamine-based dendrimers groups were anchored onto the surface of the A-SBA-15. The detailed steps were shown as follows.

Firstly, the synthesis method of A-SBA-15 was carried out as described by Wu et al. [32]: (1) 2.0 g Pluronic P123 was dissolved in 60 g HCl (2 M), followed by the addition of 4.5 g TEOS. The mixture was stirred at 313 K for 4 h and then a specific amount of aluminum isopropoxide ($C_9H_{21}AlO_3$) was added to the mixture. (2) Subsequently, the mixture was continuously stirred at 313 K for 20 h and then crystallized in a Teflon-lined autoclave at 373 K for 2 days. (3) After that, the pH of the synthesis system was then adjusted to 7.5 by adding ammonia dropwise at room temperature and the obtained mixture was hydrothermally treated again at 373 K for another 2 days. (4) The final solid was collected by filtration, washed with water, dried at room temperature, and calcined in air at 823 K for 6 h for the following using. The mesostructure of A-SBA-15 was shown in Fig. 1.

Then, the melamine-based dendrimers groups anchored onto the surface of A-SBA-15 were carried out according to a synthesis method described by Shahbazi et al. [27] and Yoo et al. [31]: (1) 1.0 g calcined A-SBA-15 was added into a closed container containing a solution of 1.4 mL APTES and 100 mL toluene. The mixture was stirred for 12 h at 298 K under nitrogen, and then the obtained solid (NH_2-A-SBA-15) was collected by filtration and washed with dried toluene. (2) Subsequently, 1.1 g cyanuric chloride and 1.42 mL DIPEA were dissolved in 300 mL dried THF and then 1 g NH_2-A-SBA-15 was added into this solution. The mixture was kept under stirring for 24 h at 273 K, and then was filtered, washed with dried methanol, dichloromethane and THF. (3) After that, the obtained solid was again transferred into a clean flask containing 1.6 mL EDA dissolved in 300 dried THF, and the mixture was refluxed for 24 h at 313 K. (4) Finally, the AG-SBA-15 was obtained by filtration, washed with dried methanol, dichloromethane and THF, and then dried at 373 K for 12 h. The schematic illustration of synthesis of AG-SBA-15 was shown in Fig. 1.

2.3. Batch adsorption experiments of AG-SBA-15

Simulate Cu(II) and $Cr_2O_7^{2-}$ ions co-existed solution used in the adsorption experiments was prepared by dissolving copper sulfate ($CuSO_4.5H_2O$) and potassium dichromate ($K_2Cr_2O_7$) in appropriate amounts of deionized water. The initial pH values of the solution were adjusting with 0.1 M NaOH or HCl solution. Adsorption experiments were performed using batch methods [3]. Typically, an amount of 0.03 g of AG-SBA-15 was added into 50 mL of a solution of known Cu(II) and $Cr_2O_7^{2-}$ species concentrations in 100 mL conical flasks, and then the flasks were placed in a water bath shaker at 150 rpm at a predetermined temperature. After a specific contact time, the adsorbent was filtered and the concentrations