Vietnam Journal of Science and Technology ***57*** *(4) (2019) 484-490*

doi:10.15625/2525-2518/57/4/13655

CHARACTERIZATION AND ADSORPTION CAPACITY OF AMINE-SiO_2 MATERIAL FOR NITRATE AND PHOSPHATE REMOVAL

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Received: 2 March 2019; Accepted for publication: 5 May 2019

Abstract. Amine-SiO_2 material was synthesized and applied as a novel adsorbent for nitrate and phosphate removal from aqueous solution. The characterizations of Amine-SiO_2 were done by using TGA, FTIR, BET, and SEM analyses. Results showed that Amine-SiO_2 had higher nitrate and phosphate adsorption capacity, i.e. of 1.14 and 4.16 times, respectively, than commercial anion exchange resin (Akualite A420). In addition, Amine-SiO_2 also had good durability with stable performance after at least 10 regeneration times, indicating that this material is very promising for commercialization in the future as an adsorbent for water treatment.

Keywords: Amine-SiO_2, phosphate adsorption, nitrate adsorption, water treatment.

Classification numbers: 2.6.2, 3.4.2.

1. INTRODUCTION

Water pollution by nutrients such as nitrogen and phosphorous is one of the most popular issue in the world. The presence of nitrate and phosphate in water source due to the ineffective treatment of domestic and industrial wastewater or excess use of fertilizer in agriculture is recognized as major reason for eutrophication, which affects seriously the quality of water and activities of living-forms in water [1]. Moreover, high nitrate concentration in water is considered as an important risk for human health, causing methemoglobinemia or forming carcinogen compounds (i.e. nitrosoamine) [2].

Various chemical, physico-chemical, and biological processes have been proposed for removal of nitrate and phosphate from water and wastewater [3-6]. Among them, adsorption and ion exchange are considered as an effective, simple, and cheap method due to the regeneration ability of adsorbent [7]. Therefore, the development of ion exchange has been recently attracted many attentions [8-10]. Moreover, mesoporous silica (e.g. SBA-15 and MCM-48) modified by amine has been proven as effective materials for removal of nitrate and phosphate in water [11-13]. However, the application of these materials is very limited in Vietnam due to the complicated procedure for synthesis and high production cost, which cannot compete with imported resins from China. Therefore, it is necessary to study on the preparation of a new, cheap, and effective adsorbent or ion exchange material which is suitable for application in condition of Vietnam.

In this study, a cheap industrial SiO_2 (China) was used as support for grafting of amine functional group and applied for removal of nitrate and phosphate in water. The adsorption capacity and durability were employed as criteria for evaluation the performance of materials, which was also compared with available commercial ion exchange resin.

2. MATERIALS AND METHODS

SiO_2 (China), triaminesilane (Sigma-Aldrich, USA), toluene, pentane, KBr, and stock solutions of nitrate and phosphate (Merck, Germany) were used for synthesis, characterization, and adsorption removal test. Commercial Akualite A420 (China), which was used as good anion exchange resin in our previous work [14], was used as comparison for as-synthesized Amine-SiO_2 material. Water used in this study was from a deionized (DI) water machine in laboratory.

Amine-SiO_2 was prepared as following procedure: a mixture of DI water and SiO_2 with ratio of 0.3 mL/g was added into a two-neck flask containing 100 mL of toluene. The flask was then immerged in a silicone oil bath set at 85 ^oC using a temperature-controlled heater system. After that, triaminesilane with ratio of 3 mL/g SiO_2 was added into the mixture and stirred for 16 h. Finally, the solid material was collected after washing with pentane and dried at 100 ^oC for 1 h [15].

Morphology of Amine-SiO_2 was obtained by scanning electron microscopy (SEM, JEOL JSM 7401F, Japan). Chemical surface property and functional group of Amine-SiO_2 were examined by Fourier transform infrared spectroscopy (FTIR, Alpha-Bruker, Germany). Amine loading on SiO_2 support was determined by thermogravimetric analysis (TGA, Q500 Thermo, USA). Specific surface area of materials was measured by Brunauer–Emmett–Teller (BET) analysis (CBET 210A Sorptometer, USA). Before BET analysis, the sample was degassed at 150 ^oC for 3 h.

In order to compare adsorption efficiency of materials (including SiO_2, Amine-SiO_2 and Akualite A420), the batch experiments were conducted using 10 ppm nitrate solution and 2 ppm phosphate solution with dosage of 30 mg of adsorbent in 50 mL of solution. After equilibrium, the adsorbent was separated by centrifuge at 10,000 rpm and the supernatant was taken for analysis by photospectrometry using sodium salicylate for nitrate (Vietnam standard TCVN 4562:1988) and ammonium molybdate for phosphate (Vietnam standard TCVN 6202:2008). All the experiments were replicated 4 times. Before each experiment, materials were activated by pretreatment with 0.1 M HCl solution for 3 h with dosage of 1 g of adsorbent/1 L of HCl solution. For durability test, the saturated materials were regenerated with HCl solution and tested for 10 times.

The removal efficiency of nitrate and phosphate were calculated as following:

$$H\% = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where C_o and C_t are the initial and equilibrium concentrations, respectively.

3. RESULTS AND DISCUSSION

3.1. Material synthesis and characterization

Morphology of Amine-SiO_2 material and Akualite A420 resin are displayed in Figure 1. While Akualite showed uniform particles with rough surface, Amine-SiO_2 was irregular particles with different sizes. Moreover, B.E.T results in Table 1 showed that surface area of based SiO_2 material did not change significantly after grafting with amine, where surface area lightly increased from 32.5 to 34.6 m^2/g.

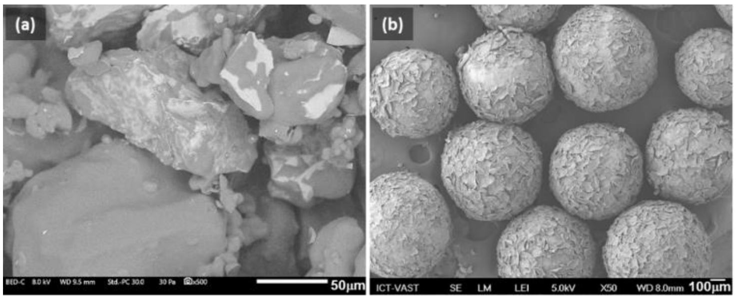

Figure 1. SEM images of (a) Amine-SiO_2 and (b) Akualite A420.

Table 1. Surface area and amine content of SiO_2 and Amine-SiO_2

Sample	Surface area (m^2/g)	Amine content (%)
SiO_2	32.5	~ 0
Amine-SiO_2	34.6	~1.6

FTIR spectra of Amine-SiO_2 and Akualite A420 ion exchange resin are plotted in Figure 2. For Akualite A420, characteristic peaks of styrene-divinylbenzene in the resin were observed. The band from 2800 to 3060 cm^{-1} is attributed to the vibration of polystyrene structure while peaks at 3018 and 2922 cm^{-1} are vibrations of C-H in benzene ring and -CH_2 in the cross-links of polystyrene, respectively [7]. Band from 3360 to 3590 cm^{-1} is O-H vibration with highest peak at wavenumber of 3457 cm^{-1} while peak at 1601 cm^{-1} is the C-C vibration of styrene ring [16]. Peak at 1481 cm^{-1} is the vibration of symmetric and asymmetric methyl in amine functional group of ion exchange resin [17, 18]. Moreover, peaks at 1039 and 1128 cm^{-1} could be vibrations of benzene ring due to the styrene-divinylbenzene matrix of resin [19]. For Amine-SiO_2, characteristic FTIR peaks were observed, including Si-H (650-840 cm^{-1}), Si-O-Si (1030-1130 cm^{-1}), C=C (1650 cm^{-1}), C-H (2930 cm^{-1}), and -OH (3420 cm^{-1}) [20]. Particularly, peak at 1481 cm^{-1} was observed in both Akualite A420 and Amine-SiO_2, proving the successful grafting of amine on SiO_2 support.

Figure 3 presents the TGA result of Amine-SiO_2 in temperature range of 30 to 975 ^oC, which can be divided into three stages. The first stage with mass loss of ~ 15 % from 30 to 150 ^oC (peak at 50 - 100 ^oC) is attributed to the release of water and low molecular weight organic compounds [21, 22]. The second stage from 150 to 550 ^oC is assigned for the loss of hydroxyl group at high temperature and the pyrolysis of organic composition in the material [22]. The pyrolysis of amine occurs in the third stage of 550 to 600 °C [23], with total mass loss reached ~ 55 % and the remaining is mainly silica [21]. The amine content was then calculated to be 1.6 % w/w, as presented in Table 1.

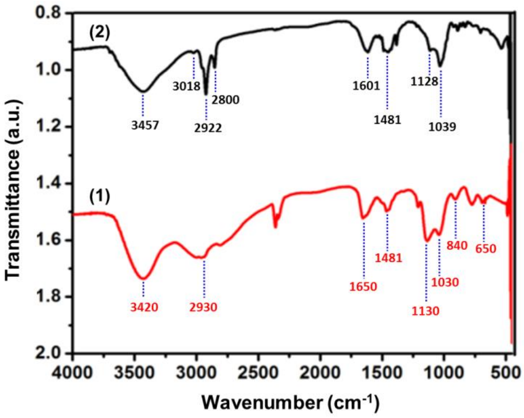

Figure 2. FTIR results of (1) Amine-SiO_2 and (2) Akualite A420.

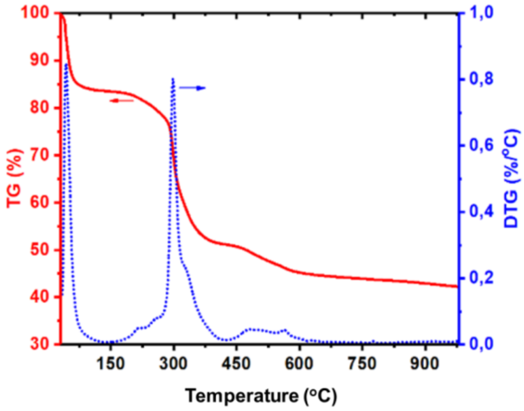

Figure 3. TG-DTG curves of Amine-SiO_2 material.

3.2. Nitrate and phosphate adsorption test

Adsorption test result in Figure 4 showed that Amine-SiO_2 material had high ability for nitrate and phosphate removal with efficiencies of 74.0 and 60.8 %, respectively, as compared to 65.0 and 14.6 % of Akualite A420. The very low adsorption efficiency of SiO_2 (i.e. 2.5 % and 1.5 % for nitrate and phosphate, respectively) proved that amine group on the surface of SiO_2 plays a major role for adsorption and ion exchange due to the strong affinity of amine group with nitrate and phosphate ions. This implied that Amine-SiO_2 is more advanced and competitive with available commercial ion exchange resin.

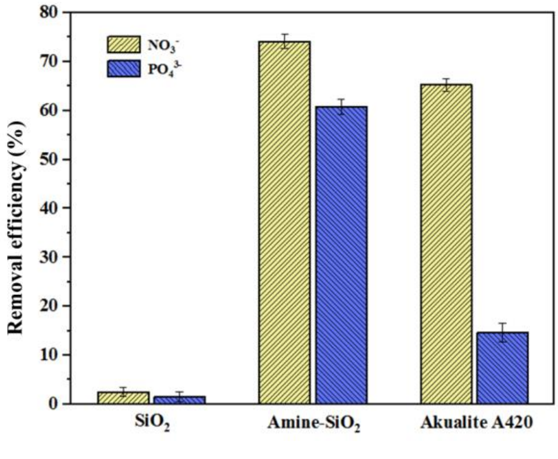

Figure 4. Nitrate and phosphate removal efficiency of adsorbent materials (n = 4).

In the durability tests, all used materials were regenerated using 0.1 M HCl solution which was similar to the pretreatment process. The durability of materials for removal of nitrate and phosphate after 10 cycles of adsorption – desorption is illustrated in Figure 5. Results showed that both Amine-SiO_2 and Akualite A420 were very stable after ten times of reuse without decline on adsorption efficiency. Thus, this is an important criterion for commercialization of the material in the future for water treatment.

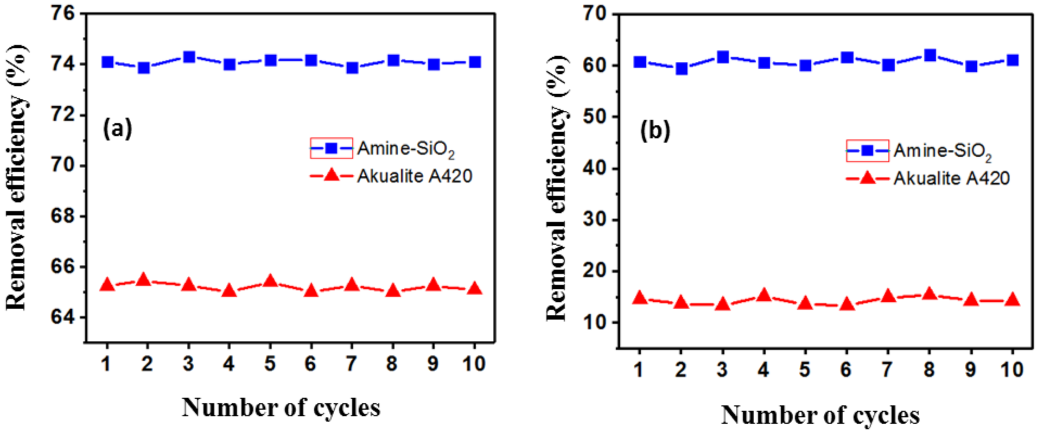

Figure 5. Durability tests of materials for (a) nitrate and (b) phosphate adsorption.

4. CONCLUSIONS

Characteristic analysis results (including SEM, BET, FTIR and TGA) examined that amine functional groups were successfully grafted on SiO_2 support. For anion adsorption experiments, Amine-SiO_2 material showed that efficiencies for nitrate (~74 %) and phosphate (~60.8 %) removals were superior that of commercial anion exchange resin-Akualite A420 (~65 % and ~14.6 %, respectively), while original SiO_2 has almost no detection for nitrate (~2.5 %) and phosphate (~1.5 %) removals. Especially, Amine-SiO_2 material also showed good durability, similar to commercial Akualite A420 (efficiency remained stable after 10 times of regeneration). All of these indicated that this novel Amine-SiO_2 material is a promising adsorbent or ion exchange material for anion removals in water environment.

Acknowledgements. This research is funded by Ho Chi Minh City University of Technology, VNU-HCM, under grant number BK-SDH-2019-1780305. The authors are grateful for support from An Giang University for experiments and analysis.

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