

A Simple Method for Synthesis of Triamine-SiO₂ Material toward Aqueous Nitrate Adsorption[#]

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ABSTRACT

This study describes a facile route for preparation of mesoporous silica at ambient condition using cheap and available commercial SiO₂ precursor. The mesoporous material was then loaded with amine (Amine-P-SiO₂) and applied for nitrate removal in aqueous solution. The materials were characterized by XRD, TGA, FTIR, and SEM to explore the properties. Effects of pH, nitrate concentration, adsorbent dosage, and temperature on the nitrate adsorption capacity were investigated. Amine-P-SiO₂ material was superior to commercial adsorbent (Akualite A420) for nitrate adsorption with capacity reaching 32.5 mg/g and relatively stable after 10 cycles of adsorption-desorption. Moreover, the adsorption follows Langmuir model, proving that this chemical adsorption could effectively remove nitrate from aqueous solution for water and advanced wastewater treatment applications.

1. INTRODUCTION

The increase of domestic water use causes a pressure on water treatment and the shortage of clean water due to climate change and water pollution from anthropogenic sources. Nitrate ion exists naturally in the nitrogen biogeochemical cycle and serves as an essential nutrient for plants on Earth. However, the increase of nitrate pollution causes many issues for both environment and human health. Nitrate concentration in drinking water is limited by WHO guideline at 45 ppm and by every country. Therefore, the removal of nitrate contaminant from water has attracted many attentions and proposed with various methods. Conventional approaches such as biological treatment, ion exchange, adsorption, reverse osmosis, electrochemical, and chemical methods show several limitations (Tyagi et al., 2018) while advanced methods using nanotechnology such as reduction by zero valent iron (Araújo et al., 2016), catalytic and electrocatalytic reduction (Martinez et al., 2017; Garcia-Segura et al., 2018), photocatalytic reduction (Tugaoen et al., 2017; Bahadori et al., 2018), adsorption (Bhatnagar and Sillanpää, 2011;

Loganathan et al., 2013; Singh et al., 2018) emerge as potential technologies. Among these methods, adsorption using new and effective nanomaterials could be a very promising technology, which can remove nitrate from water and wastewater. The development of ion exchange has recently attracted many attentions (Banu and Meenakshi, 2017; Kalaruban et al., 2016; Nujić et al., 2017). Moreover, mesoporous silica (e.g., SBA-15 and MCM-48) modified by amine has been proven as effective materials for nitrate removal from water (Hamoudi et al., 2007; Safia et al., 2012; Saad et al., 2007). However, the application of these materials is limited due to the complicated procedure for synthesis and high production cost. Therefore, the development of simple and cheap adsorbents is necessary for effective and efficient nitrate removal and recovery in water environment.

In the present work, a simple process for synthesis of new and cheap mesoporous silica was proposed from available commercial SiO₂. The materials were then grafted with amine and applied for removal of nitrate in water. The effect of

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environmental conditions on the nitrate removal efficiency and adsorption capacity was investigated, including solution pH, initial nitrate concentration, adsorbent dosage, and adsorption temperature. The adsorption capacity of the synthesized materials was compared with commercial ion exchange resin (Akualite A420) and the durability test was also conducted.

2. METHODOLOGY

2.1 Material synthesis and characterization

Analytical-grade chemicals and in-lab deionized (DI) water were used in this study. HF, SiO₂, NaOH, and HCl were from Xilong (China). Triaminesilane (N¹-(3-trimethoxysilylpropyl) dimethylene triamine), pentane and toluene solvents, KBr powder, and nitrate (stock solution of 1,000 mg/L) were from Merck (Germany). Commercial Akualite A420 resin bought from China was used as a reference material.

Commercial silica (industrial grade) was purchased from Ho Chi Minh City, Vietnam. This silica was pretreated by washing with DI water, drying at 100 °C, and sieving with mesh size from 20 to 50 μm (named as SiO₂ in this study). The mesoporous structure of silica was created by using chemical reaction of HF and SiO₂. In a typical procedure, 20 g of SiO₂ powder was added into 1 L of 5% (vol/vol) HF solution under continuous stirring at ambient condition. After 30 min of reaction, the remaining solid SiO₂ powder was filtered and washed with DI water. The mesoporous silica (named as P-SiO₂) was finally obtained by drying at 100 °C for 4 h.

The amine-loaded materials (i.e., Amine-P-SiO₂ and Amine-SiO₂) were synthesized by grafting of triaminesilane onto P-SiO₂ and SiO₂ materials, respectively, following a synthesis procedure described in the literature (Thanh, 2016). In a typical experiment, a mixture of 150 mL toluene and DI water (continuous stirring at 85 °C) was added with P-SiO₂ (or SiO₂) at ratio of 0.3 mL DI water per 1 g of P-SiO₂ (or SiO₂). The mixture was then added with triaminesilane with ratio of 3 mL/g silica and stirred continuously for 16 h. After that, the mixture was filtered and the obtained solid material was washed by toluene and subsequently pentane. The material was finally dried at 100 °C for 1 h and named as Amine-P-SiO₂ (or Amine-SiO₂).

The materials were then characterized by Fourier transform infrared spectroscopy (FTIR, Bruker), thermogravimetric (TGA, Q500), X-ray diffraction (XRD, D2 Phaser), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), Brunauer-Emmett-Teller (BET, BET-202A Porous Materials). Detailed condition of these analyses and material sample pretreatment can be found in our previous studies (Phan et al., 2018; Thanh, 2016).

2.2 Nitrate adsorption experiment

The nitrate removal ability of amine-grafted materials was evaluated using batch nitrate adsorption test. Adsorbent was added into 50 mL of nitrate solution and shaken at 120 rpm and 25±0.5 °C. After reaching the equilibrium, the solid material was collected by centrifuging at 10,000 rpm. The effects of adsorbent amount (0.005-0.10 g), pH (2-10), and nitrate concentration (5-100 mg/L) on the adsorption capacity were investigated. All experiments were replicated three times and the average results were reported. Nitrate concentration was analyzed using a SPECORD 210 Plus UV-Vis spectrophotometer (Analytik Jena) via brucine-sulfanil colorimetric method.

The regeneration of adsorbents was carried out by brine desorption technique. Typically, 1000 mL of HCl solution (0.1 M) was used to regenerate the adsorbent (1 g) for 3 h at ambient condition. The material was then washed with distilled water.

2.3 Adsorption isotherms, thermodynamics, and kinetics

In order to study the nitrate adsorption on the surface of Amine-P-SiO₂ material, both the Langmuir and Freundlich isotherm models were applied. The Langmuir isotherm is based on the monolayer adsorption of nitrate ions on adsorbent surface. The Freundlich isotherm describes both multilayer adsorption and adsorption on heterogeneous surfaces. The Langmuir model (1) and Freundlich model (2) are presented as the following equations:

$$q_e = \frac{Q_{\max}K_L C_e}{1+K_L C_e} \quad (1)$$

$$q_e = K_f C_e^{1/n} \quad (2)$$

Where C_e (mg/L) and q_e (mg/g) are equilibrium concentration and amount of nitrate adsorbed, respectively. Q_{max} (mg/g) and K_L (L/mg) are the maximum capacity and equilibrium constant. K_f ((mg/g)(L/mg)ⁿ) and n are Freundlich constants.

In this study, chi-square analysis was also applied for the calculated results from model ($Q_{max,cal}$) and experimental data ($Q_{max,exp}$) as in Equation (3).

$$\chi^2 = \sum \frac{(Q_{max,exp} - Q_{max,cal})^2}{Q_{max,cal}} \quad (3)$$

Thermodynamic parameters were calculated from equilibrium condition at different adsorption temperatures (293-318 K), as following equations (Duranoğlu et al., 2012):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

$$K = \frac{C_{Ae}}{C_e} \quad (5)$$

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

Where C_{Ae} and C_e (mg/g) are the nitrate amount on adsorbent and solution phases, respectively. ΔG° (kJ/mol), ΔH° (kJ/mol), and ΔS° (kJ/mol.K) are

Gibbs free energy, enthalpy, and entropy changes, respectively, calculated from Equation (6) using the plot of $\ln K$ vs. $1/T$.

3. RESULTS AND DISCUSSION

3.1 Material characterizations

FTIR was used for identification of surface functional groups of Amine-P-SiO₂ and Akualite A420 materials, as shown in Figure 1. The FTIR peak at around 3,442 cm⁻¹ was observed for both Akualite A420 and Amine-P-SiO₂ for -OH stretching vibration. In Akualite A420, other peaks was found at 3,018 and 2,922 cm⁻¹ of C-H bonds and -CH₂ groups (Sowmya and Meenakshi, 2013), 1601 cm⁻¹ of styrene ring C-C bonds (Lazar et al., 2014), 1481 cm⁻¹ of methyl group of quaternary nitrogen (Wołowicz and Hubicki, 2009; Gandhi et al., 2011), and 1,039 and 1,128 cm⁻¹ of benzene ring (Lee et al., 2003). For Amine-P-SiO₂, FTIR peaks were found at 1,480 cm⁻¹ of amine group, which is similar to Akualite A420. The other characteristic peaks of organic and silica were observed at wavenumbers of 3,420 (-OH), 2,930 (C-H), 1,650 (C=C), 1,030-1,130 (Si-O-Si), and 650-840 cm⁻¹ (Si-H) (Ibrahim et al., 1980), which indicates the successful grafting of amine groups onto the surface of porous P-SiO₂ material.

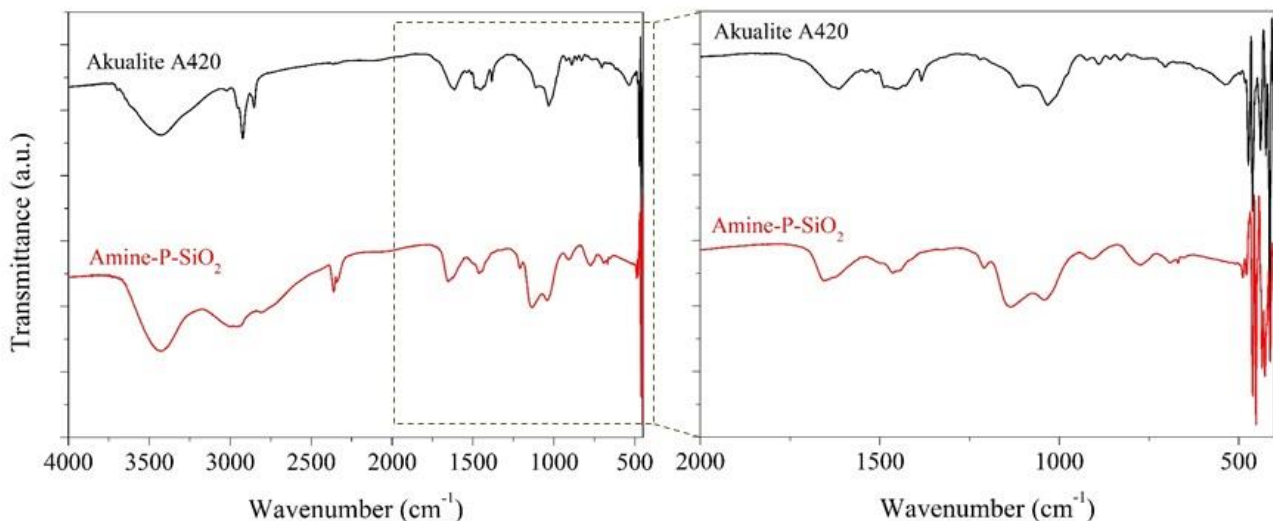


Figure 1. FTIR spectra of Amine-P-SiO₂ and ion exchange resin (Akualite A420)

The BET adsorption - desorption isotherms of nitrogen at 77 K for P-SiO₂ support and Amine-P-SiO₂ material are plotted in Figure 2, which follow type IV IUPAC isotherm for mesoporous materials.

The BET surface area of supports amine-loaded materials is summarized in Table 1. There was a remarkable increase of 20 times in surface area of silica material after treated with HF (i.e., from 32.5

(SiO₂) to 675.8 m²/g (P-SiO₂). This proves that HF treatment is a very effective method for generation of mesoporous silica from commercial silica. After loading with amine, the surface area of Amine-P-SiO₂ slightly decreased to 625.7 m²/g; however, it was still 18 times higher than that of Amine-SiO₂.

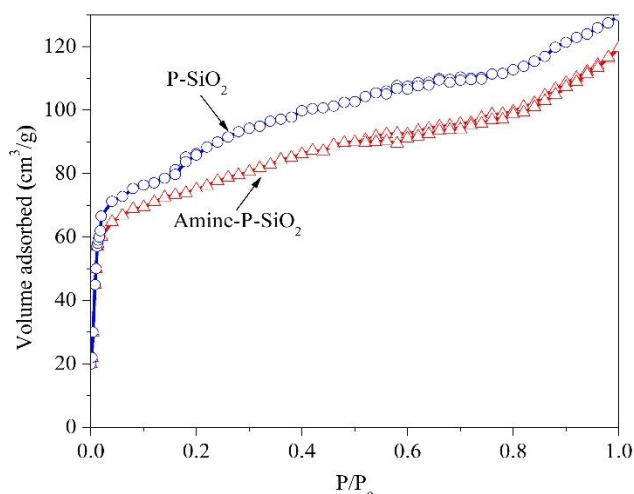


Figure 2. Nitrogen adsorption - desorption isotherm of P-SiO₂ and Amine-P-SiO₂

Table 1. Surface area and amine loading of silica materials

Sample	Surface area (m ² /g)	Amine loading (%)
SiO ₂	32.5	-
P-SiO ₂	675.8	-
Amine-SiO ₂	34.6	~ 1.6
Amine-P-SiO ₂	625.7	~ 6.4

Figure 3 presents the thermogravimetric curves of Amine-P-SiO₂ in temperature range of 30-1,000 °C. The mass loss can be divided into three stages. The first mass loss of ~16% in range of 30-200 °C with peak at 50-100 °C was the loss of water and highly volatile compounds. The second mass loss of ~34.6% in range of 200-430 °C was attributed to the hydroxyl group dehydration and other volatile compounds loss. The major loss of amine group (6.4%) was observed in the third stage with temperature range of 450-620 °C. The amine contents of P-SiO₂ and SiO₂ were then calculated to be 6.4% and 1.6%, respectively (Table 1). This was due to the higher surface area of P-SiO₂ support or silica density on silica support surface as compared to SiO₂ material.

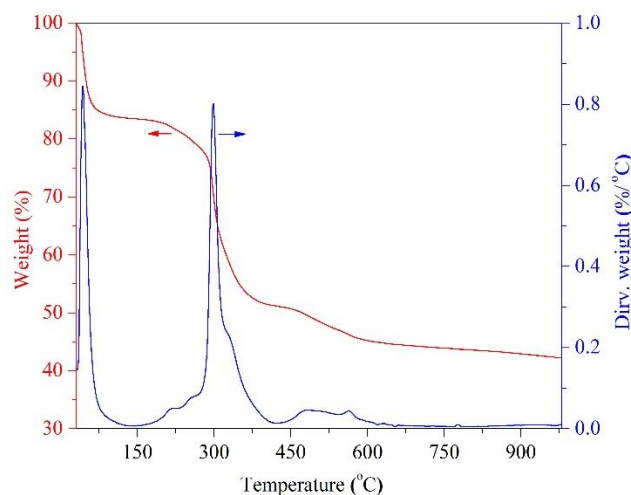


Figure 3. Thermogravimetric curves of Amine-P-SiO₂

Figure 4 displays SEM results of P-SiO₂ and Amine-P-SiO₂. It was observed that P-SiO₂ possessed highly porous structure, which was formed from the reaction of HF and SiO₂ during the synthesis of P-SiO₂. SEM-mapping results showed a relative homogeneous dispersion of amine on the surface of support and EDS results gave elemental ratios of O, C, Si, and N were 36.8, 31.6, 26.0, and 5.6%, respectively. There was not a significant change in the microstructure of P-SiO₂ after grafting with amine, as proven by XRD patterns in Figure 5 with only characteristic peaks of silica observed for both materials. The disappearance of some peaks at 73° and 77.5° and the lower intensity for other peaks of Amine-P-SiO₂ also proved the successful grafting of amine on the surface of the support material.

3.2 Adsorption tests of nitrate removal

The nitrate removal test using amine-loaded silica materials was evaluated using batch adsorption experiment. The effect of environmental conditions such as initial solution pH, concentration, dosage, and temperature on the adsorption capacity was investigated. When pH increased from 2 to 8 (Figure 6), nitrate removal capacity was higher than 18 mg/g and reached maximum capacity of 19 mg/g at pH 5. However, the capacity of nitrate removal decreased significantly to 15 mg/g at pH 10. This could be explained by the effect of solution pH value on the surface charge of adsorbent and nitrate species. Under acidic condition, NO₃⁻ ions tend to combine with H⁺ ions in solution to form HNO₃, which

reduces the electrostatic attraction between nitrate and positively charged functional groups on the surface of Amine-P-SiO₂ adsorbent (Song et al., 2016). Meanwhile, the poor adsorption capacity of Amine-P-SiO₂ under basic condition could be due to the competition of OH⁻ and nitrate ions for the same

adsorption sites (Battas et al., 2019). When the pH of the solution increases, many OH⁻ ions exist, which can make the adsorbent surface more negatively charged, thereby hindering the ion exchange of NO₃⁻ on the adsorption sites of material by electrostatic repulsion.

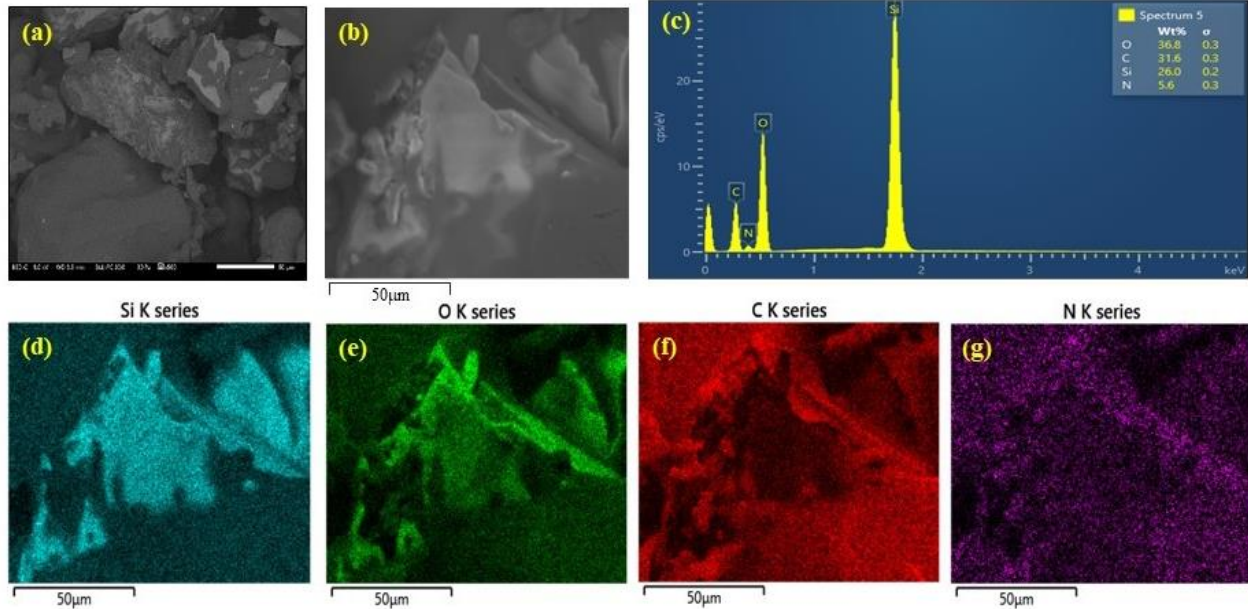


Figure 4. SEM images of (a) P-SiO₂ and (b) Amine-P-SiO₂, (c) EDS spectrum, and (d, e, f, and g) SEM mapping images of Amine-P-SiO₂ for Si, O, C, and N elements

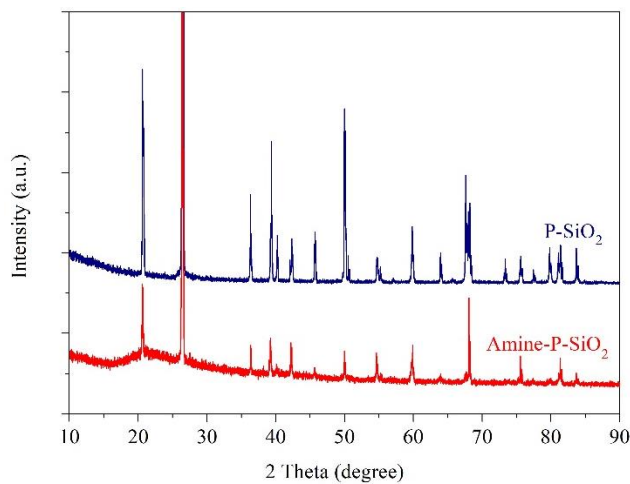


Figure 5. XRD pattern of P-SiO₂ and Amine-P-SiO₂ materials

The effect of Amine-P-SiO₂ dosage on nitrate adsorption is shown in Figure 7. It is obvious that adsorption efficiency continuously increased with the increase of the adsorbent dosage. However, the rapid increase was only observed for low dosage

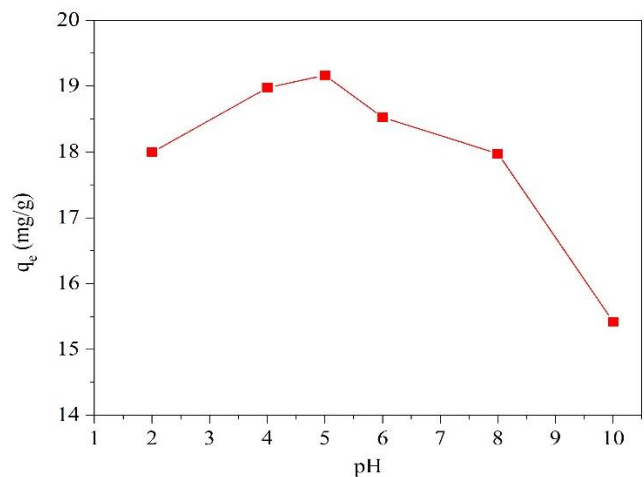


Figure 6. Effect of pH on nitrate removal using Amine-P-SiO₂ (Condition: temperature: 25±0.5 °C, dosage: 0.6 g/L, nitrate concentration: 15 mg/L)

range of 0.1-0.2 g/L and the efficiency then increased slowly in dosage range of 0.2-2.0 g/L. On the other hand, the adsorbent capacity of Amine-P-SiO₂ reached the highest value of 66.0 mg/g at the lowest dosage of 0.1 g/L, but decreased to 10 mg/g

at the highest dosage of 2.0 g/L. Since there was limited nitrate ion in the solution, adding more amount of adsorbent would result in a decrease of

adsorption capacity and an adsorbent dosage of 0.6 g/L with high adsorption capacity and efficiency was chosen for further experiments.

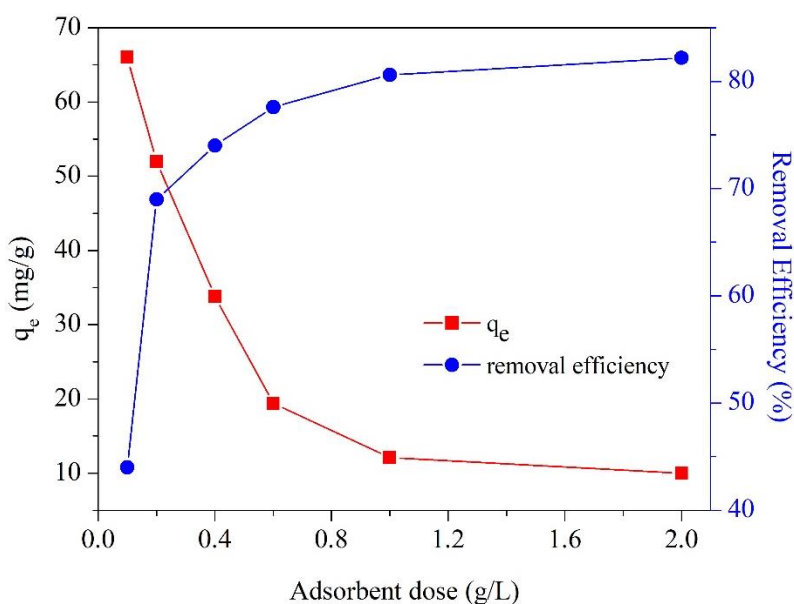


Figure 7. Effect of Amine-P-SiO₂ dosage on nitrate removal (Condition: temperature: 25±0.5 °C, pH 5, nitrate concentration: 15 mg/L)

The comparison on nitrate removal of Amine-P-SiO₂, Amine-SiO₂, and anion exchange resin (Akualite A420) is presented in Figure 8(a). Amine-P-SiO₂ showed a superior adsorption capacity of 32.5 mg/g, which was 1.71 and 1.31 times higher than that of Akualite A420 and Amine-SiO₂, respectively. The higher nitrate adsorption capacity of Amine-P-SiO₂ confirmed the successful and effective modification of SiO₂ surface by HF solution. However, the loading and utilization of amine was not effective and needed to be optimized in the future since the surface area and amine loading of Amine-P-SiO₂ was around 20 and 4 times, respectively, higher than those of Amine-SiO₂. Moreover, both amine-loaded silica materials had higher adsorption capacity than Akualite A420, proving the strong affinity of nitrate (from the solution) and amine group (on the surface of silica materials). The used Amine-P-SiO₂ and Akualite A420 were then regenerated using 0.1 M HCl solution and applied for durability test. As demonstrated in Figure 8(b), Amine-P-SiO₂ was more stable than Akualite A420 and the decline in adsorption of these materials was 20% and 50%, respectively, after 10 cycles of adsorption-desorption. This is a notorious advantage of Amine-

P-SiO₂ as compared to Akualite A420 ion exchange resin for commercialization of the product in the future

3.3 Adsorption isotherms, thermodynamics, and kinetics

Figure 9 illustrates the adsorption isotherms using Amine-P-SiO₂. Langmuir and Freundlich models were applied to understand the adsorption of nitrate. The calculated parameters for these two models are summarized in Table 2. As seen in Table 2, the Langmuir model fit better with the experimental data due to its higher correlation coefficients of 0.9849-0.9992 and smaller χ^2 values of 10.215-23.280. The maximum capacities (Q_{max}) for nitrate ion were then calculated to be 45.2-99.0 mg/g in temperature range of 288-318 K, respectively. These results indicated that nitrate removal mainly follows monolayer adsorption on Amine-P-SiO₂ adsorbent surface (Yousef et al., 2011). The adsorption process would be the chemical interaction of amine functional groups on the surface of the material and the nitrate ion. This also suggests that the improvement of the adsorption capacity in the future should be focused on the increase of surface amine groups on the material.

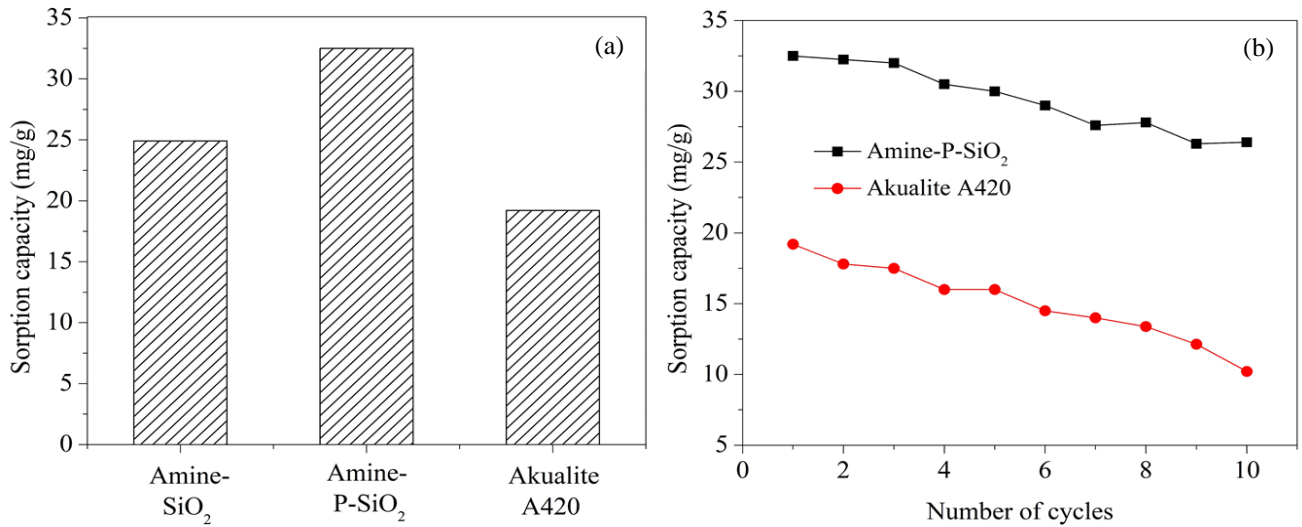


Figure 8. (a) Nitrate sorption capacities of different materials and (b) Cyclic tests for Amine-P-SiO₂, and Akualite-A420 (Condition: temperature: 25±0.5 °C, pH 5, dosage: 0.6 g/L, nitrate concentration: 50 mg/L)

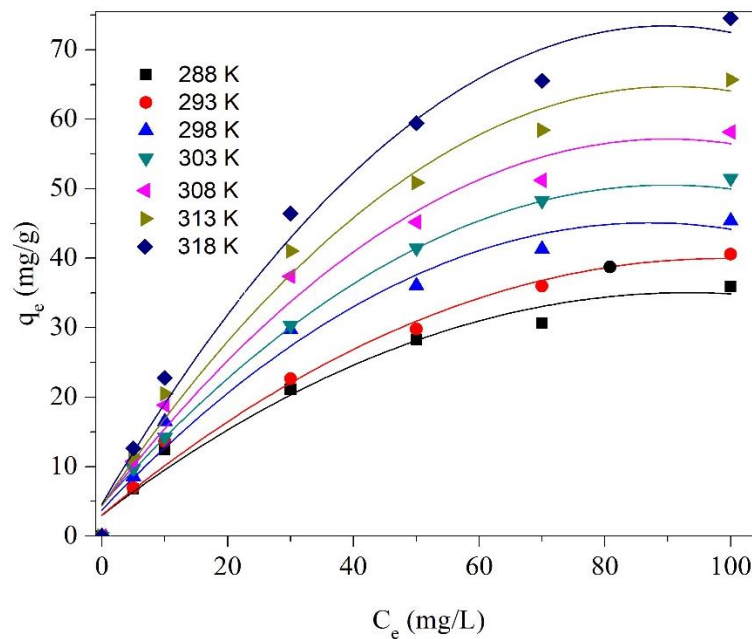


Figure 9. Adsorption isotherms at different temperatures (Condition: pH 5, Amine-P-SiO₂ dosage: 0.6 g/L)

Table 2. Parameters of Langmuir and Freundlich adsorption isotherms

Isotherm model	Model parameters	Adsorption temperature (K)						
		288	293	298	303	308	313	318
Langmuir	Q _{max} (mg/g)	45.249	53.476	57.471	70.922	74.627	86.957	99.010
	K _L (L/mg)	0.034	0.029	0.036	0.028	0.033	0.0300	0.029
	R ²	0.9911	0.9849	0.9979	0.9905	0.998	0.999	0.9992
	χ ²	10.215	15.918	11.289	12.206	16.067	20.244	23.280
Freundlich	K _f ((mg/g)(L/mg) ⁿ)	3.215	3.181	4.146	3.806	4.876	4.999	5.442
	n	1.853	1.759	1.837	1.693	1.786	1.716	1.685
	R ²	0.980	0.980	0.968	0.989	0.979	0.981	0.979
	χ ²	5.149	4.851	15.499	38.635	40.808	75.475	212.39

As observed in Figure 9 and Table 2, nitrate removal increased with the increase of temperature. Thermodynamic parameters of nitrate adsorption on Amine-P-SiO₂ at different temperatures are showed in Table 3. The values of $\Delta G^\circ < 0$, $\Delta H^\circ < 0$, and $\Delta S^\circ < 0$ indicated that nitrate adsorption is an

spontaneous but endothermic process (Milmile et al., 2011) and the adsorption increases the disorder and randomness of the system. Moreover, the adsorption of nitrate using Amine-P-SiO₂ was more favorable at higher temperatures where ΔG° value decreased and became more negative (Katal et al., 2012).

Table 3. Thermodynamic parameters of nitrate adsorption on Amine-P-SiO₂ at different temperatures (nitrate concentration: 15 mg/L)

ΔH° (kJ/mol)	ΔS° (kJ/mol)	ΔG° (kJ/mol)				R ²
		293	303	308	318	
18.852	124.5188	-17.632	-18.877	-19.500	-20.745	0.8717

4. CONCLUSIONS

A new Amine-P-SiO₂ material was successfully synthesized using a simple and low-cost route. The surface modification of silica precursor by HF reaction and amine loading was demonstrated by material characterization using TGA, XRD, FT-IR, BET, SEM and EDS-mapping. Results showed that Amine-P-SiO₂ had high nitrate adsorption of 32.5 mg/g (1.71 times higher than Akualite A420) and followed Langmuir isotherm as chemical adsorption. Amine-P-SiO₂ could be a new and very potential material for water and advanced wastewater treatment applications.

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