Selective removal of silicic acid by a gallic-acid modified resin

Shuqin Bai, Jue Han, Cong Du and Wei Ding

ABSTRACT

To remove silicic acid from aqueous solutions, a novel gallic acid-type resin (GA-type resin) was prepared by a grafting method. The effects of the adsorption capacity, pH and presence of NaCl, NaNO$_3$, Na$_2$SO$_4$, and NaCO$_3$ salts on the silicic acid removal were studied. The GA-type resin adsorbs monosilicic acid, silicate ions, and polymeric silicic acid. The adsorption capacity of 4.64–4.94 mg/g was achieved in a short adsorption time (Q_m of 8.99 mg/g) and is 30–40 times larger than that of the OH-type resin. The silicic acid removal efficiency was almost unaffected by the pH and common anions when the common anion and silicic acid contents were similar, proving the GA-type resin exhibits an excellent performance for selective adsorption of silicic acid. The Temkin isotherm model can well describe the adsorption process, which is chemical adsorption, and indicates that the adsorption heat decreases with the increasing adsorption amount. The adsorption mechanism of silicic acid on the GA-type resin involves dehydration condensation reactions of the hydroxyl groups in silicic acid and gallic acid. The GA-type resin can be efficiently regenerated and reused after treatment with an HCl solution.

Key words | adsorbent regeneration, adsorption capacity, adsorption isotherms, resin modification, selective removal

Shuqin Bai (corresponding author)
Green Intelligence Environmental School,
Yangtze Normal University,
No. 16 Juxian Road, Fuling, Chongqing 408100,
China
E-mail: *baishuqin2000@163.com*

Shuqin Bai
Jue Han
Cong Du
School of Ecology and Environment,
Inner Mongolia University,
No. 235 West University Road, Saihan,
  Hohhot 010021,
China

Wei Ding
School of Environment and Energy,
Peking University Shenzhen Graduate School,
Shenzhen 518055,
China

INTRODUCTION

Mineral scale formation in pipelines, wells, heat exchangers, and membranes is one of the main problems that hinders the wide utilization of water resource regeneration and seawater and brackish water desalination (Semiat *et al.* 2001; Zarrouk *et al.* 2014; Menzri *et al.* 2017). In particular, silica scale formation in many industrial processes can significantly shorten the lifetime of the water treatment equipment, increase the maintenance costs and energy consumption of an operation due to water flow or membrane blockages, and cause equipment corrosion, unscheduled shutdown time and system efficiency loss (Nishida *et al.* 2011; Milne

et al. 2014). Once formed, the scales are very difficult to remove and can damage equipment over prolonged periods, resulting in a reduced water production capacity (Durham 1999). Therefore, silica scale mitigation is a challenge for all water utilization systems because of the complicated deposition mechanism, insolubility in common acids, and hard, dense structures of silica scales.

The development and application of silica scale control technologies in aqueous systems has been the subject of numerous investigations (Gallup *et al.* 2003; Stathoulopoulou & Demadis 2008; Sanciolo *et al.* 2014). However, the traditional scale control methods applied to crystalline mineral salt precipitates cannot be used for silica scale because of its amorphous nature. Currently, two distinct approaches are used to control silica scaling: (a) addition of scale

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inhibitors inside the equipment and (b) reduction of the silicic acid concentration outside the equipment. Scale inhibitor methods include inhibiting silica polymerization, increasing the solubility of silica as it forms, and dispersing precipitated silica and silicate compounds using polymeric dispersants. Cationic inulin polymers and polyethyleneimine and polyallylamine hydrochloride additives inhibit silicate polymerization by covering the surface of colloidal silicate (Gallup & Barcelon 2005; Ikeda & Ueda 2017). In contrast, the small molecule tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate) doubles the solubility of silica by forming water soluble complexes with silica (Bai *et al.* 2008). However, creating colloidal silicate dispersions and increasing the silicate solubility require the addition of organic compounds to the water body, which increases the chemical oxygen demand (COD or BOD) of water and possibly increases the post-processing costs.

The silicic acid concentration outside the equipment is reduced by removing silicic acid with a pretreatment process, such as precipitation or adsorption (Den & Wang 2008; Ragueh *et al.* 2015). The precipitation of silica with various inorganic compounds such as $Fe(OH)_3$, $Al(OH)_3$, and silica gel has been investigated, and $Al(OH)_3$ is the most effective precipitant for silica, removing nearly all of the molecularly dissolved silica (Bouguerra *et al.* 2007; Cob *et al.* 2014). However, a residual amount of aluminum remains in solution, and the aluminosilicate colloids are not removed (Cob *et al.* 2014). A strongly basic anion-exchange resin also has a good performance, removing up to 94% of silicic acid, but the pH of the resultant solution is 12 (Ali *et al.* 2004). In this pH range, the other metallic ions such as calcium, magnesium, and iron precipitate as hydroxides and can block waterways. Other common anions in water, such as CO_3^{2-}, NO_3^-, and SO_4^{2-}, competitively adsorb and reduce the effectiveness of silicate ion-exchange processes. In addition, anion-exchange resins remove only silicate ions and do not remove the molecular and polymer forms of silicic acid. In fact, silicic acid mainly exists in its molecular form in natural water due to the pH of natural water, i.e., 8.3. So far, no literature has reported the selective adsorption of silicic acid. Therefore, finding a selective adsorbent for the various forms of silicic acid with a high capacity, low cost, and regeneration ability is important.

The purpose of this study was to find a new adsorbent that selectively removes silicic acid from water to achieve high water resource regeneration without silica scaling. Our past study has found that the gallic acid (which has three adjacent hydroxyl functional groups and one carboxyl group) interacts with monosilicic acid to form a complex in the water solution. Based on this result, we modified a strong-base anion-exchange resin with gallic acid by grafting method, and the resin can be used under a broad range of pH conditions for silicic acid removal from aqueous systems. Additionally, the adsorbent can be regenerated. The silicic acid uptake capacity, adsorption isotherms, adsorption kinetics, adsorption mechanism, regeneration ability, and other characteristics of the resins were tested by corresponding experiments.

EXPERIMENTAL

Materials and methods

All of the chemicals used were of analytical reagent grade. The silicic acid stock solution was prepared by dissolving sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$) in a sodium hydroxide solution (0.1 mol/L), and its concentration was determined by inductively coupled plasma atomic emission spectrometry. The gallic acid stock solution was prepared by dissolving solid gallic acid in solution, and the solution was standardized by a Shimadzu UV-3600 UV-Vis spectrophotometer under 260 nm. The strong-base anion-exchange resin (Amberlite IRA402, anion-exchange capacity: 2.0 mequiv/dry g) was purchased from Shanghai Macklin Biochemical Co., Ltd. All solutions were prepared with ultra-pure water (Milli-Q SP system, Millipore, resistance >18 MΩ). All experiments were performed at room temperature (25 ± 1 °C). The total silicic acid concentration (Si(T)) in the filtrates was measured by inductively coupled plasma atomic emission spectrometry. In addition, the monosilicic acid concentration (Si(M)) in the filtrates was measured by a spectrophotometric method (Shimadzu UV-3600 UV-Vis) based on the formation of yellow molybdosilicic acid with wave length 400 nm. Here, Si(T) − Si(M) represents the concentration of polysilicic acid. In this paper, the concentration of the silicic acid solution is represented as Si mg/L.

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Preparation of the GA-type resin

The strong-base anion-exchange resin (10 g) was added into the gallic acid solution (500 mL, 10 g/L, pH 7) and was stirred for 24 h. The resins that bound gallic acid were filtered with a qualitative paper filter, rinsed with water, and air dried at ambient temperature for 3 days and stored in a dryer. The concentration of gallic acid in the filtrate was determined by UV-Vis spectrophotometer under 260 nm. Then the amount of gallic acid on the resin was calculated by the difference in the gallic acid concentration between initial solution and the filtrate and was estimated to be 725.3 mg/g (dry).

Silicic acid uptake by the GA-type resin

The GA-type resin and OH-type anion-exchange resin (each 0.36 g) were added into silicic acid solutions (250 mL, 10 mg/L) with various pH values and shaken with 140 rpm using a thermostat oscillator (HZQ-X300C) for 67 h. The suspensions were filtrated through a 0.45 μm membrane filter at varied time intervals. The amounts of silicic acid adsorbed on the two types of resins were calculated by the difference in the silicic acid concentrations in the initial solution and filtrate. In addition, the morphologies of silicic acid adsorbed on the resin were obtained using HITACHI SU8200 Scanning Electron Microscopy after being sputtered with gold (Au). Images and data were then collected at accelerating voltage of 15 kV as presented.

Effect of coexisting anions on the uptake of silicic acid by the GA-type resin

The GA-type resin (0.36 g) was added into silicic acid solutions (250 mL, 0.356 mmol/L, equal to 10 mg/L) with various concentration ratios of salts, including Na_2CO_3, Na_2SO_4, NaCl, and Na_2NO_3. The concentration ratios of silicic acid to the anions were 1:1, 1:10, and 1:100 (as Si: anion, mmol/L).

Adsorption isotherms and kinetics

Batch experiments were carried out by shaking 0.36 g of the GA-type resin in 250 mL solutions with different initial silicic acid concentrations (10–50 mg/L). The pH values of the solutions were adjusted and maintained at 8 ± 0.2. The

silicic acid adsorption data were fitted to four two-parameter equations using nonlinear regression. Four isotherms, as described below in Equations (1)–(4), were used for fitting the results obtained from the adsorption experimental data (Langmuir, Freundlich, Temkin and Dubinin–Astakhov):

$$q = \frac{K_L Q_m C_e}{1 + K_L C_e} \tag{1}$$

$$q = K_F C_e^{\frac{1}{n_F}} \tag{2}$$

$$q = A_T + B_T \ln C_e \tag{3}$$

$$q = Q_D \exp\left\{ -A_D \left[\ln\left(1 + \frac{1}{C_e}\right) \right]^n \right\} \tag{4}$$

where q is the amount adsorbed at equilibrium (mg/g), and C_e is the equilibrium concentration of silicic acid in solution (mg/L). The other parameters are the different isotherm constants, which can be determined by a regression analysis of the experimental data. The curve fitting and statistical analyses were performed with Origin 8.5.

For the kinetic study, a nonlinear pseudo-second-order reaction model and an intra-particle diffusion model were used to fit the experimental data. The models are represented as follows in Equations (5) and (6), and the conformity between the experimental data and the model predicted values is expressed by the correlation coefficients (r^2).

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{5}$$

$$Q_t = k_n t^{\frac{1}{2}} + C \tag{6}$$

where k_2 is the rate constants for the pseudo-second-order adsorption, k_n is the intra-particle diffusion rate constant, and Q_t and Q_e are the amounts of silicic acid adsorbed at time t and at equilibrium, respectively.

Regeneration and reuse of the GA-type resin

To evaluate the possibility of regenerating and reusing the GA-type resin, sorption-regeneration cycles were performed with different eluents. Two GA-type resins, which had certain amounts of adsorbed silicic acid (silicic acid

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adsorption amount was 4.310 mg/g as Si), were eluted with HCl and NaOH solutions (0.005 mol/L) and stirred for 24 h. The resins were filtered after washing with water and grafted again with a gallic acid solution (50 mL, 5 g /L) at pH 7 to prepare the regenerated resins. The regenerated resins were used as adsorbents to adsorb 10 mg/L silicic acid from solution.

RESULTS AND DISCUSSION

Silicic acid uptake by the GA-type resin

Silicic acid is commonly found in natural water due to weathering of silicate minerals in the earth. Multiple forms of silicic acid (monomeric, polymeric, colloidal, particulate, and silicate ions) exist in natural water depending on the concentration and pH (Milne *et al.* 2014). Generally, the concentration of silicic acid in groundwater and geothermal water ranges from 10 to 60 mg/L and 200 to 500 mg/L (as Si), respectively (Bai *et al.* 2012). Silicic acid is mainly present as a monosilicic acid (H_4SiO_4) in groundwater at concentrations less than 60 mg/L. To confirm the adsorption capacity of the GA-type resin for monosilicic acid, 0.36 g of the GA-type resin and the OH-type resin was contacted with silicic acid solutions (Si 10 mg/L) at different pH values. Figure 1 shows the change in the removal rate over time at the different pH values for the two resins. For the GA-type resin, the silicic acid removal rate rapidly increased with the adsorption time and reached 80% for all the pH conditions after 67 h. In contrast, for the OH-type resin, the silicic acid removal rate slowly increased and reached only 3%–5% for all the pH values after the same contact time, which suggested that rapid adsorption of silicic acid occurred on the GA-type resin. The removal rate by the GA-type resin was almost the same at the different pH
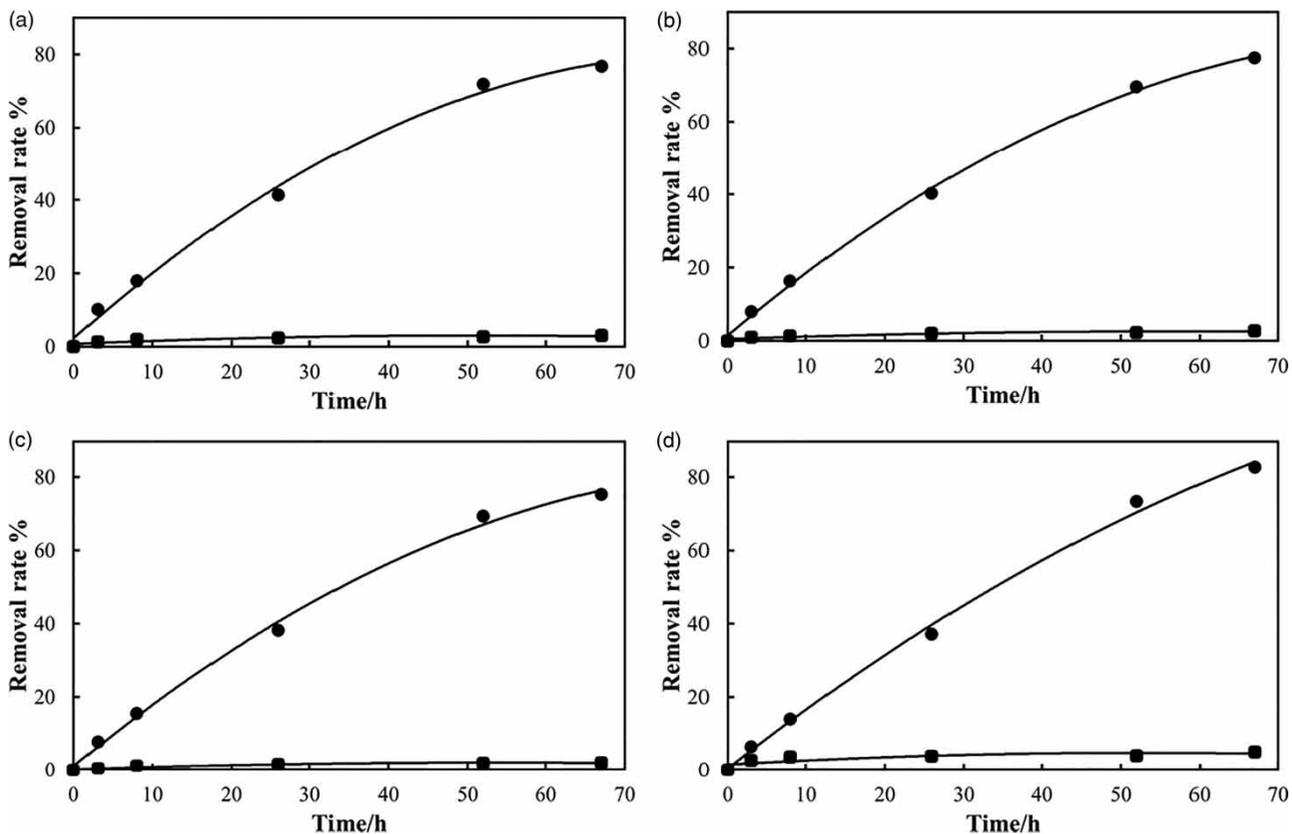
Figure 1 │ Change in the silicic acid removal rate over time with two kinds of resin at different pH values (silicic acid concentration of 10 mg/L, pH of: (a) 4, (b) 6, (c) 8, (d) 10, resin amount of 0.36 g).

values, which indicated that the adsorption behavior of silicic acid was independent of the pH. For all the pH values, the amount of silicic acid adsorbed by the GA-type resin was 4.64–4.94 mg/g, which was 30 times greater than the amount adsorbed by the OH-type resin (0.14–0.35 mg/g) and indicated that the GA-type resin has potential application value for silicic acid removal from water over a wide pH range. The adsorption amounts for the two kinds of resins at pH 10 were slightly larger than those at the other pH values, which showed that the GA-type resin adsorbs the molecular and ionic forms of silicic acid. At neutral and acidic pH values, the predominant silicic acid species is nonionic, and at higher pH values, the speciation begins to shift. At pH values of approximately 10, silicic acid deprotonates to form the silicate anion (pKa_1 of silicic acid is 9.83) (Iler 1979). Both the adsorption amount and removal rate of the GA-type resin were higher than those of the OH-type resin, which demonstrated that the newly synthesized GA-type resin can be widely used to remove silicic acid and prevent silica scale formation.

Polymeric silicic acid is present in addition to monomeric silicic acid in supersaturated solutions due to the solubility of amorphous silica (Iler 1979). In a geothermal power plant or cooling water system, the silicic acid concentration is supersaturated due to water evaporation, and polymeric and colloidal silicic acid form under this condition. Therefore, the adsorption capacity of the GA-type resin for polysilicic acid was investigated. To evaluate the adsorption behaviors of different sizes of polysilicic acid, two kinds of experiments were carried out using a 400 mg/L silicic acid solution (pH 8). In one experiment, the resin was directly added into the silicic acid solution, and in the other, the resin was added to the silicic acid solution after 5 h of the polymerization reaction (in these two conditions, the degree of polymerization was different). Figure 2 shows the change in the adsorption amount over time. The adsorption amount increased as the reaction time increased and reached 9.17 mg/g and 6.60 mg/g by direct or indirect addition, respectively, within 25 h. The direct adsorption amount was higher than the indirect adsorption amount at each time, which suggested that the GA-type resin more easily adsorbs smaller sizes of polysilicic acid. The adsorption amount of polysilicic acid was larger than that of monosilicic acid, as shown in Figure 1, even with a shorter reaction time, which indicated that each
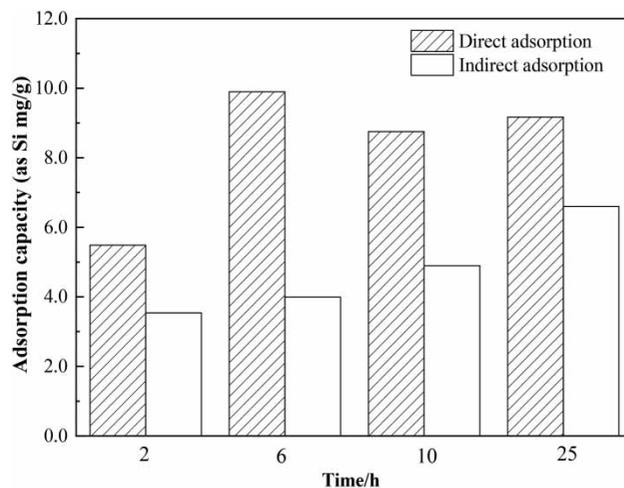

Figure 2 | The change in the adsorption amounts of polysilicic acid over time with the GA-type resin at pH 8 (silicic acid concentration of 400 mg/L, resin amount of 0.72 g).

polymer of silicic acid occupied one adsorption site on the resin surface.

In conclusion, the GA-type resin adsorbs monosilicic acid, silicate ions and the polymer form of silicic acid. The adsorption capacity was 30–40 times larger than that of the OH-type resin, which is commonly used as adsorbent to remove silicate ions from water. In addition, the adsorption capacity of the GA-type resin for silicic acid was independent of the pH and shows broad application prospects over a wide pH range for water treatment processes.

Effect of coexisting anions on silicic acid adsorption

Natural waters and industrial wastewaters contain sulfate, carbonate, and chloride anions, which may compete with silicic acid for adsorption sites and reduce the efficiency of a resin. To evaluate the competitive effect of coexisting anions on silicic acid removal with the GA-type resin, batch adsorption experiments with silicic acid (0.356 mM) were carried out after the addition of other anions, such as Cl^-, NO_3^-, SO_4^{2-}, and CO_3^{2-}, over a concentration range of 0.356–35.6 mM (from 1:1 to 1:100 molar ratios). As shown in Figure 3, the silicic acid adsorption amount in the presence of a single anion with a molar ratio of 1:1 was exactly the same as that in the absence of any anion, which showed that the same amount of a common anion does not affect the silicic acid removal by the GA-type resin. Importantly,
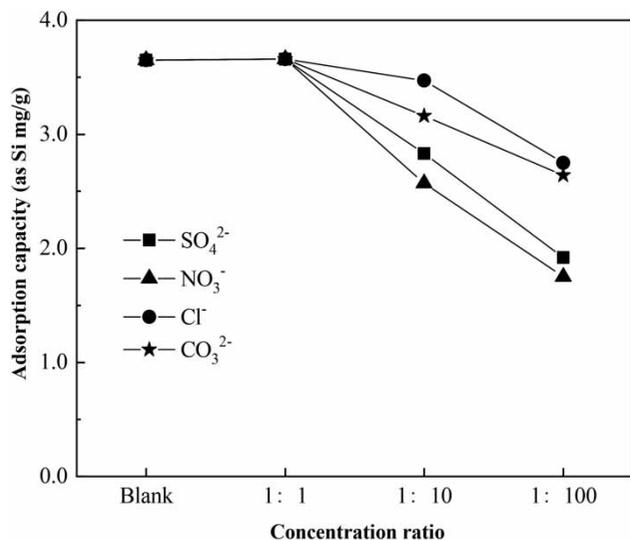
Figure 3 │ The effect of single anions on silicic acid adsorption with various molar ratios at pH of 8 after 72 h.

this result also proved that the GA-type resin has selective adsorption properties for silicic acid. However, the adsorption amount gradually decreased as the salt concentration increased, and this decrease may be caused by the formation of an ion atmosphere, which decreases the activity of silicic acid. The initial adsorption amount of 3.65 mg/g (1:0) decreased to 2.75, 2.64, 1.92, and 1.75 mg/g (1:100) for the coexisting anions CO_3^{2-}, Cl^-, SO_4^{2-}, and NO_3^-, respectively. We speculated that the different effect of different anions on the silicic acid adsorption may be caused by different charge and different form of anions.

In addition, we also investigated the effect of multiple anions on the adsorption amount using CO_3^{2-}, Cl^-, SO_4^{2-}, and NO_3^- ions, and the anion to silicic acid (10 mg/L) molar ratio was 1:1. The adsorption amount decreased from 3.65 mg/g to 3.06 mg/g, which indicated the effect of multiple anions was larger than that of a single anion (not show here). Although the concentration ratio was the same as that used to examine the effect of a single anion (1:1), many kinds of ion species and different ion charges result in a different ionic strength and effect.

Adsorption isotherms and kinetics

The adsorption process can be understood through isotherms examining the adsorbate concentration in solution and the adsorbate amount adsorbed on a unit mass of the adsorbent at a constant temperature. Compared with the double-parameters of linear adsorption isotherm models, nonlinear models can more accurately describe adsorption processes. Therefore, to estimate the adsorption characteristics and mechanism of silicic acid on the GA-type resin, the experimental silicic acid adsorption data were fitted to Equations (1)–(4) using nonlinear regression.

The adsorption isotherms of silicic acid on the GA-type resin are shown in Figure 4. As seen in Figure 4, all four isotherm models well fit the experimental data. Among the models, the Temkin isotherm had the highest r^2 value ($r^2 = 0.980$) of determination and well represented the adsorption process in the designated concentration range. This result indicated that the adsorption heat decreased as the adsorption amount increased, which is indicative of chemical adsorption; i.e., the adsorbate/adsorbate can interact with each other on the surface of the resin. This phenomenon is related to the chemical properties of silicic acid. The hydroxyl groups on silicic acid easily form silicon oxygen bonds (Si-O-Si) by a dehydration condensation reaction. According to the Langmuir isotherm analysis, the maximum adsorption capacity of the GA-type resin is 8.99 mg/g (19.12 mg/g as SiO_2), which is higher than the silicic acid uptake by the TMAMo resin (13.82 mg/g as SiO_2), as shown in Table S1, Supplementary material (Alexandratos *et al.* 2010). The data in Table S1 summarize
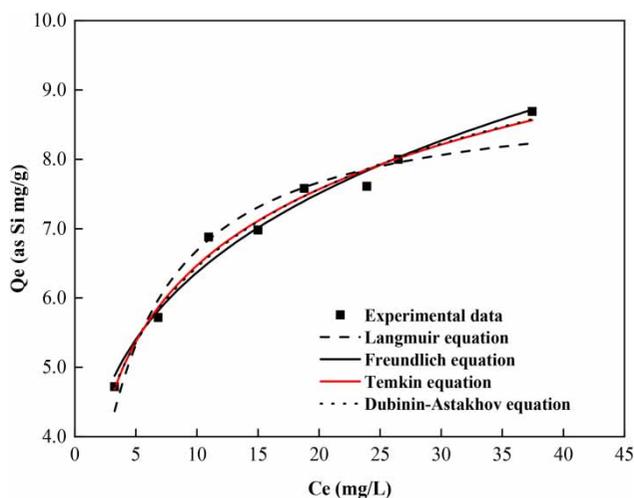
Figure 4 │ Fitting plot of the four isotherms for silicic acid adsorption onto the GA-type resin.

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the previous studies on the uptake of silicic acid by several adsorbents. Based on Table S1, the adsorption capacities of inorganic adsorbents are much greater than those of organic adsorbents such as resins, but inorganic adsorbents are difficult to regenerate and produce large amounts of sludge (Badruk & Matsunaga 2001; Ali *et al.* 2004; Li *et al.* 2008; Latour *et al.* 2015). Among the several kinds of adsorption resins, the adsorption capacities range from 0.077 to 13.8 mg/g, and the modified TMAMo resin has the largest capacity. The adsorption capacity obtained in this study was higher than that of the other resins and 35 times larger than that of a typical ion-exchange resin present in Table S1, which was consistent with the results in this study.

Considering the complexity of the adsorption process, various simplified kinetic models have been reported in the literature, and each model has its own limitations due to simplified assumptions (Peydayesh & Rahbar-Kelishami 2015; Sadegh *et al.* 2015). In this study, to investigate the adsorption mechanism and potential rate controlling steps, a certain amount of the GA-type resin was contacted with three silicic acid solutions with different concentrations (10, 20, and 30 mg/L), and a pseudo-second-order reaction model and an intra-particle diffusion model (Equations (5) and (6)) were used to fit the experimental data.

The change in the adsorption capacity for different concentrations of silicic acid and the fitting of the kinetics models are shown in Figure 5. As seen in Figure 5(a), the pseudo-second-order model k values showed a decreasing trend as the initial concentration increased. The high r^2 values of the pseudo-second-order model indicate that the adsorption process is better fit by the pseudo-second-order rate mechanism. The suitability of the pseudo-second-order model suggests that chemical adsorption is the silicic acid adsorption mechanism on the GA-type resin.

The linearity of the curves in Figure 5(b) shows the validity of the intra-particle diffusion model for silicic acid adsorption onto GA-type resin. A plot of Q_t versus $t^{1/2}$ can be divided into two parts with different slopes: the first relates to the internal micro-porous process of adsorbate diffusion into the adsorbent, and the second with a lower slope represents chemical adsorption. The result shows that the r^2 values of the two parts were 0.988–0.998 and 0.913–0.992, respectively, which is indicative of the rate-limiting stage of silicic acid adsorption onto GA-type resin being controlled by the diffusion of ions within the adsorption, and chemical adsorption reaction occurred.

Adsorption mechanisms

According to the isotherm analysis, the adsorption of silicic acid on the GA-type resin occurs via chemisorption. As shown in Equation (7), the gallic acid molecule becomes negatively charged upon deprotonation of the carboxyl
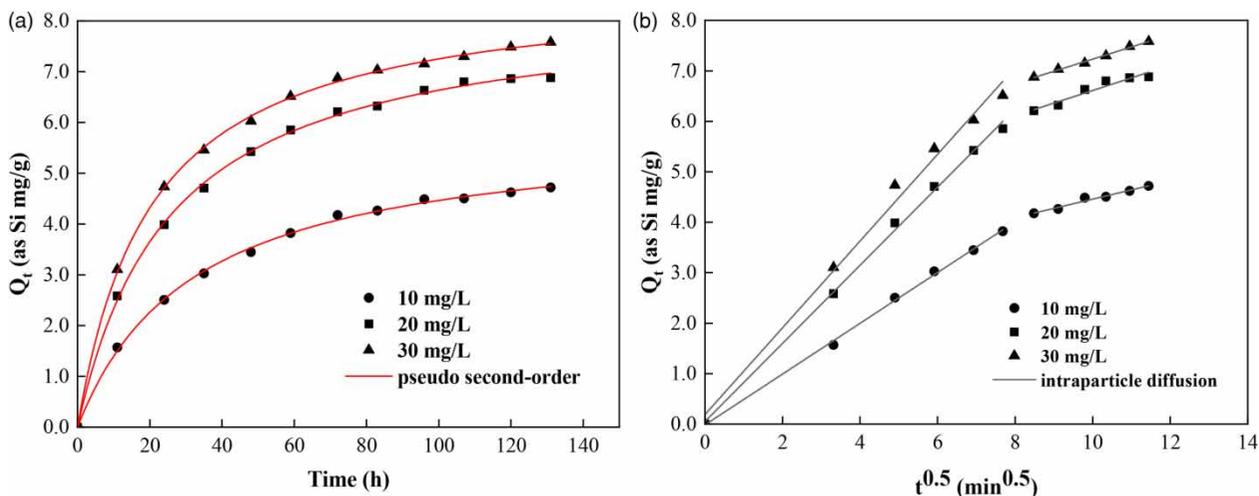
Figure 5 | Fitting plot of the two kinetic models for silicic acid adsorption onto the GA-type resin: (a) pseudo-second-order reaction model and (b) intra-particle diffusion model.

group when the pH is above 4.44 and can be grafted onto anion-exchange resins through ion exchange. The surface of the grafted resin has outward facing hydroxyl groups that can interact with silicic acid molecules to form gallate–silicate complexes and attach silicic acid to the resin (see Equation (8)).
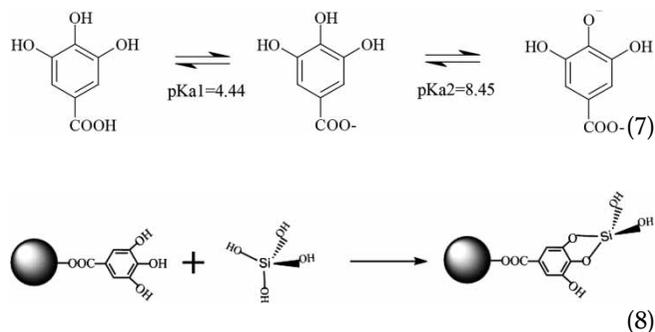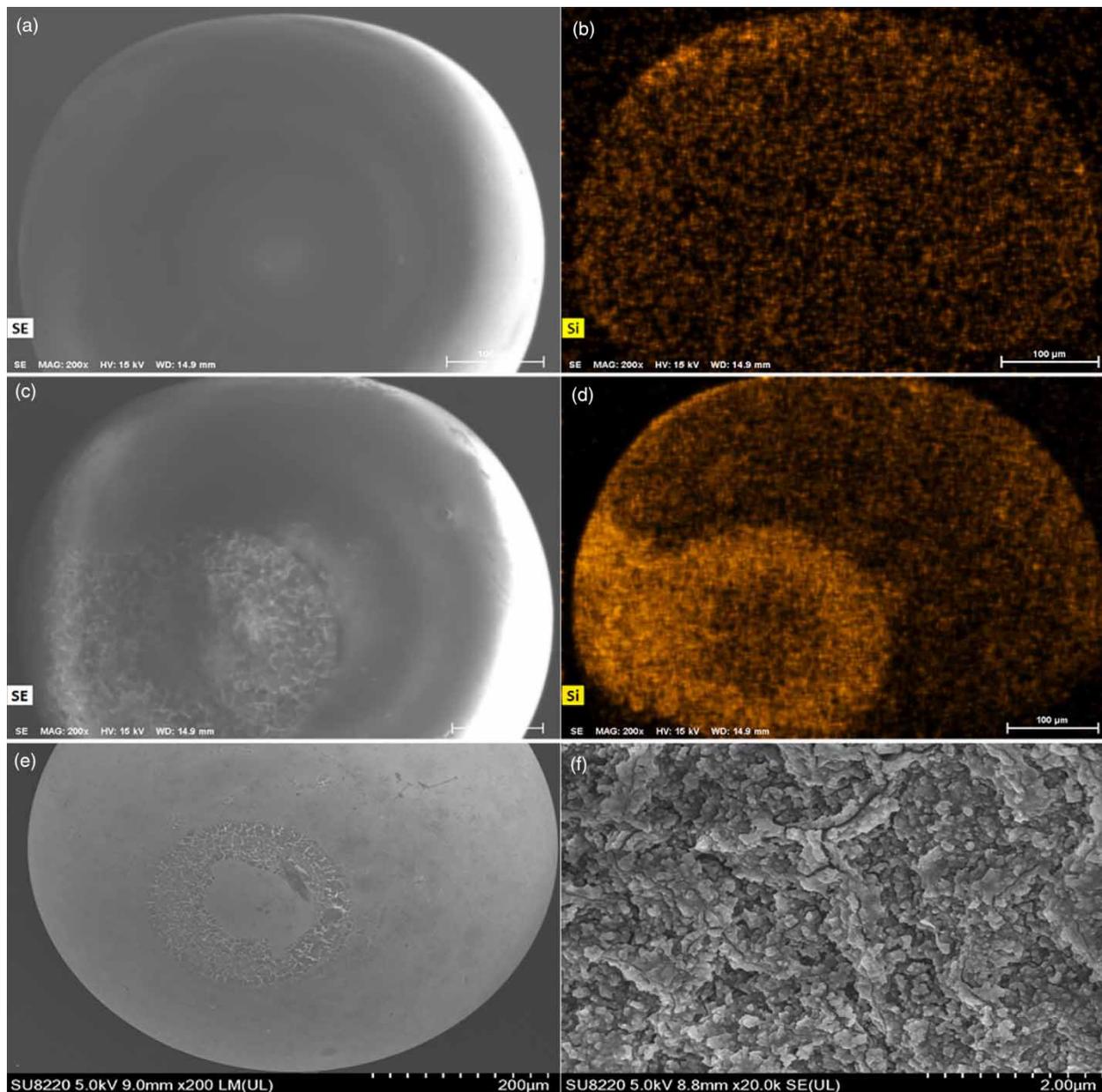

$$\text{(7)}$$

$$\text{(8)}$$

Figure 6 shows the SEM images of the GA-type resin particles after adsorption of monosilicic acid (a) and polysilicic acid ((b) and (c)). The surfaces of the particles appear to be clean and smooth after the adsorption of monosilicic acid (a), while the surfaces of the particles appear to have a film-like material on them after the adsorption of polysilicic acid ((b) and (c)). The characteristic X-ray image of silicon (d) for the resin in photograph (a) shows the silicon was uniformly distributed, which suggested that monosilicic acid uniformly adsorbs on the surface of the resin. This fact is consistent with the hydroxyl groups on silicic acid or silicate ions interacting with the uniformly distributed hydroxyl groups on the surface of the resin to form silicon oxygen bonds (resin-O-Si-OH) to uniformly attach to the resin surface. However, the characteristic X-ray image of Si (e) for the resin in photograph (b) was non-uniform, which suggested that the silicic acid species (monomeric and polymeric) non-uniformly adsorbed on the resin. Small spherical silica particles congregated together to form a silica film on the surface of the resin (see (f)), which indicated that polysilicic acid or colloidal silica adsorbed on the resin. According to the isotherm model (Temkin model), silicic acid molecules or colloidal silica adsorbed on the resin and further combined by a dehydration condensation reaction to form a film-like silica cover on the resin (Figure S1, Supplementary material).

Regeneration and reuse of the GA-type resin

Generally, the regeneration process consists of two main steps, desorption of the adsorbate from the resin using an acid or alkali regenerant and washing the resin with water. To compare the eluting effect of different eluents, HCl and NaOH solutions with the same concentration were used. Three sorption–regeneration cycles were performed to study the efficiency of the resin regeneration procedure. Each silicic acid adsorption cycle lasted for 48 h. As shown in Figure 7, in contrast with the fresh resin, the silicic acid adsorption capacity gradually decreased after multiple regeneration cycles in both cases. The decreasing adsorption capacity might be due to passivation of the grafting sites by the regeneration eluents. For regeneration with HCl, the adsorption amounts for each regeneration cycle were slightly larger (2.12 mg/g after three cycles) than those for regeneration with a NaOH solution (1.45 mg/g after three cycles), which suggested that an acidic eluent is more suitable for the GA-type resin regeneration. The silicic acid that is eluted from the resin can be in two forms, i.e., the molecular form of silicic acid (silicic acid only) and a gallate–silicate complex ($C_7O_5H_3$-$Si(OH)_2$). In the case of HCl, silicic acid can be eluted as a complex, which frees the original ion-exchange site on the resin and is beneficial for further grafting. With NaOH, silicic acid can be eluted in its molecular form because silica is soluble in alkali. Therefore, some gallic acid remains on the surface of the resin, preventing repeated grafting. In addition, gallic acid can be easily oxidized to quinone under alkaline conditions (pKa_2 of gallic acid: 8.45), decreasing the probability of a gallate–silicate complex forming and subsequently decreasing the adsorption amount of silicic acid. However, the adsorption capacity after multiple regeneration cycles was still above 1.45 mg/g (with NaOH), which was much higher than that of the original OH-type resin (0.13–0.25 mg/g) and indicated the resin can be efficiently reused. Acidic eluent was more suitable for eluting the GA-type resin for regeneration. The regeneration cycle results were slightly lower than the ideal adsorption capacity and can be improved in future research.
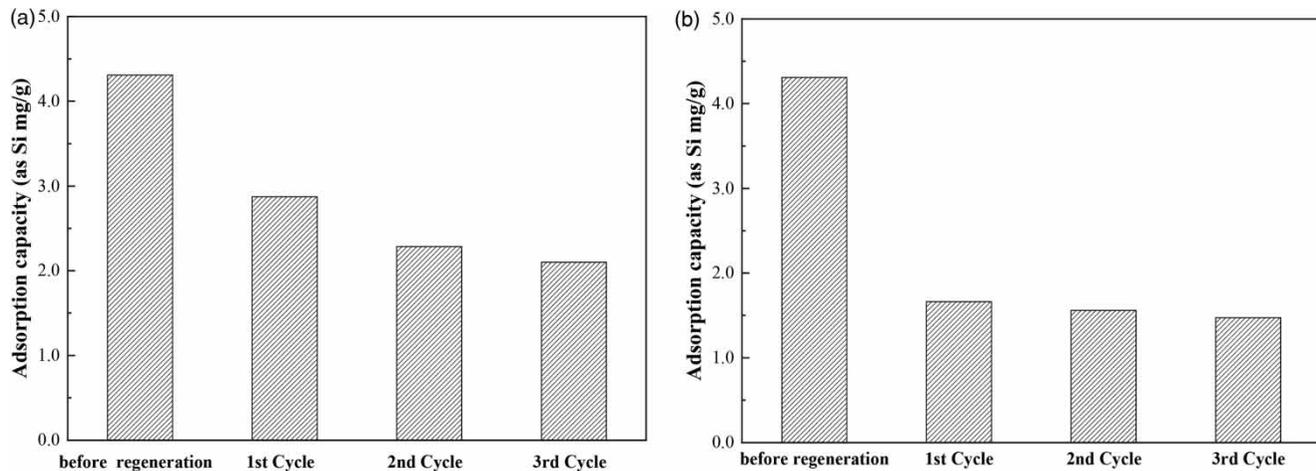
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Figure 6 │ SEM images of the GA-type resin particles after the adsorption of monosilicic acid (a), and polysilicic acid (b) and (c). Characteristic X-ray images of Si for the particles in photographs (a) and (b), also shown in (d) and (e), respectively; (f) expanded image of (c).

CONCLUSIONS

A new, selective silicic acid removal resin was prepared by a grafting method, and the resin showed good adsorption properties for silicic acid from aqueous solutions with a wide pH range. The adsorption kinetics were faster than those of commonly available ion-exchange resins. The removal of silicic acid from solutions was studied over a concentration range of 10–400 mg/L (as Si), and the results showed that the GA-type resin adsorbs monosilicic acid, silicate ions, and polymeric silicic acid. The adsorption capacity was 4.64–4.94 mg/g with a short adsorption time, which is 30–40 times larger than that of the OH-type resin. The effects of coexisting anions on the silicic acid removal were dependent on the anion content. The removal efficiency was not affected when the coexisting anion and

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Figure 7 | Silicic acid removal with the GA-type resin after multiple regeneration cycles with HCl (a) and NaOH (b) solutions.

silicic acid contents were similar, which proved the GA-type resin selectively adsorbed silicic acid. The adsorption process was best fit by the Temkin isotherm model, and the maximum theoretical adsorption capacity was 8.99 mg/g (19.12 mg/g as SiO_2), which is larger than that of other currently reported resins. The adsorption mechanism of silicic acid by the GA-type resin occurs via a complexation reaction between silicic acid and gallic acid. An acidic eluent was more suitable for eluting the GA-type resin for regeneration, and after multiple regeneration cycles, the resin still showed a good performance for silicic acid removal.

ACKNOWLEDGEMENTS

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