



Research Article

Iron removal from synthetic aqueous solution using amino functionalized commercial silica gel as adsorbent

Prawit Nuengmatcha^{1*}, Naengnoi Saengsane¹, Nongyao Teppaya¹, Nichapa Rattanakomon¹ and Piyawan Nuengmatcha²

¹Program of Chemistry, ²Program of Environmental Science, Faculty of Science and Technology, Nakhon Si Thammarat Rajabhat University, Nakhon Si Thammarat 80280, Thailand.

*E-mail: prawit_nue@nstru.ac.th

Abstract

The amino group (-NH₂) is one of the most important functional groups of ligands. Particularly, 3-aminopropyl-trimethoxysilane (APTMS) has relatively high affinity to bind various to metal ions. The present study was aimed to modify commercial silica gel (CSG) with the APTMS via silanization process to acquire amino groups (CSG-NH₂) as an adsorbent for the removal of iron from synthetic aqueous solution. For an optimal adsorption study, the effects of the initial concentration of Fe(II) (1-80 mg/L), pH of solution (pH 1-10), contact time (1-36 hours) and temperature (30-60°C) were investigated. The results showed that the adsorption capacity of the obtained CSG-NH₂ for the Fe(II) was 60.80 mg/g at pH 4, and complete adsorption equilibrium was reached within 24 hrs. The adsorption isotherm of the CSG-NH₂ for Fe(II) was well fitted by the Langmuir isotherm model. In addition, thermodynamic data demonstrated that the Fe(II) adsorption onto the CSG-NH₂ surface was mainly an exothermic spontaneous reaction. This implies that CSG-NH₂ can be used as a high potential adsorbent for the removal of ferrous ion from contaminated wastewater.

Keywords: Amino functionalized commercial silica gel, Iron removal, Adsorbent

Introduction

As one of the most abundant elements in the Earth's crust, iron always coexists with nonferrous metals in their ore bodies (Zhang et al., 2016). It is often present in groundwaters worldwide and may exist in a soluble form as ferrous iron (Fe²⁺ or Fe(OH)⁺) or complexed forms as ferric iron (Fe³⁺) forming colloidal minerals and/or associated with organic matter (Hamdouni et al., 2016). Although iron is an essential nutrient for humans and has beneficial effects on health, its presence in water may cause contaminations, particularly at high concentrations. It can influence the taste and esthetic quality of the water. Indeed, the oxygen from air induces its rapid oxidation to form ferric hydroxide or oxyhydroxide precipitates for pH>6, that can generate toxic derivatives and develop infections such as neoplasia, cardiomyopathy, and arthropathy (Hamdouni et al., 2016).

There are several efficient iron removal techniques, e.g., electrocoagulation (Ghosh et al., 2008), oxidation-coagulation (Bordoloi et al., 2013), solvent extraction (Quijada-Maldonado et al., 2016), microfiltration (Ellis et al., 2000), aerated granular filter (Bong-Yeon., 2005), ion

exchange (Vaaramaa et al., 2003) and adsorption (Seliem et al., 2016). Of the above techniques, adsorption provides an attractive alternative treatment to other removal techniques because it is more economical and readily available. This technique relies on interactions between an adsorbent and an adsorbate. Thus, a key factor in the adsorption process is a selective adsorbent with its intrinsic functional groups (Nuengmatcha et al., 2014). Although several adsorbents have been studied for iron removal from wastewater, some of these adsorbents still either have low efficiency or low adsorption capacity. Thus, new adsorbents are being developed to maximize their adsorption property with higher capacity and selectivity.

Silica gel (SG) can serve as an alternative choice of adsorbent owing to its abundant functional groups (hydroxyl), which provide anchor sites for metal ion complexation. Moreover, SG can be modified with several ligands, including ditopic zwitterionic Schiff base ligand (Wang et al., 2014), propyl-polyethylenimine (Snoussi et al., 2016), dendrimer-like polyamidoamine and 5-sulfosalicylic acid (Wu et al., 2016), making it a potential material as a super adsorbent for toxic metal ions removal. The amino group (-NH₂), in particular, has a high ability to adsorb both toxic metal ions and other pollutants. With this unique characteristic, the amino group has a great potential in the removal of pollutants from wastewater (Fellenz et al., 2017). To test the combined effects of SG and amino groups in metal removal from wastewater, we modified the commercial silica gel (CSG) with 3-aminopropyl-trimethoxysilane (APTMS, -NH₂) resulting in a functionalized CSG-NH₂. The adsorbent was then applied to remove Fe(II) from synthetic aqueous solution (see Fig. 1(a)). The effects of the initial concentration of Fe(II), pH of solution, contact time and temperature were studied. Both Langmuir and Freundlich isotherms were also investigated to fit their adsorption models for Fe(II) removal.

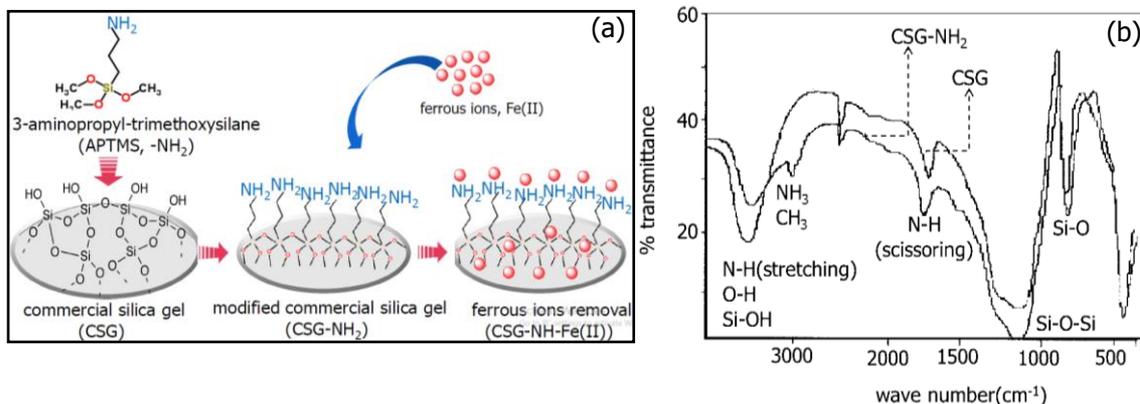


Figure 1. (a) Schematic diagram of CSG-NH₂ adsorbent preparation and their application
(b) FTIR spectra of CSG and CSG-NH₂ adsorbents

Materials and methods

3-mercaptopropyl-trimethoxysilane (APTMS) and commercial silica gel (CSG) were purchased from Sigma-Aldrich. All adsorbents were characterized by FTIR spectroscopy (Bruker, Germany). To functionalize CSG with APTMS, 200 mg of CSG was added to a round flask with 25 mL ethanol and dispersed through ultra-sonication for 30 min. Then, 4.5%w/v of APTMS was added and ultra-sonicated for 30 min. After that, the mixture was stirred at 65°C for 12 hrs. The CSG-NH₂ product was centrifuged and washed with ethanol and oven-dried at 50°C for 12 hrs. The obtained CSG-NH₂ was characterized by FTIR analysis.

For the adsorption experiment, the adsorbent (0.20 g) was accurately weighed into a 125 mL conical flask. Then, 25 mL of Fe(II) solution (various concentrations) was added and the pH of the solution was adjusted, with the solution kept at ambient temperature. For optimum conditions, various experimental parameters including the effect of initial concentration of Fe(II) (1-80 mg/L), pH of solution (pH 1-10), contact time (1-36 hrs) and temperature (30-60°C) were investigated. After a period of equilibrium adsorption, the adsorbent was separated from the solution mixture by centrifugation for 5 min and Fe(II) in the supernatant solution was determined by AAS. All experiments were conducted in triplicate under the same conditions. The adsorption capacity (q_e , mg/g) of Fe(II) at an equilibrium state was determined as follows:

$$q_e = V(C_0 - C_e) / m \quad (1)$$

where C_0 is the initial concentration (mg/L) of Fe(II) in the solution, C_e is the Fe(II) concentration (mg/L) at the equilibrium state, V is the volume (L) of the solution, and m is the mass (g) of the adsorbent. Langmuir and Freundlich adsorption models were used to describe the equilibrium nature of iron adsorption onto the CSG-NH₂ adsorbent.

Results and discussion

Characterization of adsorbents

To confirm the formation of CSG-NH₂, the prepared adsorbents were characterized using FTIR. As can be seen in Fig. 1(b), the Si-O-Si groups appeared in the range of 1250-1000 cm⁻¹. The bands at 3372 cm⁻¹, 3290 cm⁻¹ and 1600 cm⁻¹ could be assigned to N-H (stretching asymmetry), N-H (stretching symmetry) and N-H (scissoring), which confirmed the formation of the CSG-NH₂ products. From the FTIR analysis, CSG was confirmed to contain -NH₂ groups, which were to be applied as an adsorbent for wastewater treatment.

The optimum conditions for Fe(II) removal

The effect of pH on the extent of adsorption can be seen in Fig. 2(a). The result indicated that the adsorption capacity of Fe(II) dramatically increased with the pH in the range of 1.0-4.0, was constant in the range of 4.0-6.0 and decreased in the range of 6.0-10.0. The maximum adsorption capacity took place at pH 4.0 (12.0 mg/g). At pH lower than 4.0, the adsorption capacity of CSG-NH₂ was lower due to the solution being overly acidic leading to the CSG-NH₂ surface becoming positively charged and unfavorable towards the uptake of Fe(II) because of their pH_{pzc} (the pH values at the point of zero charge). On the other hand, at pH higher than pH_{pzc} (>4.0), the surface of the adsorbents became negatively charged and favorable towards the uptake of Fe(II). Therefore, the maximum adsorption capacity of CSG-NH₂ occurred at pH higher than 4.0. However, at pH higher than 6.0, the adsorption capacity reduced probably due to the formation of the iron hydroxide form. In Figure 2(b), which shows the effect of contact time of Fe(II) adsorption onto the CSG-NH₂ adsorbents with 20 mg/L of Fe(II) concentration at pH 4.0, it can be clearly seen that the rate of adsorption increased at an initial period of the contact time and the equilibrium time was established within 24 hrs. Therefore, the further experiments were carried out with a period of 24 hrs as a suitable contact time for Fe(II) adsorption on CSG-NH₂. Figure 2(c) shows a plot of equilibrium adsorption capacity versus the initial concentration of Fe(II) on CSG-NH₂. It is clear that the equilibrium adsorption capacity increased with increasing an initial concentration. The maximum

value of the equilibrium adsorption capacity at 50 mg/L Fe(II) concentration for CSG-NH₂ was found to be 12.74 mg/g. An increase in the uptake capacity of CSG-NH₂ adsorbents with increasing initial Fe(II) concentration may be due to both the higher collision probability between Fe(II) ions and the adsorbent particles and the fact that all initial active sites on the surface of CSG-NH₂ were vacant.

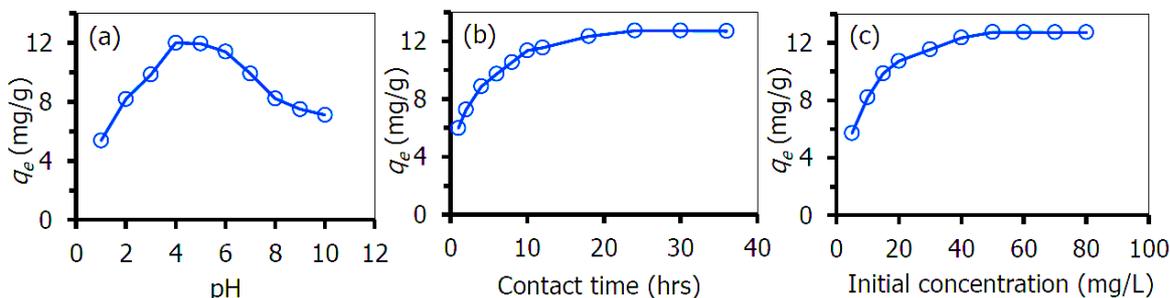


Figure 2. Effect of (a) pH, (b) contact time and (c) initial concentration of Fe(II)

Thermodynamic study

For the thermodynamic study, three basic thermodynamic parameters, the Gibbs free energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_d \quad (2)$$

$$K_d = q_e / C_e \quad (3)$$

$$\ln K_d = -(\Delta H^\circ / RT) + (\Delta S^\circ / R) \quad (4)$$

where R is a constant (8.314 J/mol K), T is the absolute temperature in K and K_d is the equilibrium constant. q_e is the amount of Fe(II) at equilibrium (mg/g) and C_e is the equilibrium concentration (mg/L) of Fe(II) in solution.

The values of ΔS° and ΔH° can be calculated from the slope and the intercept of the van't Hoff plot of $\ln K_d$ versus $1/T$. The thermodynamic parameters are summarized in Table 1.

Table 1. Thermodynamic parameters of Mn(II) adsorption using CSG-NH₂ as adsorbent

ΔH° (kJ/mol)	ΔS° (kJ/mol.K)	ΔG° (kJ/mol)				R ²
		303 K	313 K	323 K	333 K	
-8.17	-10.49	-23.54	-24.80	-25.74	-26.72	0.924

As shown in Table 1, the negative value of ΔG° indicates the spontaneity of the ongoing adsorption process. The negative ΔH° indicates that the Fe(II) adsorption using CSG-NH₂ is exothermic in nature and the negative value of ΔS° indicates a tendency to lower disorder at the solid-solution interface during the adsorption. At higher temperatures, the thickness of the boundary layer decreases due to an increase in the tendency of the Fe(II) ions to escape from the adsorbent surface to its bulk solution, resulting in a decrease in the adsorption capacity.

Adsorption isotherm

For the study of an adsorption isotherm, Langmuir and Freundlich models were used. The Langmuir model assumes that a monolayer of an adsorbate is covered on a homogenous adsorbent surface containing a finite number of the adsorption sites via uniform strategies of adsorption with no transmigration of the adsorbate taking place along the plane of the surface. In addition, the Freundlich adsorption isotherm is also an equation that assumes a heterogeneous surface energy for which the energy term in the Langmuir equation varies as a function of a surface coverage. The linear form of the Langmuir and Freundlich isotherm is given by the following Eq. (5) and Eq. (6):

$$C_e/q_e = C_e/q_m + 1/q_m K_L \quad (5)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad (6)$$

where q_m is the maximum amount of Fe(II) adsorbed per unit weight of adsorbent (mg/g) to form a complete monolayer covering the surface at the equilibrium state of Fe(II) concentration (mg/L), q_e is the amount of Fe(II) adsorbed per unit weight of adsorbent at equilibrium, K_L is the Langmuir constant (L/mg), and K_F and n are the Freundlich constant and the intensity of adsorption, respectively. The values of q_m and K_L are calculated from the slope and the intercept of the straight line plot of C_e/q_e versus C_e (Fig. 3(a)), while the values of K_F and $1/n$ can be obtained from a linear plot of $\log q_e$ versus $\log C_e$ (Fig. 3(b)). The constant values obtained from both Langmuir and Freundlich adsorption isotherms and their correlation coefficients (R^2) were calculated and are summarized in Table 2.

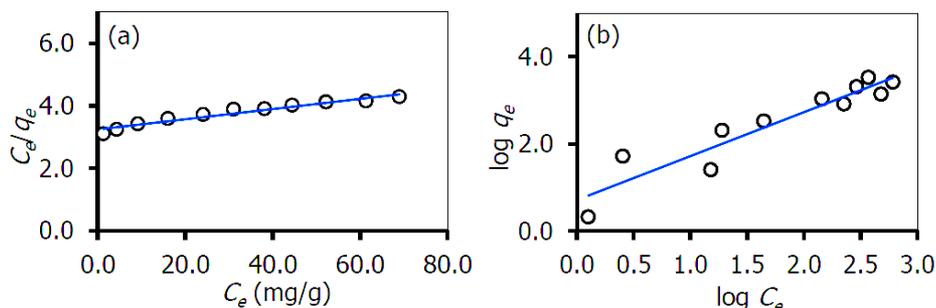


Figure 3. (a) the Langmuir and (b) the Freundlich adsorption plots.

Table 2. Isotherm parameters for the adsorption of Fe(II)

Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	q_{\max} (mg/g)	K_L	R^2	K_F	$1/n$	R^2
CSG-NH ₂	60.80	0.05	0.9494	5.12	1.01	0.8844

As shown in Table 2, it is found that the Langmuir isotherm ($R^2 > 0.94$) fitted the experimental results better than the Freundlich isotherm ($R^2 > 0.88$) as reflected in the correlation coefficient, indicating the homogenous feature is presented on the CSG-NH₂ surface and it demonstrates the formation of monolayer coverage of the Fe(II) ions on the CSG-NH₂ surface. The maximum adsorption capacity of the Fe(II) was found to be 60.80 mg/g.



Conclusion

The obtained results indicate that CSG-NH₂ is a suitable and effective adsorbent for the removal of Fe(II) from synthetic aqueous wastewater. The maximum adsorption capacity of CSG-NH₂ for Fe(II) was 60.80 mg/g under the optimum conditions. Thermodynamic parameters were also evaluated. The negative ΔG° indicates the spontaneity of the ongoing adsorption process, while the negative ΔS° indicates a tendency to lower disorder at the solid-solution interface during the adsorption. In addition, the negative ΔH° indicates that the Fe(II) adsorption using CSG-NH₂ is exothermic in nature. Therefore, the overall adsorption process was exothermic and spontaneous. It is evident that the as-prepared CSG-NH₂ can be used as a high potential adsorbent for the Fe(II) removal.

References

- Bong-Yeon C., (2005) Iron removal using an aerated granular filter, *Process Biochem.*, 40: 3314-3320.
- Bordoloi S., Nath S.K. and Dutta R.K., (2013) Arsenic and iron removal from groundwater by oxidation-coagulation at optimized pH: laboratory and field studies, *J. Hazard. Mater.*, 260: 618-626.
- Ellis D., Bouchard C. and Lantagne G., (2000) Removal of iron and manganese from groundwater by oxidation and microfiltration, *Desalin.*, 130: 255-264.
- Ghosh D., Solanki H. and Purkait M.K. (2008) Removal of Fe(II) from tap water by electrocoagulation technique. *J. Hazard. Mater.*, 155(1-2): 135-143.
- Hamdouni A., Montes-Hernandez G., Tlili M., Findling N., Renard F. and Putnis C.V., (2016) Removal of Fe(II) from groundwater via aqueous portlandite carbonation and calcite-solution interactions. *Chem. Eng. J.*, 283: 404-411.
- Nuengmatcha P., Mahachai R. and Chanthai S., (2014) Thermodynamic and kinetic study of the intrinsic adsorption capacity of graphene oxide for malachite green removal from aqueous solution, *Orient. J. Chem.*, 30(4): 1463-1474.
- Quijada-Maldonado E., Romero J. and Osorio I., (2016) Selective removal of iron(III) from synthetic copper(II) pregnant leach solutions using [bmim][Tf2N] as diluent and TFA as extracting agent. *Hydrometall.*, 159(1): 54-59.
- Seliem M.K. and Komarneni S., (2016) Equilibrium and kinetic studies for adsorption of iron from aqueous solution by synthetic Na-A zeolites: Statistical modeling and optimization, *Microporous Mesoporous Mater.*, 228(7): 266-274.
- Snoussi Y., Abderrabba M. and Sayari A., (2016) Removal of cadmium from aqueous solutions by adsorption onto polyethylenimine-functionalized mesocellular silica foam: Equilibrium properties, *J. Taiwan Inst. Chem. Eng.*, 66: 372-378.
- Vaaramaa K. and Lehto J., (2003) Removal of metals and anions from drinking water by ion exchange, *Desalin.*, 155: 157-170.
- Wang Q., Gao W., Liu Y., Yuan J., Xu Z., Zeng Q., Li Y. and Schröder M., (2014) Simultaneous adsorption of Cu(II) and SO₄²⁻ ions by a novel silica gel functionalized with a ditopic zwitterionic Schiff base ligand, *Chem. Eng. J.*, 250: 55-65.
- Wu X., Luo L., Chen Z. and Liang K., (2016) Syntheses, characterization and adsorption properties for Pb²⁺ of silica-gel functionalized by dendrimer-like polyamidoamine and 5-sulfosalicylic acid, *Appl. Surf. Sci.*, 364: 86-95.
- Zhang Y., Liu Q. and Li L., (2016) Removal of iron from synthetic copper leach solution using a hydroxy-oxime chelating resin. *Hydrometall.*, 164: 154-158.