Application of a Compound Containing Silica for Removing Ammonium in Aqueous Media

R. Darvishi Cheshmeh Soltani,[a] M. Safari,[b] A. Rezaee,[c] and H. Godini[d]

[a]Department of Environmental Health Engineering, School of Public Health, Arak University of Medical Sciences, Arak, Iran; darvishi@arakmu.ac.ir (for correspondence)

[b]Department of Environmental Health Engineering, School of Health, Kurdistan University of Medical Sciences, Sanandaj, Iran

[c]Department of Environmental Health Engineering, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, Iran

[d]Department of Environmental Health Engineering, Faculty of Health, Lorestan University of Medical Sciences, Khorramabad, Iran

In the present investigation, removal of ammonium from aqueous solutions by a compound containing silica was considered. The compound was a waste of ferrosilicon compound produced during Ferro-alloy manufacturing. The results showed that an increase in the pH of solution up to 7 caused a rapid increase in the adsorbed ammonium to 36.21 mg/g. But adsorbed ammonium was decreased to 26.51 mg/g as the initial pH reached to 10. The amount of adsorbed ammonium was increased with contact time and initial ammonium concentration. A contact time of 180 min was selected because there was no significant increment in adsorbed ammonium as contact time was further increased. The results exhibited suitability of the pseudo-second order kinetic model ($R^2 = 0.9867$). Increasing initial ammonium concentration from 10 to 180 mg/L resulted in an increment in adsorbed ammonium from 6.69 to 59.13 mg/g, respectively. The obtained data were fitted to Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) isotherm models in which the obtained correlation coefficient showed the relatively better fitness of the data to Langmuir model ($R^2 = 0.9969$) with a maximum adsorption capacity of 78.74 mg/g. © 2014 American Institute of Chemical Engineers Environ Prog, 00: 000–000, 2014

Keywords: adsorption, ferrosilicon compound, ammonium, kinetic, isotherm

INTRODUCTION

Nowadays, water contamination due to the discharge of large amounts of industrial, agricultural, and municipal wastewaters has grown drastically [1,2]. Among various pollutants, discharging nitrogen species causes adverse effects on receiving waters and human health [3]. Thus, removing nitrogen compounds is one of important issues in environmental and public health protection [4]. Ammonium is one of the major nitrogen species in several industries like fertilizers, refining, inorganic chemicals, ferroalloys, glass and steel manufacturing, together with agricultural and domestic activities [2]. The presence of ammonium ions can cause eutrophication in aqueous environments such as rivers and lakes [3,5,6]. The over-production of algae in aqueous environments due to the eutrophication and subsequently, biodegradation of dead algae can result in oxygen depletion in such environments [5]. Moreover, the presence of ammonium in drinking water can cause odor and illness in human being [1]. Several physicochemical and biological methods, including biological nitrification–denitrification, break-point chlorination, ion-exchange, adsorption, chemical precipitation, electrochemical oxidation, and air-stripping, have been widely applied to remove ammonium from aqueous media [5,6]. Among aforementioned techniques, adsorption with a variety of solid adsorbents is considered as a promising method for removing ammonium ions [2]. Comparatively, activated carbon derived from different materials has been widely used for sequestering ammonium ions from aqueous solutions [2,4,7,8]. However, with the increase of industrial effluents containing different concentrations of ammonium ions, there is a growing demand to develop new materials for the efficient removal of ammonium ions from aqueous environments rather than the high cost activated carbon in which its full-scale application has been limited [9]. Recently, application of some compounds containing SiO_2 due to its exchange property, Fe_2O_3 and Al_2O_3 due to their amphoteric properties has been considered as an efficient approach to adsorb various ions such as ammonium from aqueous solutions [10–12]. Hence, in the present work, we studied the application of a compound containing silica named ferrosilicon compound and produced during Ferro-alloy manufacturing to adsorb ammonium ions in an aqueous medium. To the best of our knowledge, the application of ferrosilicon compound has not been investigated for the removal of ammonium ions. To vigorously evaluate the capability of the compound for removing ammonium, the effects of the initial pH, contact time, and initial ammonium concentration were investigated in batch flow mode reactors. Furthermore, isotherm and kinetic studies were carried out to assess adsorptive characteristics of the studied adsorbent to a great extent.

MTERIALS AND METHODS

Materials and Reagents

The waste ferrosilicon compound as the adsorbent agent produced during manufacturing was prepared from Ferro-

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alloy industries of Iran, in Lorestan Province. The compound sample was washed with deionized water and sieved using standard sieves. All reagents and chemicals, which were of analytical grade, were purchased from Merck, Germany. The synthetic wastewater containing ammonium was simulated with deionized water and NH_4Cl.

Experimental Apparatus

Erlenmeyer flasks with volume of 100 mL were used as batch reactors for the experiments at 120 rpm to investigate the effects of the initial pH, contact time, and the initial ammonium concentration on adsorption process. The pH was adjusted to the target values by HCl and NaOH with appropriate molarity at the beginning of each experiment. To control the ammonium adsorption in the absence of adsorbent, a control batch reactor without adsorbent was used and checked. All experiments were performed twice and the mean values were written down.

Analysis

A Jenway pH meter (Model 3505, UK) was used to determine the pH of the solution. The residual ammonium ions were measured with Neslerization method using a UV–vis spectrophotometer (Unico 2100). The amount of adsorbed ammonium ions onto ferrosilicon compound was calculated by Eq. 1:

$$q=(C_o-C)V/M \tag{1}$$

where q, C_o, and C are the amount of ammonium adsorbed onto the adsorbent (mg/g), the initial concentration, and the final concentration of ammonium ions in the solution (mg/L), respectively. In addition, V and M are the volume of the solution in reactor (L) and the weight of the adsorbent (g), respectively [7,13]. Morphological characteristics of the adsorbent were gained using scanning electron microscopy (SEM) (Philips, XL30, the Netherlands). SEM images were provided by energy dispersive X-ray (EDX) microanalysis. The X-ray diffraction pattern of the sample was obtained by a diffractometer (XRD, X'Pert MPD, Philips, the Netherlands) with anode material of Cu, $\lambda = 1.54056$ Å, step size = 0.02°/s, and scanning angle = 20°–80°. Fourier transform infrared (FTIR) analysis was performed on KBr pellets by a Fourier transform infrared spectrophotometer (Nicolet IR100, Thermo Scientific Co., USA) in the wavenumber range between 400 and 4000 cm^{-1}. Additionally, an X-Ray fluorescence spectrometer (XRF, 2404, Philips, the Netherlands) was used to determine the chemical composition of the compound.

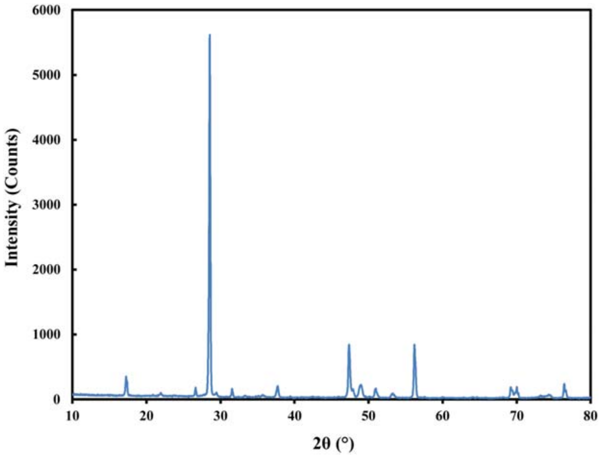

Figure 1. XRD pattern of ferrosilicon compound applied for the adsorption of ammonium ions. [Color figure can be viewed in the online issue, which is available at **wileyonlinelibrary.com**.]

RESULTS AND DISCUSSION

Structural Characteristics

The pattern of XRD analysis depicted in Figure 1 demonstrates a crystalline nature of the adsorbent. The most obvious peaks in XRD pattern are relevant to the Si and, in the next place, Fe compounds. As shown, the significant peaks at 28.53°, 47.31°, and 56.17° are related to the presence of Si compounds within the compound and weaker peaks at 17.19°, 37.47°, 48.65°, and 50.75° are associated with Fe compounds. To reach a good understanding of the composition of the studied adsorbent for the adsorption of ammonium ions, XRF analysis was conducted. The chemical characteristics of the adsorbent, based on weight percent (%), are shown in Table 1. As shown, the major portion of the compound is composed of SiO_2 and Fe_2O_3. The morphological structure of the adsorbent was studied by means of SEM analysis. The obtained image is shown in Figure 2a. SEM image indicated a rugged and porous structure for the adsorbent to remove ammonium ions from aqueous phase with a high performance. Besides, SEM analysis was provided by EDX analysis to identify its basic structure (Figure 2b). The spectrum of EDX analysis shows two obvious peaks related to Si and Fe compounds, confirming the data obtained via XRF analysis. In addition, FTIR analysis was conducted to determine the presence of various functional groups on the surface of adsorbent for binding ammonium ions in aqueous solution. As depicted in Figure 3, the presence of different significant peaks related to the active functional groups for adsorption is evident in the wavenumber range from 400 to 4000 cm^{-1}. The peaks centered at 439 cm^{-1}, 1100 cm^{-1}, 2360 cm^{-1}, 2923 cm^{-1}, and 3417 cm^{-1} correspond to Si—O—Si (bending), Si—O—Si (asymmetric stretching), S—H, C═O, and O—H groups, respectively [2,13–16]. The presence of various functional groups, especially ionizable carboxyl and hydroxyl groups, on the surface of adsorbent would be effective for the adsorption of different cations such as ammonium ions [16]. Conclusively, the results of structural analysis demonstrated an appropriate structure for the ferrosilicon compound to adsorb ammonium from aqueous solutions.

The Effect of the Initial pH

The pH of a solution is a determining factor influencing surface charge of the adsorbent and chemical properties of the solution [17]. Therefore, the effect of the initial pH on the adsorption of ammonium onto the adsorbent was studied in the range between 2 and 10. Figure 4 shows the increase

Table 1. The chemical composition of ferrosilicon compound.

	Chemical composition (wt %)											
Sample	**SiO_2**	**Fe_2O_3**	**Al_2O_3**	**CaO**	**MgO**	**Na_2O**	**SO_3**	**TiO_2**	**K_2O**	**P_2O_5**	**MnO**	**Sr**
Ferrosilicon	84.18	10.22	3.081	1.808	0.192	0.128	0.124	0.094	0.078	0.049	0.034	0.010

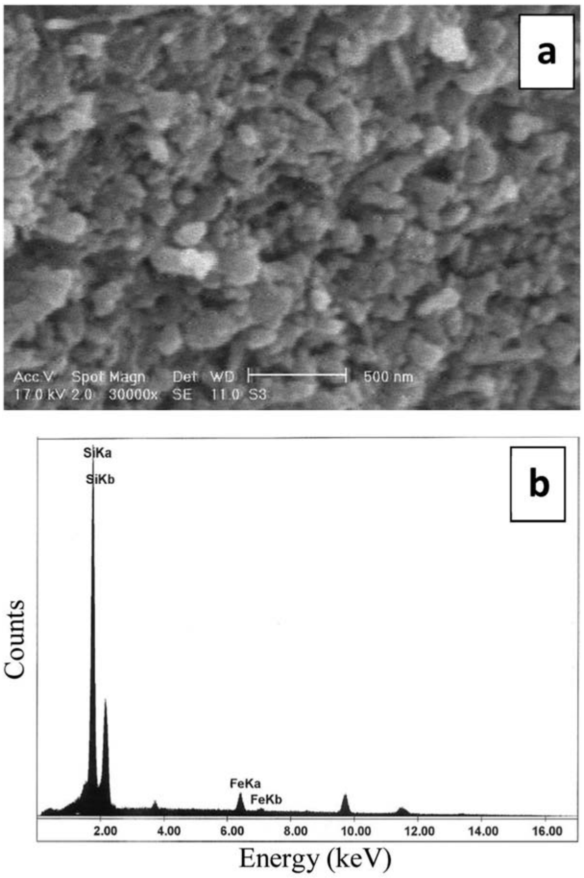

Figure 2. SEM image taken at 30,000× magnification (a) and EDX spectrum (b) of ferrosilicon compound.

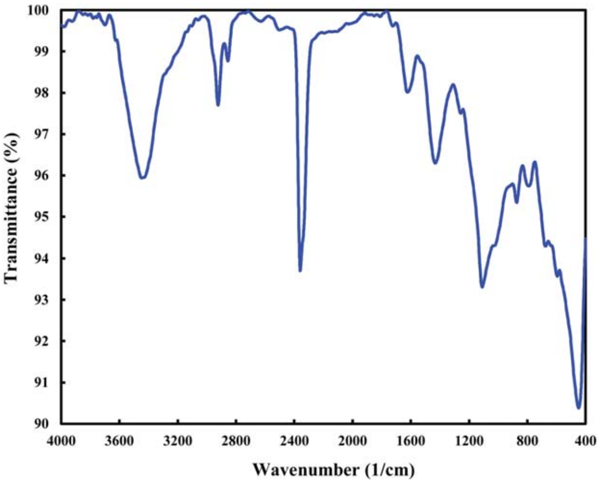

Figure 3. FTIR spectrum of the ferrosilicon compound. [Color figure can be viewed in the online issue, which is available at **wileyonlinelibrary.com**.]

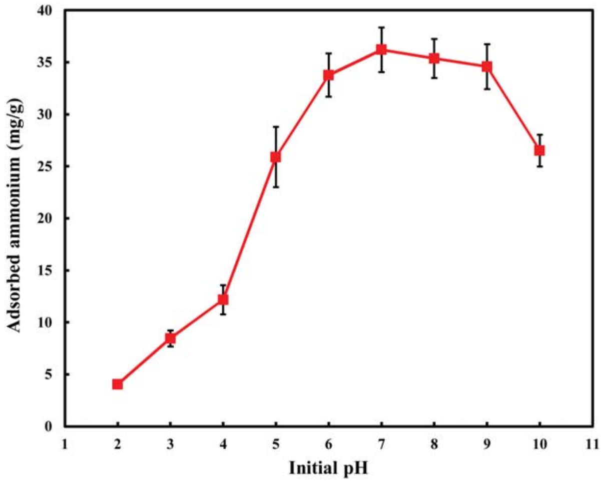

Figure 4. The effect of pH on the adsorption of ammonium ions onto ferrosilicon compound. Initial ammonium concentration = 100 mg/L, contact time = 60 min, and adsorbent dosage = 1 g/L. [Color figure can be viewed in the online issue, which is available at **wileyonlinelibrary.com**.]

in the pH from 2 to 7. It resulted in increasing the adsorbed ammonium from 4.04 to 36.21 mg/g, respectively, while increasing the pH to 10 led to decreasing adsorbed ammonium to 26.51 mg/g. The drop in adsorption of ammonium with decreasing pH values can be attributed to the competition of H^+ ions with ammonium cations for occupying active functional groups [2,18]. Initially, a decrease in the adsorption of ammonium at basic pH values may be due to the conversion of ionized ammonium (NH_4^+) to neutral ammonia (NH_3), which reduces the amount of adsorbed ammonium ions [19]. As can be seen in Figure 4, this behavior is evident at pH values up to 9, which is because the ammonia's pK_a at 25°C is 9.3 [20].

The Effect of Contact Time and Kinetic Study

An exposure time of 240 min was used to evaluate the effect of contact time on the adsorption of ammonium ions onto the adsorbent. As depicted in Figure 5, adsorbed ammonium ions were increased with time, reaching equilibrium within the contact time of 180 min. As the contact time was continued to prolong up to 180, the adsorbed ammonium ions onto the adsorbent became constant and changed little. An adsorbed ammonium of 47.61 mg/g was achieved by 180 min, while increasing reaction time to 240 min resulted in an adsorbed ammonium of 48.88 mg/g. It is related to the presence of unsaturated adsorptive sites at the beginning of the process for rapid adsorption of ammonium ions in the pores [21], while by increasing contact time, the rate of adsorption becomes equal to the rate of desorption [19]. Reaching equilibrium time indicates the formation of a monolayer ammonium ion onto adsorbent surface [11]. In agreement with our findings, Zhu *et al.*, in their study on the adsorption of ammonium ions onto activated carbons derived from rice husk, observed that increasing reaction time from 180 to 210 min caused an insignificant change in the ammonium adsorption [2]. Malekian *et al.* observed a fast adsorption of ammonium onto zeolite for the first 60 min and a slower adsorption as the process was continued [22]. According to the equilibrium time of 180 min, the kinetic of ammonium adsorption was evaluated at an initial ammonium concentration of 100 mg/L, at an initial pH of 7, and an adsorbent dosage of 1 g/L. Hence, two most widely used kinetic models, pseudo-first and pseudo-second order, were used to carry out the kinetic study. The linear form of the pseudo-first order kinetic model is presented in Eq. 2:

$$\log\left(q_e - q\right) = \log q_e - \left(k_{1,\mathrm{ad}}/2.303\right)t \qquad (2)$$

where q_e and q (mg/g) are the adsorbed ammonium ions at equilibrium and time t, respectively. In addition, $k_{1\mathrm{ads}}$

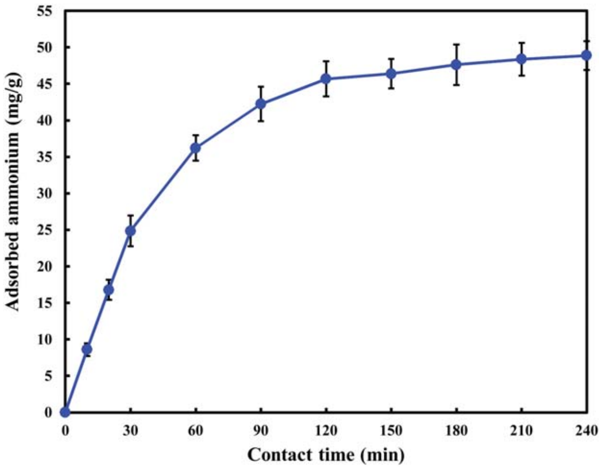

Figure 5. The effect of contact time on the amount of adsorbed ammonium ions. The initial ammonium concentration = 100 mg/L, initial pH = 7, and adsorbent dosage = 1 g/L. [Color figure can be viewed in the online issue, which is available at **wileyonlinelibrary.com**.]

(1/min) is defined as rate constant. The linear form of the pseudo-second order kinetic model is shown in Eq. 3:

$$t/q = \left(1/k_{2,\mathrm{ad}}\, q_e^2\right) + \left(1/q_e\right)\ t \tag{3}$$

where $k_{2\mathrm{ads}}$ (g/mg min) is the rate constant of the pseudo-second order model. A straight line of $\log(q_e - q)$ versus time and a straight line of t/q versus t indicate the suitability of the pseudo-first order and pseudo-second order kinetic model, respectively [13,23,24]. Figure 6 shows the obtained plots of pseudo-first and pseudo-second order kinetic models for the ammonium adsorption onto the adsorbent. To assess the suitability of the studied models, obtained correlation coefficients for each model were compared. The kinetic parameters and correlation coefficients of the kinetic models are shown in Table 2. As stated in Table 2, the correlation coefficient of the pseudo-second order model was relatively higher than that of pseudo-first order model ($R^2 = 0.9867$). In accordance with our results, Uğurlu and Karaoğlu, in their study, showed that ammonium adsorption by fly ash followed pseudo-second order kinetic model [17]. An adsorption process usually comprises various interactions between adsorptive sites and adsorbate ions including electrostatic and chemical interactions, surface adsorption, and intraparticle diffusion; hence, the pseudo-second order model displayed the best fit for describing the adsorption process of various adsorbate ions. However, the pseudo-first order kinetic model describes adsorption process when only controlled by way of diffusion through a boundary layer [2,25].

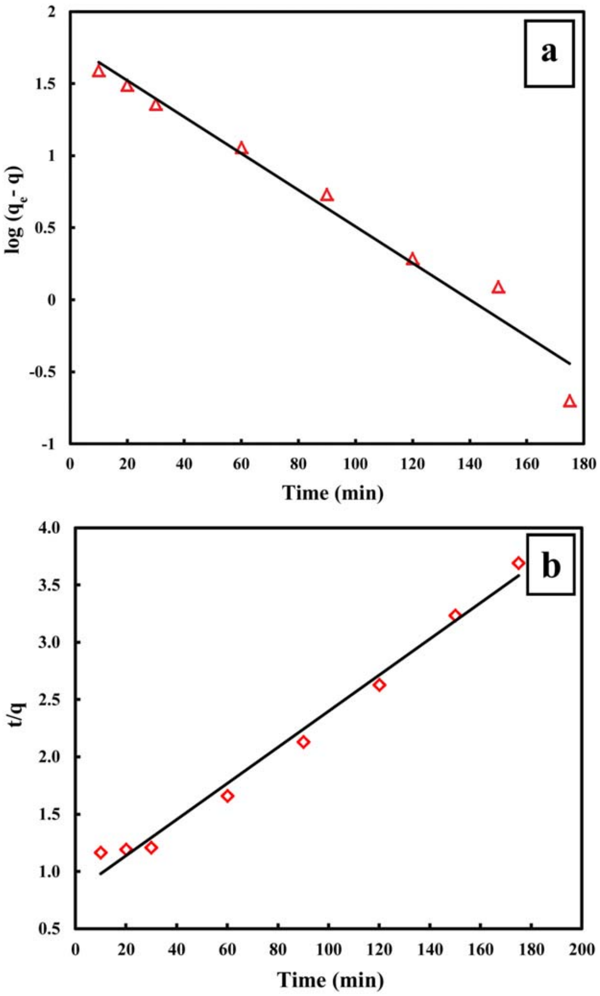

Figure 6. Pseudo-first (a) and pseudo-second (b) order kinetic models for the ammonium adsorption. [Color figure can be viewed in the online issue, which is available at **wileyonlinelibrary.com**.]

Table 2. Kinetic parameters for the removal of ammonium ions by using ferrosilicon compound.

Type of kinetic model	Value
Pseudo-first order model	
R^2	0.9709
$k_{1,\mathrm{ad}}$ (1/min)	0.0292
q_e (mg/g)	59.607
Pseudo-second order model	
R^2	0.9867
$k_{2,\mathrm{ad}}$ (g/mg min)	0.0192
q_e (mg/g)	63.291

The Effect of Initial Ammonium Concentration and Isotherm Study

Ammonium concentration was varied between 10 and 180 mg/L to assess the efficacy of the ferrosilicon compound for the removal of ammonium under different initial concentrations. As it is obvious from Figure 7, increasing initial ammonium concentration from 10 to 180 mg/L resulted in an increment in adsorbed ammonium from 6.69 to 59.13 mg/g, respectively. This can be ascribed to the increase in the driving force for ammonium ions to be adsorbed on the surface of the adsorbent [26]. Similar results have been reported by Thornton et al. for ammonium adsorption onto MesoLite [19]. Moreover, as another reason for increasing adsorbed ammonium with increasing the initial concentrations, it could be stated that at high adsorbate concentrations, more binding sites on the adsorbent are available to be occupied by adsorbate ions, yielding higher adsorbed ions [25]. Moreover, a plot of adsorbed ammonium ions (q_e) as mg/g versus unadsorbed ammonium ions (C_e) remaining in solution as mg/L could be suitable to evaluate reaching the equilibrium at different initial ammonium concentrations. As depicted via a smaller image on Figure 7, equilibrium is achievable at the initial ammonium concentration of 180 mg/L in which the

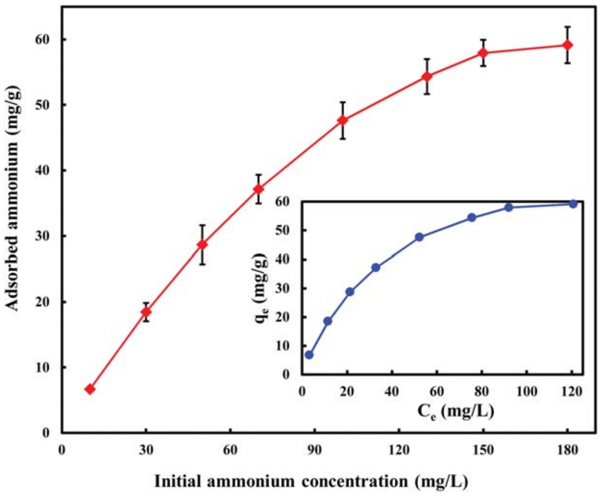

Figure 7. Variations of adsorbed ammonium ions versus various initial ammonium concentrations. [Color figure can be viewed in the online issue, which is available at **wileyonlinelibrary.com**.]

plot of q_e versus C_e becomes plateau for the range between 150 and 180 mg/L. Therefore, ammonium concentration was varied between 10 to 180 mg/L to conduct isotherm study. Three isotherm models including Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) were used to perform isotherm study. To plot linear regression for obtaining isotherm parameters, linear forms of the models were depicted and analyzed. The linear form of the Langmuir isotherm is shown in Eq. 4:

$$C_e/q_e = 1/Kq_m + C_e/q_m \tag{4}$$

where q_m (mg/g) is the maximum amount of adsorbed metal ions per unit weight of the adsorbent and K (L/mg) is the affinity of the binding sites or Langmuir constant [27]. The linear form of the Freundlich isotherm is displayed in Eq. 5:

$$\log q_e = logK_F + 1/n \log C_e \tag{5}$$

where *1/n* is a constant associated with the adsorption intensity, and K_F (mg/g) is relevant to the adsorption capacity [13,19,25]. The last isotherm model is D-R isotherm model, whose linear form is given by Eq. 6:

$$\ln Q = \ln Q_0 - k\varepsilon^2 \tag{6}$$

where Q is the moles of metal ions adsorbed per unit weight of adsorbent (mol/g), Q_0 is adsorption capacity (mol/g), and k is a constant associated with the adsorption energy (mol^2/J^2). The other parameter related to D-R isotherm is Polanyi potential (ε) as J^2/mol^2, which can be calculated by Eq. 7 [9]:

$$\varepsilon = RT \ \ln(1+1/C_e) \tag{7}$$

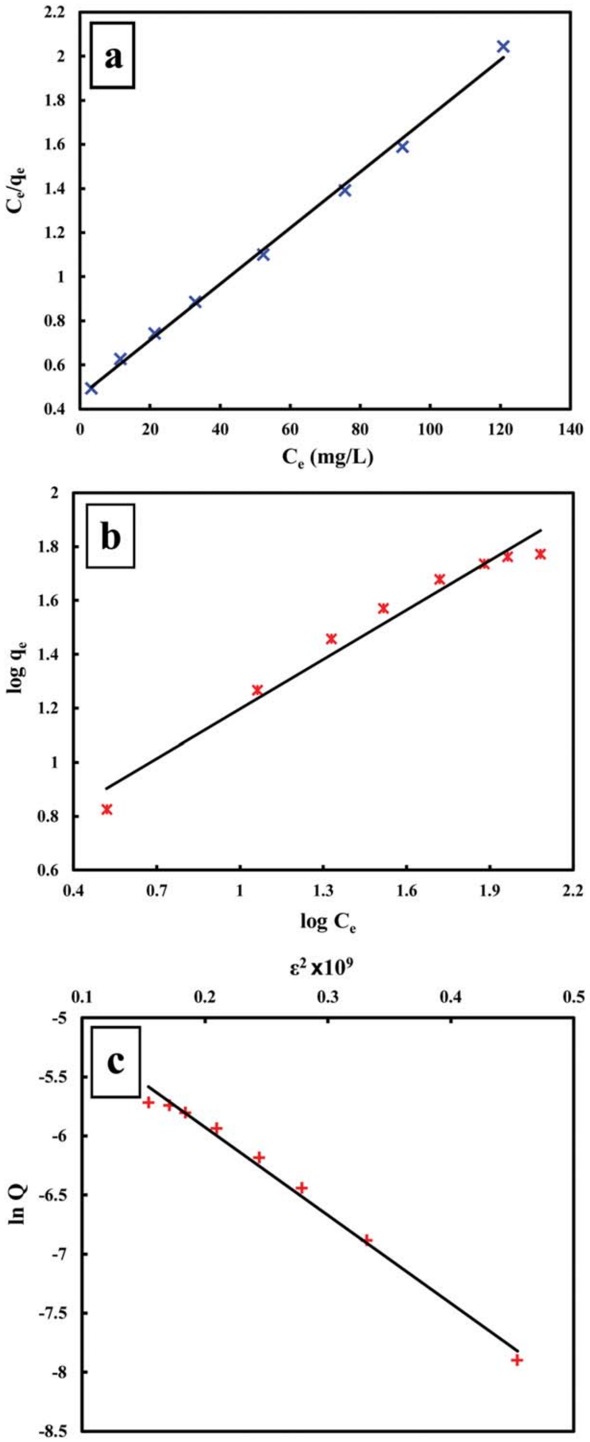

Figure 8. Langmuir (a), Freundlich (b), and D-R (c) isotherm plots for the ammonium adsorption. [Color figure can be viewed in the online issue, which is available at **wileyonlinelibrary.com**.]

where R (8.314 J/mol K) is the gas constant and T (K) is the temperature of solution. The plots of Langmuir, Freundlich, and D-R isotherm models are depicted in Figure 8. The Langmuir isotherm describes a monolayer adsorption on the homogeneous binding sites, while a non-uniform distribution of adsorbed ions onto the heterogeneous binding sites is assumed in Freundlich isotherm model [18]. Besides, D-R isotherm model would be beneficial to determine the mechanism or nature of the adsorption process. Isotherm study was carried out in such conditions where adsorbent dosage, pH of the solution, and reaction time were adjusted to 1 g/L, 7, and 180 min, respectively. The Langmuir, Freundlich, and D-R isotherm models were plotted. The corresponding parameters are shown in Table 3. As shown, a relatively higher correlation coefficient of Langmuir isotherm model ($R^2 = 0.9969$), in comparison with the other isotherm

Table 3. Isotherm parameters for the adsorption of ammonium ions onto ferrosilicon compound.

Type of isotherm models	Values
Langmuir isotherm	
q_m (mg/g)	78.74
K (L/mg)	0.0277
R_L	0.167–0.783
R^2	0.9969
Freundlich isotherm	
K_f (mg/g)	3.839
$1/n$	0.612
R^2	0.9684
Dubinin–Radushkevich (D-R) isotherm	
k (mol^2/J^2)	-7×10^{-9}
Q^o (mol/g)	1.1835×10^{-2}
E (kJ/mol)	8.452
R^2	0.9900

Table 4. Maximum adsorption capacity of some adsorbents for the adsorption of ammonium ions in aqueous solutions.

Adsorbent	q_m (mg/g)	References
Sepiolite	66.63	[1]
Activated carbons derived from rice husk	8.68	[2]
Activated carbon	17.19	[8]
Chitosan-*g*-poly(acrylic acid)/ attapulgite composite	20.76	[9]
Volcanic tuff	19	[11]
Fertilizer controlled release agent (FCRA)	85.47	[18]
Light expanded clay aggregate	0.255	[21]
Multi-walled carbon nanotubes (MWCNTs)	9.31	[26]
Natural zeolite	18.34	[28]
Ferrosilicon alloy	78.74	Present study

models, is evident. However, besides Langmuir isotherm model, Freundlich and D-R isotherm models are appropriate for describing ammonium adsorption onto the adsorbent because of high correlation coefficients obtained (>0.9). In agreement with our findings, Lin et al. found that ammonium adsorption onto natural zeolites followed Langmuir isotherm model [28]. One of the parameters related to Langmuir isotherm is defined as separation factor (R_L), which can be estimated via Eq. 8:

$$R_L = 1/1 + C_o K \tag{8}$$

The values of R_L can be arranged in three intervals including $R_L = 0$, $0 < R_L < 1$ and $R_L > 1$, which represent an irreversible, favorable, and unfavorable adsorption, respectively [22,25]. The obtained R_L value in Table 3, which was between 0.167 and 0.783, indicates favorable adsorption of ammonium ions onto ferrosilicon compound. One of the most useful parameters for comparing adsorption capacity of different adsorbents is q_m, which can be estimated by Langmuir isotherm equation. As shown in Table 3, the value of q_m for the ammonium adsorption onto the adsorbent is 78.74 mg/g. In a comparative manner, the maximum adsorption capacity of ferrosilicon compound for ammonium adsorption was compared to other adsorbent materials. The results are shown in Table 4. Although the major components of light expanded clay aggregate (LECA) utilized by Sharifnia *et al.* for ammonium removal consists of SiO_2 (64.8%), Al_2O_3 (15.05%), and Fe_2O_3 (7.45%), its application for ammonium removal involves a much lower adsorption capacity as compared to the ferrosilicon compound [21]. The higher adsorption capacity of ferrosilicon compound for ammonium removal could be ascribed to the higher percentage of SiO_2 (84.18%) and Fe_2O_3 (10.22%). It is demonstrated that the most important components for ammonium removal is SiO_2 and in the next place Fe_2O_3 in the adsorbent structure [10,21]. Agreeing with our findings, Wang *et al.* observed that high Si to Al ratio resulted in a good selectivity of the compound toward lower charged cations such as ammonium [29]. In addition, it is specified that adsorptive characteristics of the adsorbent for removing various ions including ammonium are dependent on the appropriate molar ratio of its components in the compound [10]. In the case of Freunlich isotherm, the obtained value of *1/n* is lower than 1, implying the favorable adsorption of ammonium onto ferrosilicon compound [11,18]. To determine the nature of the adsorption of ammonium ions onto the adsorbent, the mean free energy of adsorption (E) was estimated by Eq. 9:

$$E = 1/(-2k)^{0.5} \tag{9}$$

The value of E as kJ/mol was arranged in two intervals including $E<8$ and $8<E<16$, showing that the process is physical and chemical in nature, respectively [26,30]. As shown in Table 3, the value of E is found to be 8.452 kJ/mol, suggesting that ammonium adsorption onto ferrosilicon compound is close to a chemical interaction.

CONCLUSIONS

The present study was performed to evaluate the efficacy of a compound containing silica as adsorbent for the adsorption of ammonium in batch flow mode experimental reactors. The XRD, XRF, SEM, and FTIR analysis indicated the appropriate structure of the compound for the removal of ammonium ions. As a result, acidic pH values along with basic pH adversely influenced the ammonium adsorption onto the adsorbent. Increasing contact time and initial ammonium concentration led to increasing adsorbed ammonium ions. However, a contact time of 180 min was chosen as the equilibrium time because of no considerable increase in the adsorbed ammonium after this time. Among studied kinetic and isotherm models, pseudo-second order kinetic model and Langmuir isotherm model were found to be the most suitable model for describing ammonium adsorption. The results of the present study demonstrated the high efficiency of the ferrosilicon compound for the removal of ammonium ions in aqueous solutions.

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