Calcium Alginate Encapsulated Pillared Clay Beads for Adsorption of Ni(Ii) from Aqueous Solution

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In the search for new adsorbents for wastewater treatment, a modified clay-based adsorbent for the adsorption of Ni(II) was proposed in the present study. Silica pillared clays (SPCs) are adsorbents with high specific surface area and thermal stability, which have not been thoroughly investigated for their metal adsorption capacity. SPC was prepared by intercalating tetraethoxysilane (TEOS) as a silica source and a cationic surfactant (ethyl hexadecyl dimethylammonium bromide) between layers of a Na-saturated Iranian clay, followed by calcination. In order to make SPC a more efficient adsorbent for use in large-scale commercial applications, the present study addresses the conversion of a powdered SPC adsorbent into a granular one (ALG-SPC) by entrapping it in a polymeric matrix of calcium alginate and then using it for the adsorption of Ni(II) from aqueous solutions. The process of pillarization/granulation increased the specific surface area of the clay from 40 m^2/g to 506 m^2/g. A strong pH dependence of Ni(II) adsorption on pH was observed, showing the role of electrostatic interaction as the dominant mechanism in Ni(II) adsorption. The pseudo-second order model was the most appropriate kinetic model to describe Ni(II) adsorption. The isotherm models of Sips and Freundlich fit the equilibrium data best. According to the isotherm model of Sips, the maximum adsorption capacity was 52.58 mg/g. Some preliminary binary adsorption experiments were performed, which showed the negative effect of the presence of aniline in the solution on Ni(II) adsorption. Further investigations on multicomponent and continuous adsorption can be carried out.

1. Introduction

Environmental pollution and its adverse effects on the health of living beings have caused major problems worldwide (Thi, 2021). The significant increase in the use of heavy metals in various industries and the discharge of untreated industrial effluents into the environment have increased metal pollution in various water bodies (Ash et al., 2021). Nickel (II) belongs to the group of heavy metals and enters aquatic ecosystems mainly through industrial effluents from mining, electroplating, forging, painting, batteries, and refining petroleum products (Raval et al., 2016). Water contaminated with Ni(II) has become a significant concern in recent years due to its high toxicity to humans and other organisms and its tendency to bioaccumulate (Islam et al., 2019). The World Health Organization (WHO) has set the permissible limit for this contaminant in drinking water at 0.02 mg/L (World Health Organization, 2021).

Adsorption is one of the most effective and economic processes for treating heavy metal wastewaters, especially at low and medium concentrations. Clay is one of the most cost-effective and harmless natural resources to ecosystems and can be used for adsorption due to its porous structure (Mnasri-Ghnimi and Frini-Srasra, 2019). Pillared clay is a modified type of clay produced by replacing charge-balancing cations in the interstices between clay layers with polymeric (or oligomeric) cationic species. The intercalated precursors then become solid columns after the calcination process. The separation of clay layers by molecular bases in pillared clay results

in more expanded and permanent porosity, greater specific surface area, and higher thermal stability than raw clay. The main pillaring agents for the preparation of pillared clay are Al_2O_3, Fe_2O_3, ZrO_2, TiO_2, and SiO_2 (Najafi et al., 2021b).

The literature search revealed that silica pillared clays (SPCs) have the highest specific surface area, the most significant total pore volume, and the highest thermal resistance among the pillared clays produced. These properties make SPC an advantageous porous material for use as an adsorbent. Clay and its modified forms, specifically pillared clay, have shown high potential for adsorption of heavy metals from aqueous solutions. This topic has attracted the attention of many researchers for many years. The literature review shows that Ni(II) has been tested to adsorb to aluminum pillared clay (Kumararaja et al., 2017), SPC with a grafted chelating ligand (Addy et al., 2012), and aluminum pillared clay prepared with a cationic surfactant in a multi-component solution (Ouellet-Plamondon et al., 2012). Addy et al. performed a limited study on Ni(II) adsorption on a column of silica-montmorillonite modified with a chelating ligand. At an initial concentration of 5 mg/L Ni(II) in the feed, they reported only the outlet concentration of Ni(II) from the column for 6 h (Addy et al., 2012). Therefore, further studies are needed to investigate the various adsorption characteristics of the Ni(II)-SPC system.

On the other hand, conversion of powdered adsorbents into commercial granular adsorbents is essential for large-scale and bed applications of adsorbents. This can be carried out by adding binders to the primary powdered adsorbent. The literature review showed that no previous study investigated the adsorption of Ni(II) onto the granular SPC. The conversion of powdered SPC adsorbent into more common forms for commercial use, such as granules and beads, was one of the main objectives and novelties of the present study, which could help expand the application of these systems. Alginate is a natural anionic polysaccharide from brown algae with carboxyl groups that can be used to granulate powder materials due to ionic crosslinking in the presence of divalent cations. The negative charge of alginate can be effective in the adsorption of cationic species (Najafi et al., 2021a).

In the present study, Ni(II) adsorption from an aqueous system using a granular SPC was investigated, and the effects of parameters such as pH, adsorbent dosage, kinetic, and equilibrium parameters were determined. In addition to the best operating parameters for the studied range, the maximum adsorption capacity and the mechanisms involved in adsorption were also obtained. In this work, SPC was first prepared from raw clay (from Iran), and then alginate biopolymer was used to convert the powder adsorbent to beads. The following steps were to characterize and apply this adsorbent for Ni(II) adsorption from an aqueous system.

2. Materials and methods

2.1 Preparation of calcium alginate encapsulated SPC beads (ALG-SPC)

SPC was prepared by the sol-gel method using a local raw clay (Mojallali Co., Isfahan, Iran), tetraethyl orthosilicate, and ethyl hexadecyl dimethylammonium bromide (Merck Co.) as the surfactant as previously reported (Najafi et al., 2021a). A 2 % sodium alginate solution was prepared and stirred at 45 °C for 1 h until the sodium alginate was dissolved entirely. A 10 % suspension of SPC was added to the sodium alginate solution (with an SPC/alginate ratio of 1.5) and stirred for 4 h at room temperature. The mixture was added dropwise into a 2 % (wt./vol.) calcium chloride solution using a syringe to prepare the beads. The prepared hydrogel granules were stored in a refrigerator at 4 °C for 15 h. After separating the calcium chloride solution, they were washed several times with distilled water and dried at 65 °C for 18 h.

2.2 Batch mode adsorption

Ni(II) solutions were prepared by dissolving $Ni(NO_3)_2.6H_2O$ in distilled water. First, adsorption experiments were performed at pH values ranging from 2 to 7 with an adsorbent dose of 3 g/L and an initial 50 mg/L Ni(II) concentration for 24 h. Adsorption studies were performed in the range of 0.5 - 5 g/L with an initial concentration of 50 mg/L and a pH with the best performance to determine the effect of the adsorbent dose.

Once the pH and dose were determined, kinetic experiments were performed at an initial concentration of 50 mg/L for 15 min - 24 h, and equilibrium experiments were performed at initial concentrations of 30 - 400 mg/L. The temperature was considered constant and equal to 25 °C in all experiments. The concentration of Ni(II) in the initial and treated solution was determined by atomic absorption spectroscopy (VarianAA240).

For the calculation of adsorption capacity and removal percentage, Eq(1) and Eq(2), were used as follows;

$$q_t = \frac{C_0 - C_t}{m} \times V \qquad (1)$$

$$R = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2)$$

In these equations, C_0 is the initial concentration of the pollutant, and C_t is the concentration at time t; also, V is the volume (L) of the contaminated synthetic solution, and m is the mass of the adsorbent (g).

3. Results and discussion

3.1 Adsorbent Characterization

The chemical composition of the raw clay and ALG-SPC was determined by XRF analysis and is shown in Table 1. After pillaring, the weight percentage of SiO_2 species increased to more than 91 % and the decrease in the percentage of interlayer cations (mainly alkali metals and alkaline earth metals cations), including sodium, indicates that the pillaring species successfully replaced the cations in the raw clay.

Table 1: Chemical composition (wt %) of the raw clay and ALG-SPC

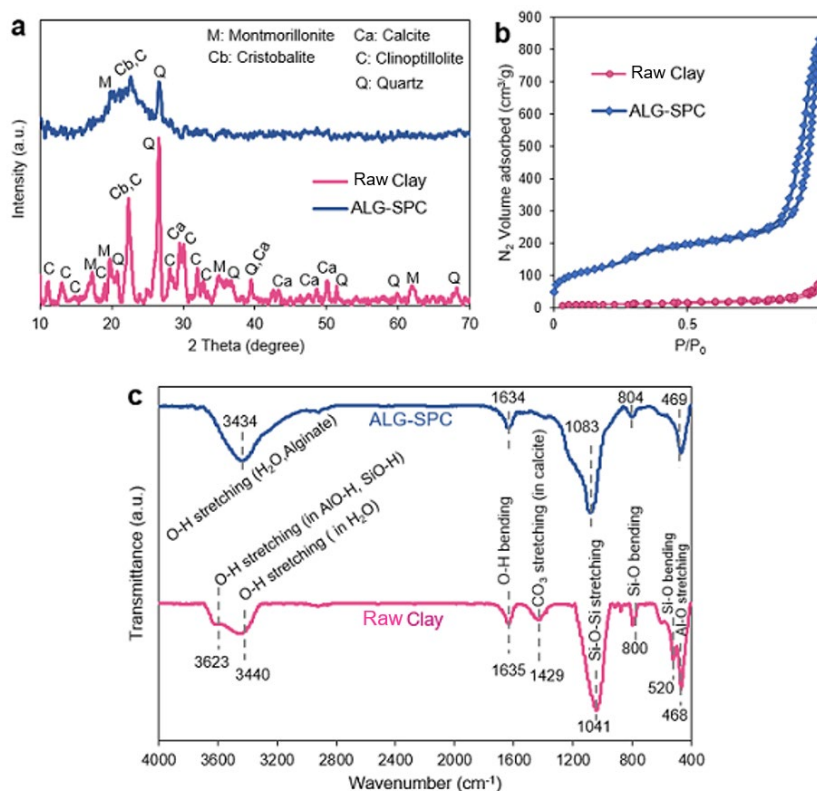| Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5
Raw Clay	76.08	12.6	1.74	1.75	4.04	2.02	1.20	0.29	0.06	0.03
ALG-SPC	91.82	3.54	0.73	0.61	2.93	<0.01	0.24	0.12	<0.01	<0.01

Figure 1: (a) XRD patterns, (b) N_2 adsorption-desorption isotherms and (c) FTIR spectra of the raw clay and ALG-SPC

The N_2 adsorption/desorption, XRD, and FTIR analyses results for raw clay and ALG-SPC are shown in Figure 1. Figure 1a shows that montmorillonite, quartz, cristobalite, clinoptilolite, and calcite were detected in the XRD spectrum of the raw clay. The degree of crystallinity of ALG-SPC was reduced by adding amorphous SiO_2 during pillarization, and the peaks associated with the calcite impurities phase were removed (it was carried out in the pretreatment stage acid leaching before the pillaring process). Figure 1b shows a significant increase in N_2 adsorption capacity related to the greater porosity of ALG-SPC compared to the raw clay. The specific surface area and total pore volume of 40 m^2/g and 0.13 cm^3/g for the raw clay were increased to 506 m^2/g and 1.29 cm^3/g in ALG-SPC. The analysis of mesopores showed that more than 95 % of the total pore volume of the ALG-SPC sample consisted of mesopores. The vibrations of chemical bonds such as -OH, Si - O- Si, Si-O, and Al-O- were observed in the FTIR spectrum of raw clay in Figure 1c. Due to the pillarization process

(introduction of SiO$_2$) and granulation process (introduction of carboxyl groups by ALG), some changes in bond vibrations were observed in the FTIR spectrum of ALG-SPC which are shown in Figure 1c.

3.2 Batch mode adsorption

The experiments showing the effects of solution pH (2 - 7) and adsorbent dose (0.5 - 5 g/L) on the adsorption of Ni(II) are shown in Figure 2. Figure 2a shows that as the pH of the solution increases, the adsorption of Ni(II) increases sharply. According to the preliminary experiments, the precipitation of nickel was observed at pH values above 9. The pH of 8 was also excluded from the range because its unexpectedly high removal percentage could be related to the formation of precipitates (which cannot be observed) in addition to adsorption. Blank tests confirmed this. In the range studied, increasing the pH from 2 to 7 improved Ni(II) removal percentage from 7.1 % to 63 %. The high concentration of H$^+$ under acidic conditions and its competition with the Ni(II) cations resulted in very low adsorption. The positive effect of increasing pH on the adsorption percentage can be related to the gradual decrease of the net positive charge on the adsorbent surface, causing an electrostatic attraction between the deprotonated functional groups, especially Si-O- (in SPC) and COO- (in ALG) with the Ni(II) cations. Therefore, the pH of 7 was chosen as the best pH under the range studied for further experiments.

Figure 2a also shows the adsorption capacity of the adsorbent for Ni(II) in the presence of aniline (50 mg/L) as an additional and competing organic pollutant in the solution. It can be seen that the presence of aniline throughout the pH range negatively affected the amount of Ni(II) adsorption, as some suitable Ni(II) adsorption sites were competitively occupied in the presence of aniline.

Figure 2b shows changing the adsorbent dose on the adsorption capacity and percent removal of Ni(II). With increasing adsorbent dose from 0.5 g/L to 5 g/L due to the increase of active sites, adsorption increased from 30.5 % to 67.4 %. However, excess adsorbent and the unsaturation of a fraction of sites led to a decreased adsorption capacity from 31.6 mg/g to 6.98 mg/g. Considering that increasing the dose from 3 g/L to 5 g/L only led to an increase in the adsorption percentage by about 4 %, 3 g/L was chosen for economic reasons as the dose with the reasonable performance.
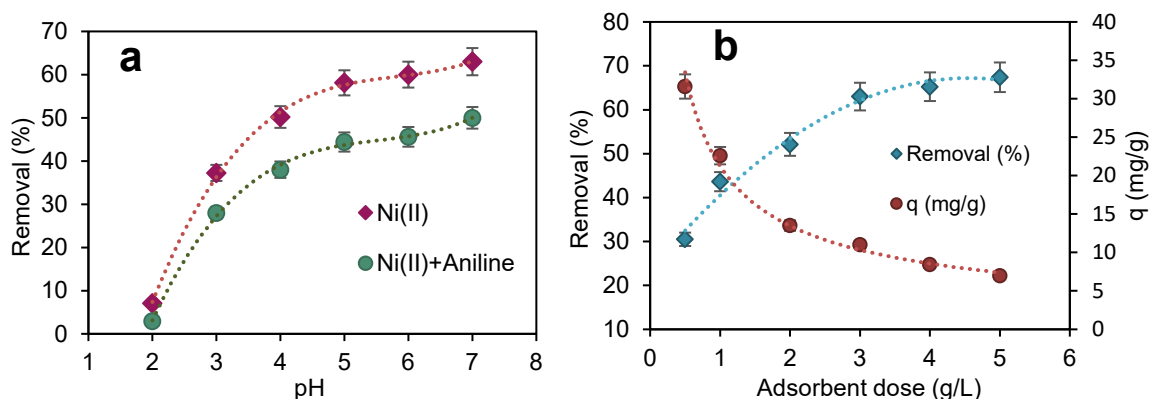

Figure 2: (a) Effects of pH and (b) adsorbent dose on adsorption of Ni(II) (contact time = 24 h, and C$_0$ = 50 mg/L) (each test was performed twice, and the error was within 5 %)

The kinetic and isothermal studies on the adsorption of Ni(II) are shown in Figure 3. From Figure 3a, the adsorption capacity increases sharply in the first few minutes and reaches almost half of the equilibrium adsorption capacity in 15 min, and then slows down until equilibrium is reached. Therefore, the time to reach adsorption equilibrium can be estimated to be about 4 h. The kinetic experimental data (sufficiently far from equilibrium) were analyzed using two kinetic reaction models, including the nonlinear forms of the pseudo-first order model and the pseudo-second order model.

Figure 3b also shows the experimental adsorption data at equilibrium. Isotherm models such as the Langmuir, Freundlich, and Sips models were applied to model the equilibrium data. It is also shown that the equilibrium adsorption capacity (q$_e$) increases with increasing initial concentration, which is due to an improvement in driving force for adsorption.

The parameters obtained from the kinetic and isotherm modeling are shown in Table 2. The statistical correlations (R^2 and RMSE) showed that the pseudo-second order model fits the experimental data better than the pseudo-first order model. Another reason for the better agreement of the kinetic data with the pseudo-second

order model is the closer proximity of the equilibrium adsorption capacity determined by the model (11 mg/g) to the experimental value.

According to Table 2, the Sips model showed the best agreement with the experimental data. The Langmuir model is the simplest adsorption model because it considers simplified approximations such as homogeneous adsorption sites and monolayer adsorption. In contrast, the Freundlich model is an empirical equation suitable for non-ideal adsorption on heterogeneous surfaces. The Sips isotherm model is a combined model that includes the approximations of both the Langmuir and Freundlich models and does not need to reach a limited equilibrium adsorption capacity at higher concentrations. According to R^2 and RMSE values, the fit with the Sips and Freundlich models was better than with the Langmuir model.
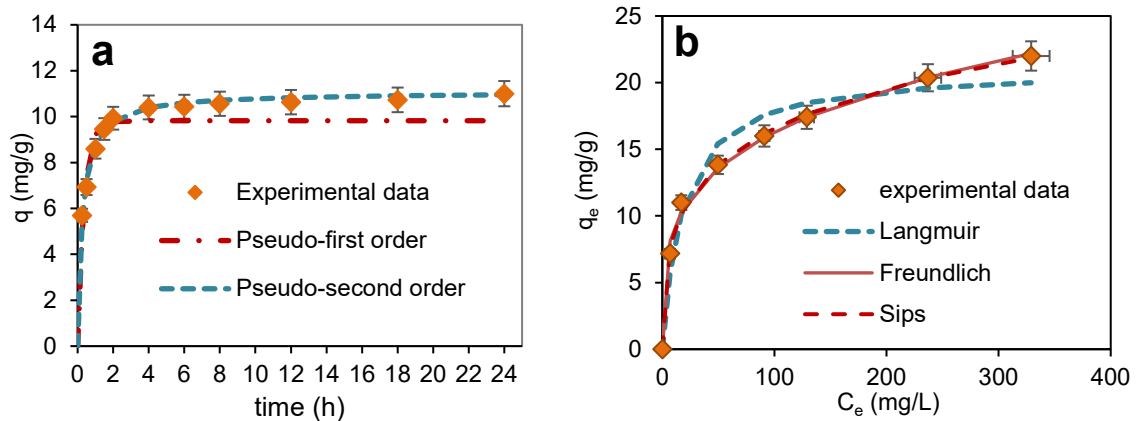

Figure 3: (a) Kinetic and (b) isotherm models for adsorption of Ni(II) onto ALG-SPC (pH = 7 and adsorbent dose = 3 g/L) (each test was performed twice, and the error was within 5 %)

4. Conclusion

Table 2: Kinetic and isotherm models parameters

Model	Parameter	Value
Pseudo-first order $q_t = q_e(1 - \exp(-K_1 t))$	K_1 (h^{-1})	2.7810
	q_e (mg/g)	9.82
	R^2	0.9799
	RMSE	0.5625
Pseudo-second order $q_t = \dfrac{q_e^2 K_2 t}{1 + K_2 q_e t}$	K_2 (g/mg.h)	0.3436
	q_e (mg/g)	11.07
	$h = K_2 q_e^2$	42.10
	R^2	0.9968
	RMSE	0.2231
Langmuir $q_e = \dfrac{q_{mL} K_L C_e}{1 + K_L C_e}$	K_L (L/mg)	0.0548
	q_{mL} (mg/g)	21.10
	R^2	0.9631
	RMSE	1.5070
Freundlich $q_e = K_F C_e^{\frac{1}{n_F}}$	K_F (mg/g)(mg/L)$^{-1/n_F}$	4.9420
	n_F	3.859
	R^2	0.9959
	RMSE	0.5052
Sips $q_e = \dfrac{q_{m_s} K_S C_e^{\frac{1}{n_S}}}{1 + K_S C_e^{\frac{1}{n_S}}}$	q_{ms} (mg/g)	52.58
	K_S (mg/L)$^{-1/ns}$	0.0856
	n_S	0.3654
	R^2	0.9971
	RMSE	0.4666

*q_e: Equilibrium adsorption capacity (mg/g), K_1: pseudo-first order kinetic constant, K_2: pseudo-second order kinetic constant, h: initial sorption rate. q_{mL}: Langmuir maximum monolayer adsorption capacity, q_{ms}: Sips model maximum adsorption capacity, KL, KF and Ks: Langmuir, Freundlich, and Sips constants, nF and nS: dimensionless exponents of Freundlich and Sips models.

In this study, a local clay was modified by silica pillaring through the sol-gel method, and then sodium alginate was used for granulating the powder adsorbent. The adsorbent beads were used to adsorb Ni(II) from an aqueous solution in batch mode. Characterization of the adsorbent showed that silica pillarization increased the SiO_2 content by more than 91 %, decreased the degree of crystallinity, and significantly increased the specific surface area (from 40 m^2/g to 506 ^{m2}/g) and total pore volume (from 0.13 cm^3/g to 1.29 cm^3/g) compared to the raw clay. an extended pH range.Adsorption studies showed that the amount of Ni(II) adsorption was strongly dependent on pH, and the highest adsorption capacity was achieved at pH 7; and electrostatic forces play an essential role in the process. The presence of aniline in the two-component adsorption system was an inhibiting factor for the adsorption of Ni(II). More than half of the equilibrium adsorption capacity of Ni(II) was reached in 15 min, and adsorption reached equilibrium in 4 h. an extended pH range. The pseudo-second order kinetic and Sips models (with a maximum adsorption capacity of 52.58 mg/g) had the best agreement with the experimental data. Based on the results, SPC is an effective adsorbent for Ni(II) adsorption, which can be used in further fixed bed studies. Moreover, to simulate the adsorption conditions in real wastewaters, the effects of other metal species (especially alkali and alkaline earth metals) on the adsorption of Ni(II) can be studied. Given the dominance of the electrostatic attraction mechanism in Ni(II) adsorption and the dependence of adsorption on pH, it is recommended that other surface treatments, such as using the metal cationic chelating agents, be applied to enhance adsorption over

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