

Pb(II) adsorption of composite alginate beads containing mesoporous natural zeolite

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Abstract

Natural zeolite beads were prepared by immersing mesoporous zeolite into alginate beads via egg box method and its adsorption properties of Pb(II) ions were investigated in aqueous solution. Crystallinity and size reduction of natural zeolite were enhanced by mechanic modification of ball milling process. FTIR and SEM-EDS analyses confirmed that mechanically modified zeolite particles were incorporated into alginate hydrogel. The highest adsorption amount of zeolite alginate beads was 87.47 mg/g after 20 h adsorption process. SEM-EDS result confirmed that adsorption process is occurred on surface of zeolite alginate beads. Adsorption isotherm data were fitted with Langmuir adsorption isotherm which showed that Pb²⁺ cation adsorbed into monolayer of adsorbent material. Moreover, we observed that calcium ion released after Pb²⁺ adsorption process in the feed solution. Therefore, adsorption mechanism of zeolite alginate beads is undergoes complex mechanism including surface sorption and ion exchange of Pb²⁺ and Ca²⁺ in beads.

Keywords: Alginate Beads, Natural Zeolite, Pb(II) Adsorption, Mesoporous, Ball milling

1. Introduction

In last decades, rapid growth of mining and industrial activity is giving a huge impact on surrounding environment worldwide. Especially, heavy metal pollution of water is serious environmental issue in Central Asia with limited water resource. Polluted water source presents a significant threat to environment problems such as toxicity in accumulation in the food chain and persistence in nature. Lead is widely used heavy metal in various industrial fields which is harmful and non-degradable¹ pollutant. Since lead is non-degradable, it is accumulated in the environment such as soil, water bodies and sediments². Due to this problem, many treatment methods have been developed for removal of heavy metals from the waste water³⁻⁷. Among them zeolite adsorbent is one of the promising technologies due to its high removal efficiency with simple treatment method, provided easy availability of low-cost adsorbent can be found locally. Source of natural zeolite in Mongolia has been estimated as 4.8 million tons. Therefore, several researchers studied about the removal of heavy metals in waste water by Mongolian natural zeolite⁸⁻¹⁰. Moreover, our previous research was focused on the adsorption ability of anionic and cationic pollutants such as Pb(II), Cd(II), Zn(II) by raw natural zeolite and As(V) by Magnesium oxide modified zeolite¹¹. The result showed that Mongolian natural zeolite has higher efficiency to adsorb Pb(II) at acidic condition than Cd(II) and Zn(II) cations and As(V) anion adsorption ability of modified zeolite was increased. Zeolite adsorption capacity of heavy metals can be enhanced with various chemical modifications. In this work, we improved zeolite structure by mechanical modification method without chemical additive. Although some chemical modification can be effective for adsorption process, but further reuse of material might be difficult. Therefore mechanical modification was carried out on natural zeolite sample due to its cost effective and environment friendly method. Moreover, powder zeolite is difficult to use in batch reactor and fixed-bed columns due to the agglomeration in solutions. Therefore, we developed zeolite beads composite material using

sodium alginate ($C_6H_9NaO_7$). Alginate, an ionic polysaccharide mainly refined from the cell walls of brown algae, is linear arranged by homopolymeric blocks of (1–4)-linked β -D-mannuronate (M) and its C-5 epimer α -L-guluronate (G) residues, making it hydrophilic, biocompatible, nontoxic, and edible^{12,13}. Preparation method of alginate bead is simple and nontoxic to environment. In these experiments, powder zeolite was encapsulated by ionotropic gelation of calcium chloride and sodium alginate and sphere shaped sorbent material has been prepared. Present work, we propose preparation of zeolite alginate beads and its adsorption performances of Pb(II) from aqueous solution. Composite beads' adsorption capacity and kinetics, initial solution pH effect, effect of contact time and isotherm models were investigated.

2. Experimental Details

2.1. Materials

Natural zeolite samples were collected from Tsagaan tsav deposit in Dornogovi province, Mongolia and it is used for alginate polymer synthesis. Average pore diameter of natural zeolite was 8.53 nm and BET surface area was 34.57 m²/g which includes in mesoporous material as described in our previous study¹¹. Main components of natural zeolite was Si, Al, Fe, K, and Ca and 0.01wt% trace elements including Ti, Sr, Ba, Zr, Mn, Rb, Zn and Y.

Sodium alginate ($C_6H_9NaO_7$, 95% purity) is used as monomer and calcium chloride ($CaCl_2$, 98% purity) is used as crosslinking agent in preparation of composite alginate beads. The reagents were purchased from Macklin Biochemical Co.Ltd, China. Lead standard solution (Pb(II) in 0.1N HNO_3 , $\geq 99\%$ purity) was used in the adsorption experiment which was supplied by Carl Roth GmbH Co.KG, Germany. Deionized water was used in all experiments.

2.2. Zeolite-Alginate composite preparation

2.2.1. Preparation of natural zeolite

Initially, the natural zeolite sample was washed with deionized water multiple times to remove

mechanical impurities and pre-treated by planetary ball mill (PM-400 Retsch, Germany) to enhance crystal arrangement with 200 rpm speed and 3 mm zircon balls in range of 5, 10, and 15 minutes.

2.2.2. Synthesis of Zeolite-Alginate composite

Sodium alginate (1 wt%) is dissolved in deionized water, then stirred by magnetic stirrer for 1 h. Natural zeolite (1 g) was added to the alginate solution and mixture was homogenized at room temperature for 6 h. Afterwards, the mixture was dropped into CaCl_2 solution (0.1 M, 50 ml) and sphere-shaped beads formed immediately. Experiment scheme showed in Figure 1. The zeolite-alginate beads (ZAB) kept in CaCl_2 solution (0.1 M, 50 ml) for 10 h in order to harden it. ZAB washed with deionized water multiple times and dried at 60°C for 3 h to remove water for obtaining accurate weight.

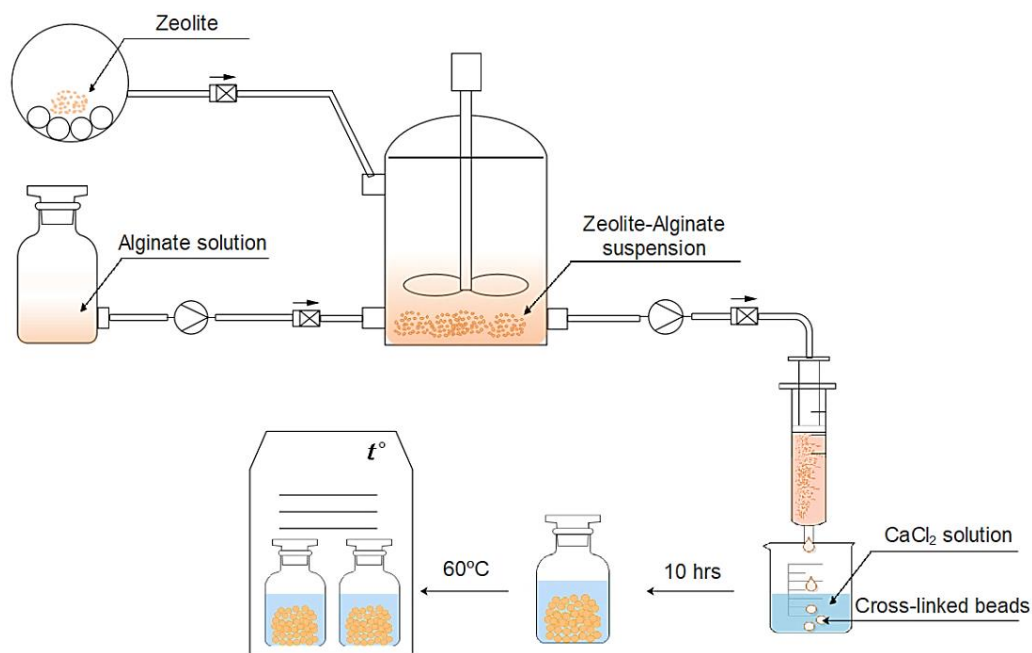


Figure 1. Preparation of Zeolite alginate beads

2.2.3. Characterization studies

The base components of natural zeolite were determined by X-Ray diffraction (XRD), PANalytical X'PERT-Pro MRD instrument via $\text{Cu-K}\alpha$ line ($\lambda = 1.5406 \text{ \AA}$) powder method on 2θ diffraction

angle (range of 5-60). Data collection and peak determination were analyzed by X'PERT High Score Version 2.0 software. Particle size analyses of powder zeolite was determined by Photon Cross-Correlation Spectroscopy (PCCS) using Nanophox, Sympatec GmbH at 293K. Surface morphology and micro detection of the element mapping of ZAB were characterized by scanning electron microscopy (SEM), HITACHI TM1000 analysis. Functional group identification of prepared beads and Pb-loaded beads were determined by Fourier Transform Infrared Spectrometer (FTIR), Thermo Scientific™ Nicolet™ iS5 at room temperature in the range of 550 - 4000 cm^{-1} . The beads were frozen in liquid nitrogen and dried in freeze-dryer (Biolab Benchtop 103aA) at -50°C for 24 h prior to characterization analyses of scanning electron microscopy (SEM) and Fourier Transform Infrared Spectrometer (FTIR).

2.3. Adsorption studies

Initial and equilibrium concentration of Pb(II) after the adsorption experiments were measured by inductively coupled plasma optical emission spectrophotometry (ICP-OES). Mass ratio of sample and solution was 30 mg adsorbent per 25 mL pollutant and adsorption reactions conducted in a batch reactor. In all adsorption experiments, zeolite alginate beads were interacted with Pb(II) solution at room temperature and prior to ICP-OES analyses, liquid and solid phases of solution were separated by a $0.45\mu\text{m}$ syringe membrane.

2.3.1. pH effect of adsorption

pH effect on Pb(II) adsorption was conducted at multiple pH values to obtain the most efficient removal condition of zeolite alginate beads. Lead standard solution (25 mL, 50 ppm) prepared and initial pH (pHi) adjusted in range of pH=2-5 by 1M NaOH or HCl solution. The solution containing ZAB was shaken at room temperature for 16 h and then Pb(II) concentration of liquid phase was measured by ICP-OES.

2.3.2. Effect of contact time

Pb(II) cations and ZAB composites' interaction time of the adsorption process was investigated at

0.5h-24h to obtain highest adsorption amount on the most effective interaction time. Initial concentration of Pb(II) solution was 100 ppm at pH=3.

2.3.3. Adsorption capacity

Adsorption capacity experiment of ZAB was carried out with various initial concentrations (10-500 ppm). The initial pH of Pb(II) solution was adjusted to 3 and interacted for 16 h. Adsorption capacity is calculated by Eq. (1).

$$Q_e = (C_i - C_f) \cdot \frac{V}{m} \quad (1)$$

Where Q_e is equilibrium amount of heavy metal adsorbed on ZAB (mg/g), C_i and C_e are initial and equilibrium concentration (mg/L) in the solution, V is total volume of feed solution (L) and m is mass (g) of ZAB adsorbent. Langmuir and Freundlich adsorption isotherms were calculated by Eq. (2) and (3), respectively.

$$Q_e = \frac{Q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

$$Q_e = K_F \cdot C_e^{1/n} \quad (3)$$

Where Q_m (mg/g) is theoretical maximum adsorption capacity, K_L (mg/g) is Langmuir equilibrium coefficient and 1 is a constant, K_F (mg/g) and n are Freundlich constants. Adsorption efficiency (%) is calculated by Eq. 4.

$$Q_{ef} = \frac{(C_i - C_f)}{C_i} \cdot 100 \quad (4)$$

3. Results and Discussion

3.1. Characterization studies

3.1.1. X-ray Diffraction (XRD)

Crystallinity of natural zeolite and mechanically pre-treated zeolite sample were investigated by XRD. Natural zeolite is determined as clinoptilolite zeolite. Clinoptilolite is one of the most abundant type among the zeolite group minerals. It included in Heulandite structure group which

has high silica content and monoclinic crystal system. Net negative charge of Clinoptilolite structure is balanced by exchangeable cations which are loosely held within the central cavities and surrounded by water molecules¹⁴. As shown in Figure 2, XRD result clearly indicates that interpretation of milled zeolite was given 2 times higher peak intensity (0-2500 u.a) than raw zeolite (0-1200 u.a). The natural zeolite consists of randomly oriented crystal particles. Increased peak intensity in milled zeolite indicates that crystal structure became arranged and ordered after mechanical treatment. Several sharper peaks were appeared in milled zeolite sample which also detected as part of clinoptilolite zeolite. This result may explain that ball-milling process increased purity of natural zeolite by removing impurities without crystal structure distortion. From XRD data, average crystallite size calculated by Debye Scherrer equation (Eq. 5).

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (5)$$

Where L is average crystallite size, K is shape factor (0.9 for spherical particle), λ is used X-ray wavelength (0.154nm), θ is Bragg diffraction angle, obtained from 2θ value of corresponding peak by dividing 2 and β is line broadening coefficient obtained from full with half at maximum (FWHM). Average crystallite size of raw zeolite 82 nm and it decreased from 56, 45, and 37 nm in 5, 10, 15 min milling process, respectively.

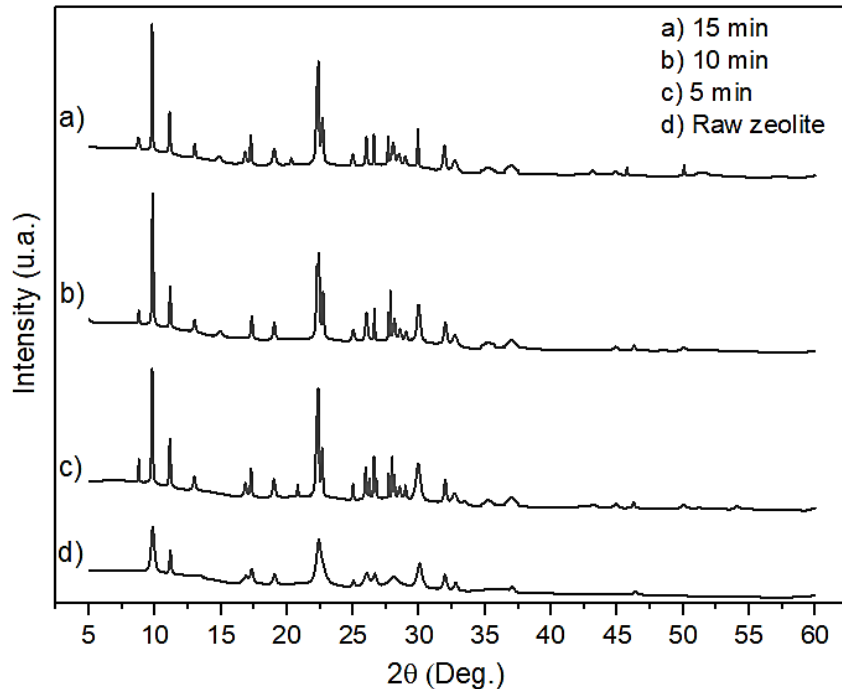


Figure 2. XRD interpretation of raw and milled zeolite by min, a) 15 min, b) 10 min, c) 5 min milled zeolite and d) raw zeolite

3.1.2. Particle size analysis

The result of particle size analyses showed that raw zeolite particle size was decreased after milling process from 0.581 μm to 0.262 μm in 0-15 minutes. Moreover, size reduction may lead to increase of interaction surface area for adsorption process.

Table 1. Comparison of particle size result by Nanophox measurement

Data type	Sample ID	Milling time, [min]			
		0	5	10	15
Nanophox result, [μm]		0.581	0.297	0.272	0.262

3.1.3. SEM-EDS

Surface morphology analyses of zeolite alginate beads (ZAB), alginate beads (AB) and Pb(II) loaded beads (Pb-ZAB) are shown in Figure 3 with magnification of 100 and 1000. From the figure 3a, we observed that alginate beads observed with homogenous smooth surface while the surface of zeolite alginate beads were rough and consisted of irregular shaped coarse parts

(Figure 3b). After Pb(II) adsorption, surface of ZAB has changed into uniform structure and agglomerated particles observed as dot shaped structure separately (Figure 3c). Moreover, Energy Dispersive Spectroscopy (EDS) analyses showed that alginate beads sample given: Ca and Cl peaks only, zeolite alginate beads given: zeolite base components such as Si, Al, Fe, K and alginate component, Ca which represented in Figure 4. Since Si, Al, Fe, K are main component of natural zeolite, this EDS result confirmed that natural zeolite particles immersed into alginate beads. As shown in Figure 4, agglomerated dark particles observed on Pb-ZAB and these dark spot was given: zeolite base components peaks and multiple Pb peaks. This result proved that zeolite particles agglomerated on surface of alginate beads and ZAB composite could adsorb Pb(II) from aqueous solution. This morphology change may indicates that Pb(II) adsorption process occurred on surface of zeolite alginate beads.

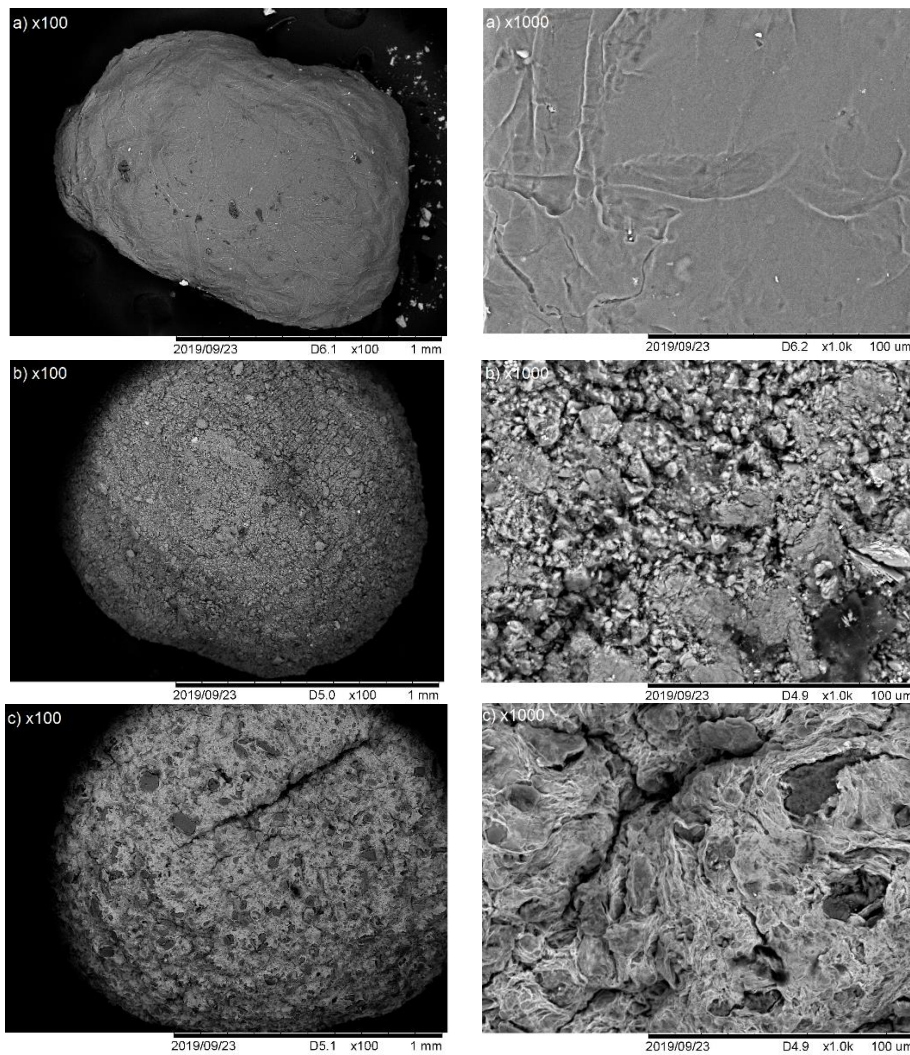


Figure 3. SEM image of beads (a) AB, (b) ZAB, (c) Pb-ZAB

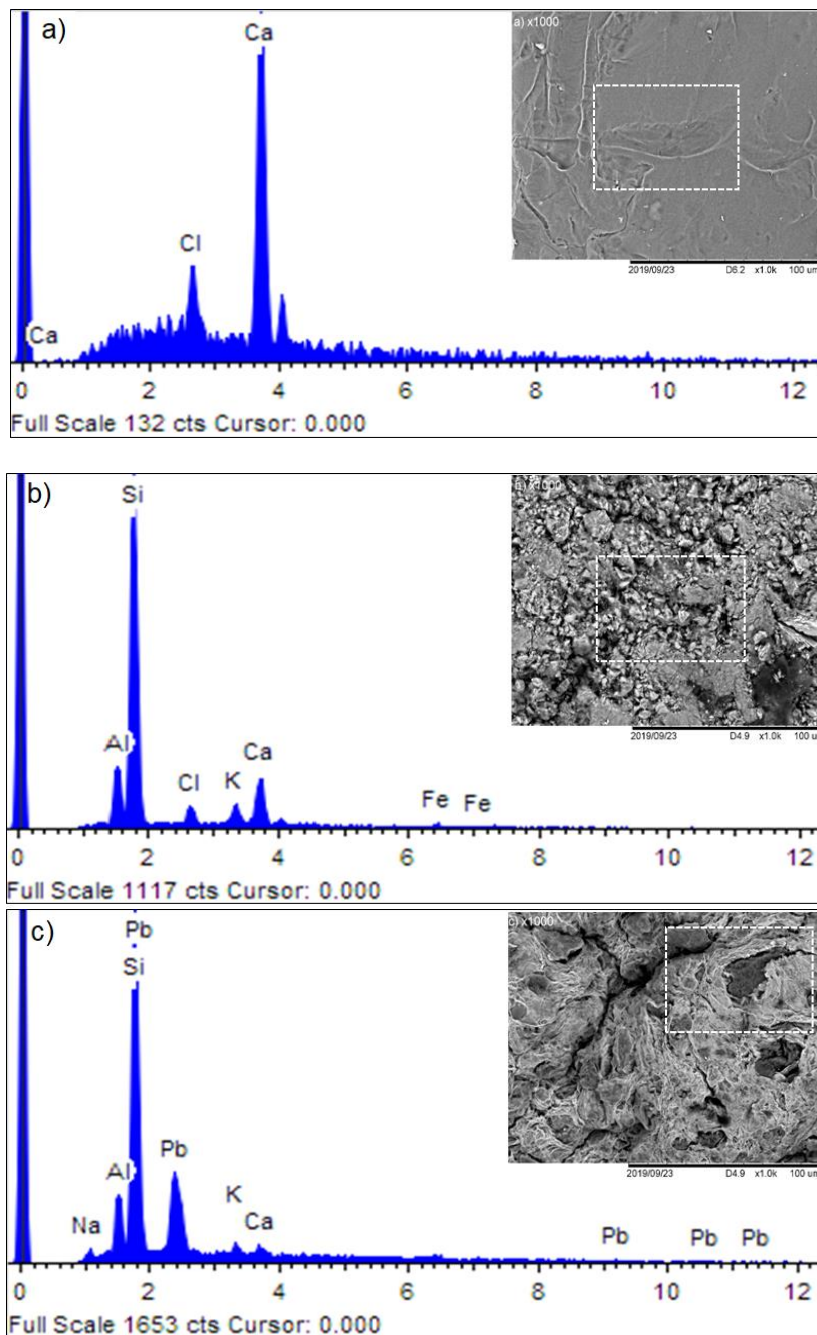


Figure 4. SEM-EDS image of beads (a) AB, (b) ZAB, (c) Pb-ZAB

3.1.4. FTIR

Alginate beads (AB), zeolite alginate beads (ZAB), and Pb(II) loaded zeolite alginate beads (Pb-ZAB) were investigated by FTIR which are shown in Figure 5. In AB spectrum, absorption peaks at 2850 and 2920 cm^{-1} showed C-H bonding vibration and absorption peak at 1590 cm^{-1} belonged

to C-O and C=O groups^{15,16}. The detected C-H, C-O and C=O bonds are included in alginate acid structure. In comparison to AB spectrum, one new peak at 1020 cm^{-1} , and broadband at 2980-3670 cm^{-1} observed in ZAB spectrum. The band at 1000-1032 cm^{-1} corresponds to Si-O-Si and Si-O-Al strong vibration which confirmed the presence of zeolite particle in ZAB. Band at 1420 cm^{-1} is assigned to stretching vibration of C=O group and peak at 1610 cm^{-1} is shifted peak of C-O and C=O groups. The broadband observed at 2980-3670 cm^{-1} indicates presence of H^+ or adsorption peak of OH^- . The peaks of Pb-ZAB were similar to ZAB peaks except C-H bonding observed at 2850 and 2920 cm^{-1} . Band at 1610 cm^{-1} shifted to 1580 cm^{-1} and 565 cm^{-1} shifted to 602 cm^{-1} . The similar peaks and intensity of ZAB and Pb-ZAB may explain that physical sorption occurred during adsorption process.

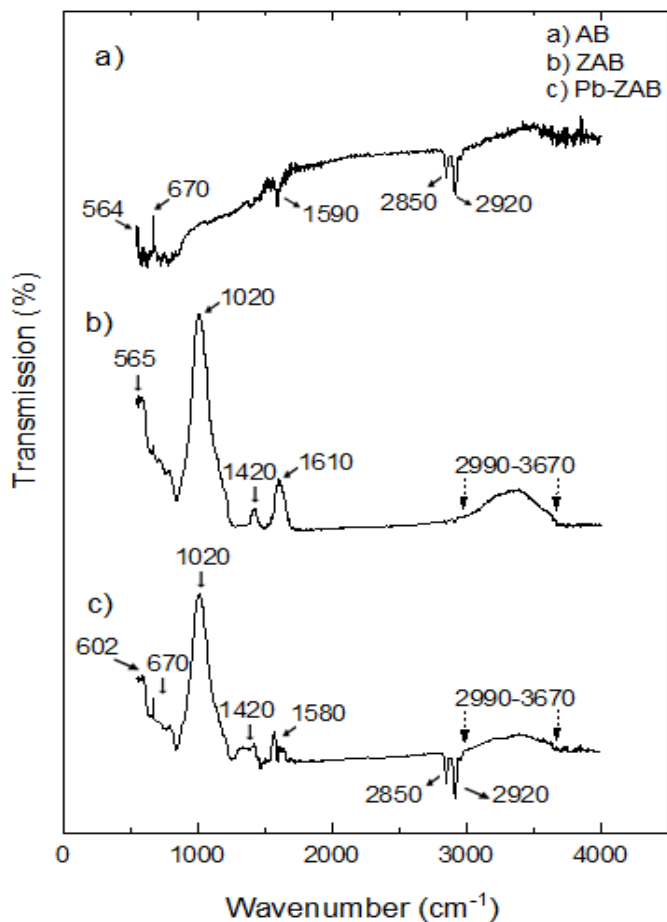


Figure 5. FTIR analyses of the beads, (a) AB, (b) ZAB, (c) Pb-ZAB

3.2. Adsorption studies

3.2.1. pH effect of adsorption

Experiments of pH effect is conducted in acidic condition (pH=2-5) because of natural zeolite adsorption behavior^{10,17} and precipitation of cations. Result of initial pH effect on adsorption is showed in Figure 6a. However there is slightly difference of Pb(II) removal in conducted pH values, zeolite alginate beads were given higher adsorption amount at initial pH=3 and after adsorption process, initial pH values increased 2.3 to 5.53 respectively (Figure 6b). In acidic condition, natural zeolite and calcium alginate's surface is protonated and it means there is competition between H⁺ ion and Pb²⁺ cation during adsorption reaction. Increase of initial pH value after adsorption process explained that Pb²⁺ cation dominated H⁺ ion and could sorb on surface of zeolite alginate beads. In the result, released OH⁻ tends to increase initial pH value of the solution. As it is shown in Figure 6c, removal efficiencies were all above 95% in all conducted pH ranges which means lower initial pH value of solution is favorable condition of zeolite alginate adsorbent.

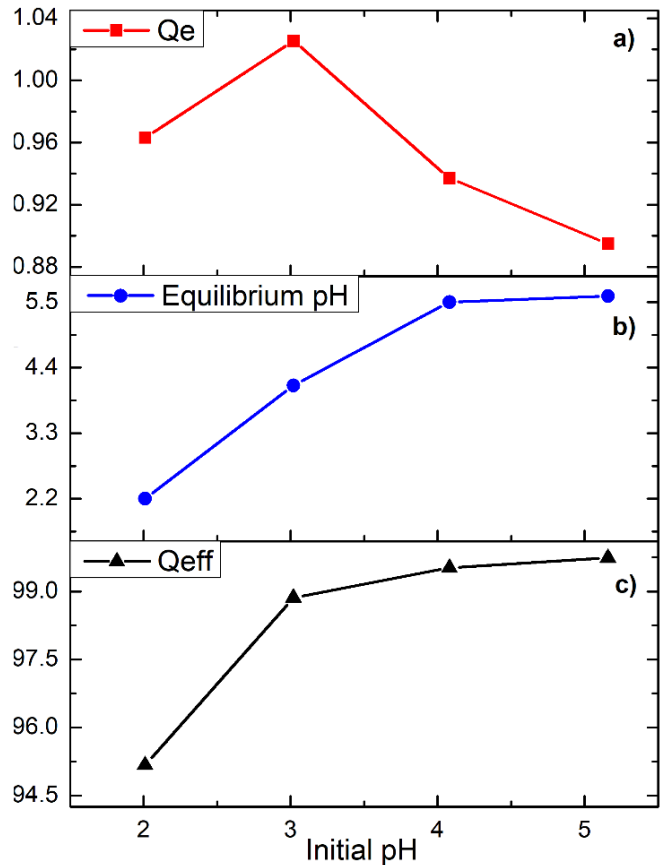


Figure 6. a) Initial pH influence on Pb(II) adsorption amount, b) Initial pH change after adsorption c) Initial pH influence on Pb(II) adsorption efficiency

3.2.2. Effect of contact time

Contact time of adsorption experiment was carried out in order to investigate maximum contact time for efficient Pb^{2+} removal in 0.5 - 24h range with initial concentration of 100 ppm. From the figure 7, adsorption amount was increased drastically from 8 h with adsorption amount of 24.57 mg/g and stabilized from 16 h with 30.57 mg/g and further increased slightly up to 31.79 mg/g at 20 h. Therefore, 20 h was found to be the most effective contact time to obtain maximum adsorption amount of Pb(II) for ZAB from aqueous solution.

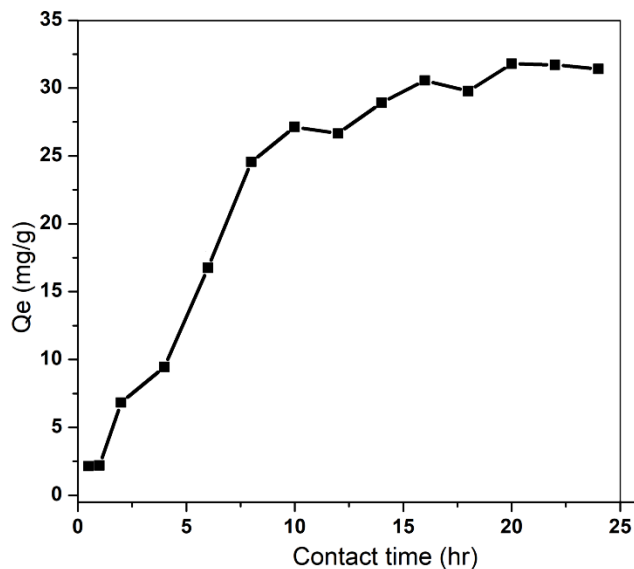


Figure 7. Effect of contact time of ZAB

3.2.3. Adsorption capacity

Zeolite alginate beads contacted with Pb(II) solution with initial concentration of 10-500 ppm. As shown in Figure 8, obtained highest adsorption amount of Pb(II) was 87.47 mg/g at initial concentration of 500 ppm. According to adsorption isotherm calculation, ZAB composite was fitted with Langmuir isotherm which indicated that adsorption process is occurred at monolayer of ZAB adsorbent. The calculation of Langmuir and Freundlich isotherm model is tabulated in Table 2 and Langmuir theoretical calculation of maximum adsorption amount was 149.3 mg/g. We found out that calcium cation was released into solution after adsorption process. Calcium initial concentration was 3.18 – 3.54 mg/L in the solution before adsorption process and it increased to 69.14 mg/L after adsorption process.

Table 2. Langmuir and Freundlich isotherm model parameters of Pb(II)

Sample ID	Langmuir Model			Freundlich Model		
	Q _{max}	K _l	R ²	K _f	n	R ²
Zeolite alginate beads	149.3	0.003	0.993	0.770	1.26	0.932

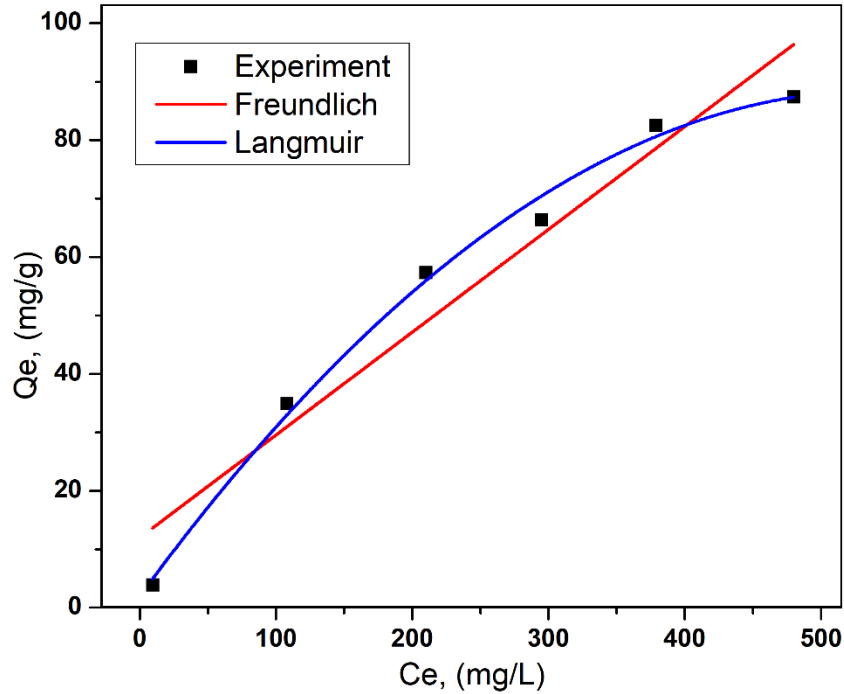


Figure 8. Adsorption isotherm of ZAB

3.2.4. Adsorption mechanism

Heavy metals adsorption ability of natural zeolite is explained by several mechanisms such as ion exchange, surface precipitation and pore impregnation due to its cation exchange properties, high surface area, and porous channel, respectively. Alginate polymer could adsorb divalent cations by their carboxyl group or hydroxyl group and cation exchange with calcium ion^{16,18,19}. Therefore, zeolite alginate beads' adsorption process can be explained by several complex mechanism not sole reason. In this study, we considered 2 adsorption mechanisms: cation exchange and surface precipitation. The result of adsorption isotherm is confirmed that Pb(II) adsorption was occurred on monolayer of adsorbent. Additionally, there was no significant change of functional group in FTIR analyses which considered as physical adsorption process occurred on surface. After adsorption process, detected calcium peak intensity was decreased on SEM-EDS. We revealed that calcium cations released into solution from zeolite alginate beads after adsorption experiments. Released calcium concentration was increased with adsorbed amount of Pb(II).

Therefore, cation exchange between calcium and Pb(II) was occurred during adsorption.

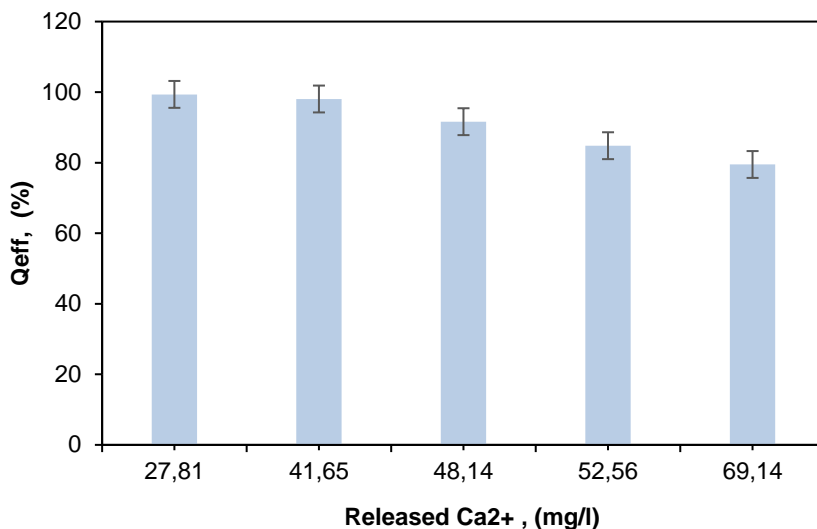


Figure 9. Released calcium amount after adsorption process

4. Conclusion

In this work, we used natural clinoptilolite sample obtained from Mongolia. Our result suggests that simple mechanical modification could increase arrangement, and crystallinity. Particle size of natural zeolite was decreased from 0.581 to 0.262 μm . Milled zeolite sample was used for preparation of alginate composite beads which prepared by extrusion technique. Zeolite alginate beads' highest adsorption amount was 87.47 mg/g and the equilibrium time of adsorption was 20 hours in acidic condition. Adsorption mechanisms of zeolite alginate beads assumed as cation exchange and surface precipitation confirmed by adsorption isotherm, SEM-EDS and FTIR result. In conclude zeolite alginate beads material can be cheap and effective material for practical application. Further study, regeneration of zeolite alginate beads will be investigated.

Acknowledgments

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