THE REMOVAL OF Cu(II) BY MODIFIED ZEOLITE FROM AQUEOUS SOLUTION

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Abstract

In this work, the removal of copper (II) from an aqueous solution using zeolite modified with silicon organic monomer (3-aminopropyltriethoxylane) was carried out depending on pH, time, temperature, and initial concentration of Cu (II) ions. The modification result was confirmed by instrumental analysis (XRD, BET, and FT-IR). The maximum adsorption capacity of the modified zeolite for Cu (II) was determined as 4.25, 7.97, 10.33, and 22.27 mg/g at the optimal condition (pH=5, t=8 hours, T=45°C) when the initial concentration of Cu(II) was 50, 100, 200, and 400 mg/l, respectively.

Introduction

Mongolia is a country with limited water resources and is ranked 22nd out of 145 countries in the world in terms of freshwater resources [1].

Nowadays, water containing heavy metals and chemicals is produced a lot in the environment due to technological and industrial rapid development. The primary resources of wastewater containing heavy metals are leather, wool and cashmere, paints, mining, and the metallurgy industry. Water is pollute d with heavy metals such as chromium, lead, copper, mercury, and nickel can cause cancer in the human body, and affect ecosystem imbalances [2-4]. Copper, one of these heavy metals, can cause brain and kidney damage in humans and living organisms, cirrhosis, chronic anemia, and gastrointestinal disorders. There is a need to treat wastewater to protect the environment and human health [5, 6].

The chemical precipitation, ion exchange, precipitation, membrane separation, reverse-osmosis , and adsorption methods are used to remove heavy metals from wastewater. From these methods, the adsorption method is the most selective and efficient if the cost of the adsorbent can be reduced [6]. Mongolia has several deposits of natural zeolite reserves. In this study, zeolite from the Tsagaantsav deposit was used as a base material. The zeolite sample was modified with silicon-organic monomer (3-aminopropyltriethoxylane) which contains amino groups with advantages such as high reactivity, low toxicity, simple structure, and low cost [10]. The purpose of this study is to investigate the properties of modified zeolite and study the adsorption properties of Cu(II) on the modified zeolite.

Methods And Materials

Modification of natural zeolite: The modification experiment was performed in two main stages: (1) pretreatment of natural zeolite sample and (2) modification with silicon-organic monomer, 3-aminopropyltriethoxysilane. The first stage: The sample was crushed and sieved to a particle size range of 0.45-0.3 mm. The sieved zeolite sample was heated in a muffle furnace at 700℃ for 3 hours to activate the surface. The temperature of 700℃ had chosen based on chemical and mineral composition of the natural zeolite [11]. Then the activated sample was washed three times with hydrochloric acid solution (5%) and distilled water, respectively, to remove fine powders and contaminants. Then dried at 110℃ for 2 hours [12].

At modification stage: 10 g of pretreated zeolite was added into 100 ml of 3-aminopropyltryethoxycylane solution (vol. 30% in toluene) and stirred for 3 hours at a temperature of 50℃. Then, the mixture was filtered, the solid residue was washed several times with distilled water and dried in the oven for 4 hours at 110℃. The modified zeolite was cooled on a vacuum desiccator for further use [13].

Adsorption experiment: Modified zeolite was thoroughly mixed with 50 ml solution of a known amount of Cu(II) in 200 ml conical flask, and the suspension was shaken in a temperature-controlled stirrer. After equilibrium, the mixture was filtered and the filtrate was analyzed to determine the remaining metal ion concentrations. Cu(II) were analyzed by ICP-OES (ICP-OES 7300DV).

Results

Effect of pH: The maximum value of the adsorption capacity of modified zeolite is 7.430 mg/g at pH = 5, which is higher than adsorption capacity of the natural zeolite, 5.4 mg/g. When the pH increased from 5, the adsorption capacity was decreased presence of Cu(II) ions species in the aqueous solution. Therefore, pH=5 was chosen as the optimal condition for the adsorption studies of modified zeolite.

Effect of initial concentration and time: The effect of time on the absorption process of modified zeolite Cu (II) at pH = 4.5 was studied using solutions with initial concentrations of 50, 100, 200, and 400 mg/l of Cu (II). The result shows that the increase of the adsorption capacity is rapid in the first 30 minutes and slow during the next 8 hours, then it becomes constant (Figure 1).

Effect of temperature: The effect of temperature on the adsorption capacity of modified zeolite was investigated at 25°C, 35°C, 45°C and, 55°C at optimum pH with different initial metal ions concentrations (Figure 2). The adsorption capacity was increased for Cu (II) adsorption with a rise of temperature from 25 to 55°C. It is further evidence of an endothermic reaction, where heat input enhances the adsorption performance.

Effect of common cations: To investigate an effect common cations, the experiment conducted under optimized pH (pH=5), contact time (i.e., 8 hours) using several concentration of Na^+, K^+, Ca^{2+}, or Mg^{2+} and combination of all 4 cations (i.e., 0, 10, 20, 50,100, and 200 mg/l). The adsorption capacity decreased by 0.5 mg/g approximately in the presence of common cations concentration increase (Figure 3). The adsorption capacity decrease was by 1.3 mg/g (20%) for the combination of all 4 cations with concentrations of 100 and 200 mg/l.

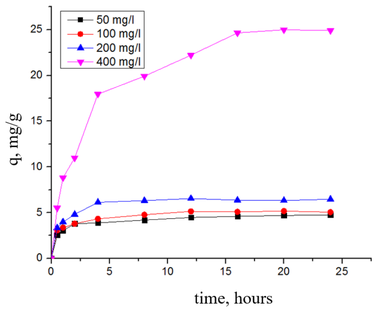

Figure 1. Effect of initial concentration and time on the adsorption capacity [pH=5, T=25°C, n =100 rpm]

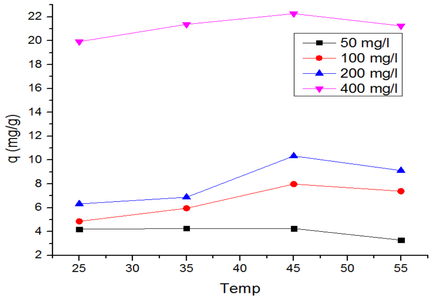

Figure 2. Effect of temperature on the adsorption capacity [pH=5, t=8 h, n=100 rpm]

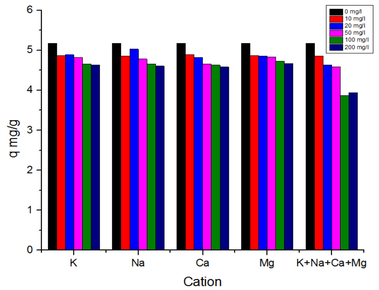

Figure 3. Effect of common cations on the adsorption capacity [pH=5, t=8 h, T= 250C, n=100 rpm]

Discussion

Characterization of natural and modified zeolite

XRD pattern showed that natural zeolite is dominated by clinoptilolite-type zeolites[14-18]. However, after the modification, the intensities of the most peaks were decreased, indicating the zeolite surface may be functionalized by 3-aminopropyltriethoxysilane [18].

The surface property of natural, pretreated, and modified zeolite was analyzed by N2 adsorption, and the result of the adsorption/desorption isotherm is shown in Table 1. The BET surface areas of natural, pretreated, and modified zeolite were 22.79, 18.28, and 9.06 m^2/g, respectively and the corresponding pore volumes were 0.058, 0.053, and 0.035 cm^3/g.

The typical peaks of FT-IR spectra of the natural and modified zeolite were found at 3620 cm^{-1} (Si-OH), 3463 cm^{-1} (OH) [18], 1642 cm^{-1} (corresponding to water molecules associated with the cations in zeolite structure) [19]. The peaks corresponding to Si-O, Al-O bond in the SiO_4 and AlO_4 tetrahedral at 1052 cm^{-1}, the peaks corresponding to Si-O-Si and Al-O-Al bond at 459 and 796 cm-1 were detected.

Table 1. The surface property of natural, pretreated, and modified zeolite

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Natural zeolite	22.79	0.058	10.188
Pretreated zeolite	18.28	0.053	11.597
Modified zeolite	9.06	0.035	15.243

Conclusions

Natural zeolite was modified with 3-aminopropyl tryethoxylane successfully, the results were confirmed by instrumental analysis. Copper ions (II) can be interacted with OH, and NH_2 functional groups of the modified zeolite. The maximum adsorption capacity of the modified zeolite for Cu (II) was determined as 4.25, 7.97, 10.33, and 22.27 mg/g at the optimal condition (pH=4.5, t=8 hours, T=45˚C) when the initial concentration of Cu (II) was 50, 100, 200, and 400 mg/l, respectively.

Future Directions

To confirm the adsorption mechanism, further investigation on the adsorption kinetics, thermos-dynamics, and isotherm studdies are needed.

Contact Information

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