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## Removal of As(V), Cr(VI) and Pb(II) from aqueous solution using surfactant-modified Sabzevar nanozeolite

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### ABSTRACT

The pollution of water environments is a challenging issue especially in developing countries. Contamination of drinking water with heavy metals has been reported in many parts of the world. Arsenic, chromium and lead are dangerous heavy metals and also common contaminants of drinking water. In this study, the capacity and performance of the surfactant-modified Sabzevar natural nanozeolite (SMSNZ) on the removal of heavy metals from an aqueous solution was investigated. Initially, the appropriate concentration of hexadecyltrimethylammonium bromide HDTMA-Br solution for modification was investigated; it was found that it must be higher than the critical concentration micelle (CMC). Then, the removal of As (V), Cr (VI), and Pb(II) from an aqueous solution was studied using SMSNZ. The results indicated that the removal efficiency was very high in different initial concentrations of heavy metals. The Linear, Langmuir and Freundlich isotherm models were used to investigate the adsorption equilibrium of the surfactant-modified natural zeolite for heavy metals adsorption. The results showed that the Linear isotherm is a better fit for the three studied heavy metals.

### 1. Introduction

Arsenic, chromium and lead are heavy metals which are potentially toxic environmental pollutants. One important feature that distinguishes heavy metals from other pollutants is that the former are non-biodegradable. Once metal ions enter the environment, their chemical form largely determines their potential toxicity [1]. Arsenic has a serious impact on human health and causes problems such as skin, lung, urinary bladder, liver and kidney cancers [2]. Dangerous concentrations of arsenic in natural water is now a worldwide problem and is often referred to as a 20<sup>th</sup>-21<sup>st</sup> century calamity [3]. This heavy metal exists in the environment in different oxidation states and in various forms, e.g., As, As(III), As(V), As(0), and As(-III). This element presents a major problem as it cannot be easily destroyed and can only be converted into different forms or transformed into insoluble compounds in combination with other elements such as iron [4]. The Maximum Contamination Level (MCL) of arsenic in water is 10 µg/L as

established by the World Health Organization (WHO) [5]. Chromium is a redox active metal element in the environment which usually exists as Cr(III) or Cr(VI). Cr(VI) may be found in the form of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), hydrochromate ( $\text{HCrO}_4^-$ ), or chromate ( $\text{CrO}_4^{2-}$ ). Cr(III) in aqueous solutions, however, may take the form of  $\text{Cr}^{3+}$ ,  $\text{Cr}(\text{OH})_2^+$ , or  $\text{Cr}(\text{OH})_2^+$ . Hexavalent chromium is more toxic to living organisms than Cr(III). Chromium(VI) is on the US EPA priority list of toxic pollutants and is present in electroplating wastewater and many other industrial discharges [1]. In epidemiological studies, an association has been found between lung cancer and exposure to Cr(VI) through inhalation. The International Agency for Research on Cancer has categorized pentavalent chromium in Group 1 which includes substances that are carcinogenic to humans (World Health Organization, 2004) [6]. The MCL of hexavalent chromium in drinking water is 100 µg/L [5]. Another contaminant investigated in this research is lead, which is not only an issue in developing countries. In Japan, lead piping has been widely used

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because it is inexpensive and easy to fabricate. This has resulted in lead seeping into tap water and has raised concerns in the society [7]. Lead disturbs hemoglobin synthesis and renal function as well as causing neurological and behavioral disturbances in children. Even low blood lead concentrations have been associated with intellectual impairment in children [8]. The MCL of lead in drinking water established by the WHO is 10 µg/L [5]. Zeolites are a widely used adsorbent for water treatment. Zeolites are hydrated alumina silicate made from the interlinked tetrahedral of alumina (AlO<sub>4</sub>) and silica (SiO<sub>4</sub>) and form with many different crystalline structures which have large open pores (sometimes referred to as cavities) in a very regular arrangement. The framework structure and high surface area of zeolites traps molecules in a cage-like structure. The widespread use of zeolites involves both types, natural and synthetic. Zeolites were first discovered at the end of the 18<sup>th</sup> century and came to prominence in the 1960's when synthetically produced zeolites were employed in large industrial applications as molecular sieves for filtration purposes and as catalysts in the cracking of crude oil [9]. In this study, we utilized natural zeolite from the Chahtalkh region surrounding the Sabzevar area in Iran as an adsorbent. Natural zeolites are abundant and low cost resources, which are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water, alkali and alkaline earth cations. Due to their high cation-exchange ability as well as their molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification processes in past decades [10]. More than 40 natural zeolites have been identified during the past 200 years. Zeolites are distinguished by the differences in their chemical compositions and the size and arrangement of their crystal structures [11]. Clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime and laumontite are very common forms whereas offretite, paulingite, barrerite, and mazzite are much rarer [16]. Working with zeolites in nanoscale depicts the significant properties of nanozeolites in comparison to typical zeolites. Nanoscience and nanoporous materials are currently attracting attention from many researchers. Microporous materials with nanometer particle size (nanozeolites) are being studied because of their outstanding properties that could not be found in the micrometer zeolites. Reducing the particle size from a micrometer to a nanometer scale leads to a significant change in material characteristics and their applications in catalysis and adsorption. The number of atoms in the unit cell increases when particle sizes decrease and nanozeolites have a large external surface area. The diffusion path length in nanozeolites is shortened as compared to that in the conventional micrometer zeolites [12]. The use of nanoscale zeolites means a reduction in weight, smaller cross sections, enhanced adsorption/desorption kinetics, and a higher

overall efficiency of the entire system [9]. Although natural zeolites have been widely used to remove cationic heavy metals in aqueous solutions, they are not useful for removing inorganic oxyanions such as chromate (CrO<sub>4</sub><sup>2-</sup>). Moreover, As, Cr and Pb exist in an anion form over a broad range of pH. The external surface charge of natural zeolites could be altered with a surfactant to make it possible to adsorb heavy metals and their oxyanions as well [13, 19]. In this study, HDTMA-Br was chosen as a cationic surfactant due to its high stability and proper interactions with the SMSNZ surface. Since the performance of surfactant on a zeolite surface is directly related to Critical Micelle Concentration (CMC), it was important to use the proper concentration of surfactant with respect to its CMC [15]. The structural formula of the used surfactant is shown in Figure 1.

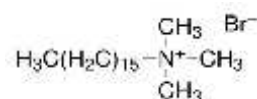


Fig. 1. Structural formula of HDTMA-Br

## 2. Materials and methods

### 2.1. Materials

The hexadecyltrimethylammonium bromide (HDTMA-Br) with a purity >99% was supplied by A-3, Okhala Industrial Area, New Delhi. The Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O (>98%) was purchased from Sigma-Aldrich while the Pb(NO<sub>3</sub>)<sub>2</sub> was provided by Merck, KGaA, Darmstadt, Germany and the K<sub>2</sub>CrO<sub>4</sub> was obtained from E. Merck, Darmstadt, Germany. Natural nanozeolite was prepared from the area of Sabzevar, Iran. All the chemicals used in this research were of analytical grade.

### 2.2. Surfactant concentration

Before choosing the best concentration of surfactant for removal, a pretest was conducted with three concentrations of surfactant. The CMC (Critical Micelle Concentration) of HDTMA-Br was 1.8 mmol/L [15]. The three concentrations included the following: lower than the CMC (0.5 mmol/L), nearly equal to CMC (2 mmol/L), and higher than CMC (30 mmol/L). The natural nanozeolite modified with these concentrations were used for treating the 1 mg/L arsenate solution. The results of the pretest are shown in Table 1.

**Table 1.** Removal efficiency of As from aqueous solution using nanozeolites that were modified with different concentrations of surfactant

Surfactant Concentration	Removal Efficiency (%)
0.5	47.5
2	57.0
30	79.0

### 2.3. Preparation of nanozeolite

The nanozeolite was manufactured using a ball mill. 10 g of nanozeolite powder was dissolved in 100 mL of 0.03 mol/L HDTMA-Br solution for surface modification. The resulting suspension was shaken for 24 h at 30°C and 150 rpm. The solid phase was separated by centrifuging and was rinsed in distilled water. The nanozeolites were dried for 48 h at 100°C and kept in the desiccator to prevent moisture adsorption. Figure 2 shows the nanozeolite after modification.



Fig. 2. Surfactant-modified Sabzevar nanozeolite

### 2.4. Removal procedure

Different concentrations of As, Pb and Cr solution were prepared using  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{K}_2\text{CrO}_4$ , respectively. For instance, the initial arsenate solution with a concentration of 10 mg/L was prepared by dissolving a sufficient amount of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  in 1000 mL of deionized water. Then the solutions with concentrations of 0.2, 0.5, 1, 2 and 5 mg/L were prepared by dilution; 0.5 g of surface modified natural nanozeolite was added to 10 mL of each solution. The batch process of heavy metal removal by SMSNZ was conducted under the following conditions: SMSNZ dosage of 50 g/L, 30°C, 150 rpm, and 24h. After the separation of nanozeolite by centrifuging at 3000 rpm for 10 minutes, the heavy metal concentration in supernatant was measured by atomic adsorption.

## 3. Results and discussion

In this study, we increased the interaction time and amount of nanozeolite in comparison to similar works in this field. Our aim was to attain the highest removal for each pollutant concentration. The adsorption percent showed that this technique was able to adsorb high levels of the mentioned ions. As(V), Cr(VI) and Pb(II) exist mainly in anion form over a wide range of pH [13]. The surface of natural zeolite has a negative charge because of its structure. For the adsorption of anion, it must be modified by cationic agents [14]. In this study, HDTMA-Br was used for modification. Three concentrations of surfactant were used for the modification of zeolite and their removal efficiency of As was investigated. The results (Table 1) showed that the removal efficiency was higher at a

concentration of the higher CMC (>CMC). Modification with this concentration formed a bilayer on the surface of zeolite and the charge on the zeolite surface was reversed from negative to positive [15]. As shown in the Figure 3, in modifications with concentrations equal to or lower than the CMC, monolayer forms on the surface of zeolite. Also, its surface charge was negative and caused a decrease in the amount of removal efficiency. Therefore, modification with higher CMC of surfactant was selected for the following study. The adsorption of heavy metal from an aqueous solution by SMSNZ in different initial concentrations of heavy metal (0.2-5 mg/L) was investigated. Figure 4 shows the results of this survey in terms of removal efficiency and adsorption capacity. According to this figure, SMSNZ can significantly remove heavy metal in different initial concentrations and the adsorption capacity of SMSNZ was about 0.1 mg/g for each of the heavy metals. Also, it indicated that the removal efficiency of Pb was higher than the two other studied heavy metals under the same condition. The equilibrium experimental data were fitted with three isotherm models, Linear, Langmuir and Freundlich. The parameters of these models can be determined by linear regression of the experimental data. The correlation coefficients ( $R^2$ ) of models for three heavy metals are summarized in Table 2. The higher values of  $R^2$  for the Linear isotherm indicated a better fitness of the Linear isotherm to the experimental data. First,  $q_e$  (mg/g) is defined as the amount of adsorption at equilibrium. In fact,  $q_e$  depicts the mg of adsorbate removed by 1gr of adsorbent. It was calculated by the mass balance equation [18]:

$$q_e = C_0 - C_e \frac{V}{m} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations (mg/L),  $V$  is the volume of solution (mL), and  $m$  is the adsorbent weight (g). The adsorption percent was calculated using the equation below [18]:

$$\text{Adsorption}\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

The logarithmic form of the Freundlich equation could be written as:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

where  $q_e$  is the adsorption amount at equilibrium (mg/g),  $K_F$  is the Freundlich constant related to adsorption capacity (mg/g)(L/g)<sup>nF</sup>,  $C_e$  is the equilibrium concentration in solution (mg/L), and  $n$  is reaction energy. The term  $1/n$  shows the curvature in the isotherm and may represent the energy distribution of the adsorption site [6, 18]. The linear form of Freundlich could be written as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

The Linear isotherm would be written as:

$$q_e = K_L C_e \quad (5)$$

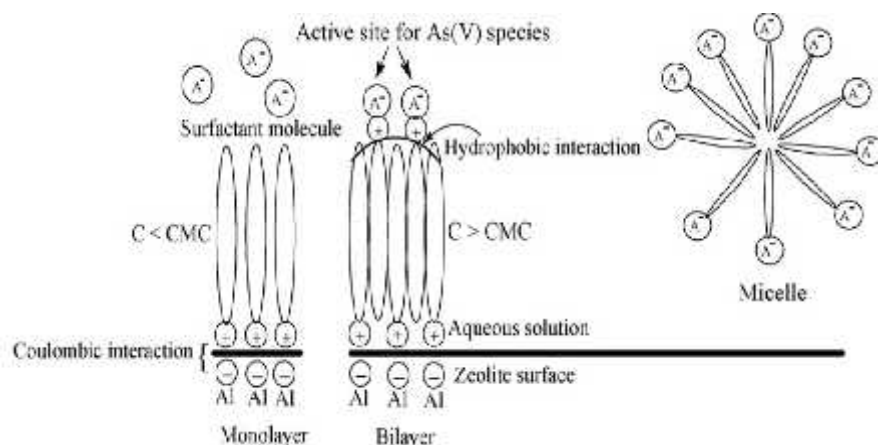


Fig. 3. The effect of surfactant on zeolite surface for higher and lower CMC [17]

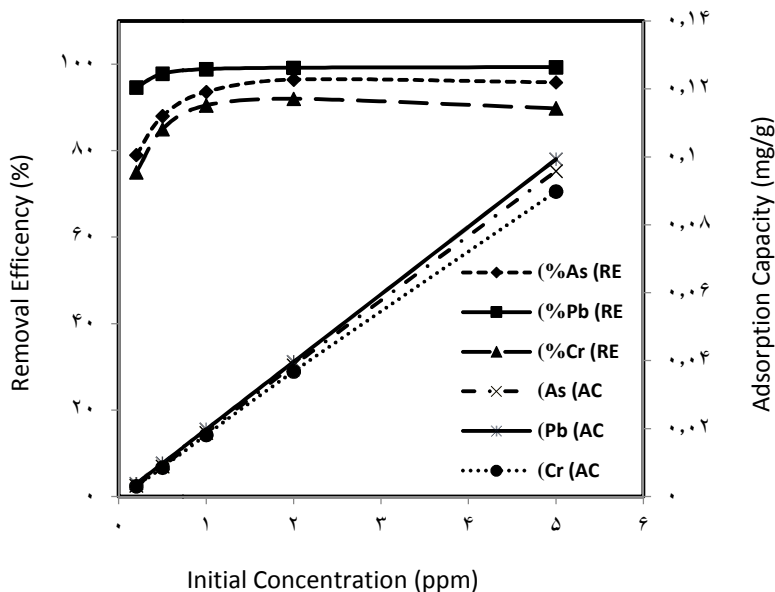


Fig. 4. Removal efficiency and adsorption capacity results for different initial concentration of arsenic, chromium, and lead solutions

Table 2. Correlation coefficients ( $R^2$ ) of Linear, Langmuir and Freundlich isotherms for heavy metal adsorption from aqueous solution by surfactant-modified Sabzevar nanozeolite

Heavy Metals	Isotherm Models	Correlation Coefficients ( $R^2$ )		
		Linear	Langmuir	Freundlich
As (V)		0.9411	0.713	0.792
Cr (VI)		0.9746	0.8463	0.9017
Pb (II)		0.977	0.4321	0.7664

4. Conclusions

Natural nanozeolite from the Sabzevar area was used for the removal of As, Cr and Pb from aqueous solutions. It was modified by HDTMA-Br. The results showed that

modification with a surfactant dosage higher than CMC had a higher removal efficiency because of the formation of bilayer on the surface of the zeolite and a change in the surface charge of the zeolite. The study of heavy metal adsorption by surfactant modified Sabzevar nanozeolite in different initial concentrations of heavy metal resulted in

the significant adsorption of heavy metal from aqueous solutions. Considering the accessibility of natural zeolites and their capability to remove heavy metals, the use of these adsorbents in future research is recommended.

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