ADSORPTION OF ARSENATE BY HEXADECYLPYRIDINIUM BROMIDE MODIFIED NATURAL ZEOLITE

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Specially dedicated to my beloved mother and father…

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ABSTRACT

The presence of arsenate (As(V)) anions in various sources of water is a prominent issue since the toxicity of this species can result in death if this species are taken either over a long period of time or present in high concentrations. In this study, a natural zeolite of the mordenite type was modified by cationic surfactant hexadecylpyridinium bromide (HDPB) to make more efficient sites for adsorption of As(V) from aqueous solutions. The natural zeolite and surfactant-modified natural zeolite (HDPB-zeolite) were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectrometer (FTIR), and BET specific surface area. The analysis of XRD revealed that the natural zeolite consists of quartz and mordenite phases, while the FTIR analysis revealed that HDPB cations has been incorporated into the natural zeolite's structure via electrostatic interaction and van der Waals forces. The results showed that the unmodified natural zeolite had little affinity for the As(V) anionic species, while the HDPB-zeolite showed significant ability to remove this anion from the aqueous solutions. The highest arsenates adsorption efficiency was obtained from the solution of pH 7 because of the dominance of the univalent species of anion. The adsorption equilibrium data were analyzed by both Freundlich and Langmuir isotherm models and the data were best fitted with the Freundlich isotherm model. The study concluded that the HDPB-zeolite can be used as alternative sorbent to remove As(V) species from water.

ABSTRAK

Kehadiran anion arsenat (As(V)) dalam pelbagai sumber air adalah isu yang terkenal semenjak ketoksikan spesies ini boleh mengakibatkan kematian jika spesies ini diambil sama ada dalam tempoh masa yang panjang atau hadir dalam kepekatan yang tinggi. Dalam kajian ini, zeolit semulajadi daripada jenis mordenit telah diubahsuai oleh surfaktan kationik heksadesilpiridinium bromida (HDPB) untuk membuat tapak permukaan yang lebih berkesan untuk penjerapan As(V) dalam larutan akueus. Zeolit semulajadi dan zeolit semulajadi yang telah diubahsuai dengan surfaktan (HDPB-zeolit) telah dibuat penciriannya dengan XRD, FTIR, dan luas permukaan spesifik. Analisa XRD menunjukkan bahawa zeolit semula jadi terdiri daripada fasa kuartza dan mordenit, manakala analisa FTIR mengesahkan bahawa kation HDPB bergabung dengan struktur zeolit semulajadi melalui interaksi elektrostatik dan daya van der Waals. Hasil kajian menunjukkan bahawa zeolit semulajadi yang tidak diubahsuai mempunyai afiniti yang kecil terhadap As(V), manakala HDPB-zeolit menunjukkan penyingkiran yang ketara terhadap spesies ini. Kecekapan penjerapan tertinggi terhadap As(V) telah diperolehi daripada larutan As(V) pada pH 7 disebabkan oleh dominasi spesies univalen anion. Data keseimbangan penjerapan telah dianalisa oleh model Freundlich dan Langmuir, dan didapati data tersebut berpadanan dengan model Freundlich. Kajian ini menyimpulkan bahawa HDPB-zeolit ini boleh digunakan sebagai penjerap alternatif untuk penyingkiran As(V) daripada air.

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LIST OF SYMBOLS

°C	-	Degree Celcius
C_o	-	Initial concentration
C_e	-	Equilibrium concentration
cm	-	Centi meter
dm	-	Deci meter
g	-	Gram
kg	-	Kilo gram
kV	-	Kilo Volt
L	-	Liter
m	-	Meter
M	-	Molar
mA	-	Mili ampere
meq	-	Mili equivalent
mg	-	Mili gram
min	-	Minute
mL	-	Mili liter
mm	-	Mili meter
mmol	-	Mili mol
N	-	Normal
nm	-	Nano meter
ppm	-	Part per million
ppb	-	Part per billion
Å	-	Angstrom
µg	-	Micro gram
µL	-	Micro Liter

LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
ASTM	-	American Society for Testing and Materials
BET	-	Brunauer, Emmet, and Teller
CCA	-	Chromated Copper Arsenate
CEC	-	Cation Exchange Capacity
CMC	-	Critical Micelle Concentration
DDTMA	-	Dodecyltrimethyl Ammonium
ECEC	-	External Cation Exchange Capacity
EPA	-	Environmental Protection Agency
FAAS	-	Flame Atomic Absorption Spectroscopy
FTIR	-	Fourier Transform Infrared
HDPB	-	Hexadecylpyridinium Bromide
HDPB-zeolite	-	Hexadecylpyridinium Bromide Modified Zeolite
HDTMA	-	Hexadecyltrimethyl Ammonium
IR	-	Infrared
LEDs	-	Light Emitting Diodes
LOI	-	Loss of Ignition
MCL	-	Maximum Contaminant Levels
ODTMA	-	Octadecyltrimethyl Ammonium
OTS	-	Octadecyltrichlorosilane
SMNZ	-	Surfactant Modified Natural Zeolite
SMZ	-	Surfactant Modified Zeolite
TDTMA	-	Tetradecyltrimethyl Ammonium
TEA	-	Tetraethyl Ammonium
WHO	-	World Health Organization
XRD	-	X-Ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

In the era of globalization, water pollution caused by disposal of heavy metals continues to be of great concern all over the world. With the rapid development in various industries, large quantities of wastewater have been produced from industrial processes and have been released into the soil and water systems. Therefore, polluted industrial wastewater treatment remains a topic of global concern since wastewater collected from the industries as well as communities must be returned to the receiving waters or land (Weber *et al.*, 1991).

There are many heavy metals pollution occurs in industrial wastewater such as that produced by metal plating facilities, battery manufacturing processes, mining operations, the ceramics and glass industries, and the production of paints and pigments. Normally, this wastewater includes cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), nickel (Ni), arsenic (As), and chromium (Cr) (Argun and Dursun, 2008).

Arsenic in groundwater is mostly due to the minerals dissolving naturally from weathered rocks and soils. In addition, it has many industrial applications and is also used extensively in the production of agricultural pesticides (Menhage-Bena *et al.*, 2004; Shevade and Robert, 2004). The increased levels of various forms of soluble arsenic in water are a result of the excess of consumption and arsenic leaching from generated waste.

The use of of water contaminated by arsenic can cause various skin and internal organs diseases (Elizalde-Gonzalez *et al.*, 2001; Menhage-Bena *et al*., 2004; Shevade and Ford, 2004). When the natural environments are exposed to toxic heavy metals, the accumulation of metal ions in the human body will occur either through direct intake or food chains. Thus, heavy metals should be prevented from reaching the natural eco-system (Meena *et al.,* 2008). In order to remove toxic heavy metals from water systems, many conventional methods have been used such as chemical precipitation, ion exchange, coagulation, solvent extraction and filtration, evaporation and membrane methods (Panayotova and Velikov, 2003). Conventional adsorbents such as activated carbon have been used extensively in many applications as an effective adsorbent for adsorption of heavy metals, and the most widely used adsorbent is the activated carbon produced by carbonizing organic materials. However, the activation process that requires high costs has restricted its use in wastewater treatment applications (Amarasinghe and Williams, 2007).

Recently, in order to produce the surfactant-modified zeolite (SMZ) for the adsorption and removal of many types of contaminants in water, clinoptilolite is the natural zeolite that is mainly used. The use of this zeolite has been working successfully for that purpose. The studies on the use of SMZ from clinoptilolite for environmental remediation were limited to the removal of organic contaminants from water until Haggerty and Bowman (1994) showed that the sorption of chromate was significantly increased by using SMZ. The sorption of chromate was attributed to anion exchange on the external surface created by the adsorbed surfactant bilayer (Li *et al*., 1998). Besides that, SMZ has also been proven to adsorb other oxyanions such as selenate (SeO_4^{2-}) and sulphate (SO_4^{2-}) (Haggerty and Bowman, 1994), nitrate (NO_3^{2-}) (Li, 2003), and dihydrogenphosphate ($H_2PO_4^-$) (Vujakovic *et al*., 2000).

The surface of natural zeolite can be modified by using cationic surfactant such as hexadecyltrimethyl ammonium (HDTMA), octadecyltrimethyl ammonium (ODTMA), and hexadecylpyridinium bromide (HDPB) because the surface of natural zeolite is the net negative charged resulting from isomorphic substitution of cations in the crystal lattice. Theoretically, when the natural zeolite contacting with cationic surfactant above the critical micelle concentration (CMC) in the aqueous phase, the cationic surfactant cations will selectively exchange with the inorganic cations on the external surface of natural zeolite framework (Li and Bowman, 2001).

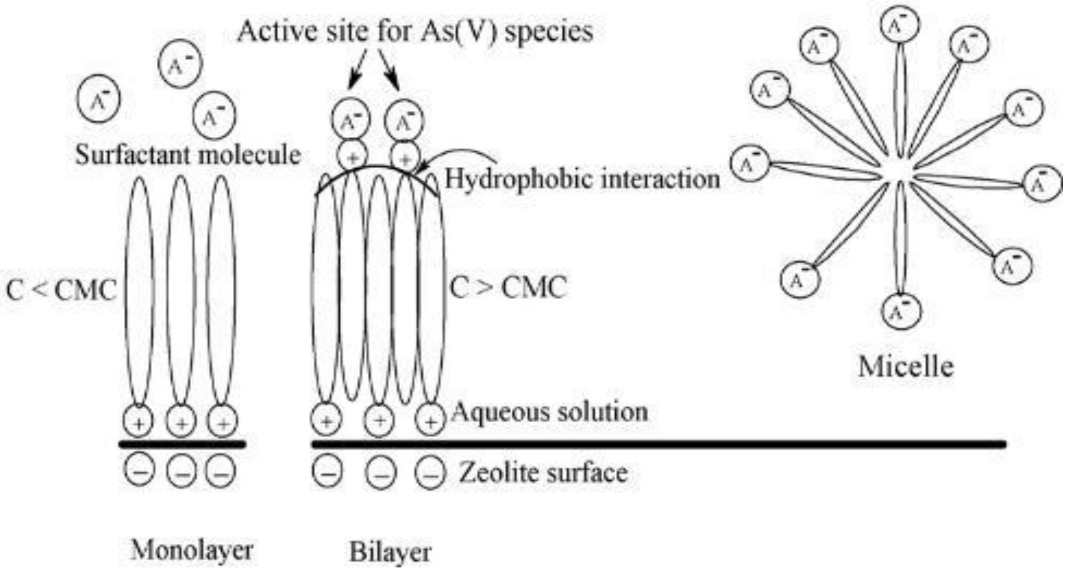

Figure 1.1 A model of modification of zeolite surface by surfactant and adsorption of As(V) species (Chutia *et al*., 2009).

The sorption of cationic surfactant onto a negatively charged surface of natural zeolite involves both cation exchange and hydrophobic bonding (Li and Bowman, 1997). It was suggested that at low loading levels of cationic surfactant exposed to a negatively charged natural zeolite surface, it will be retained by ion exchange and eventually form a monolayer at the solid-aqueous interface. At this stage, the surfactant molecules exist as monomers in aqueous solution at concentrations below the CMC which is usually below 1 mmol/L. When the surfactant concentration is greater than CMC, the surfactant molecules associate to form solution micelles in addition to monomers. As the amount of cationic surfactant increases and the initial surfactant concentration is greater than CMC, the interaction among the hydrocarbon tails causes the formation of a bilayer or patchy bilayer with the first layer retained by cation exchange and the second layer by hydrophobic bonding and stabilized by counter ions. The adsorbed surfactant creates an organic-rich layer on the natural zeolite surface and the charge on the surface is reversed from negative to positive. The positively charged head groups are then balanced by counter ions. A model of modification of natural zeolite surface by surfactant and adsorption of As(V) species is illustrated in Figure 1.1.

1.2 Statement of Problem

Arsenic is very toxic, carcinogenic, and harmful to human beings. In addition, the requirement to comply with the regulation made by the governments to remove this toxic metal in various sources before discharging it into surface water streams or for drinking water is very crucial. Consequently, in order to eliminate or reduce the quantity and concentration of this metal, extensive research to develop cost-effective methods has been carried out using different adsorbents. Generally, adsorption method is considered as a promising method amongst the different existing technologies due to easy separation of adsorbent from aqueous media after the treatment (Chutia *et al*., 2009).

Naturally occurring zeolites are hydrated aluminosilicate materials with high cation exchange capacities (Kuleyin, 2007). In late 1990's, adsorption of arsenic on natural zeolites has been studied widely due to their low cost and availability in nature (Chutia *et al*., 2009). In contrast, arsenic adsorption by surfactant-modified natural zeolites (SMNZ) has gained much less attention. Sullivan *et al*. (2003) used SMNZ to remove arsenic from soil-washing leachate for the first time. After this, very extensive work on this field has been carried out by different workers using either SMNZ or clay minerals as adsorption media (Erdem *et al.*, 2004; Chutia *et al*., 2009; Baskan and Pala, 2011).

In order to adsorb anion and cation, the modified surface must possess positively and negatively charged exchange sites. However, a natural zeolite in its natural form cannot remove or adsorb the anion species as its surface is in the negatively charges. By treating the natural zeolite with a cationic surfactant, an organic covering is created on the external surface of natural zeolite and the charge is reversed to positive charge.

There are few reports in the literature concerning surfactant hexadecylpyridinium bromide (HDPB) modified zeolite, especially on the intercalation of HDPB in natural zeolite. The adsorption of Cr(VI) using HDPB modified natural zeolites has been reported before this (Zeng *et al.*, 2010). However, the application of HDPB modified natural zeolites for the adsorption of As(V) has never being reported. In this research, the adsorption of As(V) using HDPB modified natural zeolites will be studied. The structure of the HDBP is shown in Figure 1.2.

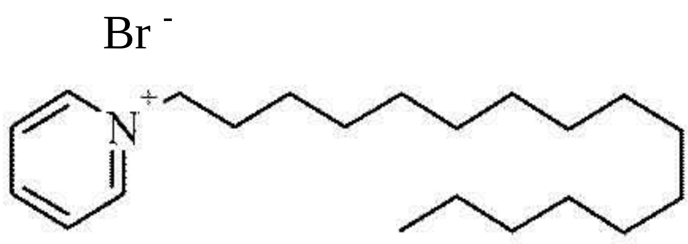

Figure 1.2 The structure of hexadecylpyridinium bromide (Kuleyin, 2007).

1.3 Objective of Study

The objectives of the studies are as follows:

1) To prepare the surfactant-modified natural zeolite by modifying the surface of natural zeolite obtained from Javanese Island, Indonesia, with cationic surfactant hexadecylpyridinium bromide.
2) To characterize the surfactant-modified natural zeolite.
3) To study the effectiveness of the modified and unmodified natural zeolite for the removal of As(V) from water.

1.4 Scope of Study

Various technologies and techniques are available for the removal of As(V) species from wastewater. The propose technique in this research was adsorption by using surfactant-modified natural zeolite. Cationic surfactant hexadecylpyridinium bromide (HDPB) was used to modify the adsorption characteristics of natural zeolites.

The samples were characterized by various characterization techniques including surface area and porosity, cation exchange capacity (CEC), external cation exchange capacity (ECEC), X-ray diffraction (XRD), and infrared spectroscopy (IR).

The adsorption studies for arsenate were done including the kinetic study based on the effect of the initial pH of solution, the adsorption behaviour and the maximum adsorption of the As(V) species by HDPB modified natural zeolite. The determination of the concentration of As(V) in the initial and final solution was carried out using the atomic absorption spectroscopy (AAS).

1.5 Significance of Study

The purpose of this study is to prepare the surfactant-modified natural zeolite by modifying the surface of natural zeolite using cationic surfactant HDPB in order to create anion adsorption sites. Furthermore, surfactant-modified natural zeolite could become an efficient source of adsorbent in the removal of arsenate as well as other heavy metals or inorganic anions in the wastewater. As a result, this study will help to solve the problems of water pollution caused by arsenate and enhance the knowledge on the adsorption of arsenate using surfactant-modified natural zeolite.

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