

ANION EXCHANGE CAPACITY OF CHROMATE ON MODIFIED ZEOLITE CLINOPTILOLITE WITH HDTMA-Br AND ITS REGENERATION

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Abstract

Zeolite Clinoptilolite from Lampung, located in South of Sumatra, had been modified with surfactant hexadecyltrimethylammonium bromide (HDTMA-Br) as chromate anion exchanger. Surfactant modified zeolite (SMZ) Clinoptilolite in particle size range of 1.5 - 2.0 mm, which contained 196.7 mmol HDTMA-Br/kg zeolite, was used for anion exchange of chromate at neutral pH. This experiment was conducted in a glass column filled with 5 gram SMZ. The breakthrough chromate exchange capacity was found 1.262 mg/g SMZ, while the total capacity was found 2.107 mg/g SMZ. The regeneration of SMZ saturated with chromate was conducted using a mixed solutions of 0.28 M Na₂CO₃ and 0.5 M NaOH, compared with using a solution of 0.01 M Na₂S₂O₄. The desorption of chromate achieved 92% with the mixed solutions of Na₂CO₃ and NaOH and 90% with the Na₂S₂O₄ solution. The regenerated SMZ with Na₂CO₃-NaOH solutions was prior washed with HCl solution to remove the carbonate from SMZ, before being used for chromate sorption again. Its breakthrough capacity was reduced to 1.074 mg/g SMZ, and to 0.724 mg/g SMZ when regenerated with Na₂S₂O₄ solution. These results indicated that regeneration of SMZ affected its exchange capacity for anion chromate. However, it is still could be acceptable, when Na₂CO₃/NaOH solutions were used for the regeneration of SMZ saturated with anion chromate.

Keywords: anion exchange capacity, chromate, regeneration, SMZ, zeolite clinoptilolite

1. Introduction

In Indonesia, the electroplating industries had grown very fast along with the growing of automotive industries. Not all of these industries have appropriate waste water treatment, although the electroplating processes need a lot of water and dispose it as waste water, especially the water for rinsing processes. In case of chrome electroplating process, its waste water effluent contains some chromium in hexavalent oxidation state, which is more toxic than the trivalent state and is known to be carcinogenic. This study was aimed to minimize the low concentration of Cr (VI) in the effluent of rinsing process, which is usually treated with ion exchange resins. Since the ion exchange resins are expensive, the development of low cost anion exchange materials based on natural zeolite would be economically implemented in the chrome electroplating industries.

The removal of toxic Cr (VI) had been studied using many kinds of adsorbent materials. The study on

implementing biosorbent, chitosan [1], showed the ultimate adsorption capacity of 153.85 mg/g chitosan, but it is not applicable for industrial waste treatment. Meanwhile the studies using low cost activated carbon derived from agriculture waste biomass [2-3] seem more applicable, but there will be problems with the Cr (VI)-contaminated carbon to solve. Modified natural and synthetic zeolites with cationic surfactants (SMZ) [4-9] offer the potential solution of removing anion chromate in aqueous and industrial effluent, since their capacities for adsorbing Cr (VI) are far higher than that of the unmodified zeolites. The potential economics applications of SMZ are related to its ability to be regenerated and the removal of Cr (VI), especially by HDTMA-Clinoptilolite can be conducted within wide solution pH range of 3.0 to 11.0 [10].

Zeolites are hydrated aluminosilicate minerals with cage-like framework structure, consists of AlO₄⁵⁻ and SiO₄⁴⁻ tetrahedra units, which are linked to each other by the sharing of oxygen atoms. Substitution of each Al³⁺ to Si⁴⁺ in the tetrahedra framework introduces a net

negative charge, which is balanced by the existence of alkali metal or alkali earth metal cations, such as Na^+ , K^+ and Ca^{2+} , found in the zeolite cavities. These cations are mobile and can be easily changed by other cations. This makes zeolite minerals possess a high cation-exchange capacity and are not suitable for anion contaminants removal in water.

Modification of the negatively charged zeolite surface can be conducted by forming layers of adsorbed cationic surfactant on the zeolite surface [11]. The sorption of cationic surfactant, hexadecyltrimethylammonium bromide (HDTMA-Br), had been thermodynamically and kinetically studied [12-13] and it proceeds in two stages. Initially the cationic surfactant, below its critical micelle concentration (cmc), is adsorbed as a monolayer by electrostatic effect. The increased of surfactant concentration exceeds its cmc in the solution will increase the surfactant sorption, caused by the hydrophobic effect, forming a bilayer of surfactant on the zeolite surface (Fig. 1). Since these surfactant aggregates look like a micelle structure, this sorption of surfactant on the zeolite surface is mentioned as admicelle.

Zhaohui Li and co workers studied the chemical and biological stability of HDTMA-modified zeolite clinoptilolite from the St. Cloud mine in Winston [14] and found some HDTMA desorption from SMZ in aqueous solution, but less desorption in higher ionic strength solution. However, HDTMA-modified zeolite has the ability to remove considerable amounts of chromate from aqueous solution through the anion-exchange with the counterion Br^- [15-19]. Like most sorbents, the uptake of chromate by SMZ reaches its maximum amount and after that it losses its effectiveness. Regeneration of chromate-saturated SMZ is therefore needed. Zhaohui Li and Robert S. Bowman studied the regeneration of chromate-saturated SMZ with a sodium carbonate/sodium hydroxide solution compared with a sodium dithionite solution [20] and found that regeneration at high-pH solution of $\text{Na}_2\text{CO}_3/\text{NaOH}$ decreased the chromate sorption capacity of the regenerated SMZ.

The aims of this study were to determine the chromate-exchange capacity of HDTMA-modified clinoptilolite and its breakthrough capacities after regenerated with a solution of $\text{Na}_2\text{CO}_3/\text{NaOH}$ compared to with a $\text{Na}_2\text{S}_2\text{O}_4$ solution.

2. Methods

The natural zeolite clinoptilolite used for this studies was obtained from CV Mina Tama, Bandar Lampung, Indonesia, which has the commercial trade name ZKK and particle sizes P-3 between 1.5 mm and 3 mm. It composed of Clinoptilolite 85%, Mordenite 7% and

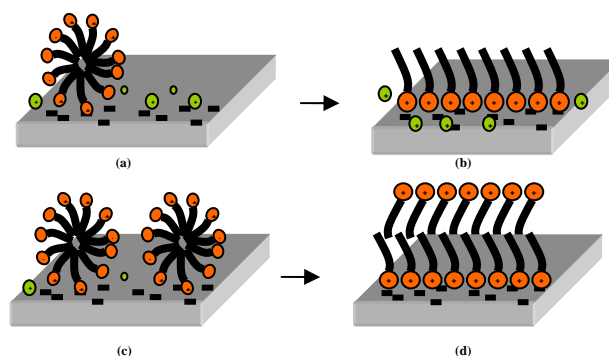


Figure 1. Adsorption of Cationic Surfactant on Zeolite Surface (b) Forming a Monolayer of Surfactant (d) Forming a Bilayer of Surfactant

Monmoroniote, Plagioglass, Quarz 8%. The chemicals composition was SiO_2 72.60%, Al_2O_3 12.40%, CaO 2.56%, MgO 1.15%, K_2O 2.17%, Na_2O 0.45%, Fe_2O_3 1.19%, TiO_2 0.16% and LOI 7.40%.

Preparation of SMZ-clinoptilolite. The natural zeolite Clinoptilolite, before was modified with HDTMA-Br surfactant, was activated at 350 °C for several hours. The modification was conducted by impregnating with HDTMA-Br at critical admicelle concentration. This cac value was determined by HDTMA-Br adsorption, which was carried out on 2.5 g clinoptilolite with 10 mL HDTMA-Br solution at varied concentrations ranged between 10 mmol/L and 90 mmol/L. The mixture of zeolite and HDTMA-Br solution was stirred for 8 hours at 25 °C and then was left for 48 hours. The solid particles were filtered and were dried at 120 °C to obtain surfactant-modified zeolite (SMZ). Furthermore, SMZ was stirred at 25 °C for 24 hours in double-distilled water to study the HDTMA-Br leaching from zeolite.

Non-adsorbed HDTMA-Br in the filtrate and the desorbed HDTMA-Br from SMZ-C were determined by spectrophotometric method using Bromophenolblue (BPB) solution.

Determination of non-adsorbed HDTMA-Br. 4 mL filtrate which contained around 0.06 mmol/L HDTMA-Br was added with 4 mL 0.03 mmol/L BPB solution in 0.01 M NaOH. The solution was adjusted to pH 8 using 0.1 M buffer phosphate solution and then was diluted to 10 mL. 5 mL of the solution was extracted with 5 mL chloroform for 20 minutes. The absorbancy of [HDTMA]₂BPB complex in chloroform phase was determined by uv-vis spectrophotometer at maximum wavelength of 605 nm.

Chromate anion-exchange. An experiment was first conducted to determine the optimum chromate anion concentration exchanged by SMZ by the following method. 0.5 g SMZ was mixed with 10 mL K_2CrO_4

solution at concentrations ranging from 40 mg/L to 900 mg/L, and was stirred for 24 hours. The SMZ was filtered and was centrifuged for 15 minutes. The amount of chromate anion in the filtrate was determined by first diluting the filtrate until 10 mL, then adding 0.2 mL 1,5-diphenyl carbazide solution in acetone and one drop concentrate HNO₃. The mixture was left for 5 minutes until a reddish-violet color appeared. The absorbancy of chromate-carbazide complex was determined by uv-vis spectrophotometer at maximum wavelength 540 nm. The anion Bromide from SMZ, which was exchanged by anion Chromate, was qualitatively determined with AgNO₃ solution.

The chromate anion-exchange capacity of SMZ was carried out using a mini-column with 5 mm diameter and equipped with a gauge. The column was filled with 5 g of SMZ and a K₂CrO₄ solution at optimum concentration was passed through SMZ. Every 5 mL effluent was collected to determine the chromate concentration, which was not exchanged by Br⁻.

Regeneration of SMZ. SMZ saturated by chromate anion was regenerated using a mixed solutions of Na₂CO₃-NaOH, compared with the regeneration using a Na₂S₂O₄ solution. The regeneration with the mixed solutions of Na₂CO₃ and NaOH was carried out at varied concentrations as follow: 0.28 M Na₂CO₃/0.5 M NaOH ; 0.28 M Na₂CO₃ / 0.25 M NaOH ; 0.14 M Na₂CO₃ / 0.5 M NaOH and 0.14 M Na₂CO₃ / 0.25 M NaOH. The exchanged chromate ion was determined in every 5 mL effluent. The regenerated SMZ was washed with excess solution 0.1 M HCl and was dried at 110 °C for several hours. Now the SMZ with chloride anion was used again for anion-exchange of K₂CrO₄ to determine its anion-exchange capacity after once regeneration.

The same method of regeneration was conducted using 0,01 M Na₂S₂O₄ solution. The regenerated SMZ without washing with HCl solution was used to determine again its chromate anion-exchange capacity.

3. Results and Discussion

Critical Admicelle Concentration of Clinoptilolite.

Zeolite has a net negative charge. Since natural zeolite clinoptilolite has cavity dimension about 4.2-7.2 Å and HDTMA-Br surfactant has head dimension around 7 Å, HDTMA⁺ will be adsorbed on the surface of clinoptilolite. The cmc value of HDTMA-Br surfactant is 0.9 mmol/L and since the zeolite modification was carried out with HDTMA-Br concentrations above its cmc value, a bilayer of surfactant molecules was built on the zeolite surface, which can be seen as the isotherm adsorption curve on Figure 2.

Figure 2 shows that HDTMA⁺ had formed admicelle on zeolite surface at initial concentration of 30 mmol/L and

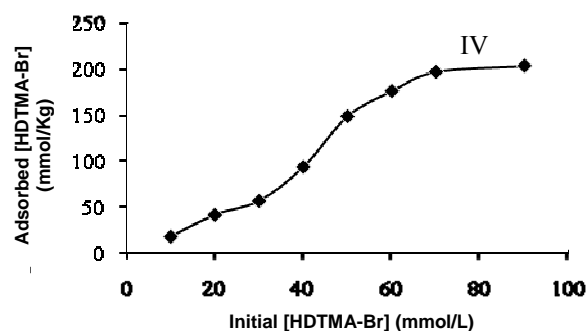


Figure 2. Isotherm Adsorption of HDTMA⁺ on Zeolite Clinoptilolite Surface

the amount of adsorbed HDTMA⁺ was 56.172 mmol/Kg. Area IV shows a constant adsorption, in which HDTMA⁺ achieved its critical admicelle concentration value at initial concentration of 70 mmol/L and 196.7 mmol/Kg HDTMA⁺ was adsorbed on zeolite.

The adsorbed of HDTMA⁺ on zeolite surface was characterized using FTIR analysis (Fig. 3). The desorbed of HDTMA⁺ from leaching of SMZ in double-distilled water was found 0.116%. This result shows that HDTMA⁺ is strongly bound to zeolite clinoptilolite.

The adsorbed HDTMA-Br on zeolite clinoptilolite was confirmed by the absorption peaks of the N-H stretching at $\nu = 3032.1 \text{ cm}^{-1}$ and $\nu = 3185.8 \text{ cm}^{-1}$ and by N-H bending at $\nu = 1472.1 \text{ cm}^{-1}$.

Chromate anion-exchange on SMZ-Clinoptilolite.

HDTMA-Br is a cationic surfactant with the head groups consist of (CH₃)₃N⁺ and counterion Br⁻. The bilayer of HDTMA-Br surfactant on zeolite surface provides positively charge sites of head groups, which are presented to the surrounding solution and are balanced by counterions. The sorption or exchange of other anion involves the replacement of the weakly held counterions by more strongly held counterions, such as the replacement of Br⁻ with anion chromate, which was qualitatively determined with AgNO₃ solution. Figure 4 shows the maximum adsorption of chromate began at the equilibrium chromate concentration of 77.76 mg/L, which was conducted at initial chromate concentration of 700 mg/L. The maximum chromate anion-exchange capacity on SMZ-clinoptilolite was calculated as follow:

$$(700-77.76) \frac{\text{mg}}{\text{L}} \times \frac{10 \text{ mL}}{2.5 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 2489 \frac{\text{mg}}{\text{kg}} \quad (1)$$

Regeneration of SMZ-C saturated with chromate.

Although chromate anion is strongly bound to HDTMA-modified zeolite, it can still be replaced by certain oxyanions, which are stronger held by HDTMA⁺, like carbonate at high pH and dithionite. In this study, before the regeneration, HDTMA-modified

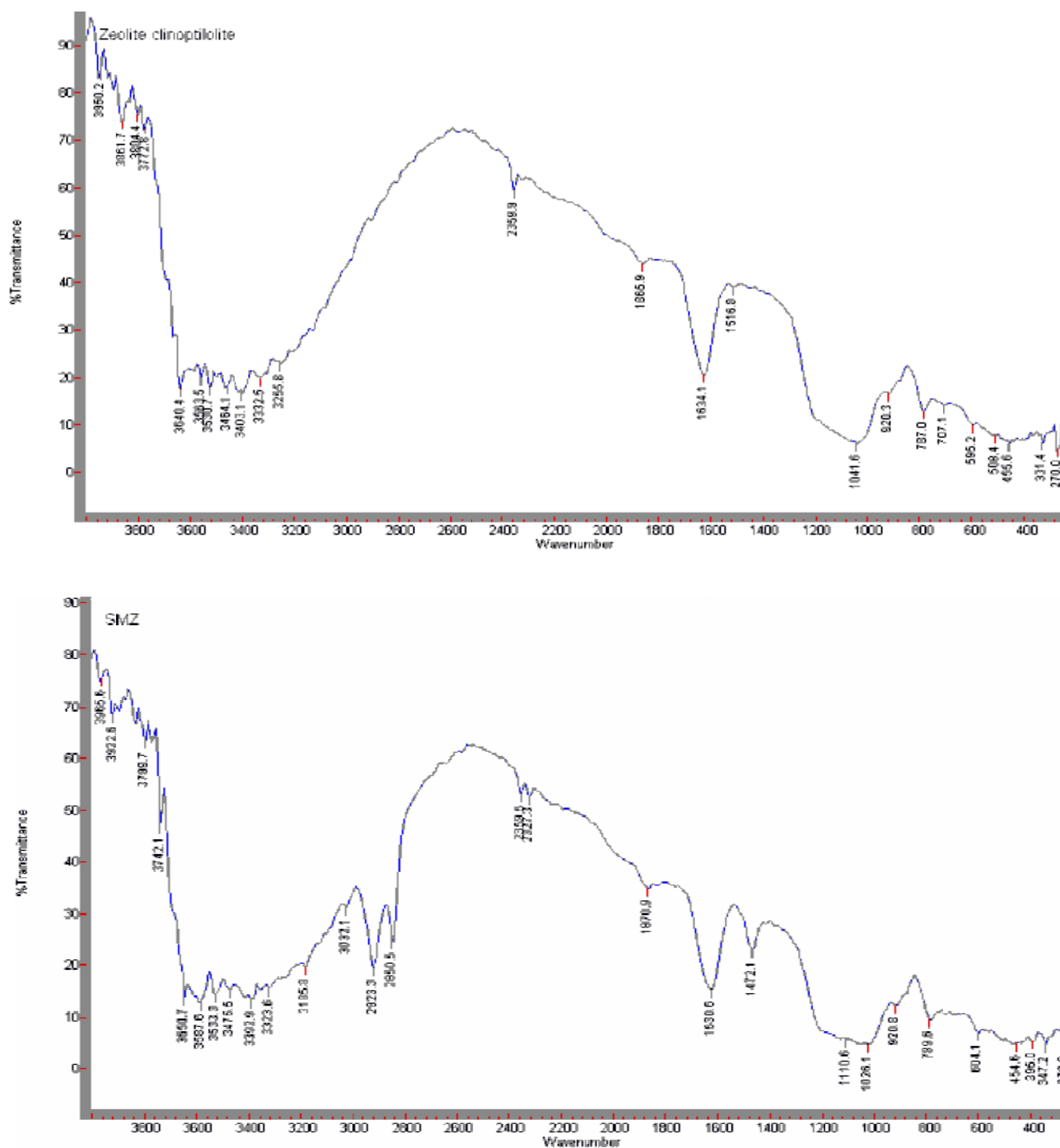


Figure 3: FT-IR spectra of zeolite clinoptilolite (above) and HDTMA-modified clinoptilolite (below)

clinoptilolite packed in a mini-column was first saturated with chromate by passing 8 aliquot of 5 mL 700 mg/L K_2CrO_4 solution. Using this method, it was found that the total capacity of SMZ-clinoptilolite was 2.107 mg/g zeolite.

The regenerations of HDTMA-modified clinoptilolite were carried out using varied concentrations of mixed $Na_2CO_3/NaOH$ solution at pH 8 and a $Na_2S_2O_4$ solution.

The results of the desorbed chromate are shown in Table 1, which shows that the solution mixture of 0.28M Na_2CO_3 and 0.50M NaOH could desorb the maximum chromate anions. Washing the regenerated SMZ-C with 0.1M HCl solution is to replace the carbonate counterions with Cl⁻ before it was again used for chromate anion-exchange. It was not necessary to replace the dithionite counterions with Cl⁻.

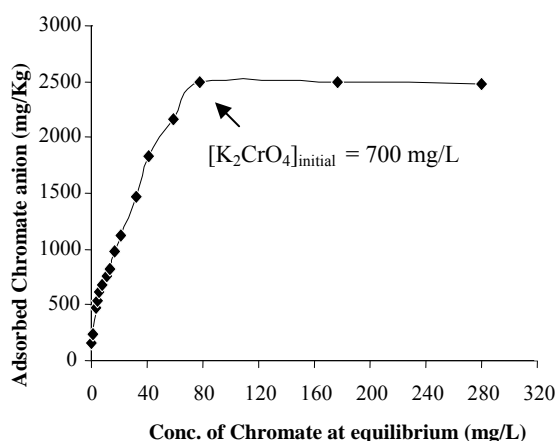


Figure 4. Chromate Anion-exchange on SMZ-clinoptilolite

Table 1. %-desorption of Chromate from SMZ-C

[Na ₂ CO ₃] (M)	[NaOH] (M)	[Na ₂ S ₂ O ₄] (M)	Chromate desorption (%)
0.28	0.50	–	92.0
0.28	0.25	–	90.0
0.14	0.50	–	87.4
0.14	0.25	–	87.4
–	–	0.01	90.0

The regenerated HDTMA-modified clinoptilolite with the mix concentration 0.28M Na₂CO₃ and 0.50M NaOH and the regenerated with 0.01M Na₂S₂O₄ were again used for chromate sorption. The breakthrough capacity for both regenerated SMZ-C were respectively 1.074 mg/g zeolite and 0.724 mg/g zeolite.

4. Conclusion

Zeolite clinoptilolite can be modified with cationic surfactant HDTMA-Br by forming bilayers admicelle sorption of HDTMA-Br on zeolite surface. The adsorbed HDTMA⁺ at initial concentration of 70 mmol/L was 196.7 mmol/Kg zeolite. This HDTMA⁺ modified zeolite clinoptilolite can be used to remove chromate anion from waste effluent with the breakthrough exchange capacity of 1.262 mg/g SMZ, while the total capacity was 2.107 mg/g SMZ. The regeneration of SMZ saturated with chromate was successfully conducted with either a mix concentration of 0.28M Na₂CO₃ and 0.50M NaOH or with 0.01M Na₂S₂O₄. The breakthrough capacities of both regenerated SMZ were 1.074 mg/g zeolite and 0.724 mg/g zeolite respectively.

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