

## Effect of pH on Adsorption of Cr(III) and Cr(VI) by zeolite A (from Fly Ash) Modified Surfactant HDTMA

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**Abstract.** Adsorption of Cr(III) and Cr(VI) in aqueous solution by the zeolite A from coal fly ash modified hexadecyltrimethylammonium bromide (HDTMAB) at various pH conditions has been carried out. Zeolite A was synthesized from fly ash through modified alkaline fusion hydrothermal process in a reactor stainless steel. The surface modification was performed using cationic surfactant HDTMAB twice as much as the cationic exchange capacity of the zeolite A resulted. The surfactant modified zeolite A was then applied to adsorption the metal ion chromium as Cr(III) and Cr(VI) in aqueous solution. The results showed that the acidity (pH) of adsorption conditions, affect the ability of adsorption surfactant modified zeolite A (SMZA) to Cr(III) and Cr(VI) in aqueous solution. The optimum pH conditions for the adsorption of Cr(III) and Cr(VI) on SMZA exist at pH 6. Surfactant modified zeolite A capable to adsorb either cation Cr(III) or anion Cr(VI). Adsorption of SMZA on Cr(III) increased from 36.30% to 97.04% with the increase the acidity of pH of 2 to 6. Adsorption SMZA to Cr(VI) is lower than the adsorption of the Cr<sup>3+</sup>, adsorption increasing from 19.63 to 64.07% with increase pH of 2 to 6.

**Keywords:** pH effect, chrome adsorption, surfactant modified zeolite A, fly ash

### INTRODUCTION

Coal is one energy source that is widely used around the world with a reserve which is still quite large. In 2025 the projected demand for coal in Indonesia will be approximately 191.13 million tones (Anonymous, 2006). Based on the amount of coal used as such, the amount of fly ash produced is estimated to reach 14.9 million tons in 2025. In general, coal ash waste stored in pools or dry landfill (Neupane and Donahoe, 2009). Coal fly ash containing a number of metal oxides to be released into the environment in the form of a metal cationic if not converted into useful materials.

Presence of heavy metals in waste water endangers human life, organisms and an environment. Water pollution by industrial waste, especially industries associated with heavy metals such as electroplating, mining, metallurgy, textile industry, industrial organic matter, pesticides and so on, bad for life. Likewise, the release and distribution of heavy metals and

radionuclides, which are toxic and spread into aquatic ecosystems, is a global problem for the world (Seliman and Borai, 2011). At a certain concentration limits, such as heavy metals, Mn, Cr, Hg, Pb, Cd, and As, so are toxic to living organisms. Hexavalent chromium compounds are toxic, carcinogenic and mutagenic and cause gastric cancer (Sikaily et al., 2007). The arsenic is declared as one of the most toxic pollutants due to mutagenic and carcinogenic effects in the human body (Jovita et al., 2011). Therefore waste water containing heavy metals processing needs to be done in advance before being discharged into the waters body.

Physicochemical changes and activity of organisms in the environment can cause changes in the metal species to their oxidation state. Metal chromium, can exist as cation of Cr(III), and the anion CrO<sub>4</sub><sup>2-</sup>, and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, depending on the acid-base conditions of the medium. Kaufman in Gajghate et al., (1992) mentioned that hexavalent Cr in high concentrations can

cause cancer of the digestive tract in humans. Compared with chrome trivalent, Cr(III), chromium as hexavalent chromate in ( $\text{CrO}_4^{2-}$ ) or hydrogen chromate ( $\text{HCrO}_4^-$ ) is more toxic and easily soluble in water in a range of pH (Swarnakar, 2011).

Chrome showed three oxidation states, i.e. 2, 3 and 6. The oxidation state of the most stable and an important chromium compound is trivalent and hexavalent chromium. Cr(II) is unstable and easily oxidized to stable form Cr(III). In solution, chromate (VI) is in equilibrium with dichromate (VI). Hexavalent chromium is more dangerous than other chromium species. Therefore it is necessary to reduce the levels of chromium in the water so it does not harm the environment. Several methods have been used to handle the chrome waste, one of them is adsorption. Various types of adsorbent have been used to adsorb contaminants in the water, and one of them is zeolite. Zeolite has a high affinity for cation because the surface is negatively charged and balanced by cation that is positively charged. The cation can be replaced or exchanged by other cation which has a higher affinity, so zeolites are widely used as cationic exchanger (Breck, 1974). For the purposes of as an adsorbent or ion exchange zeolite with lower Si/Al ratio would be more effective than the zeolite with high Si/Al ratio. The existence of isomorphous substitution of Si by Al atoms in the framework structure of the zeolite resulted negatively charge on overall the zeolite surface. With this unique nature, zeolites have a high affinity for cation, making it very suitable for use as an effective cationic exchanger. However, for the anionic species, such as  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ , these capabilities are less meaningful for the unmodified zeolite (Bansiwal et al., 2006).

The active nature of the anion can be provided on the surface of the zeolite by using

the concept of surface modification using a surfactant. For large cationic surfactants, are believed to occur due to the exchange on the outer surface of these ions is large enough to enter the zeolite pores (Bowman, 2003; Sullivan et al., 1998). By doing variations in the concentration of surfactant, the surfactant-modified zeolite can be designed to adsorb adsorbate three main classes, such as cation, anions and organic nonpolar (Majdan et al., 2006). In this study, we investigate effect of pH on adsorption of Cr(III) and Cr(VI) by zeolite A (from coal fly ash) modified surfactant HDTMA ions at various pH.

## MATERIALS AND METHODS

### Equipment and materials research

The equipment used in this study include: (a) a set of glassware (b) Orbital Shaker (c) pH meter (d) analytical balance, (e) Atomic Absorption Spectrometer, Perkin Elmer, (f) Shimadzu-XRD 6000. The materials used were (a) zeolite A synthesized from fly ash, (b) HDTMAB ( $\text{C}_{19}\text{H}_{42}\text{BrN}$ ), (c) HCl, (d) NaOH, (e)  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , (f)  $\text{K}_2\text{CrO}_4$  (e) filter paper Watman 42 and (f) aqua demineralization. The entire chemical is analytical grade, production of E-Merck.

### Experiment procedure

#### Surfactant modified zeolite A.

Modification of zeolite A synthesized from fly ash was carried out by using a surfactant HDTMAB. The zeolite A was washed with distilled water several times until the pH is about 10. A total of 2 g of zeolite A added with 50 mL of solution with a concentration corresponding HDTMAB 2 x CEC value of zeolite A, then stirred with orbital shaker for 24 hours at a speed of 200 rpm. The mixture was filtered and the solids obtained washed with demineralized aqua until the free  $\text{Br}^-$ , then dried in air at  $110^\circ\text{C}$

for 2 hours. The solids were then characterized using IR spectroscopy and XRD.

**Adsorption procedure.** In this study, the adsorption solution of chromium (III) and chromium(VI) is carried out in a pH range of 2-8, at 200 rpm, 60 minutes, the initial concentration of 20 or 30 mg / L, using adsorbents ZA and SMZA respectively 0, 01G. A total of 20 ml of a solution of Cr(III) or Cr(VI) with a particular concentration were added respectively with an adsorbent which has been prepared. The mixture was shaken with a speed of 200 rpm for 1 hour in a 50 mol Erlenmeyer flask. After the adsorption time specified, the mixture was centrifuged at 1000 rpm for 3 minutes and then separated from the solid phase by decantation. The filtrate obtained is then determined its concentration by using Atomic Absorption Spectrophotometer.

## RESULTS AND DISCUSSION

### Diffraction pattern of zeolite A(ZA) and surfactant-modified zeolite A(SMZA).

To monitor the effect of surfactant HDTMA modifications to the stability of the structure is carried out using XRD and FTIR analysis of unmodified zeolite A (ZA) and zeolite A modified (SMZA). Comparison diffractogram zeolite A and zeolite A modified surfactants are listed in Figure 1. According to Figure 1, it appears that the diffraction peaks of zeolite A modified with a surfactant HDTMA (SMZA), both synthetic and commercial results practically unchanged compared with zeolite A is not modified (ZA). This shows that the resistance and stability of the zeolite crystal structure when modified with a surfactant HDTMA.

The similar results were reported, that the surface modification of zeolite A using a surfactant HDTMA not change zeolite crystals structure (Bansiwal et al., 2006, and Kumar et al., 2007). Peaks diffraction trem showed no

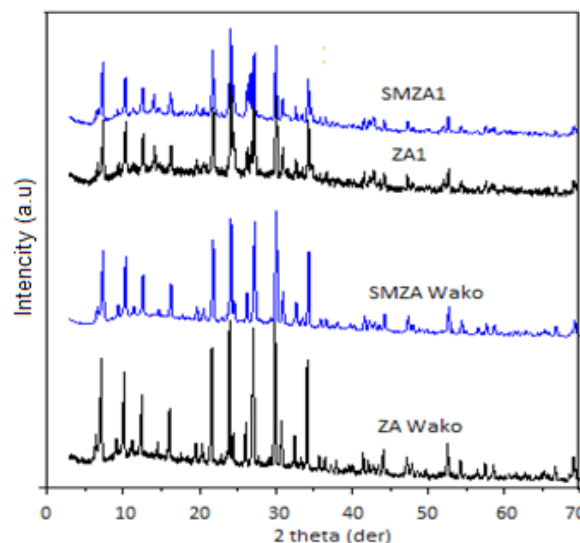


Figure 1. Diffraction term of zeolite A and zeolite A modified surfactant

significant change. In Figure 3 also shows a reduction in the amorphous phase SMZA than ZA, both for standard and custom synthesis product ZA.

### Effect of pH on Cr(III) and Cr(VI) adsorption by surfactant modified zeolite (SMZA).

Adsorption of Cr(III) and Cr(VI) using SMZA performed at pH 3-8, contact time 1 hour, ZA adsorbent amount of 0.01 g, and the initial concentration of Cr(III) 23 mg/L and Cr(VI) 30 mg/L. Plot the amount of chromium metal ion adsorption, as Cr(III) and Cr(VI) at various pH by using zeolite adsorbents A surfactant-modified HDTMA (SMZA) is presented in Figure 2. In Figure 2 it appears that the zeolite A surfactant-modified (SMZA) can adsorb Cr(III) as well as unmodified zeolite A. Even the adsorption capacity of the cationic  $\text{Cr}^{3+}$  is greater than its adsorption on anion  $\text{CrO}_4^{2-}$ .

The similar results were obtained Bolortamir, et. al., (2009), and Takashi, (2008) which showed that the modified zeolite with HDMA-Br can absorb the Cr(III) as well as the unmodified zeolite. SMZA ability to adsorb Cr(VI) in chromate species ( $\text{CrO}_4^{2-}$ ) is also shown in Figure 2. The addition of Figure 2 also

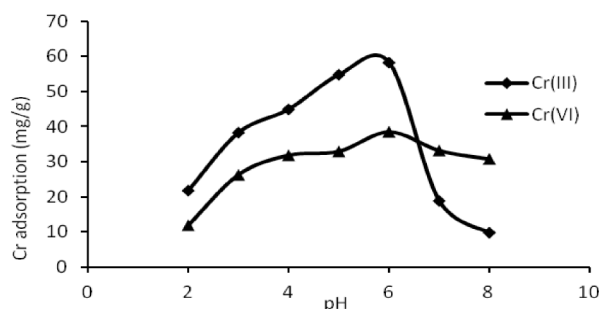


Figure 2. Effect of pH on the adsorption of Cr(III) and Cr(VI) on SMZA

appears that the adsorbent SMZA showed that adsorption increased from 36.30% up 97.04% with increasing pH from 2 to 6, then adsorption decreases at higher pH (pH 7-8). It is proved that after being modified with a surfactant HDTMA, internal parts are negatively charged pore zeolite still serves to absorb cationic  $\text{Cr}^{3+}$ . With increasing pH, the more negative SMZA internal surface due to internal deprotonation of zeolite by  $\text{OH}^-$  ions. Overall internal surface charge more negative zeolite. This causes increased electrostatic attraction between the negatively charged elite A with Cr (III) which caharged positively, thus increasing adsorption. At higher pH  $\text{Cr}^{3+}$  reacts with  $\text{OH}^-$  to form  $\text{Cr}(\text{OH})_3$ , thus drastically lowering adsorption.

SMZA dual function as an adsorbent cation and anions can be explained by the interactions that occur between the SMZA with

$\text{Cr}^{3+}$  and  $\text{CrO}_4^{2-}$ , as shown in Figure 3. In Figure 3 it appears that the surfactant-modified zeolite has two active sides which can act as an anion exchanger on the external surface of the upper balancing anionic  $\text{Cl}^-$  or  $\text{Br}^-$  with  $\text{CrO}_4^{2-}$ , and as a cationic exchanger on the internal surface of the upper counterweight ion zeolite  $\text{Na}^+$  or  $\text{K}^+$  with cationic  $\text{Cr}^{3+}$ . Therefore, beside to adsorb anionic, the surfactant modified zeolite A can also adsorb cationic species.

SMZA adsorption on anionic chrome,  $\text{CrO}_4^{2-}$ , as shown in Figure 2, lowers than the adsorption of the  $\text{Cr}^{3+}$ . This may be due to the amount HDTMA used for surface modification is not optimal, so that the ion exchange or adsorption is not optimal C  $\text{CrO}_4^{2-}$  not maximized. As for the effect of pH on the adsorption of Cr(VI) as chromate ion increasing from 19.63 to 64.07% by increased pH of 2 to 6, and further the adsorption decreases at pH 7-8. So the maximum adsorption occurs at pH 6. Similar results were also reported by Kumar, et al., 2007, the maximum adsorption of Cr(VI) occurs at pH 6. The results were slightly different obtained Swarnakar, et al., (2011), the maximum adsorption occurs at pH 7, when the Cr(VI) is in a stable state as ion  $\text{CrO}_4^{2-}$ .

At low pH form dichromate ions is larger than the chromate ions. It explained that the

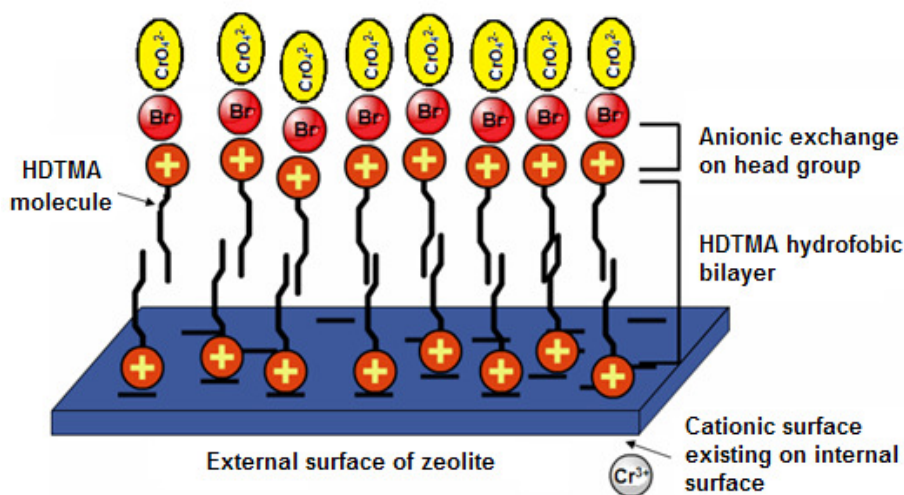


Figure 3. Interaction model of  $\text{Cr}^{3+}$  and  $\text{CrO}_4^{2-}$  on configuration bilayer of surfactant modified zeolite.



zeolite pore size is suitable for ion adsorption  $\text{CrO}_4^{2-}$  of the  $\text{Cr}_2\text{O}_7^{2-}$ . For dichromate ions  $\text{Cr}_2\text{O}_7^{2-}$  maximum adsorption of surfactant-modified zeolites occur at low pH, as reported by Hommaid and Hamdo, 2014, maximum adsorption at pH 1.5. In the surfactant modified kaolin,  $\text{Cr}_2\text{O}_7^{2-}$  maximum adsorption occurs at pH 1.5-2 (Khoirunisa, 2011). The reactions that occur in Cr species in solution are as follows:



In alkaline medium, when the pH is greater than 7 chromate ion species is converted to  $\text{Cr}(\text{OH})_3$ , which is less stable than  $\text{CrO}_4^{2-}$  species. Therefore, chromium showed maximum adsorption at pH 7 (Swarnakar, et al., 2011).

## CONCLUSIONS AND REMARKS

The pH conditions of adsorption process, affect the adsorption ability of SMZA to Cr(III) and Cr(VI) in aqueous solution. The optimum pH conditions for the adsorption of Cr(III) and Cr(VI) by SMZA exist at pH 6. The modification using cationic surfactant HDTMA affect the adsorption properties of zeolite A. Surfactant modified zeolite (SMZA) capable to adsorb either cation Cr(III) or Cr(VI). SMZA adsorption to Cr(III) increased from 36.30% to 97.04% with the increase of pH from 2 to 6, then adsorption decreases at higher pH (pH 7-8). SMZA adsorption on anion chromate,  $\text{CrO}_4^{2-}$ , lower than the adsorption of the  $\text{Cr}^{3+}$ . SMZA adsorption to Cr(VI) as chromate ion increasing from 19.63 to 64.07% by increase pH of 2 to 6, and further the adsorption decreases at pH 7-8. It can be concluded that the surfactant modified elite A (SMZA), not only adsorb anion  $\text{CrO}_4^{2-}$ , but also can adsorb  $\text{Cr}^{3+}$  cation in aqueous solution.

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