Removal of Cr(VI) and As(V) from aqueous solutions by HDTMA-modified zeolite Y

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ABSTRACT

The synthesized zeolite NaY from rice husk ash (RHA) and the commercial zeolite NaY both modified with surfactants in amounts equal to 50%, 100% and 200% of their external cation exchange capacity (ECEC) were used to remove chromate and arsenate anions from aqueous solutions. While the unmodified zeolite Y had little or no affinity for the Cr(VI) and As(V) anionic species, the surfactant-modified zeolite Y (SMZY) showed significant ability to remove of these anions from the aqueous solutions. The highest chromates and arsenates adsorption efficiency was observed from solutions of pH values 3 and 8, respectively because of the dominance of the univalent species of both anions. The adsorption equilibrium data were best fitted with the Langmuir isotherm model with the highest removal capacities observed for the SMZY initially prepared considering the hexadecyltrimethyl ammonium (HDTMA) amount equal to the 100% of the ECEC of zeolite Y. Synthesized SMZY remove Cr(VI) and As(V) more than the corresponding commercial one due to its lower silica to alumina ratio. Thus, the HDTMA-covered modified zeolite Y synthesized using RHA can be used to remove Cr(VI) and As(V) from water.

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1. Introduction

The presence of chromate (Cr(VI)) and arsenate (As(V)) anions in various sources of water are prominent issues since the toxicity of these species can result in death if these species are taken either over a long period of time or present in high concentrations. The chemical form of chromates determines their potential toxicity as Cr(VI) is believed to be carcinogenic in humans than Cr(III) species [1]. The carcinogenic and toxicity of Cr(VI) is based on its oxidation state where the chromate anion resembles the form of sulfate and phosphate [2]. Arsenate which is in the pentavalent state (As(V)) is also considered to be toxic and carcinogen to human. Arsenate is thought to elicit acute toxicity via different mechanisms where arsenate mimics phosphate and interferes with the adenosine triphosphate (ATP) production in the mitochondria [3].

Hence, the regulation for the limitation of the Cr(VI) and As(V) concentrations in water should be highlighted and emphasized in every country due to the toxicity, reactivity and probable carcinogens of these species. Acceptable limits for chromium in water differ in almost every country. As a guideline, World Health Organization (WHO) recommended a maximum level of 0.050 mg L^{-1} for Cr(VI) in drinking water [4] and the National Institute for Occupational Safety and Health (NIOSH) proposed that the levels of chromium

should be reduced to 10^{-3} mg L^{-1} [5]. For arsenic species, EPA adopted a new standard and public water must comply with the 0.010 mg L^{-1} standard beginning 23 January 2006. Since Cr(VI) and As(V) are very toxic, carcinogenic and very harmful to human beings, in addition, the requirement to comply with the regulation made by the governments, the importance of removing both toxic metals in various sources before discharging them into the surface water streams or for drinking water is very crucial and critical.

In the aqueous solutions, Cr(VI) is very soluble and exists in the form of chromic acid (H_2CrO_4) and in the form of dichromate ($Cr_2O_7^{2-}$) while in neutral solutions, Cr(VI) is present in the form of $HCrO_4^-$ and CrO_4^{2-} [6]. For arsenic species, at moderate or high redox potentials, it can be stabilized as a series of pentavalent (arsenate) oxyanions, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} [7]. Thus, to eliminate these toxic metals from water, the adsorbent must have the anion exchange properties.

Because zeolites are crystalline aluminosilicates with the structure based on tetrahedral SiO_4 and AlO_4 units, connected by shared oxygen atoms, they are one of the synthetics inorganic cation-exchangers [8]. This kind of three-dimensional structure has small pores where the exchangeable ions are located and the ion exchange reactions take place. Silicon is tetravalent and aluminum is trivalent, which result in negatively charged framework structures. Thus, each mole of aluminum produces one equivalent of cation exchange capacity for the zeolite framework. Because of this property, the zeolites cannot remove arsenate and chromate anions

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but fortunately, the modification of zeolites by the cationic surfactant can enhance the capability of zeolites to remove anions species in water.

Recently, the utilization of natural zeolites, particularly clinoptilolite modified with cationic surfactant (SMZ) with the purpose to remove multiple types of contaminants from water was studied by many researchers especially from Li and Bowman groups [9,10,11,12,13]. Recent study by Campos showed that the modification of mordenite by ethylhexadecyldimethyl ammonium (EHDDMA) and hexadecyltrimethyl ammonium (HDTMA) can remove hexavalent chromium [14]. In addition, Perez Cordoves and his co-workers [15] have studied for the first time that the affinity distribution analysis combined with the Freundlich binding model allows the characterization of the SMZ binding properties for Cr(VI). Besides that, the surfactant-modified natural zeolites such as stilbite and laumontite [16] and clinoptilolite-heulandite rich tuffs [17] were also used to remove arsenic from water and the results showed that the SMZ from clinoptilolite can remove As(V) more than As(III) [18]. Although there are many papers on the utilization of natural zeolites, especially clinoptilolite for the preparation of SMZ but the synthetic zeolites also can be used for the same purpose because the synthetic zeolites resemble the natural zeolite minerals. They possess permanent negative charges on their surface and large cation exchange capacity (CEC) depending on the types of zeolites allowing them to be modified by cationic surfactant to enhance their sorption of organic and anionic contaminants in water.

The aims of this paper is to modify the synthesized zeolite NaY from rice husk ash (RHA) with the cationic surfactant quaternary ammonium namely hexadecyltrimethyl ammonium, in order to enhance the capability of this material to adsorb anion species of Cr(VI) and As(V) from aqueous solutions. This study encompasses the effect of the HDTMA loading level, different concentration of chromate and arsenate and pH of the solution in the adsorption capacities of these anions on modified zeolites Y.

2. Materials and methods

2.1. Materials

Rice husk ash that was used as a source of silica in the synthesis of zeolite was prepared through physical combustion; the dried rice husk was burnt in the combustor at a constant temperature of $600\,^\circ$C and constant pressure for an hour. The quantity of silica present in the RHA was analyzed by X-ray fluorescence (XRF) technique (91.65%). Silica was in the form of amorphous as proven by X-ray diffractogram and infrared spectroscopy in previous study [19].

The synthesis and its physicochemical properties of the zeolite NaY were discussed in another paper [19]. The physicochemical properties values of the synthesized zeolite NaY (Zeo-NaY-S) and commercial zeolite NaY (Zeo-NaY-C) are tabulated in Table 1. The commercial zeolite NaY was supplied by Zeolyst International (CBV 100). The procedure for the determination of external cation exchange capacity (ECEC) was adopted from Bouffard [20]. The procedure for ECEC was similar to the determination of CEC but differs in the last step in which the sodium cation was replaced by HDTMA cation.

2.2. Preparation of surfactant-modified zeolite Y

Three series of surfactant-modified zeolite Y (SMZY) were prepared by reacting zeolite with HDTMA in aqueous solutions. Hexadecyltrimethyl ammonium bromide (HDTMA-Br) was supplied by Merck-Schuchardt. HDTMA was added in an amount equal

Table 1
Physicochemical properties of Zeo-NaY-S and Zeo-NaY-C

Physicochemical properties	Zeo-NaY-S	Zeo-NaY-C
Unit cell, a_o (Å)	24.76	24.67
SiO_2/Al_2O_3[a]	3.2	4.0
SiO_2/Al_2O_3[b]	3.9	5.0
SiO_2/Al_2O_3[c]	3.8	5.1
Si/Al[b]	1.9	2.5
Si/Al[c]	1.9	2.6
Specific surface area ($m^2\,g^{-1}$)	506.6	484.9
Total pore volume ($cm^3\,g^{-1}$)	0.27	0.26
Average pore diameter (Å)	21.70	21.77
Cation exchange capacity, CEC (mequiv. g^{-1})	3.15	2.55
External cation exchange capacity, ECEC (mequiv. g^{-1})	0.67	0.53

[a] From elemental analysis.
[b] From unit cell.
[c] From infrared spectrum.

to 50%, 100% or 200% of ECEC of zeolite. This experiment was to study the effect of different surface coverage of HDTMA onto zeolite in the sorption of anions in water. The SMZY was identified by a prefix stating the percentage of the ECEC of zeolite which was supposedly to be occupied, followed by the abbreviation for the type of zeolite, i.e. S and C, for the synthesized zeolite NaY and commercial zeolite NaY, respectively. HDTMA solution was prepared by dissolving an appropriate amount of HDTMA-Br in distilled water and was heated gently until all of HDTMA-Br was dissolved. After that, the HDTMA solutions were mixed with zeolite and the mixture was stirred using a magnetic stirrer for 5 days at room temperature. The mixture was then filtered by vacuum filtration and solid sample was dried at $60\,^\circ$C overnight. The resultant SMZYs were readily used for adsorption studies.

2.3. Adsorption of Cr(VI)

2.3.1. Effect of the pH solution

Cr(VI) solution was prepared by dissolving a suitable amount of potassium dichromate, $K_2Cr_2O_7$ (Merck, Darmstadt, Germany) in distilled water. pH of the solution ($10\,mg\,L^{-1}$) was adjusted with the addition of NaOH or HNO_3 solution to obtain pH 3, 5, 7, 8 and 10. pH of the solution was measured by pH meter CyberScan pH/Ion 510 pH meter (Eutech Instruments). An accurate amount of SMZY (0.2000 g) samples were mixed with the Cr(VI) solution (20 mL) in a 50 mL centrifuge tube. The samples were then shaken for 48 h on an orbital shaker (Hotech) and finally, supernatant was filtered through a Whatman filter paper No. 1.

2.3.2. Isotherm study

Isotherm study conducted on the aqueous solution using the batch method. An accurate amount of the unmodified and modified zeolite (0.5 g) was placed in a centrifuge tube 50 mL and added with Cr(VI) solutions (20 mL) having concentrations of 10, 15, 20, 30, 40, 50 and $70\,mg\,L^{-1}$. pH of the Cr(VI) solutions were kept between 3 and 4. The mixtures were shaken at room temperature at the agitation rate of 150 rpm using an orbital shaker (Hotech) for 48 h (a period shown to be sufficient to reach adsorption equilibrium). The mixture was then filtered and the filtrate was analyzed for Cr(VI) concentration by UV–vis spectrophotometry. Langmuir isotherm was used to determine the maximum adsorption capacity of Cr(VI) onto the SMZY.

2.3.3. Determination of Cr(VI)

Procedure for the determination of the hexavalent chromium, Cr(VI) in the solution was based on the standard method set up by the American Public Health Association (APHA) [21]. This pro-
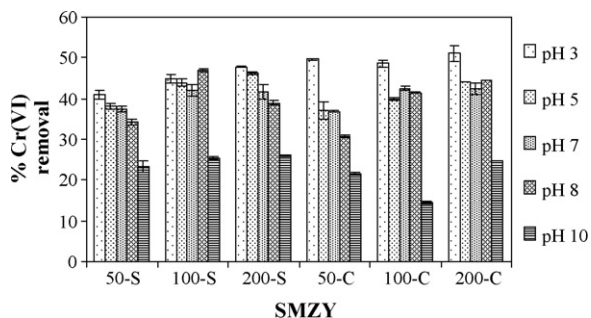
Fig. 1. Effect of pH solution on the Cr(VI) removal by SMZY.

cedure measured only hexavalent chromium (Cr(VI)) in which the Cr(VI) was determined colorimetrically by the reaction with diphenylcarbazide in acid solution. The solution was transferred to a 1-cm absorption cell and the absorbance was measured at 540 nm using an ultra violet-visible (UV–vis) spectrophotometer (PerkinElmer, model Lambda 25) and distilled water was used as reference.

2.4. Adsorption of As(V)

2.4.1. Effect of the pH solution
The stock solution of As(V) was prepared by dissolving Na_2HAsO_4 (0.0416 g) in a solution containing 0.2 g of NaOH in 10 mL and finally diluted to the 50 mL by distilled water.

About 0.2 g of SMZY sample was weighed precisely and placed in the 50 mL centrifuge tube. Solution containing 20 mg L^{-1} of As(V) (20 mL) having difference initial pH was added to the sample. The adjustment of the pH solution was carried out by the addition of NaOH or HNO$_3$ solution to obtain the pH 4, 6, 7, 8, 10 and 12. pH was measured using a CyberScan pH/Ion 510 pH meter (Eutech Instruments). Mixture in the tube was shaken for 5 h at a constant agitation rate (120 rpm) and at ambient temperature. The mixture was then separated by filtration and lastly, the filtrate was analyzed for the concentration of As(V) using flame atomic absorption spectroscopy (FAAS).

2.4.2. Isotherm study
As(V) solution was prepared with the appropriate dilution of the stock solution to get the required concentrations of As(V) of between 10 and 50 mg L^{-1}. About 0.2 g of SMZY sample was weighed precisely and added with 20 mL As(V) solution (pH 6) in the centrifuge tube 50 mL. The tubes were then shaken for 5 h and the supernatant subsequently filtered. The concentration of As(V) before and after the adsorption were measured by FAAS.
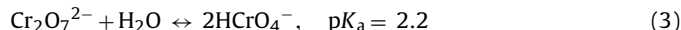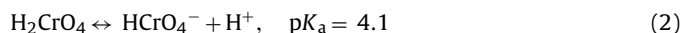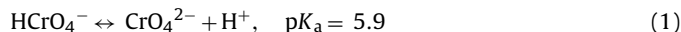
3. Results and discussion

3.1. Adsorption of Cr(VI) study

The removal of Cr(VI) from water by an adsorbent is highly dependent on the pH of the solution, which subsequently affects the surface charge of the adsorbent, the degree of ionization and the speciation of the adsorbate species [22]. In water as well, Cr(VI) anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and the concentration of the solution. Therefore, it was important to study the effect of pH on the removal of Cr(VI) onto SMZY.

Fig. 1 shows the effect of pH, ranging from 3 to 10 on the removal of Cr(VI) by each SMZY. The removal capacity of Cr(VI) by SMZY was observed to be the highest when Cr(VI) solution having pH 3

while the lowest sorption capacity at pH 10. Similar Cr(VI) removal capacity behavior from pH 5 to 8 was noted for both SMZY synthetic and commercial obtained with different initial concentration of surfactant in the solution. The Cr(VI) species may be represented in various forms such as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ in the solution phase as a function of pH. Cr(VI) speciation is affected by solution pH through the following equilibrium [23]:

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+, \quad pK_a = 5.9 \tag{1}$$

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+, \quad pK_a = 4.1 \tag{2}$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^-, \quad pK_a = 2.2 \tag{3}$$

Above pH 6, the dominant species is the yellow chromate anion, CrO_4^{2-}, between pH 2 and 6, $HCrO_4^-$ and dichromate ion, $Cr_2O_7^{2-}$ are in equilibrium [6]. From Eq. (1), the major species are $HCrO_4^-$ at pH 5 and CrO_4^{2-} at pH 7. Because of the distribution of Cr(VI) in water which is in the form of anion, it is clearly indicated that the zeolite Y that has been modified with cationic surfactant are suitable to adsorb Cr(VI) species in water at suitable pH. The adsorption efficiency of Cr(VI) was highest at pH 3 for each of the SMZY while the adsorption decreased when the pH increased. This is due to the dominant species of Cr(VI) which exist in water and the exchange capacity of the SMZY for one species. As described above, at lower pH, the Cr(VI) species are mostly in the univalent form ($HCrO_4^-$) and thus require one exchange site for one molecule of Cr(VI) species at that pH. In contrast, at high pH, the divalent form of Cr(VI) species ($Cr_2O_7^{2-}$, CrO_4^{2-}) are mostly present and necessitate two exchange sites from SMZY for the adsorption to occur. This resulted in higher removal capacity of Cr(VI) species by SMZY at lower pH than that at higher pH. In addition, the lower affinity of Cr(VI) sorption at pH 10 may also be influenced by the strong competition from OH$^-$ with Br$^-$ or chromate anion for the sorption sites since more OH$^-$ anions are present at high pH. Li [10] also found similar observations at pH 11 as more Cl$^-$ were desorbed at this pH. In addition, at pH values greater than 6, the presence of OH$^-$ ions forms the hydroxyl complexes of chromium. The Cr(VI) species are very soluble in aqueous solutions and their solubility increase with pH; therefore, it was practical to employ these series of SMZY in solutions with pH values of 8 and below.

Previous results showed that sorption of chromate anion (Cr(VI)) on the surfactant-modified zeolite followed a typical Langmuir-type isotherm [24]. The Langmuir equation is based on a kinetic approach and assumes a uniform surface, a single layer adsorbed material at constant temperature. The Langmuir equation is

$$\frac{x}{m} = \frac{bQ_oC_e}{1 + bC_e} \tag{4}$$

where x is the mass of adsorbate adsorbed (mmol); m the mass of adsorbent (kg); C_e the equilibrium concentration (mmol L^{-1}); b the Langmuir constant related to the affinity of the binding site and Q_o is the maximum adsorption at monolayer coverage (mmol kg^{-1}).

Eq. (4) can be simplified, if:

$$\frac{x}{m} = q_e = \text{amount adsorbed at equilibrium (mmol kg}^{-1}) \tag{5}$$

Therefore

$$Q_e = \frac{bQ_oC_e}{1 + bC_e} \tag{6}$$

The nonlinear form (Eq. (6)) can be evaluated by transforming to the linear equation:

$$\frac{m}{x} = \frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \tag{7}$$

When m/x or $1/q_e$ against $1/C_e$, a straight-line graph is obtained with slope is $1/bQ_o$ and intercept-Y is $1/Q_o$. Figs. 2 and 3 show the
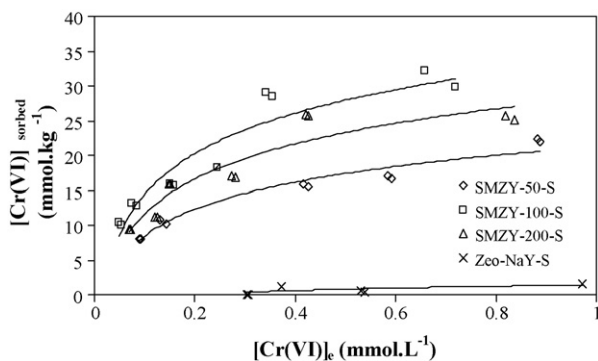
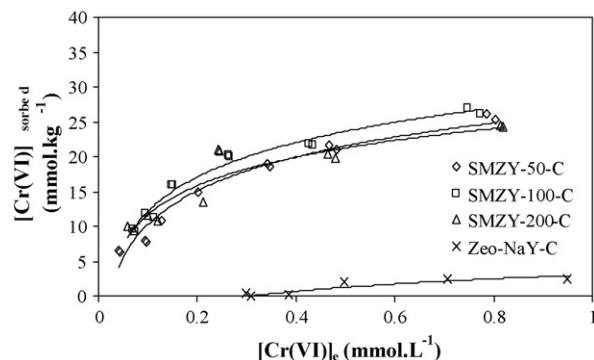**Fig. 2.** Sorption of Cr(VI) by SMZY and unmodified synthesized zeolite Y.

Fig. 3. Sorption of Cr(VI) by SMZY and unmodified commercial zeolite Y.

sorption capacities of Cr(VI) on the SMZY from synthesized and commercial zeolites, respectively. As a comparison, the sorption of Cr(VI) by the unmodified zeolites is also shown.

As shown in these figures (Figs. 2 and 3), the unmodified zeolite NaY had little affinity for Cr(VI). Zeolite Y has a net negative structural charge resulting from the isomorphic substitution of cations in the crystal lattice. Due to this negative charge, zeolite Y has little or no affinity for anionic species. In contrast, zeolite Y that had been modified with HDTMA effectively remove Cr(VI) from the aqueous solutions. The sorption of Cr(VI) by SMZY are varied based on the surfactant loading onto zeolite Y. When these data were plotted as the linear form of the Langmuir equation (Eq. (7)), a straight line was obtained showing that the isotherm data for the sorption of Cr(VI) by SMZY were well described by the Langmuir isotherm equilibrium model. Table 2 presents the values of Langmuir parameters for all the batch sorption isotherm experiments.

The results from the Langmuir isotherm study clearly showed that both zeolites treated with HDTMA at amounts equal to 100% of the ECEC of the zeolites resulted in the highest adsorption capacity for both types of SMZY. Zeolites treated with HDTMA at amounts equal to 50% and 200% of the external cation exchange capacity showed reduction in the removal capacity of Cr(VI) from aqueous solutions. The reduced sorption observed at lower HDTMA levels

Table 2
Values of the Langmuir parameters for sorption of Cr(VI) by SMZY

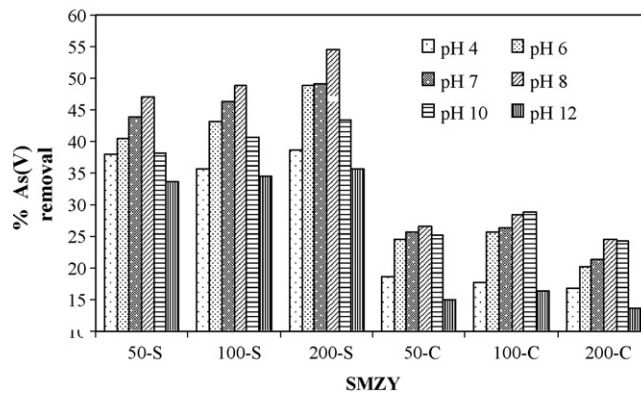| Samples	Q_o (mmol kg^{-1})	b (kg^{-1})	r^2
SMZY-50-S	21.01	6.90	0.9964
SMZY-100-S	37.59	7.19	0.9778
SMZY-200-S	30.77	6.37	0.9604
SMZY-50-C	26.04	7.25	0.9653
SMZY-100-C	31.35	6.51	0.9935
SMZY-200-C	27.10	7.38	0.9941

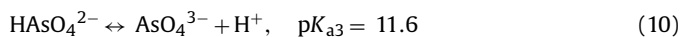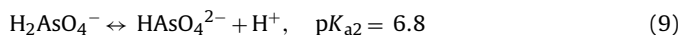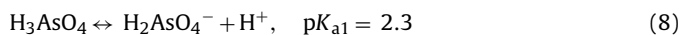**Fig. 4.** Effect of the initial pH solution in the removal of As(V) by SMZY.

(50%) might be resulted from the lower amount of HDTMA attached on zeolites. At higher HDTMA levels, the removal capacity of Cr(VI) was low may be due to the release of excess, loosely bound HDTMA from admicelles on the SMZY into the aqueous solution. This has subsequently resulted in the competition of the chromate with HDTMA in the solution to attach onto the surface of the zeolite. Haggerty and Bowman [24] also reported that the same observation occurred when the natural zeolite, clinoptilolite treated with HDTMA at an amount of 200% of the ECEC was used to remove chromate anions in water.

Table 2 also revealed that the SMZY from the synthesized zeolite Y adsorbed more Cr(VI) species than the commercial one because the synthesized zeolite Y exhibited lower ratio of SiO$_2$/Al$_2$O$_3$ and higher CEC than the commercial zeolite Y. In addition, the specific surface area of the synthesized zeolite Y was higher than the commercial one. The lower ratio of SiO$_2$/Al$_2$O$_3$ tends to offer higher exchange sites which enabled the synthesized zeolite Y to adsorb more HDTMA to cover its surface, and thus presented a higher value of adsorption capacity of Cr(VI). When compared to the organo-zeolite from the naturally occurring zeolite, clinoptilolite, the SMZY in this study showed higher sorption capacity. From a previous literature, Haggerty and Bowman [24] showed that the surfactant-modified zeolite from clinoptilolite at amounts equal to 50%, 100% and 200% of the ECEC have maximum adsorption of Cr(VI) at 2.35, 4.08 and 3.6 mmol kg^{-1}, respectively.

3.2. Adsorption of As(V)

The percentage of As(V) removal as a function of solution pH is illustrated at Fig. 4. The removal of As(V) by each SMZY occurred over a wide range of solution pH and was clearly affected by the initial pH of the solution, similar to the observation for the removal of Cr(VI) by SMZY. The trend for the removal of As(V) in different pH solution ranging from 4 to 12 was nearly identical for each of the SMZY. Favorable sorption of As(V) with SMZY from synthesized zeolite Y was found to take place at the pH region of 6–8 which is considered to be the pH for most drinking water.

As(V) speciation is affected by the solution pH through the following equilibrium:

$$H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+, \quad pK_{a1} = 2.3 \tag{8}$$

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+, \quad pK_{a2} = 6.8 \tag{9}$$

$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+, \quad pK_{a3} = 11.6 \tag{10}$$

From Eqs. (8) to (10), the As(V) species occurs mainly in the form of H$_2$AsO$_4^-$ in the pH range between 3 and 6, while a divalent anion HAsO$_4^{2-}$ dominates at higher pH values (such as between pH 8 and 11). In the intermediate region which is in the pH range between 6
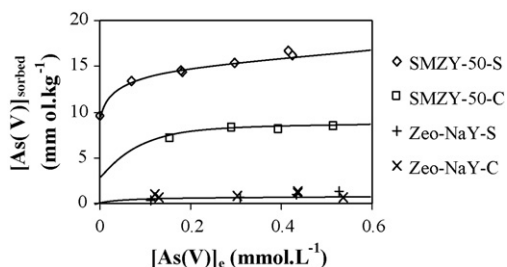
Fig. 5. As(V) sorption from aqueous solution by SMZY-50-S, SMZY-50-C and respective parent zeolite NaY.

Fig. 7. As(V) sorption from aqueous solution by SMZY-200-S, SMZY-200-C and respective parent zeolite NaY.

and 8, both species coexist with one another [25]. Thus, it is evident that the adsorption of As(V) by SMZY is pH dependent.

According to the Eq. (8), As(V) species at pH 4 exists mostly as neutral form (H_3AsO_4) and univalent form but the neutral form is much more common. As a result, the removal capacity at pH 4 is lower than that at pH 6 since the mechanism for the removal of As(V) by SMZY is mainly by ion exchange and only a little for the adsorption to occur. The removal of As(V) was lowest at pH 12 because at this stage, the dominants As(V) species exist as divalent ($HAsO_4^{2-}$) and trivalent (AsO_4^{3-}) forms which need two and three exchange sites from SMZY for the adsorption to occur. In contrast, at pH 8, the univalent ($H_2AsO_4^{-}$) form of As(V) is dominant which only need one exchange sites from SMZY, hence, more As(V) species can be adsorbed by SMZY. In addition, the abundant OH^{-} which exist in this solution at pH 12, strongly compete with the As(V) anions at the exchanges sites. Shevade and Robert [26] also obtained the same results when they used zeolite NH_4Y to remove As(V) at pH 13.2. They had studied the structure of this zeolite after contacting with the As(V) at pH 13.2 and found that the structure was unstable resulting in the formation of a poorly crystalline aluminosilicate, but the aluminosilicate solid was still present at this pH, thus, the reduced As(V) sorption was due to the competition with aqueous OH^{-}.

The As(V) exist mainly in the anion form over a wide range of pH, thus proving that the sorption of As(V) is attributable to the anion exchange provided by the reversed charge from negative to positive that was created by the double layer from the HDTMA at the zeolite Y surface in SMZY. This observation is comparable with the sorption of chromate anion by SMZY.

Previous work [13,24,27] have shown that anion sorption by surfactant-modified zeolite is well described by the Langmuir isotherm. The sorption isotherms of As(V) from aqueous solutions by SMZY-50 (50% from ECEC), SMZY-100 (100% from ECEC) and SMZY-200 (200% from ECEC) are given in Figs. 5, 6 and 7, respectively. The sorption of As(V) by unmodified zeolite Y is also given in each figure for comparison.

The sorption of As(V) by SMZY fitted very well with the Langmuir isotherm model because a straight line is obtained when these data are plotted according to Eq. (7) with the coefficient of determination
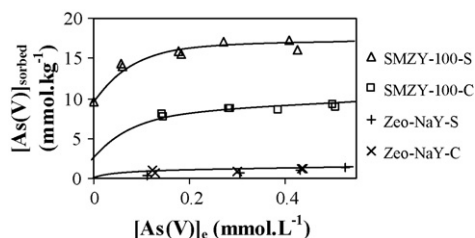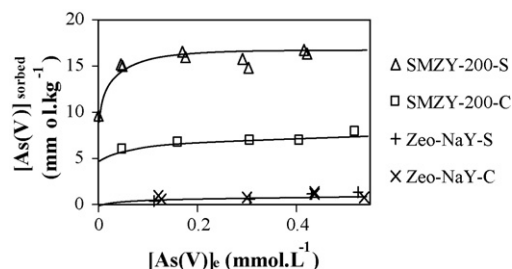
(r^2) for each set of the linearized data exceeding 0.96 as shown in Table 3.

Figs. 5–7 demonstrate that both unmodified zeolite NaY have little affinity for As(V), in contrast, the SMZY shows significant sorption of As(V) from the aqueous solution. The ability of the SMZY to sorb As(V) is due to the anion exchange at the positive sites brought about by the reversed charge resulting from the HDTMA double layer onto the zeolite surface. Because the As(V) exists in water as the anion form and analogous with the Cr(VI) species, the SMZY is able to sorb As(V) by the anion exchange. On the contrary, the unmodified zeolite NaY having a net negative charge in the structure tends to repulse the anionic form of As(V) species. This result is similar to the previous observation where the 0% surfactant surface coverage, the raw zeolite has no affinity for arsenate [18]. The SMZY prepared from the synthesized zeolite Y sorbed more As(V) than the SMZY from the commercial one. The noteworthy difference of the As(V) sorption by SMZY from the synthesized zeolite compared to the SMZY from the commercial is due to the properties of the parent synthesized zeolite Y which has higher CEC, higher surface area and lower ratio of silica per alumina than the commercial zeolite Y. These properties strongly affect the adsorption capacity of the As(V) by SMZY.

From the Langmuir analysis, the sorption of As(V) by SMZY from the synthesized zeolite Y varied slightly with each other in an ascending series as SMZY-50-S > SMZY-100-S > SMZY-200-S. SMZY prepared from the commercial zeolite Y treated by HDTMA which attained 100% of the ECEC of the zeolite, showed the highest sorption capacity. The reason for the decreasing As(V) sorption capacity for zeolites treated with HDTMA which attained 200% of the ECEC of the zeolite is similar to the sorption of Cr(VI). These results are caused by the release of excess, loosely bound HDTMA from micelles on the SMZY into the aqueous solution resulted in the competition of the As(V) with HDTMA in the solution to attach onto the zeolite Y surface. Compared to other previous literatures, SMZY from this study can adsorb As(V) more than the HDTMA-modified clinoptilolite-heulandite rich tuffs from Oaxaca (0.044 mmol kg^{-1}) and Chihuahua (0.052 mmol kg^{-1}) [17] and also more than HDTMA-modified kaolinite (9.0 mmol kg^{-1}) and HDTMA-modified clinoptilolite from St. Cloud Mine in Winston (7.2 mmol kg^{-1}) [18].

Fig. 6. As(V) sorption from aqueous solution by SMZY-100-S, SMZY-100-C and respective parent zeolite NaY.

Table 3
Values of the Langmuir parameters for sorption of As(V) by SMZY

Samples	Q_o (mmol kg^{-1})	b (kg^{-1})	r^2
SMZY-50-S	17.92	21.46	0.9949
SMZY-100-S	17.89	55.90	0.9696
SMZY-200-S	17.04	195.67	0.9981
SMZY-50-C	8.94	25.41	0.9951
SMZY-100-C	10.18	20.46	0.9980
SMZY-200-C	9.16	11.14	0.9970

4. Conclusions

Zeolite Y basically has little or no affinity to the anion species of Cr(VI) and As(V), but the modification of zeolite Y by the cationic surfactant (HDTMA) can enhance the adsorption capacities of Cr(VI) and As(V) on the zeolite Y. The removal capacities of Cr(VI) and As(V) on SMZY are dependent on the pH of the solution whereby the highest removal capacities for Cr(VI) and As(V) are observed at pH 3 and 8, respectively. At those pH, both species were in the univalent form which only need one exchange site from the SMZY, hence, more Cr(VI) and As(V) species can be adsorbed by the SMZY. The adsorption of Cr(VI) and As(V) on the SMZY fitted well on the Langmuir isotherm equilibrium with SMZY with HDTMA amount equal to the 100% of ECEC of zeolite Y showed the highest adsorption capacity. Surfactant-modified zeolite Y derived from the synthesized zeolite Y tend to adsorb more Cr(VI) and As(V) than the commercial one. This is due to the physicochemical properties of these zeolites where the Zeo-NaY-S has lower silica to alumina ratio, higher CEC and ECEC as well as higher specific surface area compared to Zeo-NaY-C which creates more exchange sites for the adsorption process to occur. Thus, the synthesized zeolite NaY from rice husk ash treated with HDTMA can be used as a potential sorbent to remove hexavalent chromium (Cr(VI)) and pentavalent arsenic (As(V)) from water.

Acknowledgements

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