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Investigation of Ammonium and Nitrite Removal by Zeolite Material Synthesized on Red Mud Base

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Abstract

The zeolite with the unit formula of $Na_8(Al_6Si_6O_{24})S.4H_2O$ was synthesized directly on red mud base with addition of single silicon (signed as RH-ZeO-Si) and both silicon and aluminum portions (signed as RM-ZeO-SiAl) to original Tan Rai (Vietnam) red mud. The structure of the zeolite was studied by X-Ray difration and FT-IR absorption spectra. The synthesized materials were studied on their adsorption ability of ammonium and nitrite ions. The results showed that, the adsorption of ammonium cation was mostly allowing ion-exchange mechanism and the zeolite crystaline forms played predominantly role besids minor one of single metal oxides. For nitrite anions, it is otherwise, the adsorption mechanism was mostly leant to electrostatic attraction between nitrite anions and electropositive effect of the hematite surface in light acidic condition. The adsorption isotherms of all ammonium and nitrite ions on both synthesized materials were nearly conformable with Freundlich model than Langmuir model. Those showed that, both materials have unhomogeneous adsorption surface. The maximum adsorption capacity of ammonium and nitrite on RM-ZeO-Si was 5.71 mg/g and 2.73 mg/g respectively, and on RM-ZeO-SiAl was 5.61 mg/g and 3.12 mg/g respectively. The initial test of competitive ions influencing on adsorption ability showed that, for all cases the competition of cations to ammonium ion was more significance than those of anions to nitrite ion in the same conditions.

Keywords: ammonium and nitrite adsorption; zeolite; Tan Rai red mud

1. Introduction

Nitrite (NO_2^-) and ammonium (NH_4^+) are most toxic compositions of inorganic nitrogen in environment which are commonly found in natural water. But they are often enriched to over the contaminant levels as a result of excessive using of fertilizers, waste water from industrial production and human life (Cengeloglu *et al*., 2006; Eturki *et al*., 2012). Excess concentrations of nitrite and ammonium ions in drinking water seriously effect to human health. According to Vietnamese National Technical Regulation on Supplied Water Quality (QCVN 01: 2009/BYT), the maximum acceptable concentration of nitrite and ammonium are 3 mg/L. In "*Guidelines for Drinking Water Quality*" of World Health Organization (WHO) showed that communities usually use polluted water with excess concentration of nitrite and ammonium may cause blue baby disease as methemoglobinemia in newborn infant (Eturki *et al*., 2012). Furthermore, nitrite ion can produce nitrosamine, a carcinogenic material within the acidic condition of the stomach of gastric cancer. Because of this toxicity to human metabolism, the removal of nitrite and ammonium ions has received increasing attention in recent years. For excess nitrite and ammonium removal, the adsorption technology with different materials such as activated alumina, modified activated carbon, synthetic ion exchange resin, materials produced from agriculture wastes such as sugarcane, bagasse, wheat and rice straw is usually used. Especially synthetical zeolites and natural zeolites are considered to be a competitive and effective materials for removal of these ions in aqueous solution (Meah *et al*., 1994; Booker *et al*., 1996; Njoroge BNK *et al*., 2004)

Red mud waste from Tan Rai Alummina Plant (in Vietnam) contains residual Al_2O_3 quatity up to 15.05%, SiO_2 5.86%, beside predonminant amount of Fe_2O_3 (more than 60%) and other minor metals' oxides such as TiO_2, MnO_2 (Pham Thi Mai Huong *et al*., 2015). Red mud has became a suitable source for synthesis of zeolites attributing to its high silicon and aluminum content, abundance and availability. There were numbers of publication used residual alummina and silicon oxide in red mud to synthesize zeolites and applied for treatment of ammonia and other polluted substances in water and waste water (Booker *et al.*, 1996; Marañón *et al.*, 2006; Nassar and Nassar, 2012). In this study, zeolites were synthesized directly in Tan Rai red mud base by hydrothermal method without alumminium and silicon pre-recovery. The adsorption ability of the zeolites for ammonium and nitrite ions was investigated.

2. Materials and Methods

2.1 The materials synthesis

The detail study of materials synthesis was presented in other work. In this paper, the optimal conditions for material synthesis were applied and main materials characterisations were summarized.

2.1.1 Material with single supplement of silicon (RM-ZeO-Si)

The red mud sample was firstly dispersed in NaOH 4M solution with the solid and liquid ratio of 1/10. The mixture was heated to temperature of 150°C and kept heating for 6 h. Then the extra silicon as $Na_2SiO_3.9H_2O$ was added to the mixture in continuously stirring to meet the molar ratio of Si/Al equal 4/1. The zeolite formation completed after 24h at a temperature of 95°C. Material then was filtered and washed by distiled water to pH equal 7 - 8 to remove dissolved ions and dried at 105°C to constant weight. The material was signed as RM-ZeO-Si.

2.1.2 Material with simulstaneously supplement of silicon and aluminum (RM-ZeO-SiAl)

The synthesis process of this material was similar to RM-ZeO-Si synthesis, but instead of only silicon addition, the $Al_2(SO_4)_3.18H_2O$ were simultaneously added and molar ratio of Si/Al was also kept the same as 4/1. The material was signed as RM-ZeO-SiAl. The zeolites' crystaline formation was characterized by XRD spectra and FT-IR absorption spectra.

2.2 Ammonium and nitrite adsorption study

The study realized by batch adsorption mode with ammonium or nitrite solution of 10 mg/L and ratio of solid (synthesized material) and liquid (ammonium or nitrite solution) phases was 1gram/100mL. The initial pHs of adsorption solution were adjusted for each experiments by HCl or NaOH solution all of 0.1 M. The adsorption mixtures were mixed around on shaker at 180 rpm for designed contact time and in constant temperature of 25°C. After contacted times the solid phase was separated by filtration though paper membrane with 0.45 µm porousity. The remained ammonium or nitrite concentrations in water phases were determined by spectrophotometric method (APHA, 1995).

2.3 Adsorption efficiency and adsorption capacity

The adsorption efficiency, H% and adsorption capacity, q were calculated by following formulas

$$H = \frac{(C_0 - C_e).100}{C_0} \quad (1)\ ;$$

$$q_e = \frac{(C_0 - C_e).V.10^{-3}}{m} \quad (2)$$

where *q* is adsorption capacity of ammonium or nitrite on the material (mg/g), *H* is the adsorption efficiency (%), C_0 and C_e are the initial and the equilibrium concentration of ammonium or nitrite (mg/L), *V* is the solution volume (L), *m* is the mass of the material (g).

The Langmuir and Freundlich isothermal models were applied for discussion of adsorption characterization and property of the adsorption processes.

3. Results and Discussion

3.1 The material charactrizations

The XRD spectrum of RM-ZeO-Si in figure 1 shows the presence of hematite (Fe_2O_3) crystal by peaks at 2Θ angle at 2.696° and 2.541°, and remarkable peaks of zeolite crystal formularized $Na_8(Al_6Si_6O_{24})S.4H_2O$ at 6.350° and 3.670°. The crystalline formation of RM-ZeO-SiAl (figure 1) was presented by peaks at 6.392°, 4.666°, 3.238°, and it has the same chemical formula as that in the RM-ZeO-Si material. It is clearly that, both materials likely contain a new kind of zeolite crystallized directly on hematite base with one sulfur atom in its crystaline unit.

The combination of XRD spectrum and IR spectrum (figure 2) showed that, in the material RM-ZeO-Si, the sodalite tetrahydrate zeolite crystaline phase was appeared on hematite base, and furthermore in the material RM-ZeO-SiAl appeared zeolite phase characterized by variations of bonds Al-O in tetrahedron AlO_4 and suggested as zeolite P.

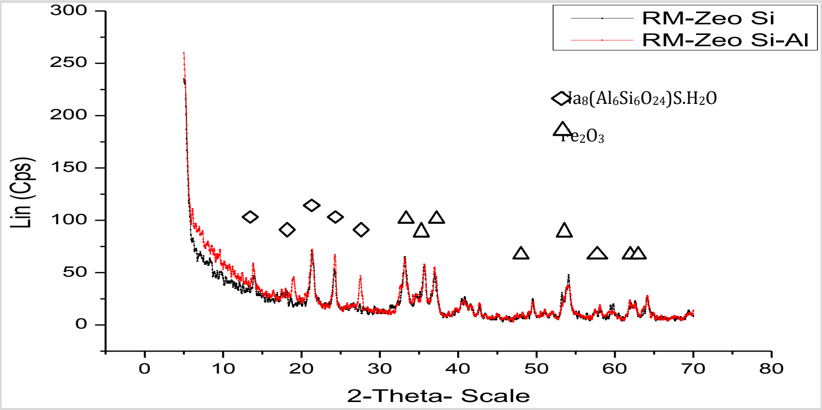


Figure 1. The XRD spectra of RM-ZeO-Si and RM-ZeO-SiAl

3.2 Study of ammonium and nitrite adsorption of the synthesized materials

3.2.1 Influence of pH on adsorption ability

The effect of pH was carried out according to the procedure presented in§2.2. The initial ammonium and nitrite concentration was 10 mg/L; the initial pH values of the adsorption solutions were adjusted in range of 2 to 12; the contact time was 180 min. The adsorption efficiency (%) was calculated as the formula (1) presented in§2.3 and the results are showed in figure 3(a) and 3(b) for RM-ZeO-Si and RM-ZeO-SiAl respectively.

As seen from figure 3, the adsorption efficiency of ammonium increased when pH of the adsorption solutions increased to 6 for both of synthesized materials. In this pH area, cations H^+ strongly compete against NH_4^+ ions and there might be also considered unstable of zeolite in acidic solution. The optimum pH for ammonium adsorption was in the range of 6 to 7 (Zhao *et al.*, 2016). The adsorption of NH_4^+ from aqueous solution on synthetic materials mainly was ion-exchange between Na^+ of zeolite section in the material with NH_4^+ in solution (equation 1), (Wen D *et al.*, 2006; Watanabe Y *et al.*, 2005)

$$\text{Zeolite-Na}^+ + NH_4^+ \leftrightarrow Na^+ + \text{Zeolite-}NH_4^+ \quad (1)$$

When the pH continuously increased to the level higher than 7, ammonium adsorption efficiency was decreased due to part of ammonium ions converted to neutral ammoniac molecules following equilibria of reaction in equation (2) as below:

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \quad (2)$$

they do not exchange with cation Na^+.

When the pH value was at 9, large portion of NH_4^+ ions are converted to less adsorption NH_3 molecules, so the adsorption efficiency of ammonium should have been more sharply decreased; but in this case it was only lightly decreased. The reason is a part of ammoniac was evaporated to the air but it was sumed to ammonia adsorbed on the material (calculated allowing formula 1). Other reason of deceasing adsorption efficiency could be the partial decomposition of the zeolite in alkaline solution.The adsorption ability of hematite in these materials to ammonium ion was negligible.

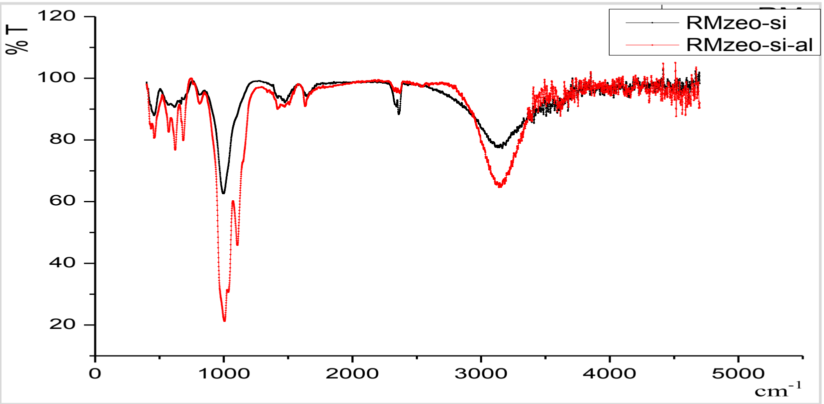


Figure 2. The IR spectra of RM-ZeO-Si and RM-ZeO-SiAl

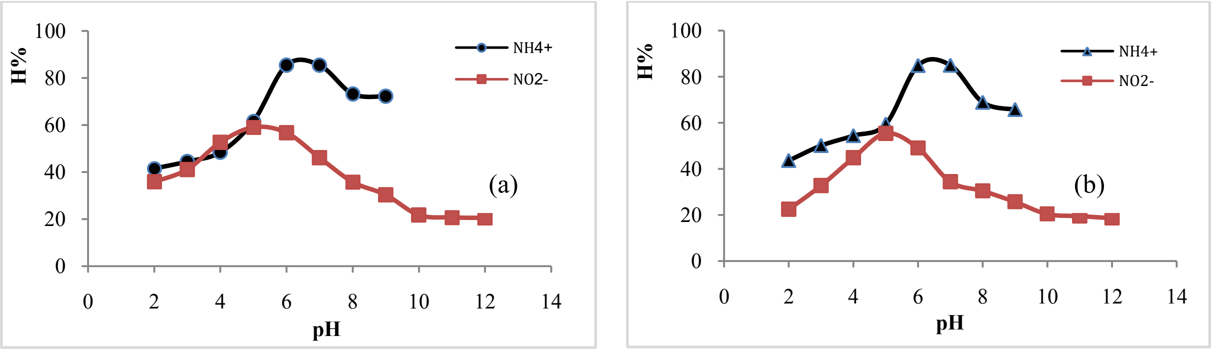


Figure 3. Influence of pH on ammonium and nitrite adsorption of RM-ZeO-Si (a) and RM-ZeO-SiAl (b)

The results at figure 3 also showed that, adsorption ability of nitrite anions was highest at pH value of 5 for both materials. At pH < 5, the most competitive effect should have consider to H$^+$ ions. There is different than ammonium ion, the nitrite adsorption mechanism is not ion-exchange, but it is possibly most nitrite anions adsorbed on hematite surface, which has electropositive effect in lower pH condition, and an other part could be attached to Na$^+$ cations on zeolite and shared them with oxygen atoms in the zeolite net. At higher pH values, the adsorption efficiency of nitrite decreased due to competition of OH$^-$ anions and loss of electropositive effect of hematite surfaces.

3.2.2 Contact time

Investigation of the contact time in adsorption equilibrium of ammonium and nitrite on synthesized materials was carried out as procedure presented in §2.2 with constant concentration of 10 mg/Lfor both ions, the initial pH of adsorption solution was 6 for ammonium and 5 for nitrite. The contact times were survayed in the range of 30 to 300 min. The results were showed in figure 4.

It could be seen that, the time necessary to get adsorption equilibrium for ammonium was about 120 min and those for nitrite was about 180 min for both materials. The different equilibrium time for ammonium and nitrite could be also a evidence of different adsorption mechanism on the adsorption processes.

3.2.3 Adsorption isotherms of ammonium and nitrite

a) Adsorption of ammonium ions on RM-ZeO-Si and RM-ZeO- SiAl

All the experiments in this investigation were carried out at 25°C with the initial ammonium concentration from 1 to 60 mg/L, pH solution was 6, contact time was 120 min. The adsorption capacity was calculated follow formula (2) in §2.2. The linear form of the Langmuir and Freundlich isotherms were given in figure 5.

The isotherms in figure 5 showed that, the adsorption surface of the materials was not homogenous. Besides adsorption mechanism as ion-exchange of sodium cations on the zeolite crystals lying on the red mud base with ammonium cations in the solution (as discussed in §3.2.1), there was contribution of ammonium adsorption of other aluminium oxide

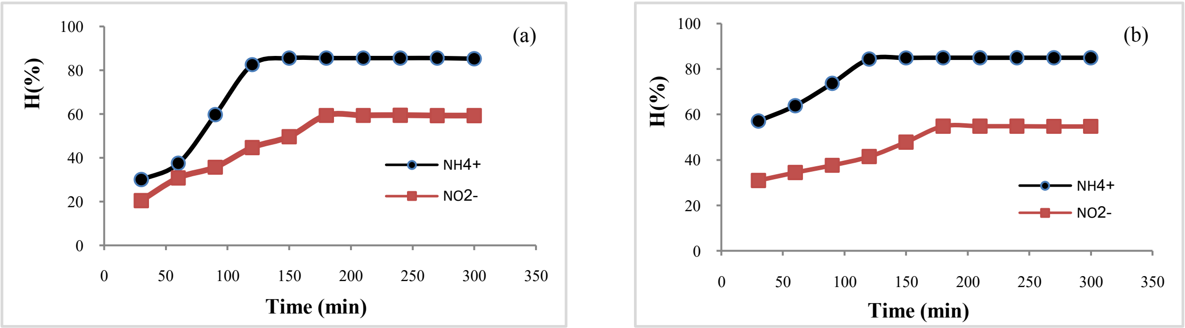


Figure 4. The contact time of ammonium and nitrite for RM-Zeo-Si (a), RM-Zeo-SiAl (b)

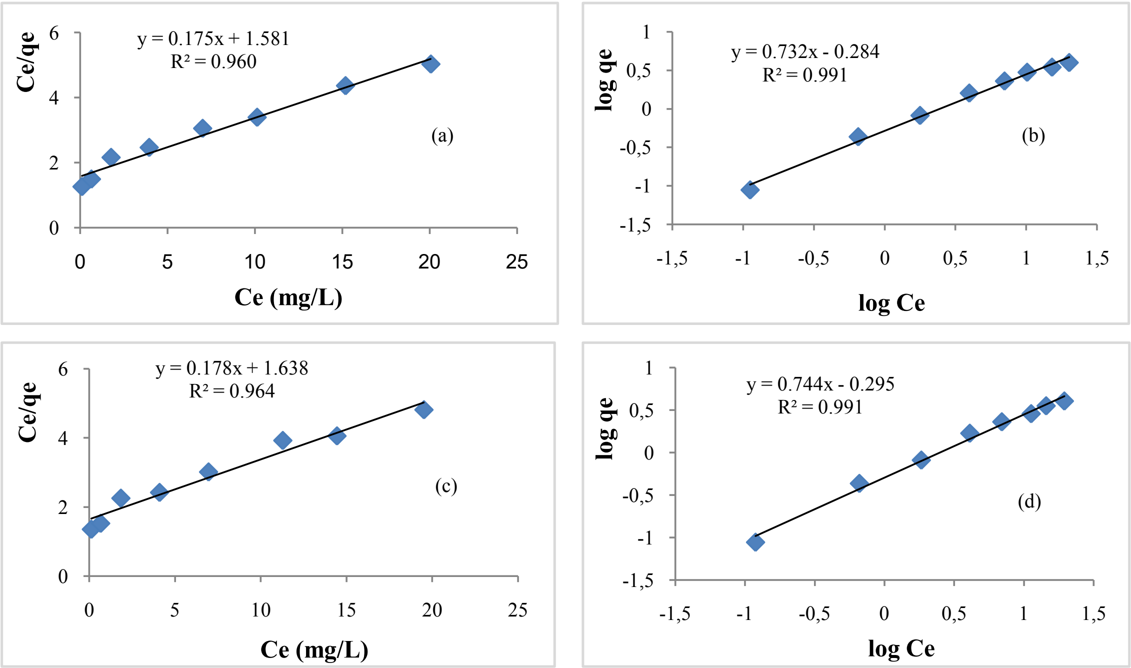


Figure 5. Linear plot of Langmuir and Freundlich isotherms of ammonium on RM-ZeO-Si (a), (b) and RM-Zeo-SiAl (c), (d)

formations in the materials. So in both cases of RM-ZeO-Si and RM-ZeO-SiAl, the adsorption isotherms have trend to accord with Freundlich isotherm than Langmuir one.

b) Adsorption of nitrite ions on RM-ZeO-Si and RM-ZeO-SiAl

For nitrite adsorption, the investigation was caried out with initial concentrations in the range of 1 to 200 mg/L, pH values of 5 and the contact time was 180 min. The results were illustrated in figure 6.

For adsorption of nitrite on both synthesized materials, there was predominantly the adsorption mechanism of electrostatic attraction between nitrite anions in solution and materials surface having electropositive effect and minor contribution possibly was coordinate binding of multi-coordinate metals such as Fe, Ti...(the transitional metals) in red mud with nitrite anions in the solution. With such complicated adsorption mechanisms occured on the materials surface, the single adsorption isotherm can not describe successfuly. Dispite, in this case, the Freundlich isotherm model could be more fitting.

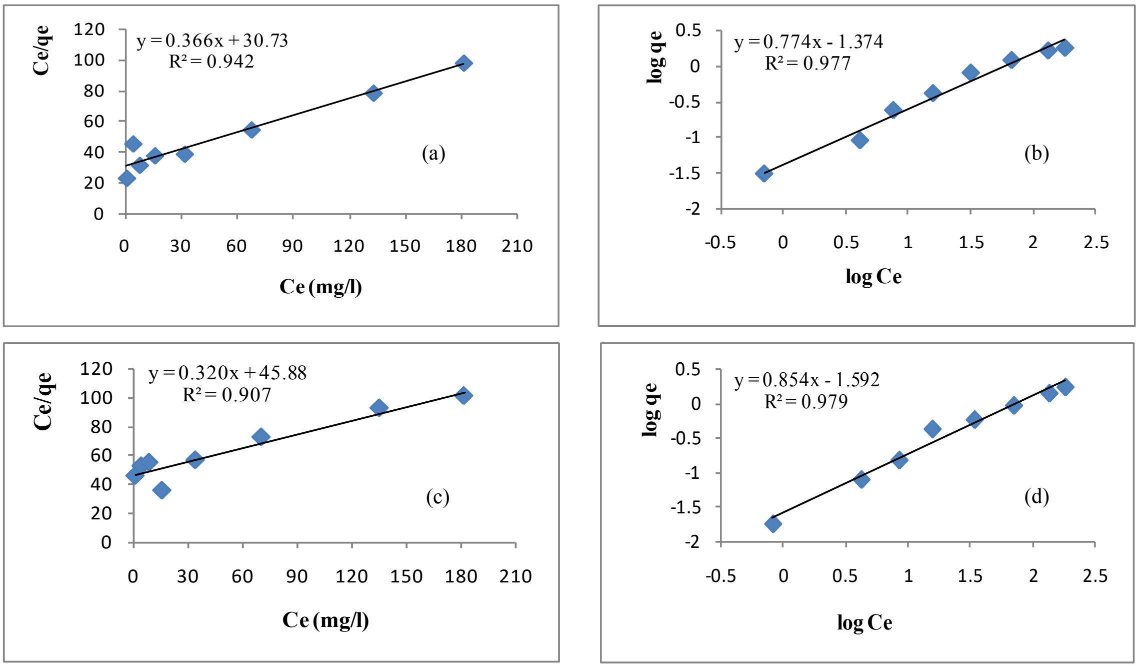


Figure 6. Linear plot of Langmuir and Freundlich isotherm of nitrite on the RM-ZeO-Si (a), (b), and RM-ZeO-SiAl (c), (d)

Table 1. Parameter of Langmuir, Freundlich isotherms for adsorption of ammonium and nitrite on the RM-ZeO-Si and RM-ZeO-SiAl

Materials	Adsorbed ions	Freundlich isotherm model			Langmuir isotherm model		
		n	K_F	R^2	q_{max} (mg/g)	K_L	R^2
RM ZeO-Si	NH_4^+	1,36	0,565	0,991	5,71	0,110	0,960
RM ZeO-Si	NO_2^-	1,29	0,042	0,977	2,73	0,012	0,942
RM ZeO-SiAl	NH_4^+	1,34	0,507	0,991	5,61	0,108	0,964
RM ZeO-SiAl	NO_2^-	1,17	0,025	0,979	3,12	0,006	0,907

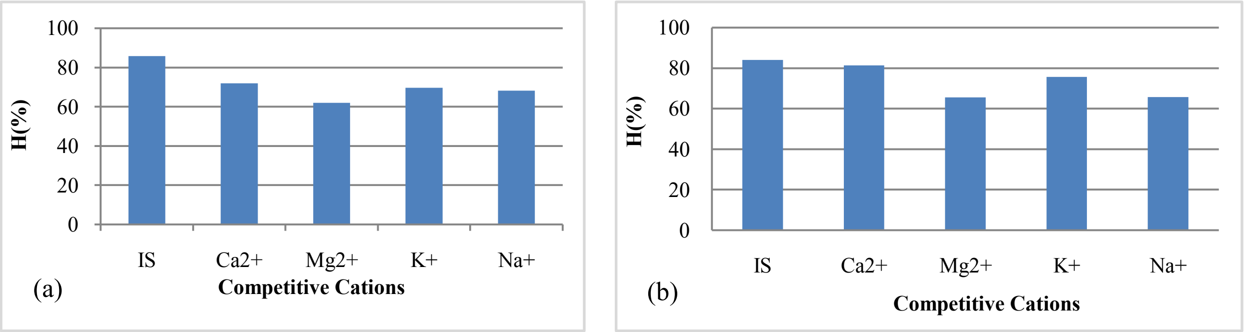
Based on the adsorption isotherms in figures 5 and 6, the maximum adsorption capacity of ammonium and nitrite on both materials and other parameters were determined and presented in table 1.

According to the data in table 1, the maximum adsorption capacity calculated following Langmuir model of ammonium on RM-Zeo-Si and RM-ZeO-SiAl was 5.61 mg/g and 5.71 mg/g respectively;the maximum adsorption capacity of nitrite on RM-ZeO-Si was 2.73 mg/g and on RM-ZeO-SiAl was 3.12 mg/g

3.2.4 Influence of competitive cations on ammonium remolval

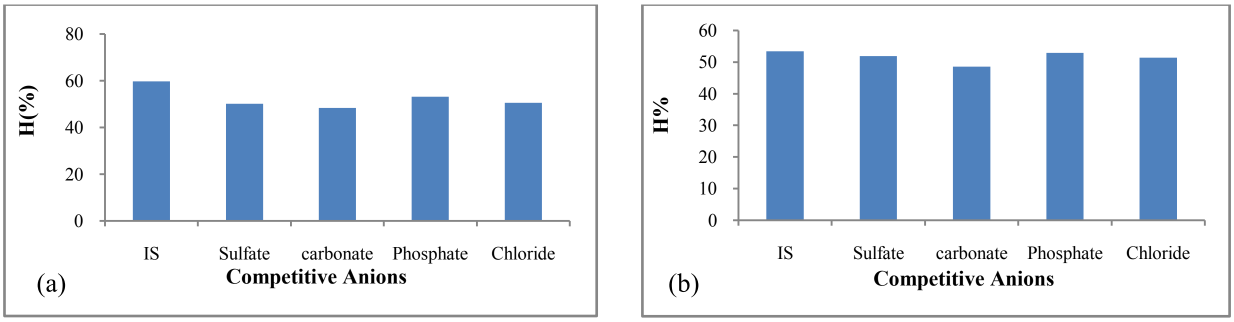
In natural water, there are usually cations such as Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Na^+...in the form of inorganic salts dissolved (Zhao *et al.*, 2016). For initial survey, influence of these cation on ammonium adsorption was tested with equal concentration of each cation as concentration of ammonium in solution (10 mg/L), and the experiment conditions of the adsorption processes were similar prevous investigation. The influence of each cation on ammonium adsorption was showed in figure 7.

As discussion above, the adsorption of ammonium ions on the synthesized materials is mainly ion exchange with Na^+cations on the zeolite forms. Therefore, presence of other cations in the solution will effect by the same mechanism. In general, the ion exchange force of a cation depends on its charge and ionic radius. If that, in the case of 4 surveyed cations, the ion exchange posibility must be increased in order of $K^+ < Na^+ < Ca^{2+} < Mg^{2+}$ (Huang *et al.*, 2010; Lei *et al.*, 2008). According to result showed in figure 7 for both materials, this order is $Ca^{2+} < K^+ < Na^+ < Mg^{2+}$. This phenomenon is just explained by the influence of environment conditions in which ion exchange occured and the sorption selectivity of zeolite to surveyed cations. The different results were also reported in other published papers, that the reduction in ammonium ion sorption capacity followed the order $K^+ > Ca^{2+} > Na^+ > Mg^{2+}$ for identical concentrations (Sarioglu, 2005; Farkaš *et al.*, 2005). This is because different zeolite has different chemical composition and structures, and thus has different cation selectivity to cations in solution (Zhang *et al.*, 2011). The zeolite studied in this work was synthesized directly on Tan Rai (Vietnam) red mud containing predonminantly hematite, so it can effect to the ion exchange ability of the material (Zhao *et al.*, 2016).



Note: IS signed as Initial Solution

Figure 7. The influence of competitive cations on the ammonium adsoprption of RM-ZeO-Si (a) and RM-ZeO-SiAl (b) materials



Note: IS signed as Initial Solution

Figure 8. The influence of competitive anions for the removal of nitrite by synthetic RM-ZeO-Si (a) and RM-ZeO-SiAl (b) materials

3.2.5 Influence of competitive anionson nitrite removal

Different than ammonium, nitrite adsorption on sythezised materials does not accordings to ion exchange mechanism, but it is mainly the electrostatic attraction one; and hematite and other metals oxides play principal role in this case. So common anions such as chloride, bicarbonate, phosphate and sulfate in natural water could compete with nitrite anion (Wan *et al.*, 2012). The experiment with identical concentrtion (10 mg/L) of bicarbonate, sulfate, phosphate, chloride and nitrite ions gave results showed in figure 8. For both materials, the competition decreased softly according to the order: Bicarbonate > Sulphate > Chloride > Phosphate.

4. Conclusion

The red mud from Tan Rai (Vietnam) alumina plant was the original material for this investigation. Adding of single sodium silicate and simultaneously sodium silicate and aluminum sulfate in zeolite synthesis process, the zeolite crystals were appeared on hematite base. The general formula of zeolite was determined as $Na_8(Al_6Si_6O_{24})S.4H_2O$. The new materials were characterized by X-ray diffraction (XRD), and FT-IR spectrum. The materials have ability to adsorb ammonium cation predominantly according to ion exchange mechanism between sodium cation in the zeolite crystals and ammonium ion in the solution, and to adsorb nitrite anion mainly by the mechanism of electrostatic attraction of metals oxide surface with nitrite anion in the solution. The adsorption capacity of ammonium achieved the values of 5.71 and 5.61 mg/g; nitrite of 2.73and 3.12 mg/g for RM-ZeO-Si and RM-ZeO-SiAl respectively. The new materials have high potencial to apply for ammonium and nitrite removal from water environment.

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