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Synthesis of zeolites from Tay Nguyen red mud and test of their adsorption ability

Nghiên cứu chế tạo vật liệu zeolit từ bùn đỏ Tây Nguyên và khảo sát khả năng hấp phụ của vật liệu

Research article

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Red mud is the waste from alumina production, contain high amount of residual alkaline, aluminate and some metals oxide such as iron oxide, silicon oxide, titanium oxide...; in which aluminum and silica proportions could be used for zeolite synthesis. The zeolite was synthesized by the hydrothermal method for obtaining RM-ZeO-Si which was signed for Si added and RM-ZeO- Si-Al for both Si and Al added. The obtained zeolites were then characterized by the XRD, EDX, SEM, BET and FT-IR methods. The results indicate that the synthesized zeolite is likely the new kind one with one surfur atom in the crystaline unit and has general formula of $Na_8(Al_6Si_6O_{24})S.4H_2O$. We tested the ability of ammonium and nitrite adsorption of the synthesized zeolites and found that the synthesized zeolites had very high adsorption capacity of both cation ammonium and anion nitrite; but the adsorption mechanism of each was different. Adsorption mechanism of ammonium was suggested as predominant ion exchange between ammonium cation in solution and sodium cation in zeolite crystals; while nitrite adsorbed on surface material by electrostatic attractive force between nitrite anion and electropositive surface of iron oxide particles.

Bùn đỏ là chất thải từ quá trình sản xuất nhôm, chứa lượng lớn kiềm, oxit nhôm và một số oxit khác như sắt oxit, silic oxit, titan oxit…trong đó tỷ lệ nhôm và silic có thể sử dụng để tổng hợp zeolit. Vật liệu zeolit được tổng hợp bằng phương pháp thủy nhiệt, thêm Si được ký hiệu là RM-ZeO-Si; vật liệu thêm đồng thời Si, Al được ký hiệu là RM- ZeO-Si/Al. Vật liệu zeolit tổng hợp được phân tích đặc trưng cấu trúc bằng các phương pháp XRD, EDX, SEM, BET và FT-IR. Các kết quả phân tích cho thấy vật liệu zeolit tổng hợp có điểm mới khác biệt so với các zeolit thông thường bởi trong cấu trúc phân tử có chứa nguyên tử S, công thức phân tử của zeolit là $Na_8(Al_6Si_6O_{24})S.4H_2O$*. Kết quả khảo sát hấp phụ ban đầu cho thấy vật liệu có khả năng hấp phụ với cả ion amoni và nitrit, cơ chế hấp phụ khác nhau. Quá trình hấp phụ cation amoni là do quá trình trao đổi ion giữa cation amoni với cation natri trong tinh thể zeolit, còn quá trình hấp phụ nitrit trên bề mặt vật liệu do tương tác tĩnh điện giữa nitrit với các cấu tử oxit sắt.*

Keywords: adsorption ability, Tay Nguyen red mud, zeolites

1. Introduction

The red mud waste from Tan Rai Alumina Plant (Tay Nguyen, Vietnam) contains 40-55% of Fe_2O_3 and others oxides such as Al_2O_3, SiO_2, MnO_2, TiO_2…[1]. Red mud has accumulated over years and it is a high potential to cause serious environmental problems due to its high alkalinity and large amount [2,3]. However, oxides in red mud in general, have high capacity adsorption of heavy metals such as Pb, Cu, As...[4,5] and anions in aqueous solutions such as NO_3^-, PO_4^{3-} [6,7]. Silicon oxide and aluminium residual in red mud have been a source for zeolites synthesis. Ying Zhao et al [8] synthesized zeolite from red mud for their study of ammonium treatment in water solutions and showed that synthesized zeolite was effective removal of ammonium in synthesized and real polluted waters [8]. However, the ratio of silicon per aluminum in red mud is commonly very low to satisfy the

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total molar ratio of Si/Al for effective zeolite synthesis. Therefore, it was necessary to add the silicon oxide to original red mud. In this study, in order to have suitable total mole ratio of Si/Al, the single sodium silicate, $Na_2SiO_3.9H_2O$ or simultaneously $Na_2SiO_3.9H_2O$ and $Al_2SO_4.9H_2O$ were added to the red mud and then dissolved them together with those remained in red mud by NaOH solution. The hydrothermal method was used for the synthesis. The characterization of the zeolites and their adsorption ability of ammonium and nitrite ions were investigated.

2. Materials and methods

2.1. Red mud sample

The red mud sample was collected from the waste area of Tan Rai Alumina Plant in Lam Dong province, Tay Nguyen, Vietnam. After screening through 0.5 mm sieve for removal of nonnative matter, the sample was neutralized by HCl down to pH 7 and washed by deionized water to remove almost sodium, chloride and other dissolved ions, then it was filtered and dried at 60^{o}C to constant weight.

2.2. Zeolite synthesis

Zeolite synthesis 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^{o}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 to 4. The zeolite formation was completed after 24h at a temperature of 95^{o}C. The material was signed as RM-ZeO-Si.

Zeolite synthesis with simultaneously supplement of silicon and aluminum (RM-ZeO-SiAl): The synthesis process was similar to RM-ZeO-Si synthesis, but instead of only silicon addition, the $Al_2(SO_4)_3.18H_2O$ were added simultaneously and molar ratio of Si/Al was kept the same as 4. The material was signed as RM-ZeO-SiAl.

2.3. Characterization of synthesized materials

The crystaline formation of the zeolite in RM-ZeO-Si and RM-ZeO-SiAl were studied by X-Ray Diffraction (XRD). The morphology of the zeolite was investigated by Scanning Electron Microscopy (SEM), the specific area was measured by BET adsorption. The interaction between different atoms in the material structure was determined by FT-IR Spectra and elemental composition was observed by **Energy Dispersive X-ray Spectroscopy (EDX).**

2.4. Initial test of ammonium and nitrite adsorption

Adsorption test was carried out with initial ammonium and nitrite concentration of 10 mg/L, solid and liquid ratio for adsorption process for both materials was 1/100, pH of solution was around 6, adsorption (contact) time was 120 min and environmental temperature was 25^{o}C. After adsorption time, remained concentration of ammonium and nitrite was determined by the photometric method with Nessler or Griess Reagent respectively.

3. Results and discussion

3.1. X-Ray diffraction (XRD) analysis

The X-Ray diffration spectra of materials RM-ZeO-Si and RM-ZeO-SiAl shows that, the appearance of a zeolite crystal with general formula of $Na_8(Al_6Si_6O_{24})S.4H_2O$ on the hematite (Fe_2O_3) base (Figure 1). The parameter of 2θ angle and d of the crystal in RM-ZeO-Si was likely coincident with those in sodalite crystal which has formula of $Na_6(H_2O)_8 Si_6Al_6O_{24}$. The pairs values of 2θ:d were 14.16:6.256 and 20.07:4.424 respectively. These parameters in X-Ray spectrum of RM-ZeO-SiAl material were nearly coincident with the values in standard spectrum of zeolite P with two pairs values of 2θ:d were in tern as 33.38:2.684 and 35.75:2.511 respectively [9,10]. The difference of other natural zeolites [11,12], in molecular structure of the synthesized zeolites appeared sulfur (S) component. The present of atom S in zeolite structure may increase its anion adsorption ability due to the reduction of their electric negative effect.

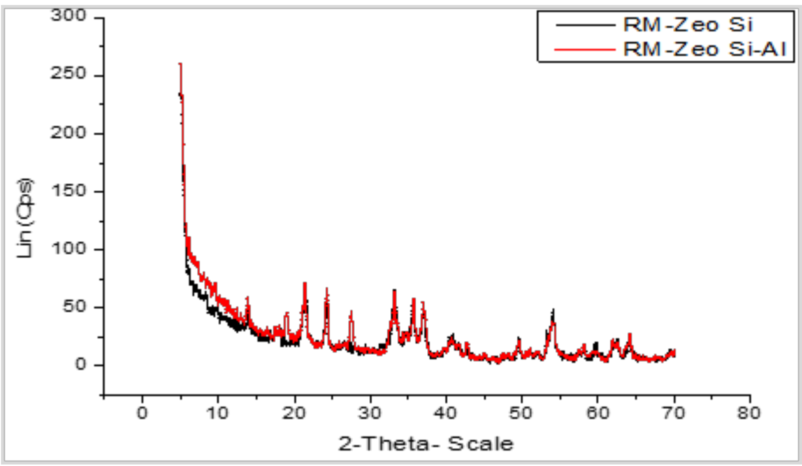

Figure 1. The XRD diffraction pattern of the synthetic zeolite RM ZeO-Si (a), RM ZeO –SiAl (b).

3.2. X-ray energy dispersive (EDX) spectra

The EDX spectra of the materials (Figure 2) showed the element composition of the synthesized zeolites and the percentage of elements were presented in Table 1. The Si/Al molecular ratio of these zeolites was then calculated.

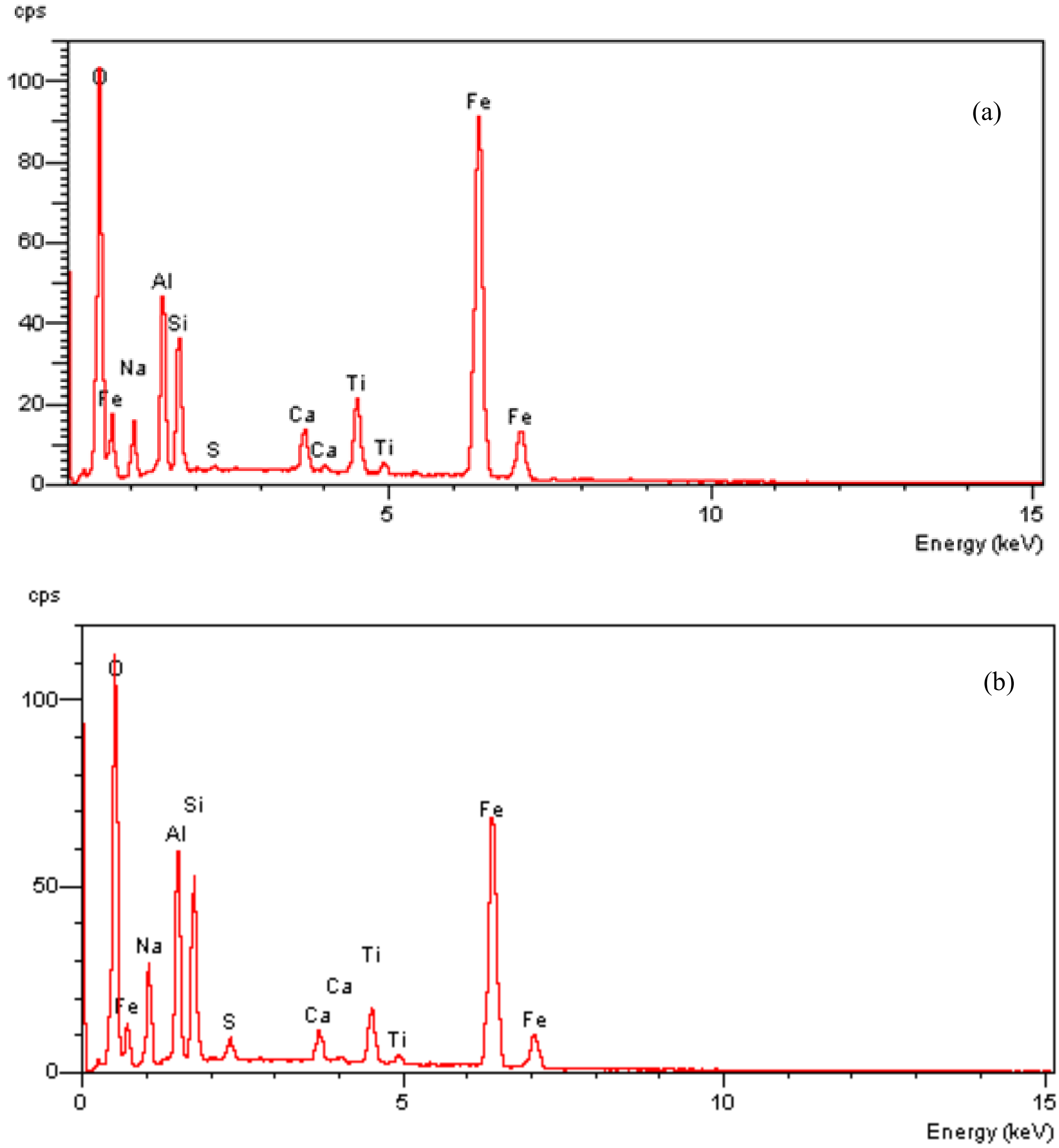

Figure 2. The EDX spectra of RM ZeO-Si (a) và RM ZeO-SiAl (b)

Table 1. The Al and Si percentage in RM-Zeo-Si and RM-Zeo-SiAl

Elements	RM-Zeo-Si	RM-Zeo-SiAl
Al	6.76	**6.49**
Si	25.96	**28.24**
Na	30.64	40.85
Fe	27.33	16.93

The molar ratio of RM-ZeO-Si:

$$\frac{[Si]}{[Al]} = \frac{25.96/28.09}{6.76/26.98} = 3.7$$

The molar ratio of RM-ZeO-SiAl : $\frac{[Si]}{[Al]} = \frac{28.24/28.09}{6.49/26.98} = 4.1$

The Si/Al ratio of both zeolites was in the range of 3.7÷ 4.1, so these zeolites could be classified in the group of medium silicon portion. Their general characteristics are high temperature supporting, homogenous micropore size, might be built with truncated tetrahedral and hexagonal (octahadra) faces [12,13].

3.3. FT-IR spectrum

The FT- IR spectra in the figure 3 show that for both materials RM-ZeO-Si and RM-ZeO-SiAl appeared peaks with intensity from weak to medium in wave number area from 3411 to 3139 cm^{-1} characterized for variations of OH groups on the materials surface. The reason is existence of adsorbed water also in the surface, so the hydrogen bridge bonds between water molecules with oxygen in OH groups hid partly bonds of OH groups on the surface. The evidence was also appearance of peaks in 1652.10 cm^{-1} and 1632.81 cm^{-1} in spectrum of material RM-ZeO-Si and RM-ZeO-SiAl respectively [13, 14].

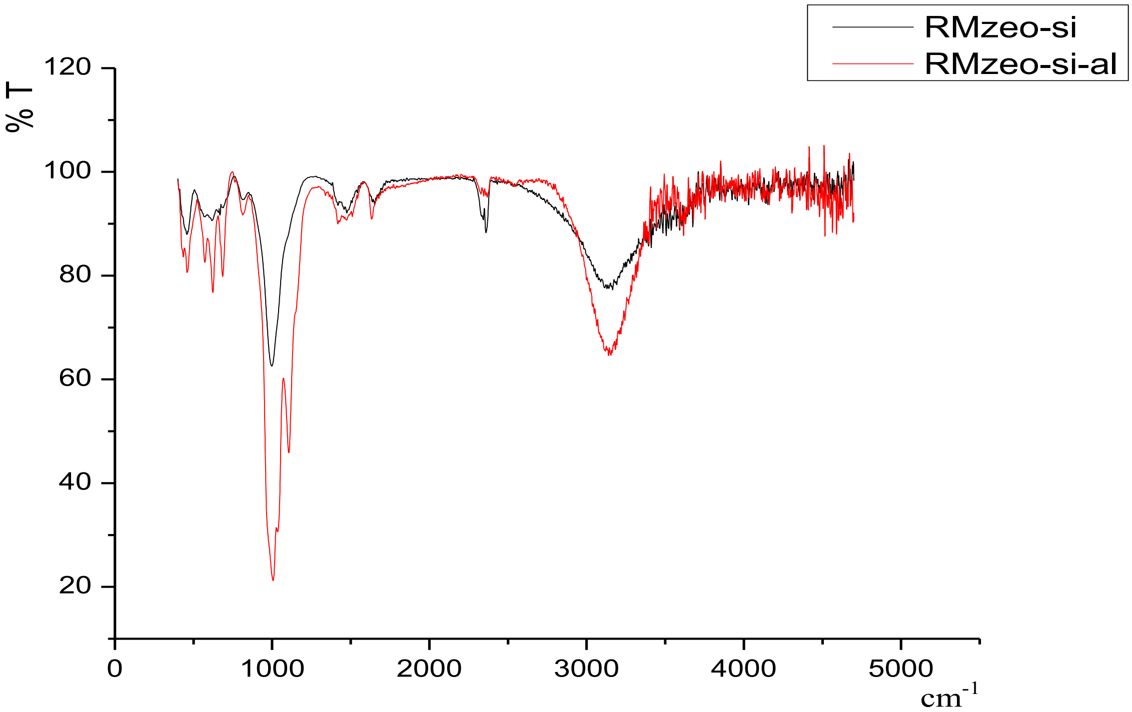

Figure 3. FT- IR spectra of RM ZeO-Si and RM ZeO-SiAl

In the wave number area from 1100 to 400 cm^{-1} appeared peaks characterized for variation of T-O and Si-O-Al bonds in the structural frame of sodalite (T is Si or Al) such 998.21, 667.40 and 1106.22, 623.03 cm^{-1} characterized for symmetric and asymmetric variations of Si-O-Al bonds in RM-ZeO-Si and RM-ZeO-SiAl [10]. In spectrum of RM-ZeO-SiAl there is still appeared peaks at wave number of 1005.92 and 1034.85 cm^{-1} characterized for variation of Si-O and Al-O bonds in TO_4 tetrahedron; and in the wave number area from 600 to 400 appeared peaks at 434.0 cm^{-1} and 571.92 cm^{-1} characterized for T-O and hexagonal frame variations [9]. While in the spectrum of RM-ZeO-Si, appeared only the peak at 568 cm^{-1} characterized for hexagonal frame variation and it proved that in RM-ZeO-Si, TO_4 bonds did not exist.

3.4. SEM images

In the SEM images (Figure 4), it's can be seen that both of synthesized materials are assemblage of spheric particles suggested as reformed hematite particles and clear microcrystals of zeolites formed in red mud base.

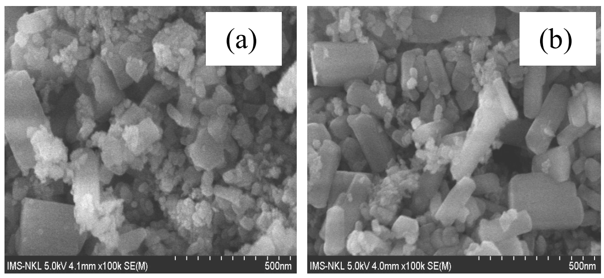

Figure 4. SEM image of RM ZeO- Si (a), RM ZeO-SiAl (b).

3.5. The BET specific surface area

The adsorbed and desorbed isotherm lines of RM ZeO-Si and RM ZeO-SiAl showed a type IV sorption isotherm, according to IUPAC classification (Fig. 5). The existence of hysteresis loop denotes the presence of mesopore. The specific surface area was determined by the BET method, showed that RM ZeO-Si was 46 m^2/g and RM ZeO-SiAl was 59 m^2/g.

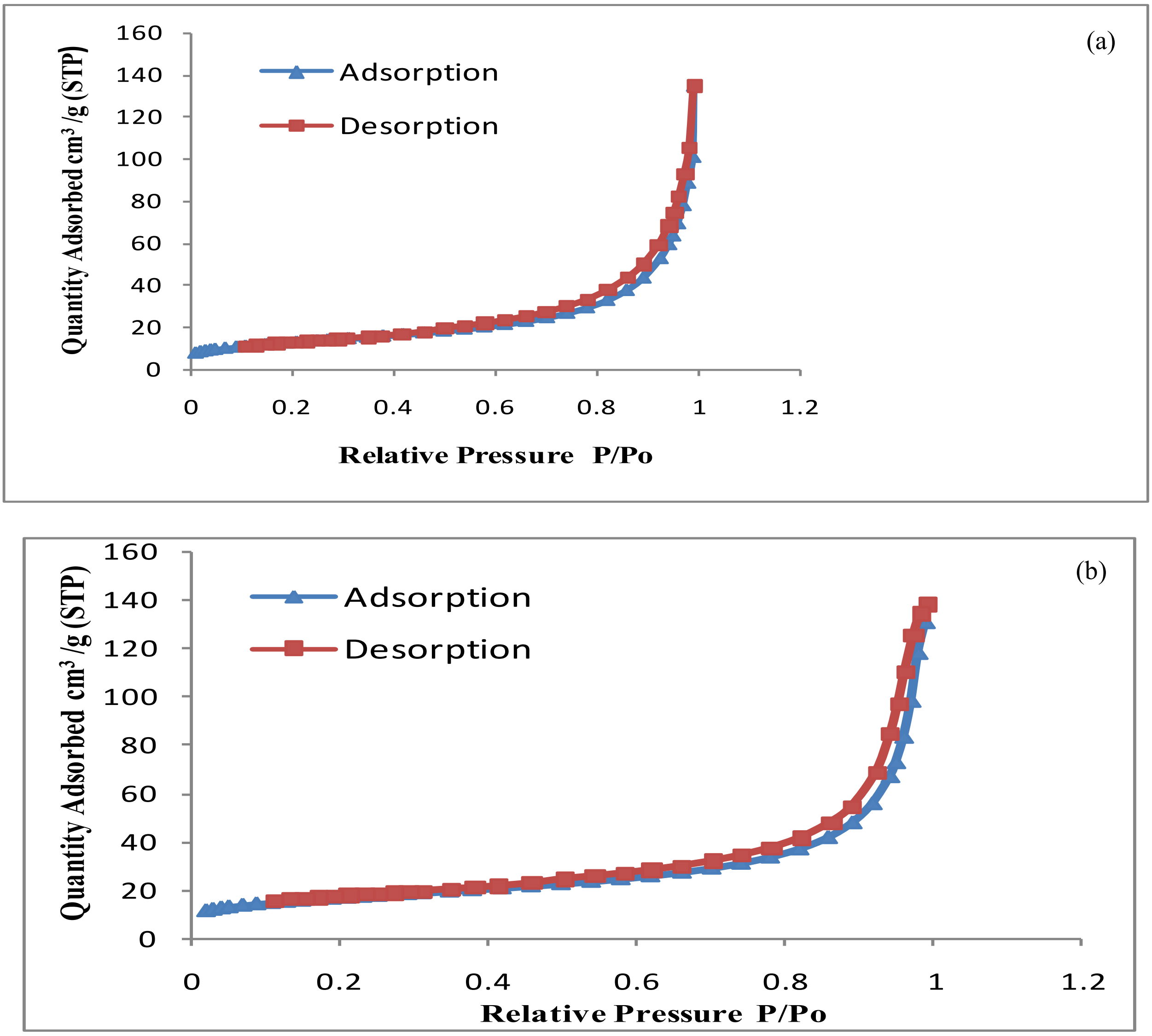

Figure 5. The adsorbed and desorbed isotherm lines of RM ZeO-Si (a) and RM ZeO-SiAl (b).

3.6. The initial adsorption test of the synthesized materials

The adsorption test was carried out according to procedure presented in the section 2.4. The experimental results are presented in Table 2.

Table 2. The adsorption capacity of ammonium and nitrite on the RM-ZeO-Si and RM-ZeO-Si,Al

Materials	Adsorbed ions	Adsorption capacity (mg/g)
RM ZeO-Si	NH_4^+	5.682
RM ZeO-Si	NO_2^-	2.976
RM ZeO-Si,Al	NH_4^+	5.568
RM ZeO-Si,Al	NO_2^-	3.214

The ammonium and nitrite adsorptions in the synthesized materials are nearly similar (Table 2). As discussed above, in both materials exist two components, they are crystals of like zeolite formed from aluminate and additional silicate, and metals oxides with predominance of iron (III) oxide in the form of hematite originated from red mud. Ammonium adsorbed on the material surface predominantly by ion exchange mechanism between Na^+ in zeolite forms and ammonium cations in the solution, while nitrite anion adsorbed mostly by adsorption on surface of metal oxide particles in the material according to electrostatic attraction mechanism. The adsorption capacity of ammonium and nitrite in our study (Table 2) are quite high in comparison with common adsorbents in the market.

4. Conclusion

The materials RM ZeO-Si and RM ZeO-SiAl were synthesized by hydrothermal method with single Si addition and simultaneous addition of Si and Al proportion from the original Tan Rai red mud. Crystaline formation in the forms of sodalite was appeared in material with single Si addition (RM ZeO-Si) and crystal of "like" zeolite P in the material RM ZeO-SiAl. The microcrystals were characterized by the XRD, EDX, FT-IR and SEM methods, and suggested that they were dispersed among hematite particles of the red mud. The initial test of adsorption ability of ammonium and nitrite on the synthesized materials showed that the adsorption ability of both ions were very high but the adsorption mechanism of each ion was different. Adsorption mechanism of ammonium was suggested as predominant ion exchange between ammonium cation in solution and sodium cation in zeolite crystals; while nitrite adsorbed on surface material by electrostatic attractive force between nitrite anion and electropositive surface of iron oxide particles. In conclusion, this synthetic zeolite obtained from red mud has potential application in removal of pollutant ammonium and nitrite ions in aqueous solutions.

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