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Modification of natural zeolite by salt to treat ammonia pollution in groundwater

Biến tính zeolite tự nhiên bằng muối ăn để xử lí amoni trong nước ngầm

Research article

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Treating ammonium pollution in ground water by natural zeolite after being modificated to the Na-form (Z-Na) is the new way of research that scientists interested in. The experiment results showed that, at pH 6, the efficient of treating ammonium in ground water is the highest. The efficient of treating increase rapidly in the first 5 minutes and remain stable after that. Higher concentration of the Z-Na will increase the treating coefficient of the process. With a water sample that has C_{N-NH4+}=27 mg/L at first, using C_{Z-Na}=13g/L and after 5 minutes, the concentration of ammonium in water was declined to 1mg/L, passed the Vietnamese standard for ground water (QCVN 09:2015-MT/BTNMT). The treating coefficient is 96.30%, the adsorption capacity is 2.07 mg N-NH_4^+/1g Z-Na. The loaded Z-Na was regenerated using 2g/L NaOH solution, the ammonium recovery ratio exceeded 92%. This means the reuse of Z-Na for ammonium adsorption is very high. The results of the experiment with groundwater samples in Phu Xuyen district, Ha Noi have a concentration of 53 mg/L. In conclusion, Z-Na material is perfectly fit for purpose of treating ammonium in ground water because of it low price, safety, easily to imitate and high efficiency.

Xử lí ô nhiễm amoni trong nước ngầm bằng vật liệu zeolite tự nhiên được biến tính bằng muối ăn (Z-Na) là một hướng nghiên cứu mới, được các nhà khoa học rất quan tâm. Kết quả thí nghiệm cho thấy, tại pH 6 thì hiệu quả xử lí amoni trong nước là tốt nhất. Hiệu quả xử lí amoni trong nước tăng rất nhanh trong 5 phút đầu tiên xử lý. Càng tăng nồng độ Z-Na thì hiệu quả xử lí amoni càng cao. Với dung dịch nước ban đầu có nồng độ amoni tính theo nitơ (N-NH_4^+) nhỏ hơn 27 mg/L và nồng độ vật liệu Z-Na sử dụng là 13g/L thì nước sau xử lí có nồng độ nhỏ hơn 1mg N-NH_4^+/L, đạt QCVN 09-MT:2015/BTNMT, hiệu suất xử lí đạt 96,30%, dung lượng hấp phụ cực đại đạt 2,07 mg N-NH_4^+/1g Z-Na. Vật liệu Z-Na sau khi xử lý được nghiên cứu giải hấp bằng dung dịch NaOH với nồng độ 2g/L cho thấy hiệu quả giải hấp đạt 92% lượng amoni được hấp phụ. Điều này chứng tỏ khả năng tái sử dụng của vật liệu Z-Na cho hấp phụ amoni là khá cao. Kết quả nghiên cứu đã được thử nghiệm xử lý với mẫu nước ngầm tại huyện Phú Xuyên, Hà Nội có nồng độ N-NH_4^+ là 53 mg/L. Vì vậy, vật liệu Z-Na hoàn toàn có thể ứng dụng vào thực tiễn để xử lý amoni trong nước ngầm rất an toàn, dễ thực hiện và hiệu quả cao.

Keywords: natural zeolite, ammonia, groundwater

1. Introduction

According to many studies, the underground water sources in many localities in the country are seriously polluted with ammonium (NH_4^+). Ammonia content in accordance with Vietnamese standards (QCVN 09-MT: 2015/BTNMT and QCVN 02: 2009/BYT) is 1 mg/L and 3 mg/l, but many places in the Red river delta and the Cuu Long river delta, groundwater contaminated with ammonium is several times higher than the permissible level [1, 5, 6].

When ammonium-contaminated groundwater is exposed to air, many species convert ammonium to nitrite and nitrate. Nitrit in the body competes with red blood cells for oxygen and causes respiratory disease (especially for pregnant women and children), on the other hand can also combine with organic substances to create substances that may cause cancer [4].

Because of the urgency of this matter that many studies have been conducted to find the best remedies possible to the best extent possible. In it, studying an NH_4^+ treatment method suitable for household level water treatment is very

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important [2,3,7,8]. To do that, we need to find a material that can be denatured in a simple, easy to apply for family size. So the study chose the material Nitto Zeolite, and modified the material with salt to treat ammonia in groundwater.

In this study, sea salt was used to modify natural zeolite into a material that is capable of treating ammonium well in water. The study also found the significance of time, pH, initial concentration on the efficiency of ammonia treatment by Z-Na.

2. Materials and methods

2.1 Materials

Ammonium contaminated water source: in the lab is modulation of ammonium solutions with different concentrations from $N\text{-}NH_4^+$ 1000mg / L solution, actual is water sample taken from a borehole of people in Phu Tuc commune, Phu Xuyen, Hanoi with $C_{N\text{-}NH4+}$ 53mg/l. Nitto Zeolite: natural Nitto Zeolite (*(Ca, K$_2$, Na$_2$) (AlSiO$_5$O$_{12}$)$_2$.7H$_2$O*), natural Nitto Zeolite activated by sea salt (Z-Na).

2.2 Methods

2.2.1 Modification of natural nitto zeolite (Z) zeolite to sodium form (Z-Na)

- Zeolite modification:
+ Add 120 g of Nitto Zeolite into 1L of sea salt solution at 6 g/L and shake well for 4 hours. Let dry we have Z-Na.

Figure 1. Activating Zeolite using sea salt

-Treatment mechanism:

$$Na\text{-}Zeolite + NH_4^+ \rightarrow Zeolite\text{-}NH_4^+ + Na^+$$

Na in the cavities of the zeolite exchanged with the NH_4^+ ion from the aqueous solution and resulted in NH_4^+ entering the zeolite and sodium Na^+ go outside.

In a water source containing concurrent cations such as Na^+, Ca^{2+}, Mg^{2+}, … competitive ion exchange occurs, which is more selective than ammonium ion, especially valence ions. Ammonia can only be exchanged when it is positive, NH_4^+ in the neutral NH_3 form is not exchangeable.

2.2.2 Research content

a. Comparison of processing efficiency between original Zeolite and Z-Na

Treatment of ammonium water samples with $C_{N\text{-}NH4+}$ = 40mg/L, Zeolite 13g/L, pH=6, t = 5 minutes with Nitto Zeolite and Z-Na.

b. Research the effect of initial ammonia to the processing efficiency

Use Z-Na with a concentration of 13 g/L of aqueous solution to treat $N\text{-}NH_4^+$ with concentration of 40 mg/L at pH 4, 6, 7, 8, 10 with 0.01M HCl standard solutions and NaOH 0.01M to adjust. Shake the sample for 1, 2, 3, 5, 10, 15, 20, 30 minutes at room temperature then filter through filter paper. Determine the remaining $N\text{-}NH_4^+$ concentration in the filtrate by spectrophotometry with nestle reagents.

c. Processing efficiency affection result with different Z-Na concentration

Treatment of ammonium solution with concentration of $N\text{-}NH_4^+$ 40mg/L (pH = 6) with Z-Na concentration of 9; 11; 13; 15; 17 and 20 mg/L. Shake the sample for 5 minutes at room temperature, filter through filter paper. Determine the remaining $N\text{-}NH_4^+$ concentration in the filtrate.

d. Research the effect of initial ammonia to the processing efficiency

Treatment of ammonium solution with $N\text{-}NH_4^+$ concentration of 15; 20; 25; 30; 35 and 40 mg/L (pH = 6) with Z-Na 13g/L, shake for 5 minutes at room temperature. Then filter through filter paper, determine the remaining $N\text{-}NH_4^+$.

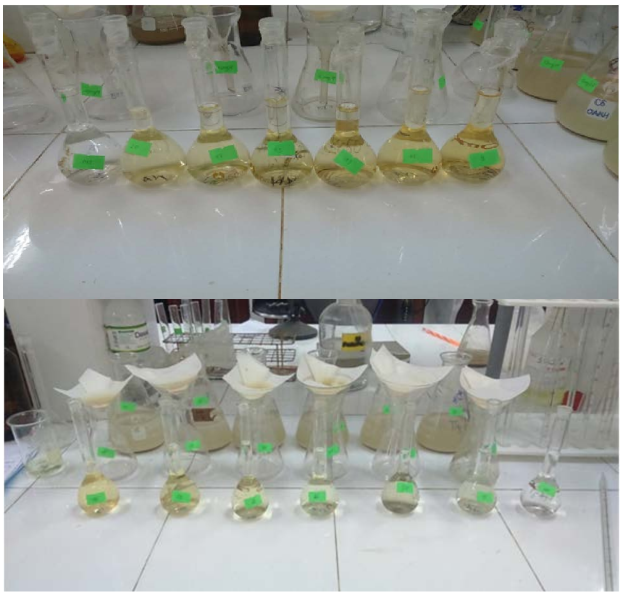

Figure 2. Examine the effect of pH, time and concentration to the processing efficiency

e. Research the desorption ability of used Zeolite

Use ammonium solution with N-NH_4^+ concentration of 80 mg/L for Z-Na 26 g/L at pH = 6. Shake for 30 minutes then filter the residue.

Add 500ml of NaOH solution with concentration of 2g/L, then shake for 30 minutes. From which, determine the concentration of N-NH_4^+ in the solution. determine the discharge efficiency of the amount of ammonia adsorbed.

f. Research of ammonia treatment in Phu Tuc commune, Phu Xuyen, Hanoi

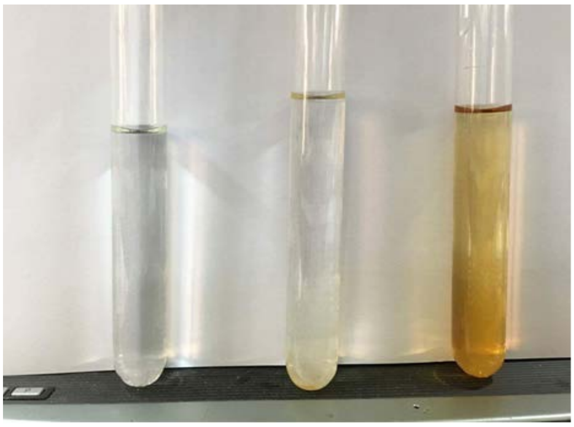

Figure 3. Treating ammonia in groundwater samples in Phu Tuc communce, Phu Xuyen, Ha Noi

(From left to right: Uncontaminated water; Ammonium contaminated water after treatment; Ammonium contaminated water before treatment).

Use Z-Na to treat the real sample (third test-tube) that has ammonia concentration of 17.5 g/L and 25 g/L.

Treatment of ammonium water samples (Figure 3) with C_{Z-Na}= 25g/L (first test-tube) and 17.5g/L (second test-tube), pH=6, t = 5 minutes.

3. Results and discussion

Currently, in Vietnam and on the world, water contaminated with ammonium is usually treated with methods such as chlorination to the mutation point, ion exchange method and biological method. These processes require high technology and large processing costs. So the study of modified zeolites has opened up a new way of dealing with household-scale ammonium contamination when similar studies in Vietnam and the world are relatively modest.

3.1. Research results on Nitto Zeolite

+ Structure: (Ca, K_2, Na_2) $(AlSiO_5O_{12})_2.7H_2O$
+ Chemical composition of Nitto Zeolite (analysed with X-ray diffracted spectrum from VNU analytical center).

The results of table 1 show that the SiO_2 content of zeolite is 65.15; Al_2O_3 is 10.07 and Fe_2O_3 is 2.37 %. These are important elements that help zeolite process well NH_4^+ in water.

Table 1. Chemical composition of Nitto Zeolite

Chemical Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	MgO
Concentration (%)	65.15	10.07	2.37	2.41	2.07	1.35	0.22

• X-ray result of Nitto Zeolite material

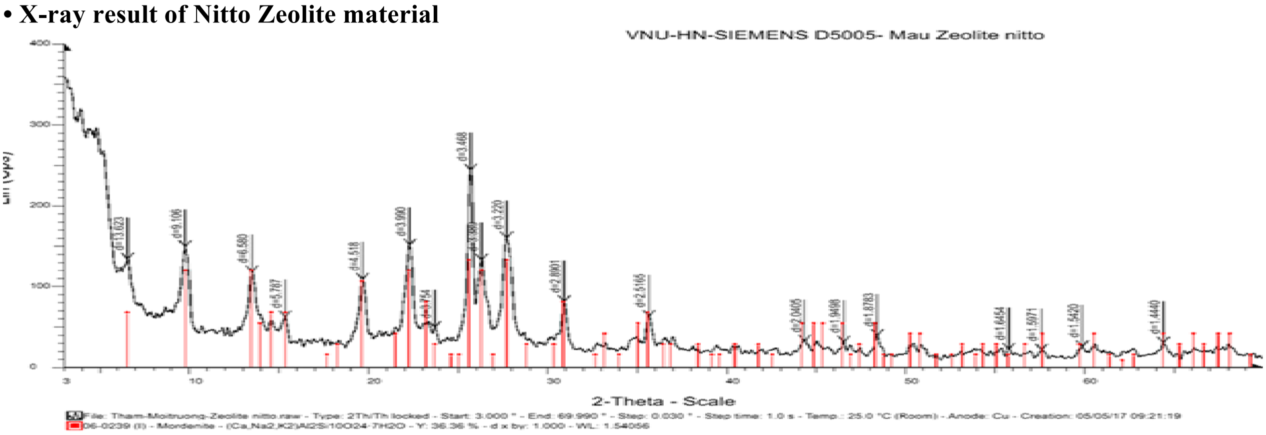

Figure 4. Diffracted spectrum X-ray of Nitto Zeolite

The XRD patterns confirmed Nitto Zeolite as the only phases present for the cocrystallized materials (Fig. 4). In the case of cocrystallized Nitto Zeolite the X-ray pattern showed the 8. 36, 14.56, 25.67, 27.03, 28.47, and 29.78 •, 2θ line characteristic of Nitto Zeolite. Nitto Zeolite showed peaks characteristic of completely dehydrated.

3.2 Comparison of treating ammonia result between Zeolite and Z-Na

Treatment of ammonium water samples with CN-NH_4^+ = 40 mg/L, results after treatment:

+ Nitto Zeolite: CN-NH_4^+ after treatment = 4.97 mg/L, processing efficiency = 87%

+ Z-Na: CN-NH_4^+ after treatment = 2.22 mg/L, processing efficiency = 94.46%.

The results above show that the treatment efficiency of Z-Na is higher than nitto zeolite.

3.3 Processing efficiency affection result of ammonia with different pH and time

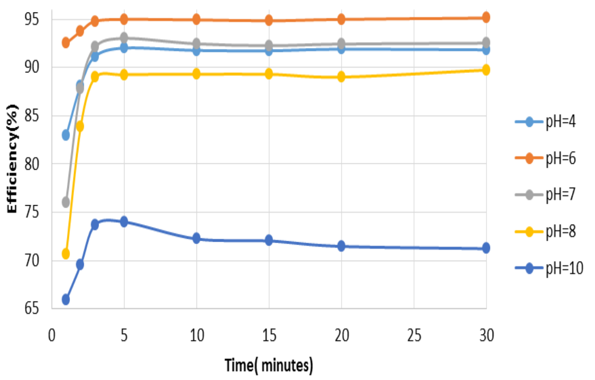

Figure 5. Processing efficiency result of ammonia with different pH and time

The results of the study in Figure 5 show the effect of ammonium treatment with Z-Na as follows:

+ The efficiency of ammonia treatment in water with Z-Na increased rapidly in the first 5 minutes and almost did not increase much later. In the first 5 minutes, ammonia removal efficiency was over 96% during the process, a litte bit lower than 99% in comparison with NaCl-modified Yemeni zeolite (Alshameri et al. 2014) but their processing time is up to 120 minutes.

+ The best performance at pH = 6. At other pHs, processing efficiency is still high, for example at pH = 4, processing efficiency is 92%, or at pH = 7, the processing efficiency is 93%. However, at pH 6, the highest ammonium treatment efficiency was up to 95%.

3.4 Processing efficiency affection result with different Z-Na concentration

According to the results shown in Figure 6, the ammonium treatment efficiency increased as the concentration of Z-Na increased.

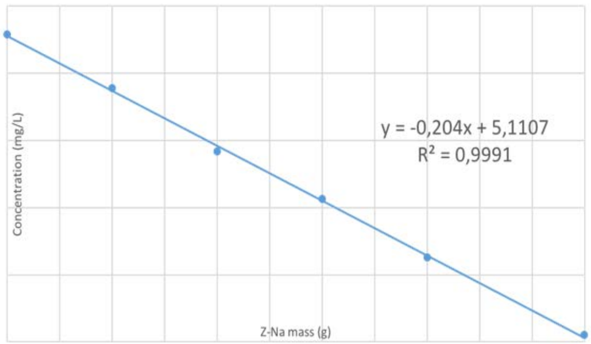

Figure 6. Processing efficiency with different concentration of Z-Na

3.5 Processing efficiency affection result with different initial ammonia concentration

Table 2. Concentration of amonia after treating and calculated data for Langmuir isotherm equation

Initial ammonia concentration (mg/l)	Ammonia concentration after treatment, Ce (mg/l)	Amount of adsorbed substance (mg/g)	Ce/Qe (g/l)	QCVN 09-MT:2015 BTNMT	QCVN 02:2009 BYT
40	2.21676	37.78324	0.05867	1	3
35	1.7199	33.2801	0.05168	1	3
30	1.20393	28.79607	0.041809	1	3
27	0.99372	26.00628	0.038211	1	3
25	0.86572	24.13428	0.035871	1	3
20	0.53169	19.46831	0.027311	1	3
15	0.31024	14.68976	0.021119	1	3

To determine the ammonium adsorption of Z-Na material, study the effect of initial ammonium concentration on the ammonium removal efficiency in water by Z-Na. Results are shown in Table 2.

From the data in Table 2, it is possible to determine the Langmuir isotherm adsorption equation as follows:

$$Qe = Q_{\max} \frac{b.C_e}{1+b.C_e} \quad (1)$$

In which: Q_e is the adsorption capacity at the time of equilibrium (mg/g), Q_{max} is the maximum absorption capacity (mg/g), C_e is the concentration at equilibrium (mg/l), b is the constant that characterizes the interaction of the absorbent and the adsorbent.

The equation 1 can be transformed into the following form:

$$\frac{Ce}{Qe} = \frac{1}{Q\max}.Ce + \frac{1}{b.Q\max} \quad (2)$$

The equation 2 is the linear equation representing the linear dependence of Ce/Qe on Ce. Replacing the empirical data from Table 2 into equation 2 we can establish the arsenic isothermal adsorption equation shown in Figure 7.

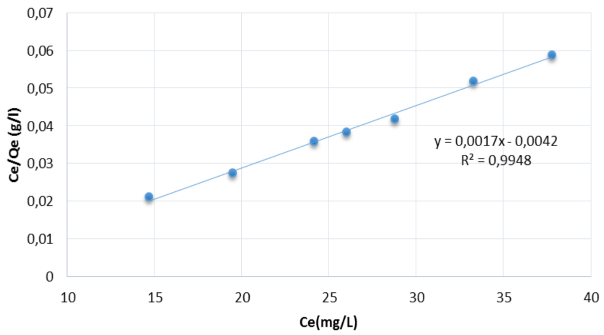

Figure 7. Langmuir isotherm line

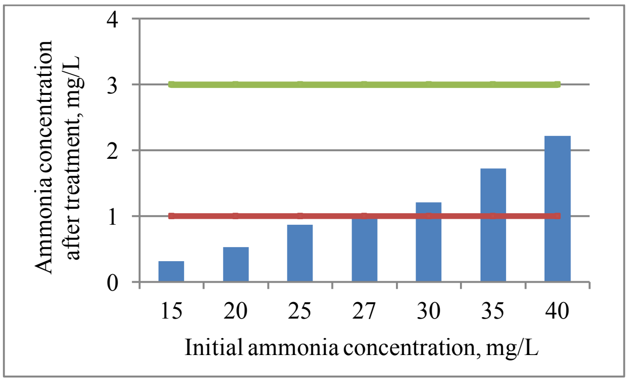

Figure 8. Ammonia concentration after treatment by Z-Na with different initial ammonium concentrations

According to the results of the study in figure 6, it was found that at each ammonium concentration a suitable amount of Z-Na was required to reach the standard. With initial water solution with C_{N-NH4+} <27 mg/L, C_{Z-Na} = 13g/L, after 5 minutes can be treated with C_{N-NH4+} = 1mg/L to QCVN 09:2015-MT/BTNMT. The processing efficiency was 96.30%, the adsorption capacity was 5.88 mg N-NH_4^+/1g Z-Na. With C_{Z-Na} = 13g/L, all concentrations of C_{N-NH4+} <50mg/L are possible to decrease down to C_{N-NH4+} <3mg/L, passed QCVN 02: 2009 / BYT.

3.6. Z-Na desorption ability

After treatment of ammonium containing solution C_{N-NH4+}= 80mg/L by Z-Na concentration of 26 g/L, a solution containing C_{N-NH4+} = 2.96 mg/L was obtained. After treatment of Z-Na steaming with 2 g/L NaOH, the solution obtained was C_{N-NH4+} = 70.96 mg/L. Discharge efficiency is 92% of the amount of ammonia adsorbed. It was higher than 89% by ultrafine coal fly ash (Elizabeth M. van der Merwe et al., 2017) and 88% by illite flotation (Hao Jiang et al., 2018)

3.7. Ammonia treatment in real sample

After actual treatment with ammonium concentrations of 53 mg/l with Z-Na concentrations of 17.5 and 25 mg/l, we have aqueous solution of ammonium with the concentration of 2 mg/l, passed QCVN 02: 2009/BYT.

4. Conclusion

According to research results, at pH = 6, the efficiency of ammonium treatment in water is the best, the efficiency is over 95%. The processing efficiency increased rapidly during the first 5 minutes, and remained almost unchanged, accounting for over 96% during the process. The higher the Z-Na concentration, the higher the processing efficiency. With the initial solution concentration of N-NH_4^+ <27 mg/L, CZ-Na = 13 g/L, after 5 minutes can be treated with solutions of N-NH_4^+ <1mg/L (passed QCVN 09-MT:2015/BTNMT). The processing efficiency was 96.30%, the adsorption capacity was 5.88 mg/g. Z-Na's desorption efficiency was 92%.

5. Recommendations

Applying Z-Na material into real-life to treat ammonia in groundwater at family scale is needed to cary out. Producing liquid fertilizer from the solution that has a high concentration of NH_4^+ after N-desorption of Z-Na is recommended.

6. References

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