

## REMOVAL OF AMMONIUM IONS FROM WATER BY RAW AND ALKALI ACTIVATED BENTONITE

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Ammonium ions in water poses adverse effects on aquatic life and in elevated level presents risk for human health. Zeolites as low cost and ecofriendly sorbent, has very good capacity to remove ammonium ions. The purpose of the present study was to examine the efficiency and comparison of raw and alkali modified bentonite as low cost sorbent for removal of ammonia nitrogen ( $\text{NH}_4\text{-N}$ ) from water. Natural calcium bentonites originating in Iran were treated with 6.0M NaOH aqueous solution at the temperature of 150°C under atmospheric pressure for 6 hours. The alkali modified bentonite were washed several times with distilled water, dried in an oven at a temperature of 110°C and then used as sorbent. Batch experiments were conducted to delineate effect of initial ammonium concentration (5,10 and 50ppm) and bentonite dose (1.0,5.0 and 10.0  $\text{gL}^{-1}$ ) on removal and sorption capacity of raw and alkali activated bentonite. Results showed that time required to reach equilibrium in removal of ammonium by the examined bentonites was 30.0 Min. Removal efficiency of raw and modified bentonites for ammonium removal with 45.0 Min. contact time was 25 to 50 percent. By increasing contact time to 4 and 18h ammonium removal efficiency for both raw and modified bentonite didn't changed definitely. Increasing bentonite dose from 1.0 to 10.0  $\text{gL}^{-1}$  slightly increased sorption efficiency. Increasing ammonium concentration from 5.0 to 50.0  $\text{mgL}^{-1}$  didn't clear effect of removal efficiency. Bentonite can be used for ammonium removal from water environment

Keywords: ammonia, water, Bentonite.

### INTRODUCTION

Ammonia in surface water supplies often is a result of runoff in agricultural areas where fertilizer applied to the ground. Another way that high levels of ammonia in water appear is from aquifers in animal feed lots. Ammonia is oxidized to nitrate by bacterial action. In drinking water the maximum ammonia concentration Of 1.5 $\text{mgL}^{-1}$  is recommended by the World Health Organization (WHO) to avoid changes of taste and odor of water. Natural levels of ammonia in ground waters are usually below 0.2 $\text{mgL}^{-1}$ . Higher natural contents (up to 3 $\text{mgL}^{-1}$  are found in strata rich in humic substances in forests. The presence of ammonia at higher levels is an important indicator of fecal pollution (Mažeikien et al., 2010). The removal of  $\text{NH}_4^+\text{-N}$  can be accomplished by physical, chemical, biological or a combination of these methods. Available technologies include adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification and denitrification. Each of these methods has its own specific limitation (Hussain et al., 2006). There are many researches that show the zeolite can be used to remove ammonia from water. Among the zeolites, Clinoptilolite was used most frequently as ammonia sorbent (Abd El-Hady et al., 2001, Miladinovic et al., 2004, Liu et al., 2008, Rahmani et al., 2006, Asilian et al., 2007). Bentonite is a clay mineral which is largely composed of Montmorillonite, which is mainly a hydrous aluminum silicate. Bentonites typically exhibit a cation exchange capacity (CEC) of 70 -100meq/gram (Kashani Motlagh et al., 2008; Karimi et al., 2009).The chemical and mineralogical structures of the bentonites, which are activated by heating in strong acids, undergo considerable transformations. The surface acidity and the porous structure of bentonites can be changed to the desired extent by acid activation (Onal et al., 2011). Many studies performed on the alkaline

reaction of bentonite have been directed, obviously, to the montmorillonite alteration. Previous studies on the reactivity of montmorillonite in alkaline solutions indicated the collapse of expandable smectite layers, in particular the formation of illite or illite/smectite mixed-layers (Cuevas et al., 2006).

The aim of the present study was to investigate the effect and adsorption behavior of raw and alkali activated calcium bentonite to remove ammonium ion from aqueous solution.

## MATERIALS AND METHODS

Natural Calcium Bentonite mined in Iran was used as starting material. Bentonite was washed several times with distilled water to remove impurities, dried in an oven at 110°C for 24h and then used as raw bentonite. The modification of raw bentonite was performed under alkaline condition. The mixture consisting 50 g of a raw bentonite and 500 mL of 6.0 M NaOH solution was placed in a reflux vessel and heated in an oven at 100°C under atmospheric pressure for 6.0h. Then the mixture was placed in a cone to settle out. The settled product was washed several times with distilled water until the pH of supernatant became natural (around 7), dried in an oven at 105°C for 24h and then used as modified bentonite.

The batch study was conducted to establish the removal pattern of ammonium ions using raw and alkali activated bentonite. The investigations on the adsorption capacity of bentonite for ammonium ions were conducted in two phases: (1) the preliminary investigations and (2) the main investigations. The preliminary investigations aimed at the evaluation of the impact of selected amounts of bentonite on the removal degree of  $\text{N-NH}_4^+$  in the following concentrations 5.0, 10.0 and 50.0  $\text{mg L}^{-1}$   $\text{N-NH}_4^+$ . The samples with the addition of 0.1 g of bentonite were shaken for 10 minutes. The removal degree of ammonium ions was evaluated. With the reference to the obtained results from the preliminary investigations, further experiments were conducted with 0.1, 0.5 and 1.0 g of raw and modified bentonite separately in order to achieve higher degree of ammonium ions removal. Also, the contact time of the sorbents and the solution was extended to 4.0 and 18.0h to determine the effect of contact time on the amount of removed  $\text{N-NH}_4^+$  ions.

Three solutions with the following concentrations: 5.0, 10.0, and 50.0  $\text{mg L}^{-1}$   $\text{N-NH}_4^+$  were prepared from the standard solution of ammonium chloride at concentration of 1  $\text{g L}^{-1}$ . Samples of 0.1, 0.5 and 1.0g of raw and alkali activated bentonite were weighed separately and 100 ml of  $\text{N-NH}_4^+$  solutions were added. The prepared samples were shaken for 10,20,30,45 and 60 minutes and after that the samples were centrifuged at 4000 rpm for 15 min. Each solution was prepared in triplicates.

Equilibrium isotherm were determined by contacting a fixed mass of sorbent (0.1, 0.5 and 1.0 g separately) with 100 mL of  $\text{NH}_4^+\text{-N}$  concentrations (5.0, 10.0 and 50.0  $\text{mgL}^{-1}$ ) were tested. The isotherm constants and least squares correlation coefficients ( $R^2$ ) of both models were compared to determine the best-fit isotherm model for this study. All experiments were conducted at room temperature ( $23 \pm 2^\circ\text{C}$ ). Ammonia nitrogen concentration was measured by EPA Method (350.2) using a HACH DR/2800 Spectrophotometer set at 425 nm wavelength.

## RESULTS AND DISCUSSION

The equilibrium time determined (time after that bentonite did not remove further ammonium from solution) for both raw and alkali activated bentonite was 30.0 Min. In the Figure 1 removal efficiency of raw bentonite and alkali modified bentonite was compared. As it can be seen from Figure 1 with ammonium concentration of 5.0 ppm, by increasing sorbent dose efficiency has been increased. Also the figure shows that modification of bentonite by alkaline solution has increased ammonium sorption efficiency.

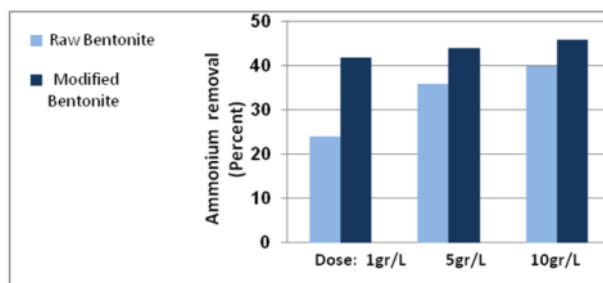


Figure 1. Comparison between percent of ammonium removal by different dose of raw and modified bentonite with initial concentration of ammonium ( $C_i=5\text{ppm}$ ) and contact time ( $t=45\text{Min.}$ )

Yujiro Watanabe et al. (2005) reported that the structure of natural zeolite such as mordenite and clinoptilolite after treatment with 3.0M NaOH solution at 150°C was changed to Phillipsite and by this type of modification the amount of ammonium removal from solution by modified zeolite was two-fold greater ( $1.92\text{ mmol g}^{-1}$ ) than that taken up by the starting material. Figure 2 shows that ammonium removal efficiency of sorbents for 10 ppm initial concentration of  $\text{NH}_4^+\text{-N}$ , are slightly lower in comparison with Figure 1. The results also shows that modified bentonite has greater ammonium sorption efficiency.

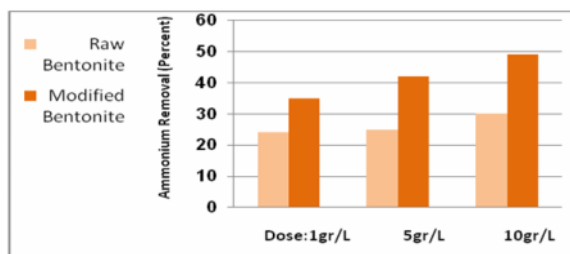


Figure 2. Comparison between percent of ammonium removal by different dose of raw and modified bentonite with initial concentration of ammonium ( $C_i=10\text{ppm}$ ) and contact time ( $t=45\text{Min.}$ )

In another study, J. Cuevas et al. (2006), reported that Spanish reference bentonite (FEBEX) was modified with alkaline solution (mixture of NaOH, KOH and  $\text{Ca}(\text{OH})_2$ ) with pH in the range of 12-13. The solid/alkaline solution ratio was 1/3 or 80 g of

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bentonite and 240 ml of solution and time of contact was from 7 days up to 365 days at 35, 60 and 90°C. The aim of their work was to clarify the effect of the alkaline plume induced by concrete on bentonite. By their of modification, they observed that the pH of solution was decreased after two month of contact and concluded that “One of the most important observations made during the interaction between alkaline solutions and bentonite was that montmorillonite can be considered as an important buffer agent of the pH in the bentonite. The pH decrease is mainly due to the dissolution of montmorillonite and the deprotonation of aqueous silica (i.e.  $\text{H}_4\text{SiO}_4 \rightarrow \text{H}_2\text{SiO}_4^{2-} + 2\text{H}^+$ ), and also to the incorporation of  $\text{OH}^-$  in the structure of newly-formed minerals or the retention of  $\text{OH}^-$  in the external surface of smectite may play a significant role”. Also they reported that the change in structure of bentonite was dependent to temperature and contact time and it can be resulted that the cation exchange capacity of alkaline modified bentonite was greater than raw bentonite (J. Cuevas, et al. 2006).

In the another research it is reported that three modified bentonites, hydroxy-aluminum pillared bentonite (Al-Bent), hydroxy-iron pillared bentonite (Fe-Bent), and cetyl trimethylammonium exchanged organo-bentonite (CTMAB-Bent) were prepared, characterized, and its adsorption properties for ammonia nitrogen were evaluated in batch experiments. The results showed that the ability of ammonia nitrogen adsorption of modified bentonites was far more than that of raw bentonite. The adsorption capacity followed the order: Al-Bent > Fe-Bent > CTMAB-Bent > raw bentonite (Liangguo Yan et al, 2009). In the Figure 3 efficiency of different dose of raw and modified bentonite for removal of 50ppm ammonium was compared. As it can be seen from this figure, with increasing the initial concentration of ammonium, the removal efficiency of sorbent didn't changed compared to Figure 1. Moreover with different dose of sorbent, the removal efficiency was in the range of 35 to 40 percent. As it can be seen from all figure, ammonia removal efficiency of alkaline modified bentonite was higher than raw bentonite. alkali activated bentonite has more cation exchange capacity than raw bentonite.

The effect of increase in contact time on removal efficiency of bentonites has been shown in Figure 4. As it can be seen from this figure, by increasing the contact time to 4 and 18 h, the ammonium removal efficiency of raw bentonite did not change very definitely compared to previous results.

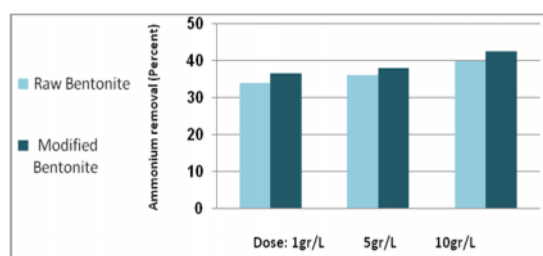


Figure 3. Comparison between percent of ammonium removal by different dose of raw and modified bentonite with initial concentration of ammonium ( $C_i=50\text{ppm}$ ) and contact time ( $t=45\text{Min.}$ )

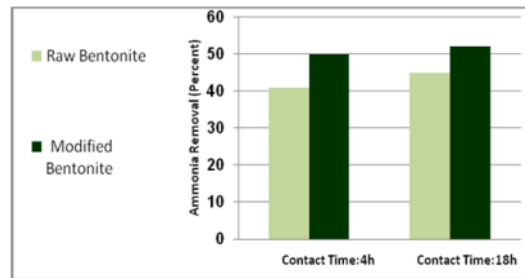


Figure 4. Comparison between contact time for ammonium removal by raw and modified bentonite with dose 10gr/L and initial concentration of ammonia( $C_i=50\text{ppm}$ )

It is reported that zeolites and bentonite due to their adsorption properties and high affinity to ammonium ions, are capable of removing ammonium and undesirable odors from the environment and because of that can appear beneficial in the treatment of animal excrements (Venglovsky et al., 1999). In another research it is reported that addition of bentonite counteracted the inhibitory effect of ammonia during thermophilic anaerobic digestion of cattle manure. The effect was observed only when the ammonia concentration was increased gradually. In batch experiments bentonite had a similar stimulatory effect leading to a decreased Lag phase and increased methane production rate. This results indicating that bentonite can remove ammonia from solution which is toxic for methanogenesis bacteria (Angelidaki et al., 1993). In order to decide which type of isotherm fits better the sorption experimental data, we plotted the quantities  $\log(x/m)$  vs.  $\log C_e$  for the Freundlich isotherm and  $1/q$  vs.  $1/C_e$  for the Langmuir isotherm. The  $R^2$  values (goodness of fit criterion) computed by linear regression for the two types of isotherms are presented in Table 1 for both sorbents. The data of Table 1 indicate that the Langmuir and Freundlich isotherms are best suited for sorption of  $\text{NH}_4^+ - \text{N}$  by both raw and modified Ca-Bentonite.

Table 1. Goodness of fit of the Freundlich and Langmuir isotherms to the sorption experimental data

| Sorbent      | $R^2$ Values        |        |      |                   |        |      |
|--------------|---------------------|--------|------|-------------------|--------|------|
|              | Freundlich isotherm |        |      | Langmuir isotherm |        |      |
| Raw Ca-Bent. | M=0.1g              | M=0.5g | M=1g | M=0.1g            | M=0.5g | M=1g |
|              | 0.98                | 0.94   | 0.95 | 0.99              | 0.88   | 0.91 |
| Mod.Ca-Bent. | 0.98                | 1.0    | 0.99 | 0.96              | 0.99   | 0.99 |

T.C. Jorgensen and L.R. Weatherley (2003), reported that ammonia removal from wastewater by zeolite clinoptilolite via ion exchange are best fitted with Langmuir adsorption model. They reported that the Langmuir model provided a close fit for the ion-exchange equilibrium. The Langmuir model assumes only one solute molecule per site and also assumes a fixed number of sites. Whilst the Langmuir model was developed for adsorption process, it can be seen that the experimental data in this ion exchange process are in accordance very well with adsorption model (Jorgensen and Weatherley, 2003).

## CONCLUSION

From the results of this study it can be concluded that, raw calcium bentonite can remove around 25 to 45 percent (depending on sorbent dose and sorbate concentration) of ammonium ions present in aqueous solution. Treatment of raw bentonite in the NaOH 6.0 M solution at 100°C for 6h will cause increase around 25 to 50 percent (depending on ammonium concentration) in ammonium sorption efficiency. Raw or treated bentonite can be used for ammonia removal in many places such as animal farms, sludge digestion plants and biogas reactors.

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