

A Study on the Ammonium Adsorption by using Natural Heulandite and Salt Activated Heulandite

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ABSTRACT: In this paper, the optimum conditions for the activation of Heulandite for the most effective parameters such as sodium concentration, stirring time and temperature was determined. The most efficient conditions was selected according to the highest ammonium removal capacity. The Activated Heulandite were investigated and compared with that of Natural Heulandite. The Activated Heulandite revealed the highest ammonium removal efficiency based on stirring time, zeolites loading, initial ammonium concentration, temperature and pH. The parameters revealed that the exchange of ammonium ion by Activated Heulandite occurred spontaneously at ambient conditions (27°C). It was concluded that when Heulandite is activated under the condition of 1M NaCl, 60°C and stirring time of 20 minutes, an excellent removal of ammonium was obtained.

KEYWORDS: Heulandite, Ammonium adsorption, Activated zeolite, Ammonium removal.

1 INTRODUCTION

Ammonium discharged together with municipal or industrial effluents is responsible for harmful effects such as eutrophication, toxicity to aquatic life and increased corrosion rate of soil materials. The toxicity of ammonium to aquatic life can cause convulsion, coma and death [1]. Traditionally, biological systems have provided an economical solution with the retrofitting of biological ammonium removal facilities to existing organic treatment systems [2]. While often effective, these systems require large land areas, due to the slowness of biological conversion of nutrients, thus imposing high capital costs. Physico-chemical wastewater treatment offers a high rate alternative to the conventional biological processes, requiring relatively small land areas for equivalent influent flows. Among the processes proposed to reduce ammonium ion concentrations in wastewater is ion exchange or adsorption using zeolite material which has been recognized as an efficient and cost competitive in both laboratory scale and commercial plants [3]. Increased awareness and understanding of the deleterious effects of ammonium, released from wastewater treatment facilities into natural water systems has resulted in stringent laws restricting ammonium discharge.

The raw water with high ammonia concentration must therefore be treated before it reaches the consumer and also the wastewater discharge into the receiving water. The most widely used methods for removing ammonia from wastewater are air stripping, ion exchange, breakpoint chlorination and biological nitrification denitrification [4]. Ion exchange has been demonstrated to be competitive with other methods both in terms of performance and cost [5][6].

The discovery of natural Zeolite deposits has led to an increasing use of these minerals for the purpose of eliminating, or at least reducing, many long standing pollution problems. Both natural and synthetic Zeolites have shown their ability for removing several cations from solutions concerning adsorption and ion exchange features. In order to comply with the increasingly strict limits being placed on ammonia levels in sewage discharged into receiving waters, a high-rate ammonia removal process was needed.

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents. They are known to have an affinity for ammonium (NH_4^+) and other cations and possess a unique framework. Overseas studies have established that zeolites have the potential to remove NH_4^+ from municipal, industrial, and aqua cultural wastewaters. The capacity of zeolites to remove NH_4^+ from wastewaters has been found to vary, depending on the type of zeolite used, zeolite particle size, and wastewater anion-cation composition.

The main features of Zeolites are high level of ion exchange capacity, adsorption, porous structure, molecular sieve, dehydration and rehydration, low density and silica compounds. However, the structural characteristics (e.g., porosity, density, and channel length) and the composition and exchangeability of Ca, Na, K, and Mg cations in Zeolites, amongst other factors (e.g., zeolite particle size and zeolite concentration in the host rocks) Natural zeolites such as clinoptilolite, mordenite, phillipsite from different deposits have been widely reported as an ion exchanger in wastewater ammonium removal installations owing to their ammonium ion selectivity and low cost [7][8].

Although the use of zeolites as adsorbent for ammonium removal from water was investigated by many researchers over the last decades, still research on the removal of ammonium by zeolitic materials are ongoing. In a recent paper, Juan and his team [9] used powdered and granulated forms of zeolites NaP1, K-F and K-chabazite/phillipsite synthesized from coal fly ash to uptake ammonium in wastewater from a sewage treatment plant. In other recent papers dealing with the removal of ammonium in water, Liang and Ni [10] found that the modification of natural zeolite clinoptilolite can improve and enhance the uptake of ammonium ion. The modification process includes pretreatment by grinding and sieving, modifying by sodium salt and finally, calcination. These modifications can improved the pore size and surface area of clinoptilolite which eventually increased the ammonium ion uptake by clinoptilolite. Therefore, it is important to improve the ammonium uptake from the waste water using an economical approach such as utilizing activated zeolite synthesized and naturally occurring zeolite.

Heulandite is a $(\text{Ca}, \text{Na})_{2-3}\text{Al}_3(\text{Al}, \text{Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O}$, Hydrated Calcium Sodium Aluminum Silicate is one of the naturally existing zeolites. It is rich in silica and has a high ion exchange capacity than other zeolites. It generally exhibits a high selectivity for ammonium and metallic ions. Heulandite's structure is sheet-like. Although still a true tectosilicate where every oxygen is connected to either a silicon or an aluminum ion and the structure is a framework, there still is a sheet-like structural organization. The sheets are connected to each other by a few bonds that are relatively widely separated from each other. The sheets contain open rings of alternating eight and ten sides. These rings stack together from sheet to sheet to form channels throughout the crystal structure. The size of these channels controls the size of the molecules or ions that can pass through them and therefore a zeolite like heulandite can act as a chemical sieve, allowing some ammonium ions to pass through while blocking others ions. Heulandite's sheet-like structure produces the prominent pinacoid faces, the perfect cleavage and the unique luster on those faces. So keeping in view all the distinct characteristics of the heulandite it has been selected in this study for the ammonium removal.

The main aim of this study is to determine the optimal conditions for the activation of heulandite to get the best results for the adsorption of ammonium by salt treatment and to realize the value of low cost activated heulandite, as an efficient alternative sorbents for the removal of ammonium. The main focus of the study is the transformation of heulandite to a high cation exchanger under appropriate activation conditions. A comparison was made with naturally occurring heulandite in powdered forms. An understanding behavior of these materials provides insights into its expected capacity as an adsorbent. Comparison on the efficiencies of the adsorbent investigated is also discussed in relation to ammonium removal.

The specific objectives of this research is to study the sodium activation of zeolite samples and the effect of various parameters on zeolite activation such as sodium concentration, stirring time, and temperature and to identify the key processes controlling the rate of ammonium adsorption by zeolite. In addition, the effects of pH, stirring times, initial concentration, adsorbent dosages and temperature on ammonium removal for both natural heulandite and activated heulandite were investigated and compared.

2 EXPERIMENTAL

MATERIALS AND METHODS

All the glassware used in the present study was pyrex quality, Manufactured by Borosil Glassware Ltd and Mumbai. Distilled Water was used for all the experiments. Reagents were prepared from Analytical Grade chemicals, using double Distilled water. Stock solutions of the ammonium ions Concentrations were prepared from analytical grade ammonium chloride, NH_4Cl . Naturally occurring heulandite samples was obtained from a large deposit in pune, Maharashtra. India.

2.1 EQUIPMENTS

The instruments used for carrying out the present study included digital pH meters (Hach) for pH measurements and conductivity meters (Hach), uv-visible spectrophotometer (Analytic jena spekol 2000), Shaker (Isi-2005rIn), Kjeldahl instrument (kps 020).

2.2 PREPARATION AND ACTIVATION OF HEULANDITE

The collected Natural Heulandite (NH) samples were grounded and sieved and the fractions between U.S. standard mesh numbers 20 and 40 (i.e 0.84 mm and 0.42 mm) were used for the study. The material was washed with distilled water to remove any non-adhesive impurities, and then dried in an oven at 100°C for 24 h and finely crushed. The activation process was carried out by mixing NH powder material with an aqueous solution of sodium chloride under the different conditions detailed below:

2.3 EFFECT OF SODIUM CONCENTRATION

To study the effect of sodium concentration and batch activation, the sodium chloride concentration was varied from 0.5 to 2.0 mol/L with zeolite/ solution ratio maintained as 1 g/10 ml. The suspension was stirred in conical flasks (500 ml) using a magnetic stirrer water bath at a rate of 100 rpm and 80°C for 2 h. Subsequently, the suspension was filtered and washed with distilled water. The wet activated material was dried at 60°C in an oven for 24 h and used in batch adsorption experiments at an initial ammonium concentration of 100 mg/L with a pH 7 at 25°C and stirring time of 24 h. The best sodium ion concentration for the activation of zeolite was selected as that corresponding to the highest ammonium removal capacity (mg/g).

2.4 EFFECT OF TIME

For determining the optimum time required for activation zeolite from aqueous solution, a weighed quantity of heulandite (1 g) was added into the solution of 1 mol/L sodium chloride concentration and stirring time ranging from 0.5 to 3 h. The conditions applied above on the effect of sodium concentration experiment were repeated. The optimum stirring time for the activation of zeolite was selected as that corresponding to the highest ammonium removal capacity (mg/g).

2.5 EFFECT OF TEMPERATURE

The effect of temperature on activation of zeolite was investigated at different temperature values ranging from 10°C to 100°C. The sodium chloride concentration and stirring time were kept constant at 1 mol/L and 0.5 h, respectively. The optimum temperature for the activation of zeolite was selected as that corresponding to the highest ammonium removal capacity (mg/g).

2.6 BATCH ADSORPTION STUDIES

All adsorptions in batch experiments were carried out using stopper conical flasks (500 ml), zeolite/liquid ratio of 1 g/100 ml, magnetic stirring water bath, a stirring rate of 120 rpm and a temperature at 25°C. A stock solution (1000 mg/L) was prepared by dissolving NH₄Cl in distilled water. For determining the optimum time required for ammonium removal by natural heulandite (NH) and activated heulandite (AH) from aqueous solution, a weighed quantity of adsorbent (1 g) was added into solution of 80 mg/L ammonium concentration and was stirred for 10–420 min and 5–60 min of NH and AH, respectively, at a fixed pH of 7.0. The effect of initial ammonium concentration in batch adsorption experiments was carried out by using initial ammonium concentration in the range of 10–250 mg/L and 10–400 mg/L for 280 min and 35 min for NZ and AH, respectively. The effect of pH on adsorption was investigated at initial ammonium concentration of 80 mg/L and performed in different pH values (2–10) at 25°C. Batch adsorption was conducted at 300 and 40 min for NZ and AH, respectively. The pH of the solution was adjusted by 1 M HCl or NaOH solution. For determining zeolites loading effect, zeolite loading was varied from 0.2 to 2.2 g/100 ml at initial ammonium concentration of 80 mg/L. The zeolite–liquid was then stirred for 300 and 40 min for NZ and AH, respectively, at temperature 25°C. Temperature of adsorption isotherms was studied at 25, 35 and 45°C. A 100 ml of ammonium chloride solution of 80 mg/L concentration was equilibrated with 1 g zeolite for 40 min for AH. The concentration of ammonium and the removal efficiency (%) of zeolite was determined by Kjeldahl Method [11].

3 RESULTS AND DISCUSSION

3.1 ACTIVATED HEULANDITE (AH)

Due to different results in activation of different zeolite samples, parameters, such as sodium concentration, stirring time and temperature, had to be investigated to obtain optimum activation conditions, and the results are shown in Fig. 1a–c. As can be seen from batch adsorption experiments (Fig. 1a–c), the temperature of 70°C, stirring time of 30 min and 1 mol/L concentration of NaCl were the most effective in adsorption of ammonium ions on Natural Heulandite (NH). The optimum conditions obtained above for the activation of zeolite using NaCl were applied on NaOH for the adsorption of ammonium ions at 100 mg/L of ammonium concentration, pH 7 and 25°C. Its ammonium adsorption capacity (mg/g) was compared with NaCl activation as shown in Table 1. The results showed that NaCl-activated heulandite (AH) had a higher ammonium adsorption capacity value than NaOH-activated zeolite. Higher ammonium adsorption capacity means higher Na⁺ content [12][13][14] From the above discussion, it can be concluded that ion exchange promoted by NaCl-activated heulandite (AH) is a more attractive zeolite preparation method than that of NaOH-activated zeolite. Therefore, NaCl-activated zeolite (ActZ) was selected for further study.

3.2 EFFECT OF STIRRING TIME

As shown in Fig. 2a and 2b, the removal efficiency of ammonium ions increased with increasing stirring time. 40% and 92% of ammonium ions removal were completed within 10 min for NH and AH, respectively, which also confirmed larger adsorption capacity of AH compared to NH. The experimental data show that NH could exceed 78% percentage removal at 300 min, but then, the removal efficiency plateaus. As to AH, the ammonium removal rate exceeds 98% percentage removal at 40 min and became increasingly slow with increasing stirring time. This may be attributed to the utilization of the most readily available adsorption sites of the zeolite that leads to a fast diffusion and rapid equilibrium attainment. On the basis of these results, 300 min and 40 min stirring period was selected for all further studies of NH and AH, respectively. Beyond this level there is no noticeable increase in the adsorption and it is thus fixed as the equilibrium time. It can be said that the Ammonium ions were adsorbed by the exterior surface of the adsorbent. When the adsorption of exterior surface of the adsorbent reached the saturation point, the ammonium ions enter the adsorbent pores and are adsorbed by the interior surface of the particles [14][15][16].

3.3 EFFECT OF INITIAL AMMONIUM CONCENTRATION

As shown in Fig. 3a and 3b, the increment of removal efficiency was achieved in the ranges of 10–50 mg/L of ammonium concentrations for both Natural heulandite and Activated heulandite. This result is similar with that reported by sarioglu [17] who concluded that the increase in removal efficiency was achieved between 8.8 mg/L and 40 mg/L of ammonium concentrations, indicating that the initial ammonium concentration plays an important role in the adsorption of ammonium onto zeolites. Increasing the initial ammonium concentration would increase the mass transfer driving force and therefore the rate at which ammonium ions pass from the bulk solution to the particle surface [16]. After 50 mg/L ammonium concentration of both zeolites, the removal efficiency of ammonium decreased with increased initial ammonium concentration. This is because the high initial ammonium concentration provided a greater driving force [18]. As a result, the ammonium ion could migrate from the external surface to the internal micropores of the zeolite within a given stirring time. The equilibrium was achieved when all the exchangeable ammonium and cation on the external and internal surfaces of the zeolite were reached [19] Fig. 3a and 3b shows that the adsorption capacity of the activated heulandite was higher than that of natural heulandite at each initial ammonium concentration.

3.4 EFFECT OF SOLUTION P^H

The pH of the aqueous solution is an important factor controlling ammonium adsorption [20] As shown in Fig. 4 pH played an important role for ammonium adsorption of Natural Heulandite and Activated Heulandite. The removal efficiency of both zeolites increased with increasing pH. from 2 to 7 and then it decreased gradually from pH 8 to 10 with the maximum value being achieved at pH 7. An almost similar trend has been reported for ammonium adsorption onto zeolite by different researchers [20][22]. The behavior of ammonium as a function of water's pH can be explained by considering the change in density of hydrogen ions, the dominant ionic species of ammonium and the surface charge of zeolite as a function of water's pH. The pH of natural heulandite and activated heulandite were 7.7 and 7.8, respectively, implying that the zeolite particle's surface is uncharged at water pH of 7.7 and 7.8 of natural and activated zeolites; the zeolites particle's surface has a positive charge at water pH below 7.7 and 7.8, and it is negatively charged at water pH above 7.7 and 7.8. This indicates that the

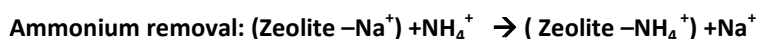
surface of zeolite is negatively charged at pH of above 7 [21]. For ammonium adsorption, according to the relation of ammonium dissociation in water as a function of pH, ammonium ions is the dominant species of ammonia nitrogen in water at pH of below 7 while the molecular form, ammonia (NH₃) is dominant at alkaline pH. By considering the above facts, the increase in adsorption of ammonium with the increase in water's pH up to the maximum point (pH 7) can be attributed to a decrease of hydrogen ions in solution corresponding to an increase in pH, and thus a reduction of the competition between hydrogen ions and ammonium ions for adsorption/exchanging sites onto zeolite particles [23]. The decrease of ammonium adsorption with the increase of water's pH above 7 is related to the increase in percentage of molecular ammonium, which resulted in the reduction of ion-exchange potential [24].

3.5 EFFECT OF ADSORBENT DOSAGE

As illustrated in Fig. 5, the removal efficiency of ammonium ions by both zeolites increases with increasing amount of both zeolites. This effect can be attributed to an increased surface area and number of adsorption sites [25] As can be seen in Fig. 5, the ammonium removal rate of activated heulandite (AH) increases more rapidly than that of natural heulandite (NH) and attains a plateau at 98.73% when the adsorbent dosage was 1 g indicating that the ammonium ions removal was negligible at higher adsorbent dosage. The natural heulandite attains a plateau at 94.5% when the dosage was 1.8 g as shown in Fig. 5. Thus, both of them reached a balance of approximately 98% when the adsorbent dosage for AH and NH was 1 g and 1.8 g, respectively. This may be attributed to a large adsorbent amount which effectively reduces the unsaturation of the adsorption sites and correspondingly, the number of such sites per unit mass comes down resulting in comparatively less adsorption at higher adsorbent amount [16][25]. Hence, when the ammonium is exchanged completely with cations on the zeolite surface at a certain amount of zeolite loading, the Ammonium removal reached equilibrium.

3.6 REUSABILITY AND DESORPTION

Accordingly, the ion-exchange and electrostatic adsorptions are probably the main mechanisms for ammonium ions removal by zeolite under the selected conditions, through the following reaction



In this study, adsorption experiments were performed using 1 g zeolite and 100 ml of 60 mg/L ammonium at 25°C for 40 min, and desorption of adsorbed ammonium onto zeolite was studied using 1 mol/ L NaCl, with zeolite/liquid ratio of 1 g/10 ml for 30 min at 70°C, and consecutive adsorption-desorption cycles were repeated four times. The results are shown in Table 2. There was a slight decrease with the increase of cycle times in adsorption efficiency from 6.630 mg/g for the first cycle to 2.10 mg/g for the fifth cycle. The activated zeolite that was regenerated by four cycles in sodium solution had high ammonium-removal efficiency with its adsorption efficiency of 2.10 mg/g which is close to that of Natural zeolite (2.34 mg/g).

4 CONCLUSIONS

The characteristics of natural heulandite (NH), activated heulandite (AH) and their efficacy in removing ammonium were investigated. The following conclusions were made from the experimental results:

- 1 mol/L of NaCl, stirring time of 30 min and 70°C were found to be the optimum activation conditions for the zeolite with excellent removal of ammonium .
- The highest adsorption capacity was obtained at pH 7.0 for both Zeolites (NH & AH) and the maximum ammonium adsorption was rapidly attained within 40 min and 300 min for activated Heulandite and natural heulandite, respectively.
- The adsorption capacity of activated zeolite is decreased to 2.10 mg/g which is close to that of natural zeolite (2.34 mg/g) after being regenerated four times. Based on these results, the study shows that activated heulandite can be used as cheap, efficient and ecofriendly adsorbent for removing ammonium from water and wastewaters.

ACKNOWLEDGEMENT

The financial support of the University Grants Commission, Rajiv Gandhi National Fellowship Scheme is gratefully acknowledged.

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