Removal of Ammonia from wastewater by ion exchange technology

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Abstract- **Nitrogen in ammonia form can have deleterious effects including accelerated eutrophication, dissolved oxygen depletion due to bacterial oxidation in receiving water and fish toxicity. Ammonia also reacts with chlorine used for disinfection in wastewater treatment to produce chloramines. Chloramines are less effective disinfectants and are toxic to aquatic life in the receiving water. There are various methods available for removal of $NH_4 – N$ from wastewater like ammonia stripping, breakpoint chlorination, struvite precipitation, nitrification-denitrification, ion exchange etc. This paper presents a study of $NH_4 – N$ removal by ion exchange method using synthetic resin from industrial wastewater. Much of the literature is concerned with clinoptilite, a naturally occurring zeolite however modern exchanger are polymer based. Clinoptilite is cheaper than synthetic resin but durability, ion exchange capacity and regeneration capacity of synthetic resin is higher than clinoptilite. Ammonium removal from aqueous solution by a natural ion-exchange resin was investigated by considering the factors affecting the ammonium-exchange capacity including the zeolites' particle size, the loading flow rates and the impact of a number of regenerations upon the ion-exchange capacity.**

Index Terms- **Ammonical nitrogen removal - ion exchange –Natural zeolite – clinoptilite - synthetic resin.**

I. INTRODUCTION

With the dramatic development of economy and improvement of human life, much more wastewater is producing nowadays. On the other hand, people are concerned about environmental protection more than ever and relevant legislations or regulations are becoming more critical. The ammonia sources, which are municipal, agricultural and industrial, contribute to accelerated eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water. Free ammonia (NH_3) and ionized-ammonia (NH_4^+) represent two forms of reduced inorganic nitrogen which exist in equilibrium depending upon the pH and temperature of the waters in which they are found. Of the two, the free ammonia form is considerably more toxic to organisms. This free ammonia is a gaseous chemical, whereas the NH_4^+ form of reduced nitrogen is an ionized form that remains soluble in water. Ammonia nitrogen contributes to BOD (Biochemical Oxygen Demand) in water due to its biologic oxidation by nitrifying bacteria, which can have a significant dissolved oxygen requirement for the breakdown of NH_3 into NO_3^-. In addition to the presence of nitrates, the principal end product of nitrification stimulates algal growth and eutrophication in waterways [1]. The maximum limit of ammonia set by the Bureau of Indian Standards for drinking water is 0.5 mg/l (IS 10500 : 2012). Discharge Standard set by central pollution control board of Ammonia Nitrogen in surface water, public sewer and marine/coastal areas is 50 mg/l.

A variety of biological and physicochemical methods and technologies have been proposed for the removal of ammonia from the environment and industrial water systems. Removal of ammonium can be accomplished through the use of air stripping, breakpoint chlorination, ion exchange, and biological nitrification–denitrification. The efficiency of the process of air stripping, biological nitrification and denitrification are significantly impaired by low temperature in winter [2],[4]. The traditional method for removal of ammonium and organic pollutants from wastewater is biological treatment, but ion exchange offers a number of advantages including the ability to handle shock loadings and the ability to operate over a wider range of temperatures. Biological methods (nitrification) do not respond well to shock loads of ammonia, and unacceptable peaks in effluent ammonium concentration may

result in such cases. The ion exchange method usually employs organic resins, which are very selective. However, they are very expensive. Ion exchange with natural zeolites is more competitive because of its low cost and relative simplicity of application and operation. Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity and compatibility with the natural environment [5].

II. MATERIALS AND METHODS

2.1 ION EXCHANGE

Removal of ionic substances using the principle of adsorption by ion exchange resin has been used quite commonly in wastewater treatment. There are two types of resins: natural resins such as zeolite and synthetic resins like silica powder. For the removal of ammonium ion from wastewater and culture medium, Clinoptilolite, a type of natural zeolite from volcanic rock has been used extensively and proved to be efficient. The effectiveness of the resins depends on the affinity towards the cations as follow:

$$K+ > NH4+ > Ca2+ > Fe3+ > Mg2+$$
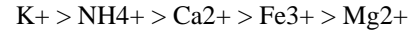
As the capacity of the resins will reach saturation point when all the ions in the resins are replaced by ammonium ions, regeneration is needed from time to time. Chemical regenerants such as sodium hydroxide and hydrochloride acid are normally used. Thus, two modes of operation system could be used – batch and continuous. In batch system, the resin is stirred with wastewater in the reactor until the reaction is completed. The saturated resin is then removed and regenerated. For continuous mode, the resin is stored in a pack column where the wastewater is passing through it. Upon exhaustion, the column is backwash with regenerants as shown in Figure 1. The shortages of this method are the high maintenance cost for the exchange of ion exchange media and the complication regeneration system.
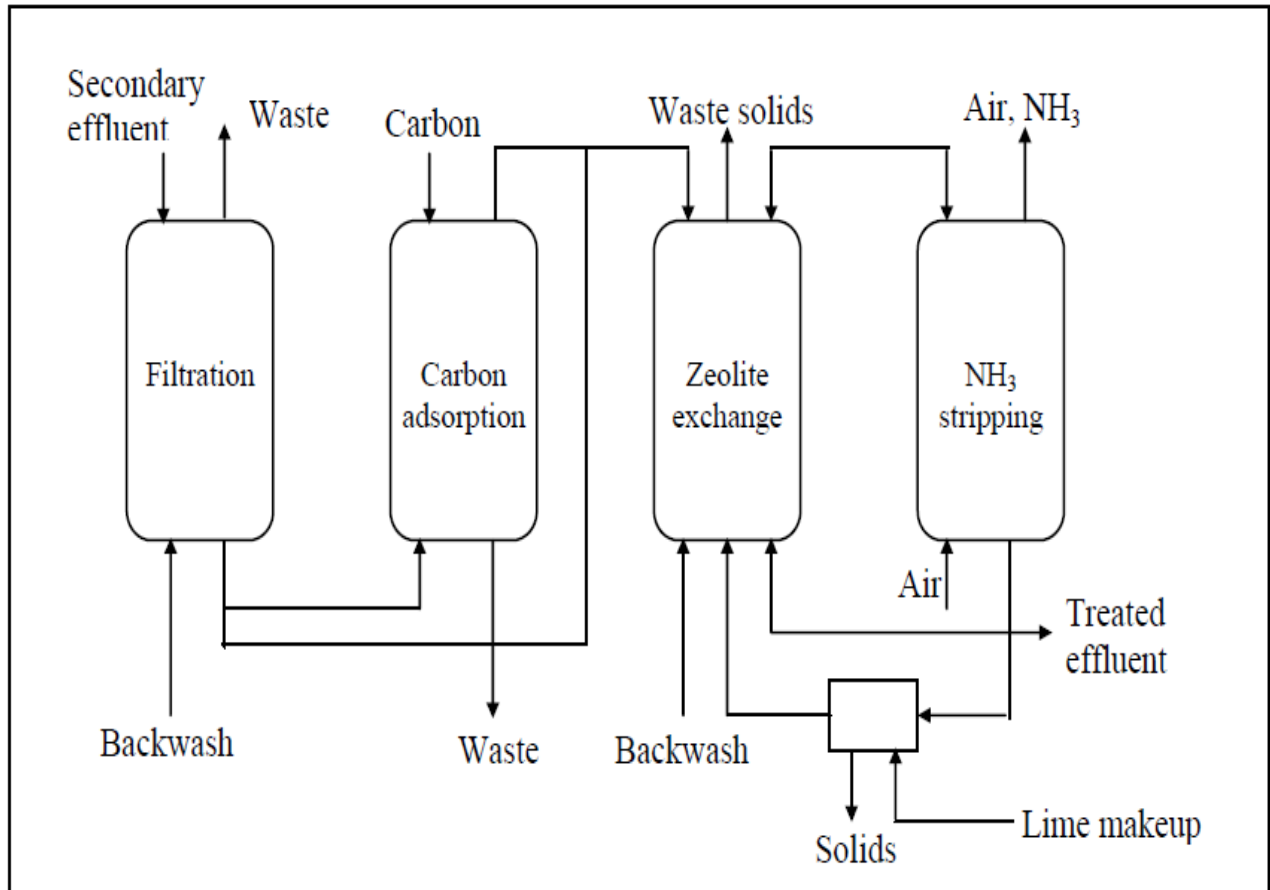

Figure 1: Flow diagram for the removal of ammonia from wastewater by zeolite exchange

2.2 Literature review

In this study, two different clinoptilolite forms were used. One of them was raw clinoptilolite and the other a conditioned clinoptilolite which was used after the first regeneration. The experiments were conducted in two phases with investigations using batch sorption and column studies.

Chemical and physical properties of the zeolite clinoptilolite

The ion-exchanger used in the experiments was obtained from Bigadiç, in the north-western part of Turkey. The natural zeolite was chosen on the basis of its good ammonium-ion selectivity and potentially low cost. The chemical properties of the clinoptilolite used in this study are given in Table 1. The effective particle size was 0.18 mm with a uniformity coefficient of 2.98 for the fine particles. The sieve analysis is provided in Table 2. Zeolite was broken into pieces and sieved into a diameter of (-1.00+0.125) and (-2.00+1.00) mm (numbers in the parentheses indicate sieve size in mm through which particles passed and were retained, respectively). The zeolite was then washed with distilled water to remove turbidity and after drying in an oven for over an hour at 70°C, was put in a desiccator.

Test chemicals and analysis

Ammonium chloride stock solution (1 000 mg/l NH4+) was prepared by dissolving NH4Cl in deionized water. The solution was further diluted before use. The ammonium chloride and other chemicals used were of analytical grade. Synthetic samples were prepared to give ammonium concentrations of 10, 20, 40 and 80 mg/l by adding appropriate amounts of ammonium chloride stock solution to distilled water. The ammonium concentration of the samples was determined by the standard Nesslerisation method using Pharmacia LKBNowaspec- spectrophotometer (*Standard Methods*, 1983). It should be noted that no more than 10 ml of sample was taken for measurement of ammonium, and hence the total volume of the aqueous solution was affected insignificantly by sampling.

TABLE 1
Chemical properties of Bigadiç zeolite tuffs

Component (%)	Yücel and Çulfaz, 1985	Çelenli et al., 1994	Sirkecioglu and Senatlar, 1995
SiO_4	-	67.96	-
SiO_2	67.6	-	64.99
Al_2O_3	11.3	10.74	9.99
K_2O	2.17	3.01	1.95
CaO	3.26	0.74	3.51
Na_2O	-	0.81	0.18
MgO	1.18	1.49	1.01
Si	-	15.36	-
Fe_2O_3	0.77	-	3.99
MnO	0.02	-	-
TiO_2	0.07	-	-
NaO_2	0.3	-	-
H_2O	13.4	-	14.47

TABLE 2
Sieve analysis of fine zeolite particles

Sieve opening, mm	1.00	0.60	0.50	0.30	0.25	0.125
% Passing sieve	100	64	54	28	20	0

Batch studies

In the first phase of runs, batch sorption isotherms for the removal of ammonium were investigated. Batch sorption isotherms were determined in 500 ml conical flasks. Weighed amounts (0.4 g) of clinoptilolite were introduced into four conical flasks, to which 400 ml of ammonium solution concentrations of between 10 and 80 mg/l were added. The flasks were shaken for 30 min and samples were taken periodically for measurement of aqueous-phase ammonium concentration. Preliminary tests confirmed that a 30 min contact time was enough to reach a steady-state ammonium concentration.[6]
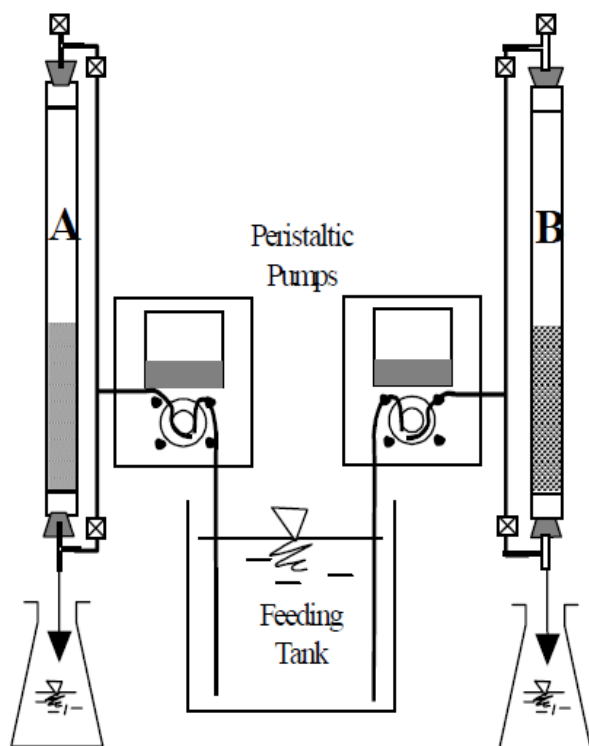
Figure 2: The experimental set-up[6]

Column studies

In this study, two columns (A and B) each with an inner diameter of 15 mm were used. The bed height and volume of the columns were 140 mm and 25 cm3, respectively. Column A was filled with fine zeolite (-1.00+0.125) mm and Column B was filled with a coarse zeolite (–2.00+1.00) mm. In the column studies, operation and regeneration parameters, and ion-exchange capacity of clinoptilolite were investigated. Two peristaltic pumps (Watson Marlow 505L) were employed to feed the stock solution to the ion-exchange column at the desired flow rate. The ammonium concentration of the samples collected from the column exit was monitored. No stratification in the combined scheme was observed under the flow rates employed. The basic experimental setup is shown in Fig. 1.

The resin column was exhausted by down flow at three different superficial velocities of 25, 50 and 75 bed volume (BV)/h, until an ammonium breakthrough of more than 2 mg/l NH4 +-N was achieved. The columns were then regenerated with two different NaCl solutions (10 g NaCl/l and 20 g NaCl/l) and at two different superficial velocities,

namely, 16 BV/h and 25 BV/h. The regenerant was passed through the column in the up flow mode. The absence of ammonium in the effluent indicated the completion of regeneration. Another loading cycle was then carried out.

Regeneration

Columns were prepared by complete regeneration with 35 BV of regenerant containing 10 and 20 g NaCl/l and a pH of 12.3 adjusted by using NaOH. Ammonium elution by 10 and 20 g NaCl/l regenerant solutions is shown in Figs. 8 and 9, respectively. 15 BV of regenerant, corresponding to the use of 20 g NaCl/l were sufficient to reduce the effluent ammonium concentration in the regenerant to less than 20 mg/l for the fine zeolite column (Fig. 9a). On the other hand, after feeding 15 BV of regenerant to the coarse zeolite column containing 10 and 20 g NaCl/l, effluent ammonium concentrations were about 200 and 150 mg/l, respectively. The coarse zeolite column needs more regenerant solution than the fine zeolite column for complete regeneration. It is concluded from Figs. 8 and 9 that a volume of 15 BV-0.35 M NaCl solution is sufficient for nearly complete regeneration of the zeolite column of (-1.00+0.125) mm particle size. The coarse zeolite needs more regenerant solution than the fine zeolite for complete regeneration and regeneration seems to be completed when 25 to 35 bed volumes of regenerant solution pass the ion exchanger bed for both of the columns. Results of the experimental investigation are used to develop optimum operational conditions for clinoptilolite exchangers.

III. RESULTS AND DISCUSSION

The initial ammonium concentration provides the necessary driving force to overcome all mass-transfer resistances of ammonium between the aqueous and solid phases. The removal of ammonium is high in the initial 5 min, but thereafter the rate significantly levels off and eventually approaches zero, i.e. when equilibrium is attained. These changes in the rate of removal might be due to the fact that, initially, all adsorbent sites were vacant and the solute concentration gradient was high. Afterwards, the ammonium uptake rate by the zeolite decreased

significantly, due to decrease in adsorption sites. A decreasing removal rate, particularly towards

the end of the experiment, indicated a possible monolayer of ammonium ions on the outer surface and pores of the zeolite and pore diffusion onto the inner surface of zeolite particles through the film due to continuous agitation maintained during the experiment. The adsorption rate of ammonium by both raw and conditioned clinoptilolite was initially fast, during the first 5 to 10 min, depending on the initial ammonium concentration, and then gradually decreased with increase in contact time. With the increase of ammonium concentration in solution, the adsorption capacity of the ammonium ion also increases. Singh and Prasad (1997) observed that with high concentrations of ammonium (98.76 mg NH4+ /100 ml), adsorption by 13X molecular sieve synthetic zeolites becomes constant, possibly because of complete removal of Na+ by NH4+ cations.

IV. CONCLUSION

The removal of ammonium from synthetic solution was demonstrated successfully on a laboratory scale with a selective ion-exchange process. The following conclusions can be drawn
from this study:

- The particle size of (-1.00+0.125) mm zeolites gives higher ammonium adsorption capacity than that of (-2.0+1.0) mm particle size of zeolites. The adsorption capacities calculated by graphical integration of the area above the breakthrough curves are about 0.57 and 0.38 meq/g NH4 + for particle sizes ranging between (-1.0+0.125) and (-2.0+1.0) mm, respectively.
- The capacity to 1 mg/l NH4+ breakthrough was reached in 450 BV for the fine clinoptilolite (1.00+0.125) column with superficial velocities of both 25 and 50 BV/h. On the other hand, the capacity of 1 mg/l NH4 + breakthrough was reached in 350 BV for the fine zeolite column with superficial velocity of 75 BV/h. A flow rate of 25 to 50 BV/h loading is advocated. It is a reasonable velocity and has no negative effect on adsorption capacity.
- The capacity increases considerably with the first regeneration. It seems that the clinoptilolite has been activated by the regenerant containing 10 and 20 g/l NaCl and a pH of 12.3 adjusted by using NaOH. Regeneration can be accomplished

with about 10 BV of regenerant containing 20 g/l NaCl applied at a rate of 16 BV/h for fine clinoptilolite. After the 2nd and 3rd regenerations ammonium adsorption capacity of zeolite remained constant. The columns could be regenerated a number of times without loss of ammonium adsorption capacity.

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