

Ammonia Removal from Nitrogenous Industrial Waste Water Using Iranian Natural Zeolite of Clinoptilolite Type

M.M. Jafarpour, Ar. Foolad, M.K. Mansouri, Z. Nikbakhsh, H. Saeedizade

Abstract— Ammonia nitrogen is one of the most hazardous water pollutants, discharging into water receptors through industrial effluents. Negative environmental impacts of such chemical species in hydrosphere include accelerated eutrophication, water toxicity and harming the aquatics. Natural zeolite clinoptilolite has very high selectivity & capacity for ammonium cation sorption. It occurs in high abundances and rich mines of this zeolite exist in different parts of Iran and thus are available more cheaply and with different sizing. The aim of this study is to investigate ammonia nitrogen removal over this natural sorbent from real samples of high polluted wastewater discharging from a fertilizer producing plant. The experimental results showed that this natural sorbent without even any pre treatment system & with the same particle size available in Iranian markets has still high capability & selectivity in ammonia nitrogen removal both in batch and continuous tests.

Keywords—Ammonia nitrogen removal, Clinoptilolite, Natural zeolite, Waste water.

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 in Iran. 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.

M.M. Jafarpour is with the Shiraz Petrochemical Complex Research Center, Shiraz, P.O.BOX#111 7348197515 IRAN (corresponding author to provide phone: +989173165114; fax: +987118200099; e-mail: m.jafarpour@spc-ir.com).

AR. Foolad is with the Shiraz Petrochemical Complex Research Center, Shiraz, P.O.BOX#111 7348197515 IRAN (e-mail: ar.foolad@yahoo.com).

M.K. Mansouri is with the Shiraz Petrochemical Complex technical services department, Shiraz, P.O.BOX#111 7348197515 IRAN (e-mail: mansouri_kazem@yahoo.com).

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 European Association for drinking water is approximately 0.5 mg/l (AWWA, 1990) and also a guide level is given as 2.5 & 1.0 mg/l for discharge to surface waters & wells respectively according to Iran Environmental protection Agency (IEPA) [2]-[3].

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 [11].

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].

Zeolites are hydrated aluminosilicates that possess a three-dimensional framework structure. This structure is formed by AlO_4 and SiO_4 tetrahedrons that are connected by sharing an oxygen atom. When an AlO_4 tetrahedron is substituted for a SiO_4 tetrahedron, a negative charge appears which is

neutralized by the exchangeable cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}). 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 [8].

Both natural and synthetic zeolites have ability for removing several cations from solutions concerning adsorption and ion exchange features. 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. One ion exchanger with a high affinity for ammonium ion is clinoptilolite, a naturally occurring zeolite [5]-[7].

Among natural zeolites, clinoptilolite occurs most frequently both in the worldwide & Iran in specific. Clinoptilolite is a silica-rich zeolite and has a general formula of $(\text{K}_2, \text{Na}_2, \text{Ca}, \text{Mg})_3 \text{Al}_6 \text{Si}_{30} \text{O}_{72} \cdot 24\text{H}_2\text{O}$. Further more, there are impurities like quartz in most of the clinoptilolite deposits. These factors reduce the uptake of ammonium ion onto natural clinoptilolite. Fusion with sodium hydroxide prior to hydrothermal reaction is the method to transform low-grade natural materials to high cation exchanger. In addition to ion exchange capacity, selectivity is also an important character for zeolites. Although the ion exchange capacity of clinoptilolite is lower than some other zeolites, it generally exhibits a high selectivity for NH_4^+ ion. The ammonia ion-exchange capacity varies depending on the presence of other cations in the aqueous phase and initial ammonia concentration [9].

Clinoptilolite has been found very effective in removing ammonia from water by means of its excellent ion exchange capacity since the 1970s of last century. Many researchers have investigated ammonia removal from water by ion exchange. Koon and Kaufman studied ammonia removal from municipal wastewaters by clinoptilolite. Jorgensen et al. investigated the dependence of the efficiency and capacity of a European clinoptilolite on different parameters. Klieve and Semmens examined the effect of pretreatments on the performance of clinoptilolite for ammonia removal from wastewaters. Booker et al. studied the value of a natural Australian clinoptilolite as an efficient alternative to existing treatment processes of ammonia removal [1],[10].

In petrochemical complexes producing ammonia, effluent streams often contain high amounts of ammonia nitrogen & because of probable technical or location map restrictions these effluents run into rivers or water resources nearby. On the other hand, due to financial constraints to invest on high technology filtration units in old age industries, it is of high importance to find & apply natural low cost & feasible sorbents for ammonia removal from waste water streams.

The present work considers ammonia removal by a sample of natural clinoptilolite extracted from Iran mines. This investigation concentrates on testing the zeolite functionality on some real wastewater streams producing in old ammonia & urea plants containing different amount of ammonia nitrogen.

Besides, the bench test conditions were set up in a way so

that parameters important in determining the quality of treated industrial wastewater would be monitored in this research and it would be as economical as it could be for the probable industrial scale up in the future.

II. EXPERIMENTAL SECTION

A. Materials and Methods

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In this study the Clinoptilolite was supplied from "Firooz Kooh" mines in the north part of Iran grinded & sized to a range of 1 to 3 mm by "Afrand Tuska" Company. At the time being, this zeolite is extracted, processed & bagged by few mining companies & sold with cheap prices (0.03-0.04 US\$) to Livestock and poultry food industries with different size ranges according to the final application. The chemical properties of the Clinoptilolite used in this study are given in Table I. The provided Clinoptilolite samples were used with the available size range in Iran market & without any pre treatment recommended in different articles like activation with sodium chloride or sulfate solution and calcinations in order to justify the probable future industrial applications in bulk scales. The bulk density of the meshed zeolite was 0.88 g/cm^3 .

TABLE I
CHEMICAL ANALYSIS OF NATURAL ZEOLITE APPLIED IN THIS STUDY

Constituent	Weight %
SiO ₂	66.5 %
Al ₂ O ₃	11.81 %
TiO ₂	0.21 %
Fe ₂ O ₃	1.3 %
CaO	3.11 %
MgO	0.72 %
K ₂ O	3.12 %
Na ₂ O	2.01 %
MnO	0.04 %
P ₂ O ₅	0.01 %
L.O.I.	12.05 %

Waste water samples belong to a urea & ammonia plant streaming continuously with 10-40 m³/h volumetric flow to offsite lagoons and can contain a minimum of 100 mg/l to 5000 mg/l of ammonia nitrogen in a pH range of 9.5 to 10.5. One of the streams includes a few concentrations of molecular urea up to maximum of 200 mg/l. No other remarkable impurity found in the streams. In the recent technologies of the plants these streams are mostly recovered in the same process; however old technologies like the ones in this study should inevitably drain them to offsite.

Material safety data sheet (MSDS) of clinoptilolite shown in table II indicates non toxicity & environmental friendly nature of the compound.

TABLE II
CONCISE REVIEW ON CLINOPTILOLITE MSDS

HEALTH HAZARD DATA
Hazardous Ingredients: NONE
Health Hazard: NONE
Skin Contact: NO FIRST AID MEASURE NEEDED
FIRE AND EXPLOSION DATA
Flammable Limits: NONE
Extinguishing Media: NONE
Unusual Fire and Explosion Hazards: NONE
REACTIVITY DATA
Stability: Stable
Conditions to avoid: Not applicable
Incompatibility (Materials to avoid): None
Hazardous Polymerization: Will not occur
Conditions to avoid: Not applicable
ECOLOGICAL CONSIDERATIONS
Waterfowl toxicity: NONE
Aquatic toxicity: NONE
Food chain concentration potential: NONE
Biochemical oxygen demand: None, products are not biodegradable.
Atmospheric: Contain no ozone depleting substances.

B. Isotherm Studies

Batch adsorption isotherm for the ammonia removal was investigated. Batch adsorption isotherm was determined in 250 ml conical flasks. Weighed amounts (1-5 g) of clinoptilolite were introduced into five conical flasks, to which 150 ml of ammonium chloride solution with fixed concentrations of 700 mg/l NH_4^+ at pH of about 6.5 were added. The conical flasks were shaken for 11 hours using a shaker device.

Preliminary tests had confirmed that 4 hours of contact time was sufficient to make ammonium concentration in solution steady, which was assumed to reach equilibrium. The final ammonia concentrations remaining in solution were analyzed & by considering the initial ammonium amount, the adsorbed amount is also determined. Afterwards using Freundlich & Langmuir equations, experimental data were fitted using linear regression in Mat Lab curve fitting software.

C. Column Studies

In the column studies, ammonia nitrogen concentrations plus some other parameters mostly important in the quality of waters involving in industry such as solution conductivity, total dissolved solids (TDS), total carbonate alkalinity (TAC), pH & in some tests sodium, potassium and calcium (or total hardness) were monitored over the number of bed volumes (BV) of waste water treated and investigated. Thus nearly 450 g of washed zeolite in size range of 1-3 mm were transferred to a glass column having 6.31cm internal diameter and 16cm length. An ascending flow was applied to pass the waste water stream with initial ammonia concentration between 150-2500 mg/l & preset pH of 6.5-7.5 through the column. The experimental setup is shown in Fig.1.



Fig. 1 Experimental set up in column studies

D. Regeneration of Zeolite

The columns were then regenerated with 1 mol/l NaCl solutions. The regeneration was also passed through the column in the up flow mode. The ammonia concentration in the effluent indicated the completion of regeneration.

III. RESULTS AND DISCUSSIONS

A. Isotherm Studies

Adsorption isotherm are essential for the description of how NH_4^+ concentration will interact with zeolites and are useful to optimize the use of zeolites as adsorbents. Therefore, empirical equations (Langmuir and Freundlich isotherm model) are important for adsorption data interpretation and predications. Both Freundlich and Langmuir models were used for the evaluation of experimental results. The Langmuir isotherm relates Q_e (mg of ammonia absorbed per gram of zeolite) and C_e (the equilibrium ammonium concentration in solution) whereas K and b are Langmuir coefficients. The said equation is shown in (1):

$$Q_e = \frac{KbC_e}{1 + KC_e} \quad (1)$$

Q_e was calculated from the volume of ammonia solution, the mass of the material exposed to the solution and the equilibrium ammonium concentration in the solution (C_e).

The Freundlich model describes a logarithmic relationship between the solid and solution concentrations, and is normally written as (2):

$$Q_e = kC_e^{1/n} \quad (2)$$

Here again k and n are defined as Freundlich coefficient. When $\log Q_e$ is plotted against $\log C_e$ the coefficients k and n can be calculated. Knowing all coefficients and using experimental data for C_e , the Langmuir and Freundlich theoretical Q_e can be calculated. Fig. 2 and 3 shows the equilibrium isotherms data that indicates good fit for the data to Langmuir and Freundlich uptake models. Values for the coefficients calculated by experimental data are given in Table III.

TABLE III
 ISOTHERM EQUATIONS' COEFFICIENTS EXTRACTED FROM THE LINEARIZED CURVES IN FIGURE 2

FREUNDLICH COEFFICIENTS		LANGMUIR COEFFICIENTS	
k	1/n	b	K
0.20	0.75	67.77	0.0009

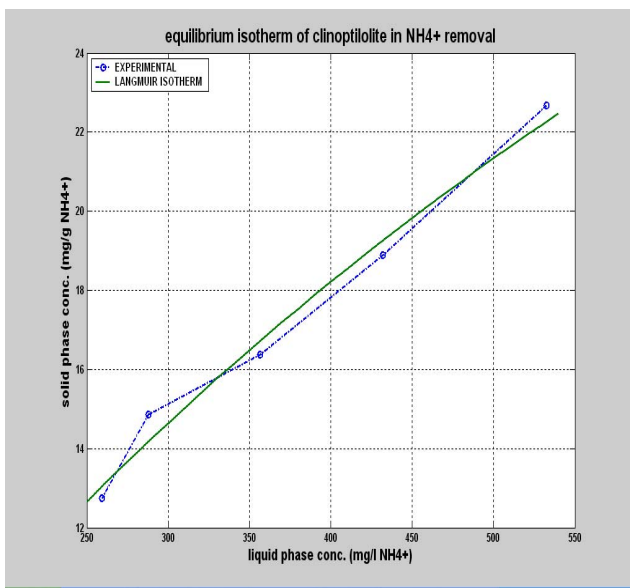


Fig. 2 Langmuir isotherms for the clinoptilolite samples obtained in batch experiments

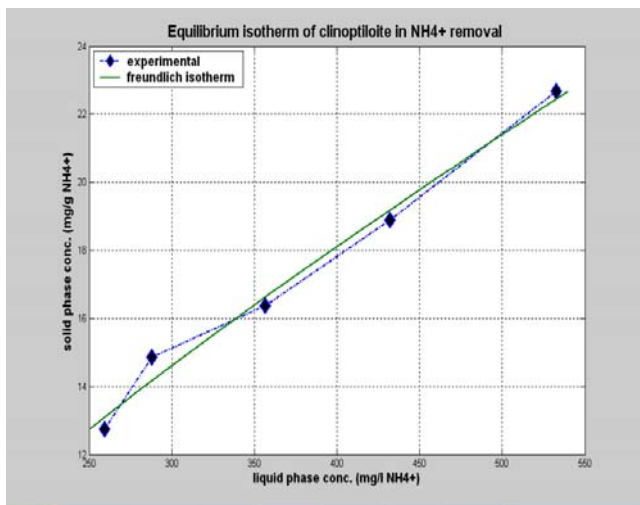


Fig. 3 Freundlich isotherms for the clinoptilolite samples obtained in batch experiments

B. Column Studies

Quite enough continuous runs with a wide range of initial ammonium concentrations and stream flows were performed in this research which proved the capability of the natural sorbent to remove 70-90 % of the ammonia nitrogen while applying waste waters with ammonium conc. Higher than 1000 mg/l. Whilst in interaction with lower ammonium concentration, complete removal had occurred.

Fig. 4 concerns on the results came from the encounter of a 1700 mg/l ammonium containing waste water stream from an ammonia plant having a pH of 7.7 and average up flow of 11 cm³/min. with the zeolite column described in the experimental section. Up to 90% of removal has occurred after passing almost 1.2 bed volume of the sample and there is still a removal of over 80 % even in 5.4 BV. Conductivity (or somehow TDS) and TAC variations indicate a perceptible decrease in the first BV and an almost constant trend afterwards. pH does not experience any appreciable variation.

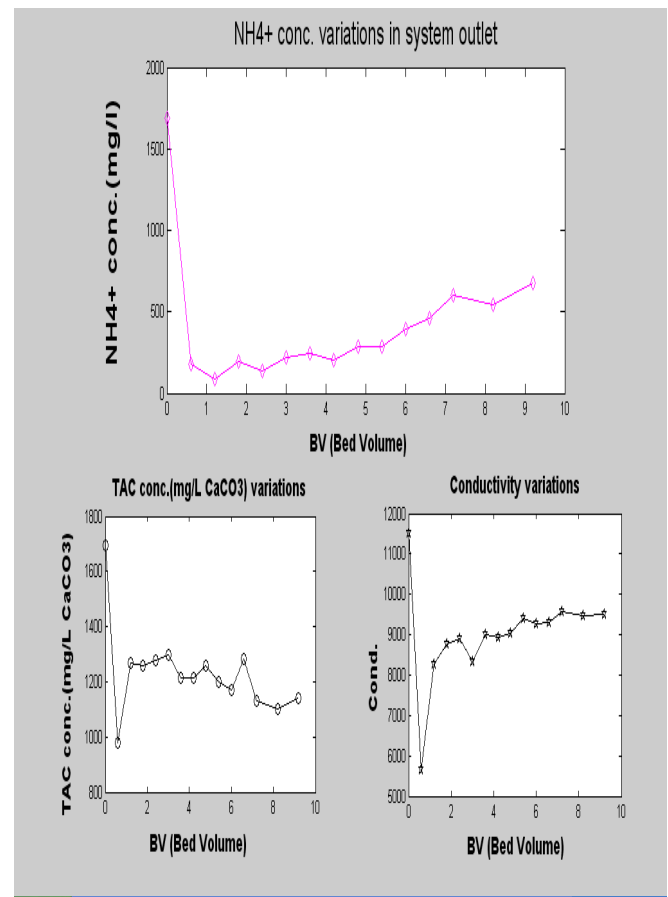


Fig. 4 Ammonium, TAC and Cond. Variations in the outlet of system- high ammonia inlet case

Monitoring the amount of sodium, potassium & calcium cations in the outlet of the system demonstrates an interesting relationship between the two alkaline cations in a way that around the third BV where sodium begins to diminish in amount, potassium starts to increase in the outlet. This proves the selectivity of the clinoptilolite for the exchange of these

cations. Calcium cations didn't prove to have as high tendency as alkaline cations in exchange with ammonium.

In fig. 5 results of flowing another sample of ammonia plant wastewater with lower initial ammonium conc. of 170 mg/l (lowering occurred by using a pre air stripping of ammonia in the sample before passing through the column), 15cm³/min up flow rate and pH=7.5 over the zeolite column are shown. Total removal of ammonia nitrogen has occurred even with higher flow rate. Cond., TAC and pH show almost similar variations.

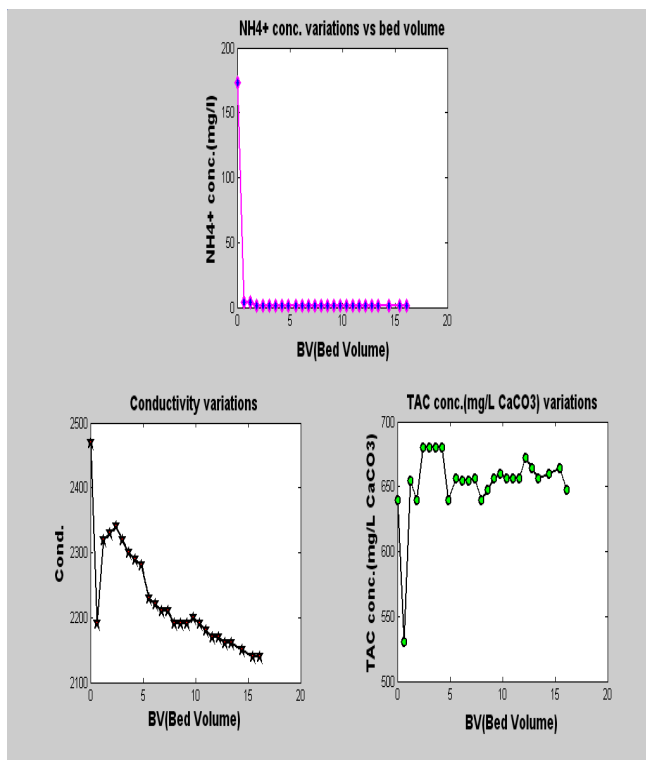


Fig. 5 Ammonium, TAC and Cond. Variations in the outlet of system- low ammonia inlet case

C. Regeneration of Zeolite

Columns were prepared by complete regeneration with 1 mol/l NaCl solution which has already been proved to be the optimum concentration for this process on clinoptilolite zeolite.

Ammonia elution by regenerate solutions and also the regeneration completion percent are shown in Fig. 6 and 7. It is concluded that a volume of 4.5 liter 1 mol/l NaCl solution with a flow rate of 45cm³/min is sufficient for nearly 90% complete regeneration of the zeolite column. The results indicated that high level of regeneration (95-98%) can be achieved with consumption of nearly 16 liters of the regenerate solution to reduce the ammonia conc. of ammonia from 4800 mg/l to 85 mg/l in the outlet.

Another continuous run was rendered using the regenerated column while a sample of waste water from urea plant with initial 630 mg/l ammonium concentration and flow rate of 45cm³/min and pH of 7 passed through the sorbent.

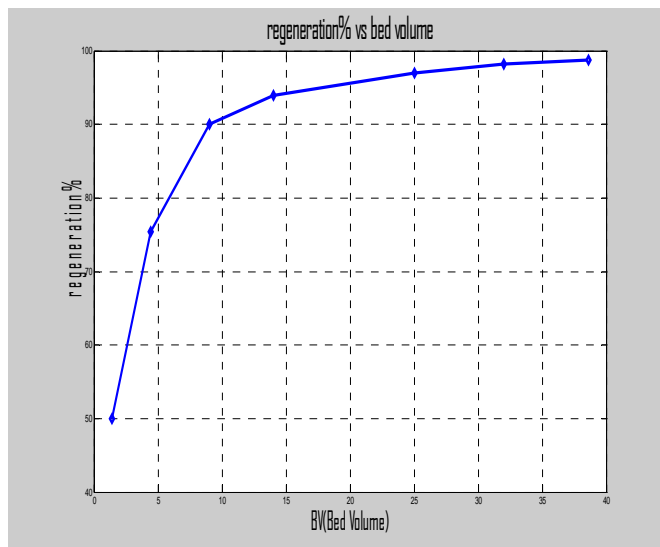


Fig. 6 Regeneration completion percent in one of regeneration process

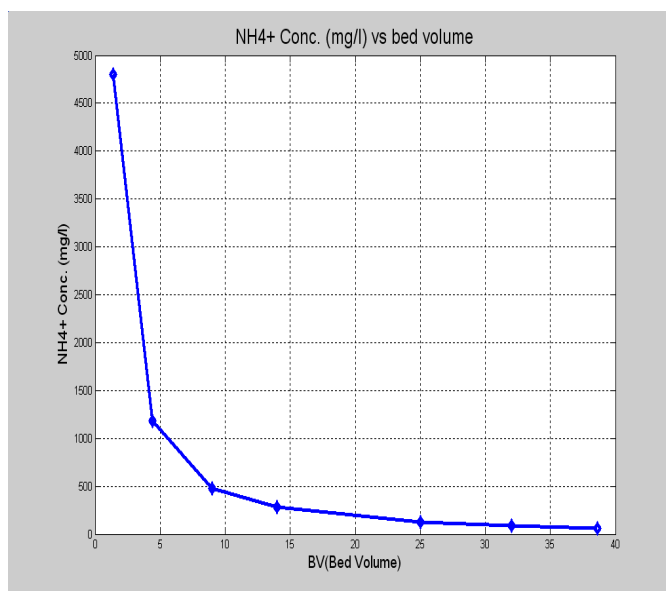


Fig. 7 Ammonia elution and regeneration completion percent in one of regeneration process

Fig. 8 and 9 follow the performance of regenerated clinoptilolite in ammonia reduction from the said sample. TDS, TAC and pH like the other runs showed no special trends during this test which can be seen in fig. 10 and 11.

Considering the bench flow rate & the bed volume, space velocity & retention time of the process is 5.4 hr⁻¹ & 11 min respectively

Considering the actual flow of the wastewater used in this latter experiment which is nearly 40 m³/hr, a zeolitic bed with volume of around 7.5 m³ is anticipated in the probable scale up.

Comparing to the cation exchange resin beds with 14 m³ volume in SPC utility plant, the above anticipation seems reasonable

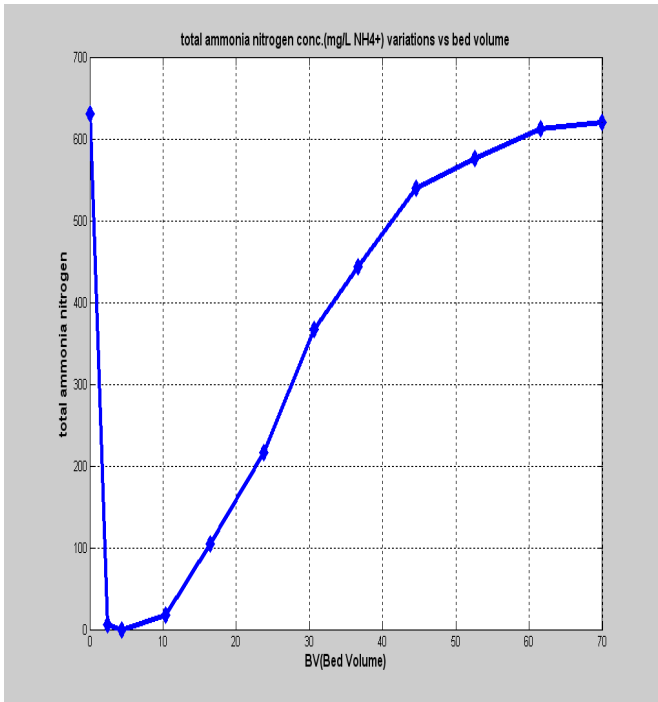


Fig. 8 Ammonia elution concentrations in a run after the regeneration process

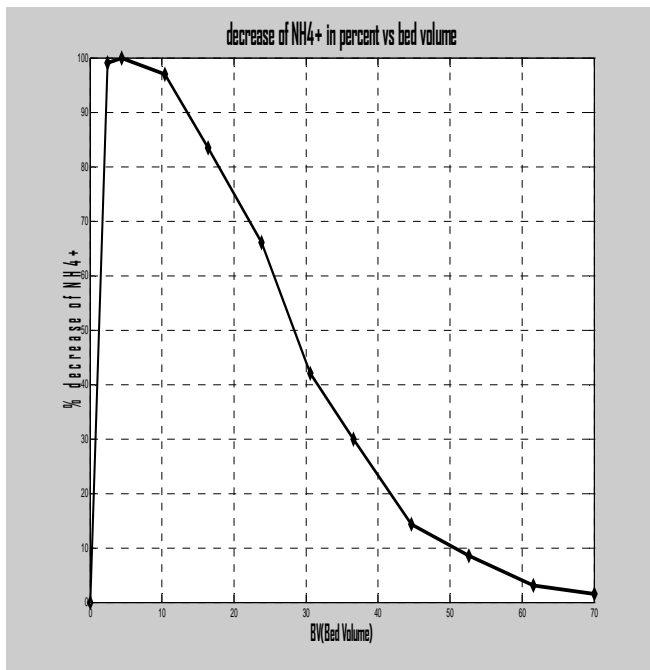


Fig. 9 Ammonia adsorption completion percent in a run after the regeneration process

IV. CONCLUSION

The Iranian clinoptilolite has proved its superiority in ammonia removal from actual waste water samples on a laboratory scale. The results obtained from column studies showed that the total exchange capacity of the Clinoptilolite sample was about 25 mg NH₄⁺/g of Clinoptilolite weight with

an efficiency of 50-65 % in column studies depending on flow rates. As the flow rate of the aqueous solution decreases, the hydraulic residence time increases, resulting in more NH₄⁺ being removed by the ion exchange sorbent. However in a predictive view for future scale up & application in industry, we tried to compromise the bench flow in a range where gives us reasonable space velocity and retention times for the future industrial ammonia removal operation. Therefore considering the actual flow of the waste streams we have focused on in this research, no larger than 8 m³ bed volumes is required for the drum to be designed.

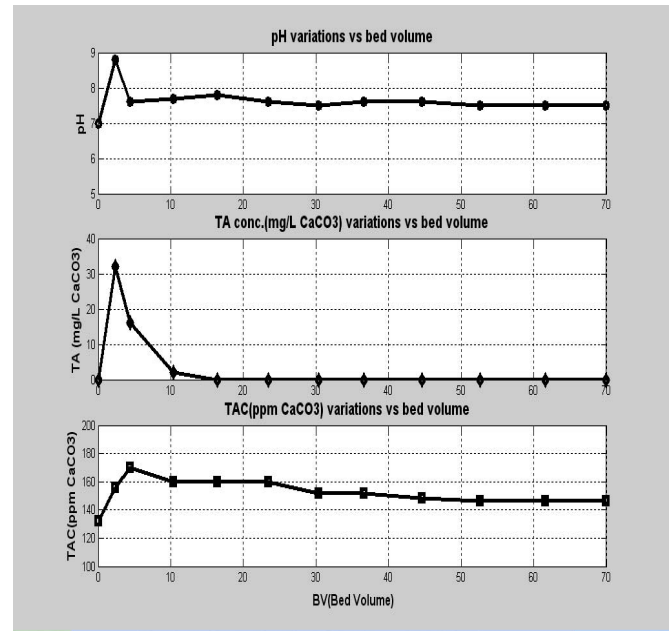


Fig. 10 Variation of pH, TA and TAC via treating the sample with a regenerated Clinoptilolite

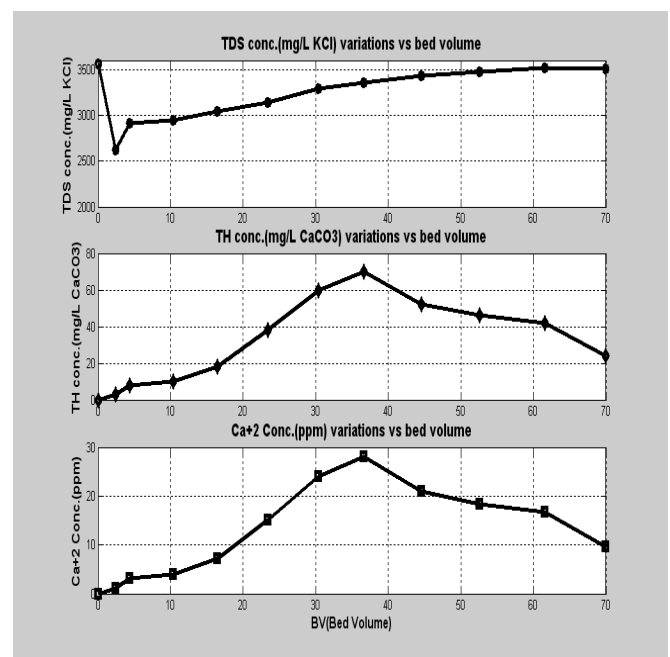


Fig. 11 Variation of TDS, TH and Ca²⁺ ion conc. via treating the sample with a regenerated Clinoptilolite

Using pre air-stripping process would reduce the amount of ammonia loads on the sorbent and as a result will increase the time the column can be in service with optimum functionality.

The results indicated that high level of regeneration (90%) might be achieved with relatively small amount of solution of NaCl. Running the column after the first regeneration shows that the Na ions have activated the zeolite column. On the other hand, the first regeneration process can improve the ammonia removal capacity of clinoptilolite because clinoptilolite can be converted to single ionic sodium-form during regeneration process. After the second and third regeneration process, the ammonia removal capacity of clinoptilolite can remain constant. This indicates that using NaCl solution, the regeneration of the column could be done repeatedly without loss of ammonia adsorption capacity.

Since this natural cheap sorbent is completely non toxic and environmental friendly, after several application , it is even possible to mix it with chemical fertilizers as ammonium enriched soil amendment additive, in order to return it to the nature with an extra useful application.

ACKNOWLEDGMENT

The authors wishes to express his sincere gratitude to Shiraz petrochemical senior managements, research center management and crew, HSE office crew and service laboratory managements and technicians for their kind and dedicated scientific and technical support in this research.

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