Sustainable Treatment Method of a High Concentrated NH₃ Wastewater by Using Natural Zeolite in Closed-Loop Fixed Bed Systems

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Abstract: The aim of this study is to investigate ammonium removal from a wastewater resulted after homogenization and anaerobic digestion of a mixture of wastes and wastewater from animal processing units and sewage sludge, by using natural zeolite clinoptilolite. Batches as well as closed loop fixed bed system (CLFB) are studied, offering an alternative to conventional fixed bed systems. The experimental results showed that the optimum pH is in the vicinity of 6.48, where the achieved removal in the batch system reached 46%. The CLFB system, under the same experimental conditions and relative flow rate of 2.56 BV h^{-1}, reached a removal of 55%, which is almost 22% higher. In the CLFB the removal of ammonia could be further increased by diluting the initial solution by 1/8, reaching the level of 96%. The achieved zeolite loading, for all studied systems, is between 2.62 and 13 mg g^{-1}. This kind of operation is very useful for relatively high concentration and small volumes of wastewater and in systems that there is no need for continuous flow operation.

Keywords: Zeolite, clinoptilolite, ammonia removal, closed-loop fixed bed, environmental friendly technology, sustainable technology.
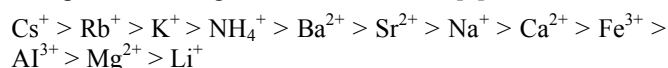
INTRODUCTION

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. Complete removal of ammonia from process or waste effluents is required due to its extreme toxicity to most fish species. A variety of biological and physicochemical methods and technologies have been proposed for the removal of ammonia from the environment and industrial water systems [1]. 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. Lastly, this free ammonia is a gaseous chemical, whereas the NH_4^+ form of reduced nitrogen is an ionized form that remains soluble in water.

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 results show that in most of the cases studied, the presence of organic compounds enhances the uptake of ammonium ion onto the ion exchangers [2].

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. The use of natural zeolites for the removal of ammonia from water and wastewater appears to have potential due to the advantages and peculiarities over some conventional and expensive ion-exchange resins [3]. Zeolites are used for several purposes. Natural zeolites, except removing ammonium, are used mostly for removing heavy metal ions from water [4]. There are several types of them as natural and synthetic. 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. Several studies have shown that clinoptilolite, and certain other natural zeolites can be effective in removing ammonia from wastewater [3,5]. The selectivity order of natural zeolite clinoptilolite among cations is as follows [4] :

$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+$

One of the cation, on which the natural zeolites have high selectivity, is ammonium ion. The use of a clinoptilolite unit would be a very good tool for compliance with stringent standards of ammonia or alternatively total inorganic nitrogen. Such a unit may be used as an upgrade in existing systems as well as in new treatment plant designs.

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Several researchers experienced with the usage of zeolite filters for ammonium removal in effluent of wastewater treatment plants [4]. Cation exchange capacity is dependent on the nature of the cation (size, load, etc.), temperature, concentration of cation in solution and structural characteristics of zeolite. When ion exchange is used as an ammonium removal process in wastewater treatment, a lab-scale or pilot plant testing program is usually required. Lab-scale study allows evaluating the influence of variables, such as pH, contact time, etc. on ammonium performance.

The aim of this study is to investigate ammonium removal from wastewater by using natural zeolite supplied from Greece. Apart from classic batch systems, a closed loop fixed bed system is studied, offering an alternative to conventional continuous flow open fixed bed systems.

EXPERIMENTAL SECTION

Materials and Analytical Methods

The zeolite is originated from Greece and was ground and sieved and the particle size of 0.5-2 mm was used for this study. The chemical analysis of the mineral is shown in Table **1**.

The XRD analysis of the natural clinoptilolite is shown in Fig. (**1**).

The wastewater is a mixture of wastes and wastewater from animal processing units and sewage sludge as shown in Table **2**.

The waste is first homogenized and then it follows an anaerobic digestion treatment for 12-14 days. In Table **3** the

physicochemical analysis of the resulting wastewater is shown. It has to be noted that the physicochemical characteristics exhibited some fluctuations during the sampling period and the average values are presented.

Table 1.   Chemical Analysis of the Zeolite.

Oxide	% w/w
SiO_2	70.08
Al_2O_3	11.72
TiO_2	0.14
Fe_2O_3	0.67
MgO	0.71
CaO	3.18
Na_2O	0.55
K_2O	3.50
LOI	9.45

Batch Experiments

Kinetic runs were conducted on natural clinoptilolite and the experimental details are as follows. The ion exchange of NH_4^+ on clinoptilolite is examined in batch mode experiments. A measured quantity of zeolite (2.5–10 g) was added in a vessel, containing measured volumes (25 ml) of the waste. Liquid samples were withdrawn at 2-4-6-24, and analysis of NH_4^+ remaining in the solution was performed. In
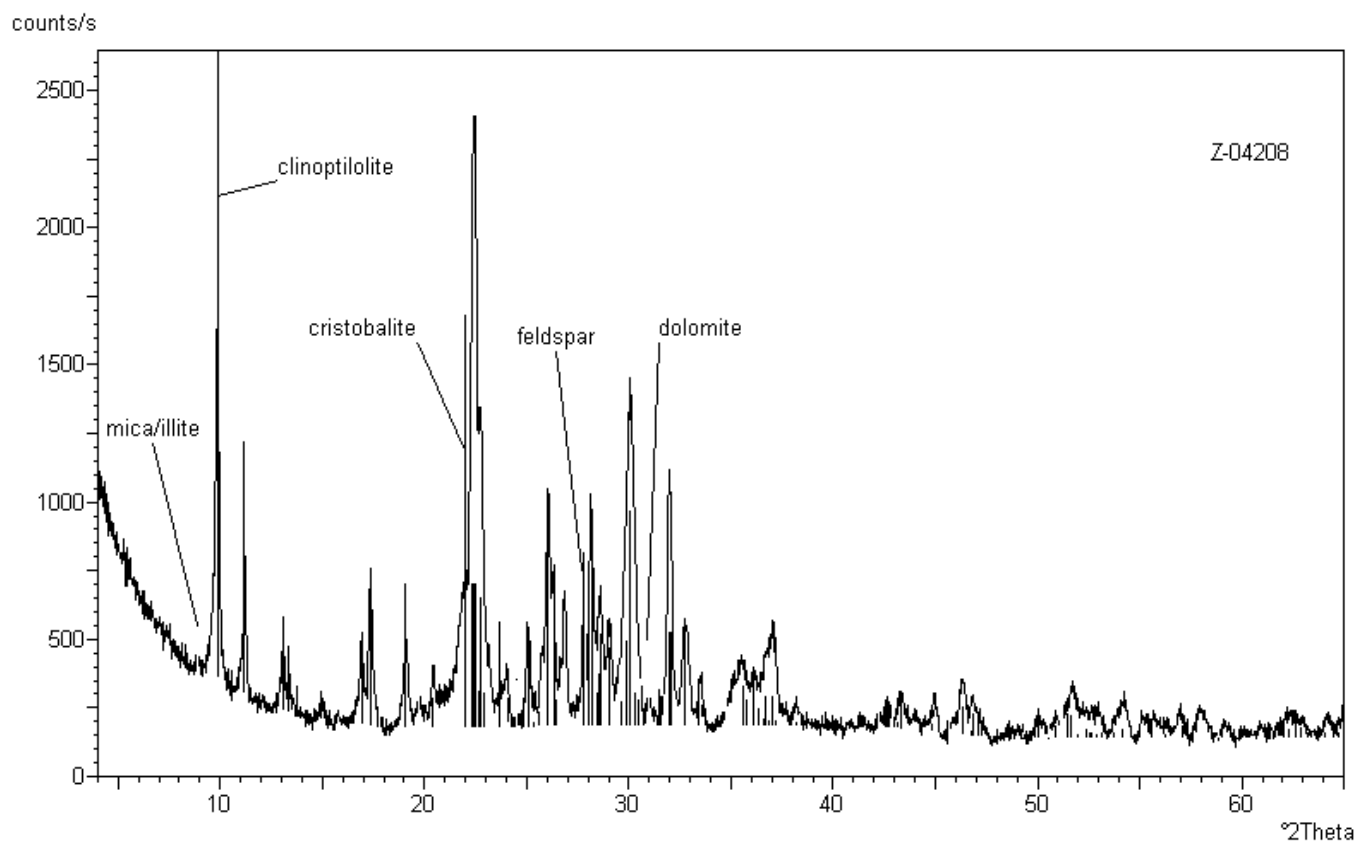

Fig. (1). XRD analysis of the natural clinoptilolite.

all experiments the temperature and pH of the solutions were continuously recorded. The exchange temperature was kept constant during the batch reaction time at 25±1 and no agitation was applied. The effect of pH is assessed in the region of 5-9. The acidity was initially regulated by using H_2SO_4 or NaOH.

Table 2.   Raw Waste Composition

Waste	Feed Flow (tn d^{-1})
Piggeries wastewater	60
Poultry manure	21
Blood (poultry slaughterhouse)	0.6
Solids (poultry slaughterhouse)	3.3
Sewage sludge	6

Table 3.   Wastewater Characterization (Homogenized and Digested Waste)

Parameter	Mean Value of 20 Samples
Ammonia concentration (mg l^{-1})	4500 ± 200
pH	6.48 ± 0.09
Electronic Conductivity (mS/cm)	30.1 ± 0.5
TSS (g l^{-1})	5.52 ± 0.66
VSS (g l^{-1})	4.40 ± 0.35
COD (mg l^{-1})	11400 ± 650
K (mg l^{-1})	1428.1 ± 11.5
Na (mg l^{-1})	361.5 ± 34.3
Ca (mg l^{-1})	120.2 ± 5.3
Mg (mg l^{-1})	117.1 ± 1.5

Closed Loop Fixed Bed Experiments

Fixed bed experiments were conducted in a closed-loop system. Fixed bed experiments were conducted in order to examine the NH_4^+ uptake by natural clinoptilolite, under a volumetric flow rate of 2.56 BV h^{-1} or 9.27 ml min^{-1} (where BV is a volume of liquid equal to the volume of the empty bed), under a initial concentration of ammonia of 544, 2160 and 4700 mg l^{-1} and initial pH value equal to 6.48 and ambient temperature (25°C). pH was monitored throughout the experiment in order to assure that the waste has the appropriate acidity conditions, i.e. the ammonia to be in NH_4^+ form (pH<7). The ion exchange process was conducted in 0.7 m long plexiglass columns of 0.02 m internal diameter (Fig. **2**) (V_{bed}=216.66 ml, depth of the bed equal to 0.69 m). The solution was introduced at a constant volumetric flow rate (Q) and concentration (C), using a peristaltic pump in up-flow mode in order to assure complete wetting of the zeolite particles (Fig. **2**). Liquid samples were withdrawn waste tank at certain time intervals and analyzed for ammonia (2-4-6-24 h).

The operational parameters have been chosen in such a way that a direct comparison between the closed-loop fixed bed and classic batch system is possible. In particular the fixed bed results were compared with batch for zeolite mass to waste volume ratio of m/V = 5 g/25 ml and the same treating time (2-4-6-24 h). Thus, 222.52 g of zeolite were conducted with 1112.58 ml of waste. This volume of waste corresponds to 5.14 BV. Furthermore, the volumetric flow rate was regulated that way in order for 2 h to have one pass of the whole waste volume. Thus, 24 h of treatment is equivalent to 12 solution passes through the fixed bed.
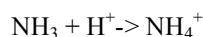
RESULTS AND DISCUSSION

Batch Experiments

In Fig. (**3**) the effect of pH on NH_4^+ removal is presented (m/V= 5g/25mL, t = 2h).

It is clear that the optimum pH is the natural one of the waste, i.e. in the vicinity of 6.48. This result is in agreement with other studies. The highest adsorption capacity of the sample was reached in the range of pH 4-7 [4,6,7]. However, the most studies indicate that pH=6-7 is the optimum [6,7]. pH has little effect on ammonium removal in the range of 6–8 and the highest value was obtained at pH 7, while for the pH value of above 8 and below 6, ammonium removal is decreased sharply [7].

The free (NH_3) and ionized (NH_4^+) forms of reduced nitrogen exist in a chemical equilibrium whose relative distribution is governed by the water's pH and temperature. For example, as the pH of water drops (i.e., the H^+ ion concentration becoming higher), free ammonia (NH_3) will tend to combine with this additional, thereby shifting this chemical equilibrium towards the ionized, NH_4^+, form, as follows:

$NH_3 + H^+ \text{->} NH_4^+$

However, given that this reaction is transformation is maintained as an equilibrium reaction, the ionized ammonium form (NH_4^+) may also drop a proton (H^+) as the pH increases, thereby reforming free ammonia (NH_3), as follows:

$NH_4^+ \text{->} NH_3 + H^+$

The higher the pH and temperature the lower is the percentage of the un-ionized ammonia in water. Furthermore, for pH lower than about 7.5 all the ammonia in water exists in its ionized form, irrespectively of the temperature, in the range of 10-30 ^{o}C.

The adsorption capacity for ammonium of clinoptilolite id found to be significantly impacted by pH value of ammonium solution. The reason is that pH can influence both the character of the exchanging ions and the character of the clinoptilolite itself. At lower pH, the ammonium ions have to compete with hydrogen ions among the exchange sites; however, when the pH is higher, the ammonium ions are transformed to aqueous ammonia as is neutralized by hydroxyl ion rendering it uncharged. On the other hand, a variety of impurities that occupy micropores and macropores of clinoptilolite, such as calcium carbonate, unaltered glass, etc., are perhaps removed by hydrogen ions at lower pH. This might contribute to improving the exchange capacity of clinoptilolite [6].
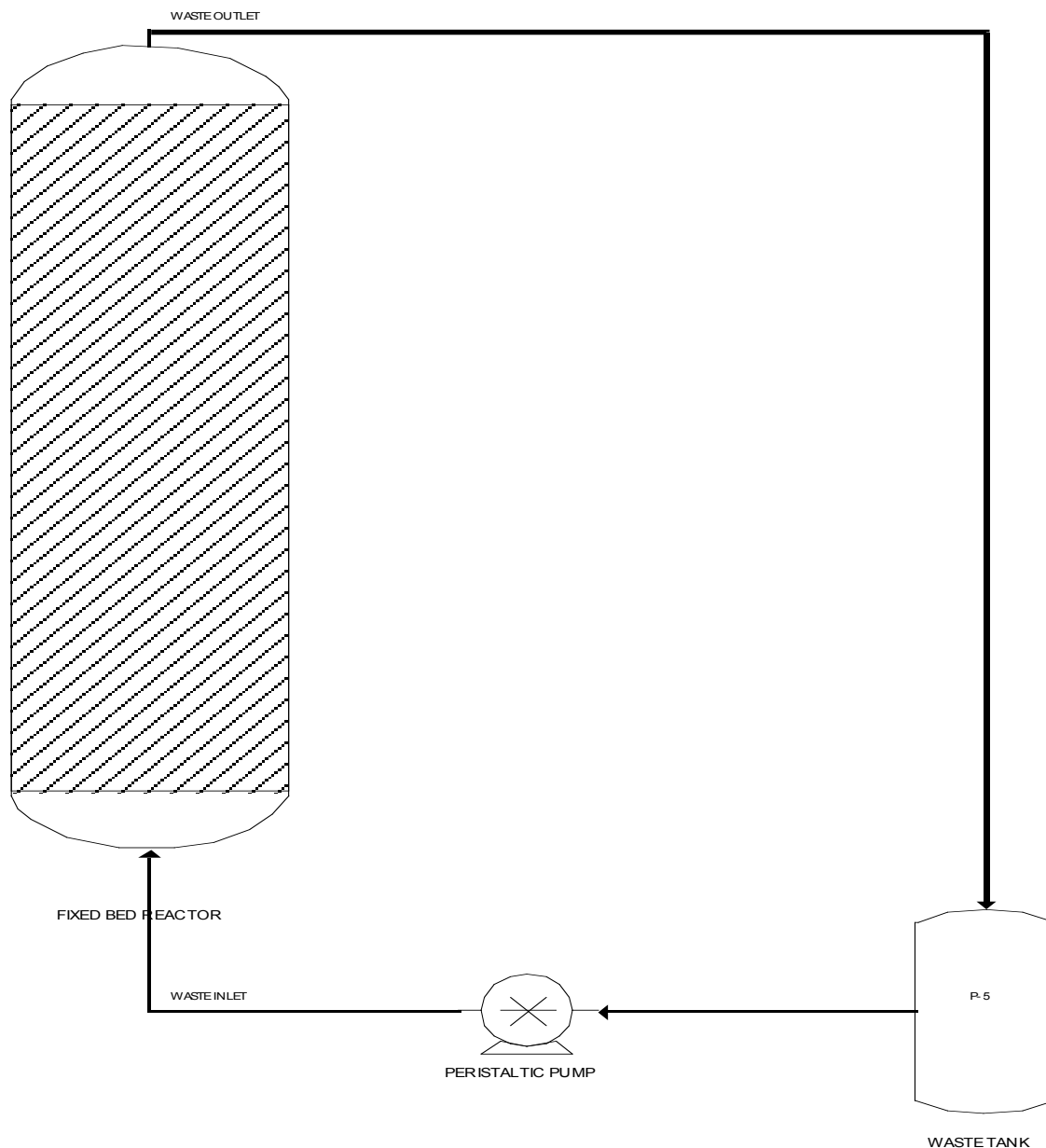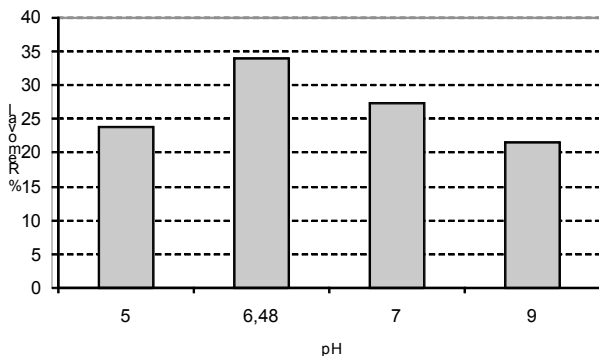
Fig. (2). Experimental set-up.

Fig. (3). The effect of pH on NH$_4^+$ removal (m/V= 5g/25mL, t = 2h).

According to authors knowledge, there is no published data on the same system (clinoptilolite – aminal waste) in the related literature. On the other hand, there is a number of studies on the removal of ammonia from either single-component, synthetic and municipal wastewater and leachates under initial concentrations up to 4000 ppm approx [4-9]. It can be concluded that the results are qualitatively comparable but in the same time direct quantitative comparison is not possible due to the different nature and composition of the wastewater treated in the present study.

In Fig. (**4**) the effect of contact time on NH$_4^+$ removal is presented (m/V= 5g/25mL, pH = 6.48).

The amount of exchanged NH$_4^+$ increased with an increase in the contact time and equilibrium was established in 24 h. It was observed that more than 34% of final NH$_4^+$ uptake was completed within the first 2 hours and then removal rate became slow with the increase of contact time, reaching almost 46% after 24 hours treatment. This is caused by fast diffusion onto the external surface then followed by

fast pore diffusion into the intraparticle matrix to attain equilibrium [5].
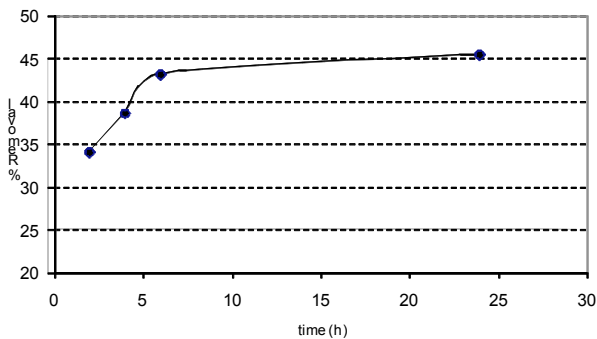

Fig. (4). The effect of contact time on NH_4^+ removal (m/V= 5g/25mL, pH = 6.48).

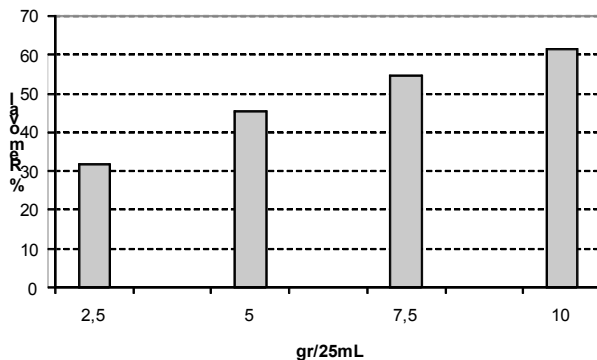In Fig. (**5**) the effect of zeolite mass to waste volume ratio (m/V) on NH_4^+ removal is presented (t= 24h, pH = 6.48).

Fig. (5). The effect of zeolite mass to waste volume ratio (m/V) on NH_4^+ removal (t= 24h, pH = 6.48).

As expected, the amount of exchanged NH_4^+ increased with an increase m/V. It was observed that more than with an increase of m/V by a factor of 4 the uptake was almost doubled, reaching the level of 61.36%.

Closed Loop Fixed Bed Experiments

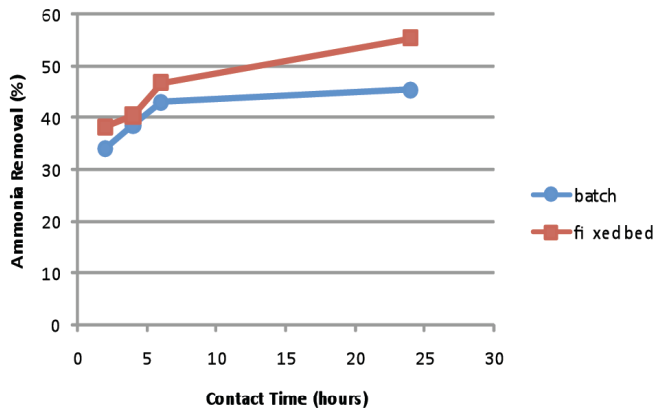In Fig. (**6**) the ammonia removal in fixed bed and batch systems is compared (m/V=0.2, pH =6.48, Q = 2.57 BV h⁻¹).

Fig. (6). Ammonia removal in fixed bed and batch systems (m/V=0.2, pH =6.48, Q = 2.57 BV h⁻¹).

It is clear that the closed-loop fixed bed operation leads to higher ammonia removal for all the range of contact time.

This result indicates that passing the waste through layers of zeolite is of benefit for the ion exchange mechanism. The reason for this behavior is that in batch system no agitation exists and so, the mass transfer in the liquid film is quite slow in comparison to the fixed bed operation where the flow of the liquid minimizes the adherent liquid film around zeolite particles, increasing thus the mass transfer rate. Furthermore, another reason is probably the different pattern in concentration profiles in the two different operation arrangements. While in fixed bed, in each layer, the solution concentration increases gradually with time, the opposite holds for the batch system. In 24 hours the removal in the fixed be operation is reaching the level of 55.32%, which is almost 22% higher than the achieved removal in the batch system.

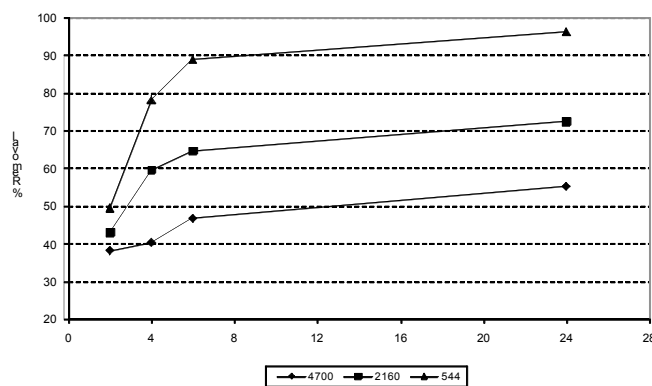In Fig. (**7**) the ammonia removal in fixed bed for different initial concentrations is compared (m/V=0.2, pH =6.48, Q = 2.57 BV h⁻¹).

Fig. (7). Ammonia removal in fixed bed for different initial concentration (m/V=0.2, pH =6.48, Q = 2.57 BV h⁻¹).

As in the case of the batch system is evident that the phenomenon is rapid in the first 8 hours and the removal is slowing down from 8 to 24 h. Furthermore, it is clear that for ½ and 1/8 dilution the solution the uptake is reaching the level of 73% and 96%, respectively. This is a considerable increase in comparison to the removal achieved for the initial solution, about 55%. The results are similar in continuous flow open fixed beds, as for example for the treatment of sanitary landfill leachate by using clinoptilolite, where the performance of the operation is considerable lowered when the inflow concentration increases from 200 to 400 ppm [7]. The same holds for batch systems, as for example in a batch system by using clinoptilolite under ammonia concentrations between 8.8 and 885 mg l⁻¹ (1g zeolite/100 ml solution). The results indicated that there is a considerable decrease of ammonia removal, from 90% at 8.8 mg l⁻¹ to 25% at 885 mg l⁻¹ initial ammonia concentration [4]. However, we have to take into account that the volume to be treated in the diluted solution is multiple. In the Table **4** the situation is summarized for 24 hours of treatment.

In Table **5** the loading of zeolite for the three different concentrations is presented. It should be noted that not batch neither closed loop fixed bed (CLFB) experiments were reached equilibrium and thus, the loading of clinoptilolite presented here is only a part of the real capacity of the material.

Table 4. Comparison of Waste Treatment with Different Initial Concentration (24 h Treatment Time)

Parameter	Raw Waste	½ Diluted Waste	1/8 Diluted Waste
Volume to be treated (ml)	1123	2225	8900
Initial concentration (mg l^{-1})	4700	2160	544
Initial pollutant load (mg l^{-1})	5229	4806	4842
Final concentration (mg l^{-1})	2100	590	20
Final pollutant load (mg)	2336	1312	178
Total load decrease (%)	55.32	72.69	96.32

Table 5. Zeolite Loading (24 Hours Treatment Time – Per Cycle)

Initial Wastewater Concentration (mg l^{-1})	Zeolite Loading (mg g^{-1})
4700	13 (CLFB) 10 (Batch)
2160	7.85
544	2.62

In literature, ammonium capacity increased with increasing of concentration [7]. It should be noted that the wastewater used in the present study contains considerable amount of competitive cations influencing in a negative way the uptake of ammonium.

Concerning the clinoptilolite capacity, it varies in the related literature due to the different experimental conditions and could be found between 0.94 and 25 mg g^{-1} [2,4,6,9]. A major difference between the relevant studies is that single component as well as synthetic and real wastewater samples have been used. Concerning real wastewater, the maximum equilibrium concentration of zeolite has been determined about 21 mg/g for a leachate at 3750 ppm ammonia concentration, in a batch system [7]. In the same study, fixed beds have reached a capacity of 8.74-16.32 mg g^{-1}. Similar values for fixed beds are found elsewhere, between 17.31 to 18.98 mg NH_4^+/g of dry clinoptilolite weight [9].
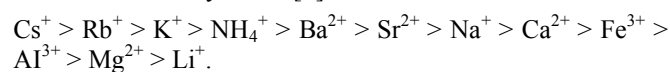
Furthermore, it is well known that the flow rate and other operational conditions have significant impact on the fixed bed performance [10]. In practical terms the fixed bed operation rarely achieves the maximum exchange level (capacity) that is achieved for the zeolite in batch systems (repeated equilibrations). On the other hand, the closed-loop fixed bed is a process between batch and fixed bed, where the contact time is fixed and the agitation is replaced by constant flow. Thus, it is expected that the closed-loop fixed bed is possible to reach the batch saturation capacity of the zeolite.

The waste volume to be treated is 2 and 8 times more and thus, the operation has to be run twice and eight times, respectively, thus treatment time and the zeolite mass needed is twice and eight times higher, respectively. However, the benefit is quite high as the removal of the pollutant load could be reduced as much as 96%. Furthermore, taking into

account that many studies have indicated a capacity up to 25 mg g^{-1} for ammonia in the specific zeolite, it is evident that the zeolite has not reached its capacity: 52%, 31% and 10% in the raw, ½- and 1/8- diluted wastewater, respectively. This means that the zeolite could be re-used and so, the fresh zeolite mass needed could be significantly lowered. Based on these percentages, the theoretically (maximum) number of cycles that a zeolite batch can be used is 1.92, 3.18 and 9.54 for the raw, 1/2- and 1/8- diluted wastewater, respectively. This in turn means that the same zeolite can treat the resulted from dilution volume for both 1/2- and 1/8-diluted wastewater. However, the efficiency in each successive cycle is expected to be lowered due to the stepwise saturation of the zeolite. Thus, the use of zeolite could not be evaluated by using the maximum capacity (25 mg g-1) and the results in a single-used batch of material.

It is clear, this more experiments are needed in order to have certain quantitative results. Furthermore, the treatment time could be reduced, for the same number of solution passes through the fixed bed, by (a) using smaller particle size or (b) using higher flow rate. It should be mentioned that the effect of flow rate is not expected to influence the process considerably as the contact time is fixed and thus not influenced by the flow rate. This means that theoretically, the treatment time as well as the zeolite mass needed could be lowered significantly for the treatment of the diluted solutions. Finally, closed-loop fixed operation should be experimentally compared with the classical fixed bed operation in order to draw clear comparative results. Thus, an optimization study is needed. Another significant issue for further study is the possible regeneration of zeolite with NaCl or with heating treatment, which could be a method for simultaneous production of ammonia gas.

Finally, it is usefull to note that is probable wastewater to contain other cations (e.g. Cd^{2+}, Zn^{2+}, Fe^{2+}, Cr^{3+}) that might interfere with the uptake processes described in the present paper and alter the process efficiency. In general, the presence of ther cations is expected to lower the uptake of ammonia, but it is not possible to fully predict the impact given the information available in the present study. However, animal waste it is not expected to have such metals in significant concentrations and it is not expected that small concentrations (at least an order of magnitude lower than ammonia) would alter the results because clinoptilolite exhibit very high affinity of for ammonia in comparison to other cations. Indicative is the following standard selectivity series [4]:

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Ba^{2+} > Sr^{2+} > Na^+ > Ca^{2+} > Fe^{3+} > Al^{3+} > Mg^{2+} > Li^+.$$

CONCLUSIONS

The experimental results showed that the optimum pH is the natural one of the waste, i.e. in the vicinity of 6.48, where the achieved removal in the batch system reached 46% (m/V= 5g/25ml, t = 24h). The closed loop fixed bed system (CLFB), under the same experimental conditions (m/V=0.2, T=24h, pH=6.48), and relative flow rate of 2.56 BV h^{-1}, reached a removal of 55%, which is almost 22% higher. In the CLFB the removal of ammonia could be further enhanced by diluting the initial solution by 1/8,

reaching the level of 96%. The achieved zeolite loading, for all studied systems, is between 2.62 and 13 mg g^{-1}.

CLFB is offering an alternative to conventional continuous flow open fixed bed systems. The advantage of this kind of operation is that the available capacity of material could be highly utilized by passing the waste repeatedly from the fixed bed, leading it to almost complete saturation. This kind of operation however, could be useful for relatively high concentration and small volumes of waste and in systems that there is no need for continuous flow of the waste (batch treatment cycles).

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