

Nitrogen and phosphorus removal using a novel integrated system of natural zeolite and lime

SILVIO J. MONTALVO¹, LORNA E. GUERRERO², ZHENIA MILÁN³ & RAFAEL BORJA^{4,*}

¹ *Departamento de Ingeniería Química, Universidad de Santiago de Chile, Santiago de Chile, Chile.*

² *Departamento de Ingeniería Química y Ambiental, Universidad Técnica Federico Santa María, Valparaíso, Chile.*

³ *Laboratorio de Biotecnología Ambiental, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile.*

⁴ *Instituto de la Grasa (C.S.I.C.), Sevilla, Spain*

ABSTRACT

Nitrogen and phosphorus can cause eutrophication problems in receiving waters. These nutrients can be eliminated by different wastewater treatments but they tend to be costly or require complex operations. With these reasons in mind, this work set out to study the behavior of a novel combined or integrated system with zeolite and lime for the removal of these chemical species. With the integrated treatment, excellent removals - 98% NH_4^+ , 100% total phosphorus (TP), 79% chemical oxygen demand (COD), 71% BOD_5 , 99% of total suspended solids (TSS) and 100% of fecal coliforms - were obtained. A sludge production of 4.4% and 4.8% of the wastewater total volume

* Address correspondence to Rafael Borja, Instituto de la Grasa (C.S.I.C.), Avda. Padre García Tejero, 4. 41012-Sevilla, Spain (Phone: +34 95 4689654, Fax: +34 95 4691262, E-mail: rborja@cica.es).

treated with lime was achieved. The final liquid effluent of the integrated system of natural zeolite and lime had a composition which was suitable for its discharge into sewerage systems and marine or continental waters (according to Chilean regulations), as far as the concentrations of nitrogen, phosphorus and total coliforms were concerned. Validated curves with their corresponding equations were obtained in this study for the removal of ammonia nitrogen and total phosphorus. These equations can theoretically be applied to estimate the removal of both parameters in studies or practical applications undertaken with operating conditions similar to those used in this work.

Keywords: Ammonium nitrogen, phosphorus, removal, zeolite, lime.

INTRODUCTION

Nitrogen and phosphorus compounds are essential nutrients to all forms of life, but when present in substantial quantities in receiving waters such as lakes and rivers can cause their eutrophication, resulting in excessive growth of algae and other microorganisms, as well as in increased dissolved oxygen depletion and fish toxicity.^[1-5] Therefore, these nutrients must be removed from wastewaters to control eutrophication in lakes and similar stagnant water bodies. This is an important factor in environmental sustainability.

Commonly, nitrogen removal is achieved by a biological-nitrification-denitrification process, where ammonium (NH_4^+) is transformed first into nitrite, then into nitrate, and finally into nitrogen gas. However, since biological methods do not respond well to shock loads of ammonia,

unacceptable peaks of the discharging levels may frequently appear in the effluent NH_4^+ concentrations.^[6] In addition, this biological method has its own limitations such as proper oxygen transfer, pH control and the chemical addition for biochemical oxygen demand removal under seasonal conditions, especially in cold water conditions. Moreover, the treatment of ammonium nitrogen wastewater with low organic content by a biological process usually needs to be supplemented with a carbon source, which may add to the treatment cost.^[6] In such a situation, ion-exchange offers an alternative method for the removal of NH_4^+ .

Ion-exchange has been used in various types of wastewater treatment for the removal of NH_4^+ .^[6] However, ion-exchange processes using organic resins as exchanger are very expensive. Hence, cheaper materials such as zeolite are needed. The use of natural zeolite for the removal of NH_4^+ is considered to be a competitive and effective treatment method due to its low cost and the relative simplicity in its application and operation.^[7-9] Natural zeolites are hydrated aluminosilicates with symmetrically stacked alumina- and silica- tetrahedral which result in an open and stable three-dimensional honeycomb structure possessing high cation exchange capacity (CEC), cation selectivity, higher void volume and great affinity for NH_4^+ . Although some previous studies have focused on the use of zeolite for NH_4^+ removal, each specific zeolite material has its special characteristics (depending basically on its origin) and requires individual research.

Crystallization of N and P in the form of struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) has been used for nutrient removal and for obtaining a valuable fertilizer.^[10-13] However, since wastewaters tend to be low in magnesium ion, it is usually necessary to add this mineral so as to enhance the process. Another disadvantage of this process is that struvite crystallization rate is slow and it requires a large reactor and pH adjustment.^[14]

The removal of phosphate, the main form of phosphorus in most wastewaters, can be achieved by chemical precipitation using ferric chloride or ferrous sulphate. As ferric and ferrous salts are hydrolyzed at a high pH, the use of the acidic solution of iron salts for phosphate precipitation requires the addition of some alkali and the use of stainless steel equipment for the storage and dosing of ferric salts. The high cost of the iron salts and alkalis is the main disadvantage of this process.^[14]

The biological method is a low-cost system for removing phosphorus from wastewater, but the fluctuation in chemical composition and wastewater temperature makes the process running unfeasible.^[15,16] Techniques such as adsorption and chemical precipitation are more economical than others such as electrodialysis.^[16-18]

Lime is an effective and cheap substance that has been previously used for P removal from piggery effluents and effluents from activated sludge processes achieving P removal efficiencies higher than 89%.^[19,20]

Therefore, finding an attractive and effective system for removing ammonium and phosphorus is a highly desired goal. The aim of this work was to study a novel combined or integrated process consisting of two steps: the first is an ionic exchange for removing NH_4^+ by using zeolite and the second is to remove P by precipitation and sedimentation using lime.

MATERIALS AND METHODS

The residual effluent used was prepared from the supernatant of the primary sedimentation step of the urban wastewater treatment plant "La Farfana" located in Santiago of Chile (Chile). Its main characteristics are summarized in Table 1. Nitrogen and phosphorus were added to this wastewater

in the appropriate quantities to achieve the desirable concentrations according to the experimental design. These amounts were in the ranges of 40 and 80 mg total phosphorus (TP)/L and between 100 and 500 mg NH_4^+ /L. The sources of phosphorus and ammonium were ammonium phosphate and ammonium chloride, respectively.

The final wastewater used (after N and P were added) was firstly subjected to a treatment with natural zeolite, which was supplied by the company “Minero Formas” (Chile). Table 2 shows the main characteristics and chemical composition of the Chilean natural zeolite used in the present work. This first series of experiments was developed according to a factorial (3^2) experimental design, shown in Table 3. The experiments were carried out in jar test reactors, which consisted of precipitate glasses with a volume of 600 mL using an agitation time of 30 minutes at 100 rpm and leaving the reactor content to decant for 1 hour prior to analyzing the floating of the decantation to evaluate the efficiency of the process. The concentration of the zeolite used was 40.65 g/L of liquid effluent. This value was assumed according to the characteristics of the zeolite used and to the recommendations of the “Minero Formas” company.

The samples obtained were analyzed to determine the chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), ammonium, phosphorus, total suspended solids (TSS), fecal coliforms and pH. These analyses were carried out according to the recommendations of the Standard Methods for the Examination of Water and Wastewater.^[21] Specifically, COD, BOD_5 , TSS and ammonium were analyzed according to the Standard Method numbers 5220 C, 5210 A, 2540 E and 4500 A, respectively. Total phosphorus was measured by spectrophotometry at 880 nm using the standard method 4500 P. The content of fecal coliforms was determined following the method of multiple tubes and Most Probable Number (MPN). Finally, the pH was analyzed with a pH-meter

(Crison, model basic 20). For the processing of the experimental data the Stat graphics plus 5.0 computer program was used.

The effluents obtained during the first experimental series (zeolite), at the conditions for which the maximum nitrogen and phosphorus removals were achieved, were subsequently subjected to a second treatment with lime. This second experimental run was carried out in similar jar test glasses using lime concentrations of 30 g/L and increasing the pH up to 10.5. The mixing time and agitation rate were 1 hour and 200 rpm, respectively. The decantation time was 1 hour in this case and after this period the supernatants of the decantation were analysed to evaluate the efficiency of the second step of the integrated process.

RESULTS AND DISCUSSION

The experimental values of NH_4^+ , phosphorus, COD, BOD_5 , TSS and total coliforms obtained after application of the zeolite are shown in Figure 1.

As can be seen in Figure 1 the highest ammonium removal obtained was 95%. It was reached in the effluent that contained the smallest initial ammonium concentration (100 mg NH_4^+ /L). On the other hand, the lowest ammonium removals (83% and 85%) were achieved for the effluent that contained the highest ammonium concentration (500 mg NH_4^+ /L). This may be due to the fact that the larger the quantity of ammonium ions in the medium, the more difficult it is that they all form part of the ionic exchange, because only a certain quantity of negative loads exists and is available as part of the oxygen present in the zeolite structure. At the same time, only certain quantities of pores exist in the mineral, which it makes possible to harbour a smaller percentage of molecules in an effluent that contains a higher ammonium concentration.

Similar behaviour was observed by Rozic et al.,^[22] who found the highest N-NH₄⁺ removal efficiencies (61.1%) at an initial ammonium concentration of 100 mg/L. With the increase of the initial concentration of ammoniacal nitrogen, the removal efficiency quickly decreased. This was expected as zeolites and other clays have limited sorption capacities,^[22] which is important from a practical point of view. In addition, for municipal wastewater, the ammonium removal efficiency was enhanced by over 27% when the influent ammonium concentration was between 24.7 and 50.5 mg/L.^[23] Lower ammonium removal efficiencies from wastewater (47.3%) were achieved when natural zeolite was used with a dosage of 10 g/L at a contact time of 40 minutes.^[24] However, the ammonium removal increased up to 88.1% when zeolite was activated by salt (0.3 mol/L of NaCl) and heat (at 100 °C).^[24] Higher contact times (105 minutes) and shaking speed (200 rpm) than those used in the present work (30 minutes and 100 rpm, respectively) were needed to remove similar ammonium concentrations from landfill leachate using low-cost activated carbon zeolite composite adsorbent.^[25] Other modified zeolites, such as NaCl modified zeolite allowed for ammonium removal efficiencies as high as 93.2%,^[26] a value somewhat lower than that achieved in the present study.

In the case of total phosphorus (TP), the tendency observed was similar to that found for ammonium. For the highest influent TP concentrations (80 mg TP/L) phosphorus removals were lower (58%) than those achieved for the smallest TP concentrations (40 mg TP/L) for which the highest removals (67%) were obtained. This may be due to the fact that zeolite possesses a specific capacity of pores for the adsorption of substances, and when a greater amount of phosphorus is present, not all the phosphorus can be adsorbed in a similar way as previously outlined for ammonium.^[27]

In phosphorus removal, besides the dependence shown with its own concentration in the medium, a slight dependence with the ammonium concentration was also observed when this concentration was increased in the medium. This may be due to the fact that, because of the attraction of loads that exists among these positive ions, ammonium enters the pores of the mineral before the other molecules to the sectors where negative loads generated by oxygen atoms are present. During the formation of the mineral, Al^{3+} replaces Si^{4+} , which is connected to four oxygen atoms. This substitution leaves an uncombined oxygen atom generating a negative available load to be combined with the ammonium, leaving the molecule electrically neuter. Therefore, it is possible that due to this attraction of loads the ammonium ions enter first and those that were not linked to the oxygen atoms may be retained in the pores, giving priority to the retention of other substances. This is all from the point of view of the attraction of loads. However, when analyzing the size of the ions, it should be pointed out that because ammonium ions are smaller than phosphate ions, they enter the pores of the mineral more readily.^[20]

The potential of the struvite crystallisation process for treating anaerobic supernatant rich in phosphorus was reported for effluents of anaerobic co-digestion of sludge with other organic wastes.^[28] 80% removal of phosphorus was observed in all the tested conditions. Similar phosphorus removal percentages through struvite precipitation were obtained from anaerobically digested swine wastewater.^[27]

In relation to COD and TSS removals, an increase in both was observed when decreasing the initial ammonium and phosphorus concentrations, with maximum COD and TSS removals at 52% and 84%, respectively. These values were lower than those obtained for ammonium removal, which can be attributed to the fact that the ammonium is quickly ionically exchanged and, in addition, ammonium and phosphorus have a smaller size than the molecules responsible for COD and TSS.

Therefore, both ammonium and phosphorus join to zeolite more easily and faster, which makes it difficult for other molecules to enter.^[27]

Coliform removal is considered much more difficult than the removal of other parameters due to its high size and because the coliform bacteria can adhere to each other forming colonies.

The BOD₅/COD ratio of the effluent prepared semi-synthetically from the La Farfana urban wastewater treatment plant was 0.68. However, after treatment with zeolite, the effluent or floating liquid of this process increased the value to 0.82. This result can be attributed to a higher removal of COD than of BOD₅ probably due to the fact that before the application of zeolite, certain compounds may have hindered the process of biological degradation developed during the BOD₅ test but that were adsorbed by the zeolite.

By means of a regression analysis, an equation that relates the ammonium removal with the initial ammonium concentration was found ($R^2 = 0.9862$):

$$\text{Ammonium removal (\%)} = 100.09 - 0.053 * [\text{NH}_4^+] \quad (1)$$

where: $[\text{NH}_4^+]$ is the ammonium nitrogen concentration of the prepared effluent before being treated with zeolite. Equation (1) was validated from the results obtained in experiments carried out with two initial ammonium concentrations (100 mg/L and 150 mg/L) without using phosphorus because the model did not show any influence of the phosphorus concentration on ammonium removal.

By a regression analysis the following equation that correlates the phosphorus removal with the initial ammonium $[\text{NH}_4^+]$ and initial total phosphorus concentration $[\text{TP}]$ was also found ($R^2 = 0.9784$):

$$\text{TP removal (\%)} = 78 - 0.014 * [\text{NH}_4^+] - 0.24 * [\text{TP}] \quad (2)$$

This equation was validated in two experiments carried out with two combinations of NH_4^+ and TP concentrations: a) 40 mg/L of TP and 100 mg NH_4^+ /L and b) 60 mg TP/L and 150 mg NH_4^+ /L (data not shown in Table 3).

The results obtained from the integrated treatment with zeolite and lime are summarized and plotted in Figures 2 and 3, which show the removal efficiencies for high initial concentrations (500 mg NH_4^+ /L and 80 mg TP/L) and low initial concentrations of nutrients (100 mg NH_4^+ /L and 40 mg TP/L), respectively.

In the treatment with zeolite, it can be observed that the higher removal efficiencies were obtained when treating the effluent with lower concentrations of nitrogen and phosphorus. This can be explained by the fact that when a high amount of compounds exists, the lower the capacity of the mineral to adsorb, given that zeolite has a limited number of pores.

In the treatment with lime, the removal efficiencies obtained for the effluents with high and low nutrient concentrations were very similar, which can be attributed to the fact that lime has a high density and weight, which means that it can drag most of the compounds found during the sedimentation step, allowing for a clarified liquid once the mixing has stopped.

Phosphorus removal efficiencies of 98% and 99% were obtained in the treatment with lime. This is mainly due to the chemical reaction that takes place between these chemical substances with the formation of precipitates of probably hydroxi-apatite and/or struvite that are dragged during the settling step.^[13, 29]

It was previously reported that more than 95% of total phosphorus was removed from recycled piggery effluent when physico-chemical treatment followed settling with lime.^[19] This physico-chemical treatment decreased total phosphorus mainly by reducing the number of suspended particles in the effluent and by precipitating some total filterable P as iron, aluminium or calcium

compounds.^[19] Phosphorus removal efficiencies of between 90% and 95% from aerated lagoons were obtained using lime. Seasonal temperature variations in wastewater did not have a detrimental effect on the coagulation and flocculation processes.^[30]

Coliform removal efficiencies of practically 100% were obtained in the treatment with lime in the present work. These high removals can be explained by the action of lime in the microorganisms provoking an increase in pH to very alkaline values and its consequent drag during the sedimentation step. Ammonium, BOD₅, COD and TSS removal efficiencies of 74%, 56%, 61% and 96% respectively were obtained after treatment with lime. These removal efficiencies were obtained as a consequence of the molecules being dragged when the lime precipitate was formed with the possible precipitation of the lime with some compounds responsible for TSS, COD and BOD₅, which also helps to remove compounds from the liquid.

Somewhat lower COD removal efficiencies (45%) were obtained in the treatment of the effluents from the soy sauce industry with lime as coagulant at a pH of 12. These effluents are characterized by their high COD and colour.^[31] The combined treatment of this wastewater with polyaluminium chloride and lime was very effective with 93% colour elimination and 28% sludge production decrease.^[31]

After the treatment with lime, the BOD₅/COD ratio increased to 0.96, which can be explained by a higher removal of refractory rather than biodegradable compounds, probably because some organic compounds which are difficult to biodegrade reacted with the lime facilitating their precipitation and/or sedimentation which generated a more biodegradable clarified settled liquid. This fact can be attributed to a higher removal of COD than BOD₅ as a consequence of the existence of compounds in the initial effluent (prior to zeolite application step) which make the biological degradation during the analysis of BOD₅ difficult and so were adsorbed by the zeolite.

Table 4 summarizes the sludge production generated during the integrated treatment of the effluent with zeolite and lime. When the mixing was stopped, the zeolite used in the treatment (18.29 g) took 50 minutes to settle, forming a sediment 8.5 cm high in the recipient, after clarifying the effluent. In the case of lime, the 11 mL added to the effluent with low nutrient concentrations took 5.5 minutes to settle, while the 24 mL added to the residual with high concentrations took 9 minutes. This is due to the fact that although zeolite has a larger volume than lime, it is less dense (1800 kg/m^3 for zeolite and 3300 kg/m^3 for lime) and it is porous.

As can be seen in Table 4, during the treatment with zeolite the percentage of sludge generated for the effluent with the highest ammonium and phosphorus concentrations ($500 \text{ mg NH}_4^+/\text{L}$ - 80 mg TP/L) was 2.3% higher than that obtained for the effluent with the lowest nutrient concentrations ($100 \text{ mg NH}_4^+/\text{L}$ - 40 mg TP/L). This result is a consequence of the higher amount of compounds present in the more concentrated substrate as compared to the more diluted one, which generates a lower amount of sediment in the latter.

For the effluent with the highest nutrient concentrations, the amount of sludges generated in the treatment with zeolite was 3.1% higher than that obtained in the treatment with lime. For the most diluted effluent the quantity of sludges generated was 1.2% higher than that obtained in the treatment with lime. This result is due to the fact that zeolite is a porous material and can retain compounds in its cavities.^[7] By contrast, lime is a substance that generates chemical reactions for the conversion and removal of compounds. Furthermore, both materials can remove compounds by dragging at the moment of precipitation and by sedimentation in the case of lime, and only by sedimentation in the case of zeolite.

The quality of the final effluent treated with zeolite and lime in relation to the phosphorus, ammonium and TSS contents is adequate for dumping in sewage systems according to Chilean

regulations, where values of 10 mg/L, 80 mg/L and 300 mg/L, for P, NH_4^+ and TSS respectively are the maximum values acceptable. This is also applicable to dumping in marine and continental superficial waters. In this case, the maximum limits allowed for phosphorus and TSS are 10 mg/L and 80 mg/L, respectively. This last regulation does not demand values of dumping for ammonium nitrogen but a value of total Kjeldahl nitrogen (TKN) equal to or less than 50 mg/L is compulsory. Assuming that the usual percentage of NH_4^+ in TKN is 70%, then a maximum quantity of around 34 mg TKN/L would be expected as maximum value in the treated effluent, which would comply with current Chilean regulations.

CONCLUSIONS

In the treatment with Chilean natural zeolite the highest ammonium, phosphorus, COD, BOD_5 , TSS and coliform removals were obtained for the effluent with low concentrations of ammonium and phosphorus. When the concentrations of ammonium and phosphorus in the sewage effluent decreased, an increase in the removals of ammonium, phosphorus, COD, BOD_5 , TSS and coliforms was observed. Treatment with lime generated excellent removals for all the parameters analyzed. Therefore, the integrated treatment (zeolite and lime) generated high removals for all the above-mentioned parameters. The final effluent obtained after the integrated treatment with zeolite and lime possesses appropriate characteristics for it to be poured into the sewage systems or into marine and continental superficial waters according to Chilean Regulations.

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FIGURE CAPTIONS

Figure 1. Removals of NH_4^+ , phosphorus, COD, BOD_5 , TSS, and total coliforms after application of chilean natural zeolite.

Figure 2. Removal efficiencies (%) at high initial concentrations of nitrogen and phosphorus.

Figure 3. Removal efficiencies (%) at low initial concentrations of nitrogen and phosphorus.

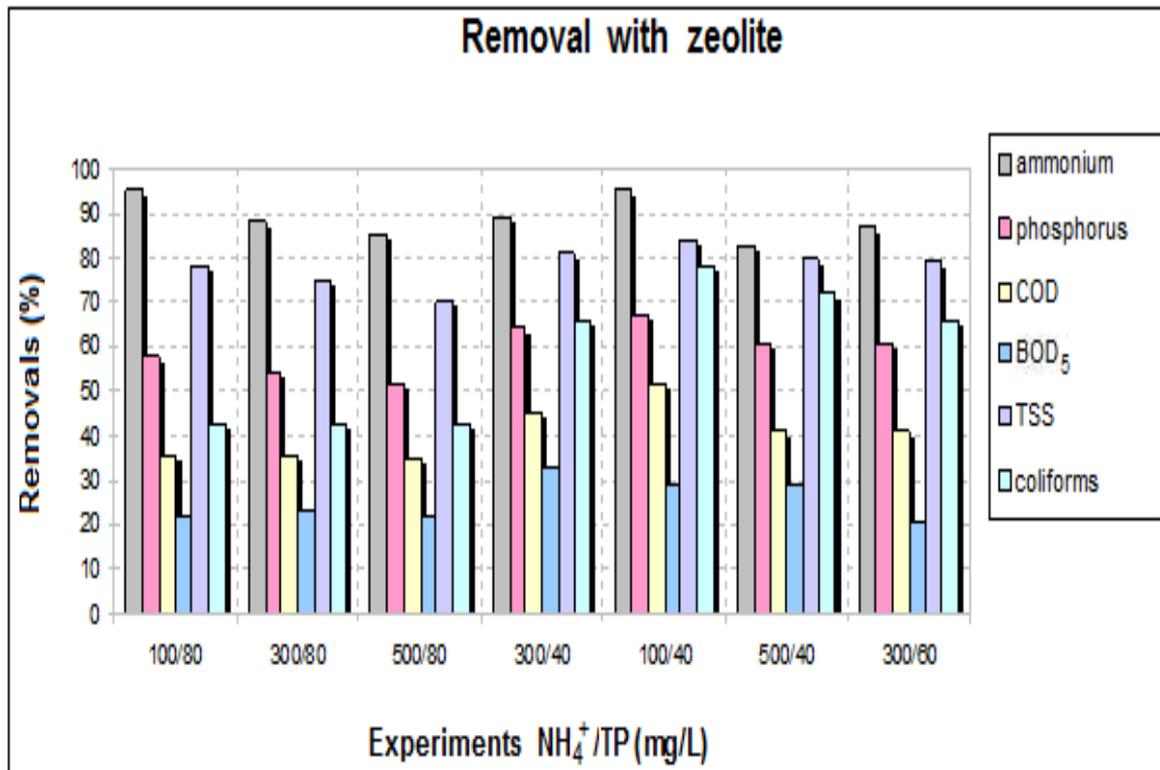


Figure 1

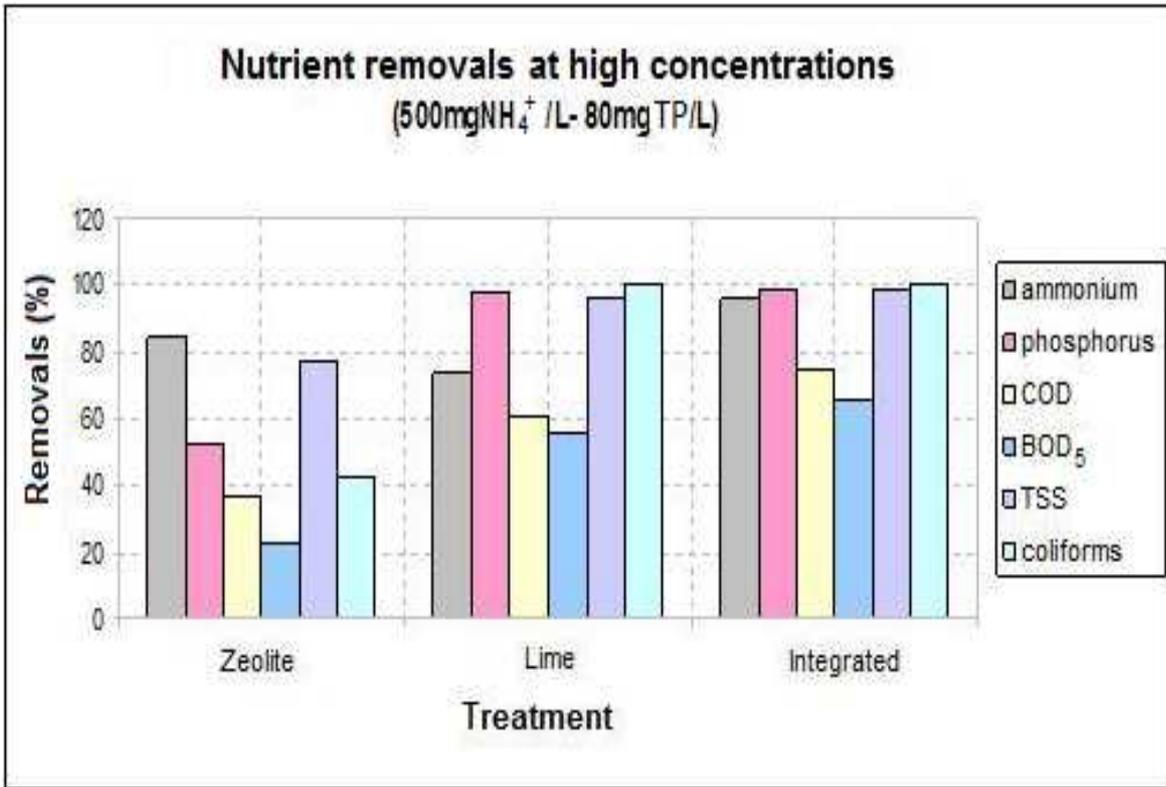


Figure 2

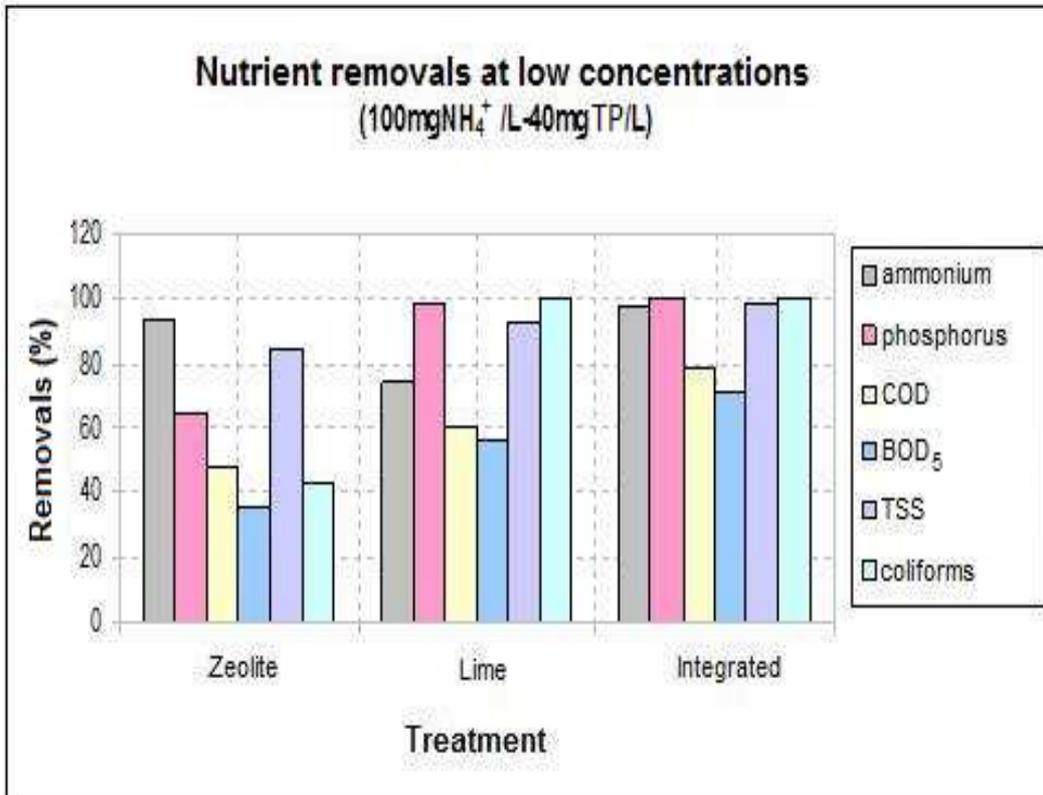


Figure 3

Table 1. Characteristics of the effluent used (effluent from the primary settling step of the Chilean urban wastewater treatment plant located at la Farfana, Santiago de Chile, Chile).*

Parameters	Concentration
BOD ₅ (mg/L)	290
TSS (mg/L)	225
COD (mg/L)	510
Mean temperature in summer (°C)	23
Ammoniacal nitrogen (mg/L)	27.4
Kjeldahl nitrogen (mg/L)	39.5
Total phosphorus (mg/L)	7.7
Faecal coliforms (MPN/100 mL)	1 x 10 ⁷
pH	7.4

* Values are averages of four determinations; there was virtually no variation (less than 3%) between analyses.

Table 2. Composition and main features of the Chilean natural zeolite (clinoptilolite type) used.*

Component	Composition (%)
SiO ₂	67.00
Al ₂ O ₃	13.01
Fe ₂ O ₃	3.60
CaO	3.46
Na ₂ O	1.32
TiO ₂	0.28
MgO	0.78
K ₂ O	0.53

* Particle size: 1 mm; SiO₂/Al₂O₃ ratio: 5.15; average diameter of pores: 170.7 Å, 0.017 µm; ionic exchange capacity: 1.57 meq/g; ammonium adsorption capacity: 12.3 mg NH₄⁺-N /g of zeolite.

Table 3. Combination of the concentrations of ammonium and phosphorus studied and obtained from the experimental design.

Number of the experiment	Ammonium (mg NH₄⁺/L)	phosphorus (mg TP/L)
1	100	80
2	300	80
3	500	80
4	300	40
5	100	40
6	500	40
7	300	60
8	100	80
9	300	80
10	500	80
11	300	40
12	100	40
13	500	40
14	300	60

Table 4. Volume of sludges generated during the integrated treatment with zeolite and lime.

Experimental Conditions	Sludges generated with zeolita			Lime used	Sludges generated with lime			Total production of sludges
	Wet (mL)	Dry (g)	% ¹	Wet (mL)	Wet (mL)	Dry (g)	% ²	%
100 mg NH ₄ ⁺ /L - 40 mg TP/L	25.0	20.0	5.6	11	18.8	1.8	4.4	9.7
500 mg NH ₄ ⁺ /L - 80 mg TP/L	35.5	20.5	7.9	24	20.1	2.4	4.8	12

¹ Percentage of sludges generated of the total liquid effluent treated, after zeolite treatment.

² Percentage of sludges generated of the total liquid effluent treated, after lime treatment.