

Application of Zeolitized Coal Fly Ashes to the Depuration of Liquid Wastes

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1 INTRODUCTION

The cationic exchange capacity of natural and synthetic zeolites is well-known, and thus this material has been used for solving different environmental problems, generally in the field of waste water depuration, removing such metals as Pb, Zn, Ni and others in borehole waters, acid mine waters or even process wastewaters. In addition, the utilization of some zeolites like ammonium compounds absorbents has also been described, justifying applications as soil fertilizers, which can produce a slow release of the previously retained ammonium.

Synthetic zeolites may be obtained from coal fly ashes. Many patents and technical papers have proposed different hydrothermal activation methods to synthesize zeolites from fly ashes. All the developed methods are based on the dissolution of aluminum-silicate phases from coal fly ashes in an alkaline solution (mainly NaOH and KOH solutions) and the subsequent precipitation of the zeolitic material¹.

Fly ash from coal combustion is a reduced-size particle material, showing adsorbent properties for some pollutants. For this reason, fly ashes have been used for treating wastewaters, achieving important reductions in parameters such as the chemical oxygen demand, COD, organic matter content and metals concentrations². High LOI fly ash can also be processed for absorbing organic and organometallic compounds from dyes and residue dye effluents^{3,4}. The removal of COD from textile mill effluent by using fly ash has also been studied in batch experiments, achieving a removal efficiency of 90%⁵. Fly ashes in an acidified form were studied with respect to removing color and organic materials from the effluent of a municipal wastewater treatment plant. In the acidified situation, coagulation of colored colloids in the effluent takes place. Carbon sorption and calcium precipitation of tannins and humic substances varied with pH and the chemical composition of the fly ash used⁶.

The major potential environmental impacts related to landfill leachate are pollution of groundwater and surface waters. Existing data show high leachate concentrations of all components (dissolved organic matter, inorganic macrocomponents and heavy metals) in the early acid phase due to strong decomposition and leaching. In the long methanogenic phase a more stable leachate, with lower concentrations and a low BOD/COD-ratio, is observed. Generally, very low concentrations of heavy metals are observed. In contrast, the concentration of ammonia does not decrease, and often constitutes a major long-term pollutant in leachate⁷.

Power plant coal bottom ash was used in column and batch experiments to investigate its adsorption capacity to reduce the concentrations of various pollutants in landfill leachates. Thus, maximum removal efficiencies for COD (50%), N-NH₃ (39.4%), N-total (31.1%), P (92.9%), Fe³⁺ (96.5%), Mn²⁺ (95.4%) and Zn²⁺ (82.2%) were determined⁸. An artificial zeolite generated from coal fly ash was used as adsorbent and was compared with activated carbon and their adsorption removal rates of N-NH₄⁺ and heavy metal ions from municipal landfill leachates were analyzed. The artificial zeolite removed >50% of N-NH₄⁺ and higher percentages (>80%) of Mn(II), Zn(II), Cd(II) and Pb(II)⁹.

A naturally occurring zeolite (clinoptilolite) was studied to find out its potential for ammonia removal from the composting leachate collected from a pilot-scale composting plant treating the solid waste coming from a greenhouse vegetable facility¹⁰. Through batch experiments, the ammonium adsorption capacity of zeolite was determined to be 14.35-14.58 mg N/g for the composting leachate. Three particle size zeolites were tested, showing that the powdered zeolite with the smallest particle size had the highest ammonium adsorption capacity. The adsorption capacity also increased with increased contact time. The same authors have studied the possibilities of using the same zeolite in a packed column¹¹. Thus, packed zeolite columns were set up and operated to investigate the continuous removal of ammonium ions from the compost leachate. The effects of hydraulic retention time and particle size of the zeolite on the ammonia adsorption capacity were studied. The powdered zeolite packed column consistently removed over 90% of the ammonia from the influent after 6 bed volumes of influent flow.

In two recent papers the use of zeolites has been described in relation to the waste water treatment in biological reactors. Lee et al (2002)¹² describe a new hybrid biological reactor using among others clinoptilolite powders as a bio-carrier and compare it with conventional activated sludge. The authors conclude that the high ammonium exchange capacity of the clinoptilolite enable nitrifiers to colonize favorably in the biofilms of this mineral and consequently increase nitrification. In other article, an activated sludge process was combined with coagulation and a zeolitic rock (clinoptilolite) pre-treatment process to treat leachate having a high concentration of ammonium nitrogen¹³. Higher COD and ammonium nitrogen removal efficiency were achieved when the influent was pretreated with coagulant and zeolite, compared with a system without ammonia pre-removal system.

Recently we studied the utilization of two synthetic zeolites for the treatment of the leachate produced in a municipal waste treatment plant, in the first phases of a

composting process. The zeolite treatment was combined with a coagulation-flocculation treatment using aluminum sulfate and a polyelectrolite. The study was carried out to see the reduction in the metal content, organic matter (COD), total nitrogen (TKN), suspended solids and colloid matter contents of the liquid waste after the zeolite treatment. In the paper¹⁴, a comparison is made between a commercial synthetic zeolite and a zeolitic material, obtained after the hydrothermal alkaline attack of fly ashes coming from the pulverized coal combustion in a power plant.

The results obtained in the above-mentioned study showed a great reduction in the nitrogen content of the leachate as a result of the treatment with zeolites. The results obtained using zeolitized fly ash were particularly remarkable. In this paper, our aim is to study both the removal of nitrogen and the possibilities of zeolitized ashes as water depuration agents more carefully. We describe a second phase in the treatment of the same landfill composting leachate using synthetic zeolites. We studied the reduction of nitrogen, phosphorus, DQO and DBO in the leachate as a result of the treatment with the partially zeolitized fly ash and with the commercial synthetic zeolite described in the previous paper. We also carried out a detailed study of the elimination of ammonia N in the same leachate as well as in a liquid cattle farm waste that had a very high concentration of ammonia N after being treated with different synthetic zeolites. In this last study, commercial synthetic zeolites were compared with other zeolitic products obtained after alkaline treatment of different coal ashes, using two different methods.

2 MATERIAL AND METHODS

2.1 First stage. Treatment of a MSW landfill leachate

2.1.1 Sample preparation

The leachate was from a collection pool of the liquid waste produced by the solid waste organic fines fraction in a storing unit, before being submitted to composting, in an integrated municipal solid waste plant.

Given the high suspended solids content of the original leachate sample and the enormous difficulty to be submitted directly to the zeolite treatment, we decided to dilute the original leachate sample up to 10% using water from the urban supply system, so that this diluted leachate (AB) would be the influent water to the zeolite adsorption treatment.

2.1.2 Preliminary study. Stirred tank test

The filtered effluent water (sample ABF) was first subjected to two alternate adsorption treatments: a stirred tank test (comparing a zeolitized fly ash and a commercial zeolite) and a column test, using the CV-Z zeolitized fly ash material, resulting from the alkaline activation of fly ashes from the Narcea power plant (Spain). The CV-Z product is composed of different zeolites (mainly Na-P1, and lower levels of analcime and

chabazite) and the fly ash remaining after the alkaline activation¹.

The treatment scheme is shown in Figure 1.

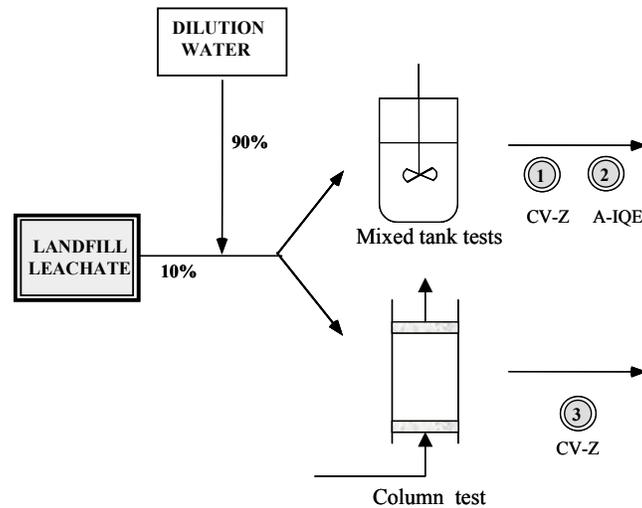


Figure 1. Zeolite adsorption treatment. Stirred tank and column tests

The stirred tank test consisted of the addition of 30 g / L of the CV-Z zeolite or the commercial zeolite A-IQE (Industrias Químicas del Ebro / IQE, Zaragoza, Spain) (sample 3). The volume of ABF sample used was 500 mL. The resulting suspensions were then stirred for 30 min at 150 rpm, and finally were decanted for 24 h.

2.1.3 Preliminary study. Column test

The column used in this experiment was 23 cm in height, had an inside diameter of 3 cm, and was made of glass. For the column study, 30 g of CV-Z zeolite was packed into the column, filling about 10 cm between two porous plates in order to support the zeolite bed and prevent the zeolite from being lost through the column. The column was operated in an upflow mode with continuous flow-through of the composting leachate. A peristaltic pump (Watson Marlow 505U) was used to feed influent from the center of the bottom of the column. The flow rate used was $100 \text{ mL} \cdot \text{min}^{-1}$ and the volume collected was 1 L, in order to maintain the same S/L proportion as with the stirred tank test. The attempts to repeat the tests in the column with the A-IQE zeolite were unsuccessful due to the change that is caused in the zeolite particles when they come in contact with the leachate. This makes it impossible for the leachate to pass through the zeolite bed without great head losses through the column due to clogging. Thus, the column tests were only carried out with the CV-Z zeolite.

2.1.4 Zeolite adsorption treatment: Variables studied

In view of the results from the first tests, we designed other tests to better define the extent of depuration and see the influence of certain parameters. A new sample of

leachate (AB and ABF) was subjected to the zeolite adsorption treatment described above. In the case of the stirred tank contact, apart from the type of zeolite (ZEO), the influence of the amount of zeolite (XX), the mixing (YY) and the sedimentation time (ZZ) were also studied (the nomenclature used for the different cases studied is: ZEO_{XXYYZZ}). With regard to the column test, which was only carried out using CV-Z zeolite as in the preliminary tests, two different flow conditions (WW) were essayed (samples CCV-Z_{WW}).

2.2 Second stage. Determination of the ammonia-N removal with different zeolites

In the next phase of the study, in view of the good results obtained from the elimination of nutrients from the landfill leachate, we decided to better define the extent of the elimination of N and broaden the study to treat other types of liquid effluents with similar problems. We chose to study a liquid waste from a cattle farm.

In this second phase, instead of the elimination of total N, we studied the adsorption capacity for ammonia N using different synthetic zeolites. We used the same zeolites as in phase 1 as well as a few others: two commercial zeolites—A-IQE and X-IQE (Industrias Químicas del Ebro, Zaragoza, Spain)—and three obtained from fly ashes—CV-Z and two other synthetic zeolites, PU4II and PU4III, manufactured using a different process. The synthesis of PU4II and PU4III was carried out by the hydrothermal alkaline attack on Puertollano coal fly ash, the extraction of Si and removal of the unattacked fly ash, and the subsequent synthesis of pure zeolite by combining the resulting Si extract with a residual high alumina solution¹⁵. The samples used, where they came from and the resulting zeolites are shown in Table 1.

Table 1. Ammonium Adsorption. Zeolites used

Sample	Fly ash	Zeolite
A-IQE		A
X-IQE		X
PU4II	Puertollano	X
PU4III	Puertollano	A
CV-Z	Narcea	NaP1

We performed the treatment by leaving different amounts of the zeolites from Table 1 in agitation for 4 h with the same volume of sample AB or with the liquid farm waste sample. After the agitation, the samples were allowed to decant for half an hour; then they were centrifuged and their ammonia N content was determined.

2.2.1 Liquid pig-farm waste

The liquid pig-farm waste tested was from the Les Masies de Voltregà plant in Barcelona, which is owned by the Guascor Group. The sample under study was obtained at the exit of the flotation treatment, and it had already been filtered when it arrived at the laboratory. This kind of substance contains a mixture of excreta, feed, and bedding material; it later undergoes chemical transformations as a result of

microbial fermentation via hydrolysis, and when mixed with the cleaning water and the products used in disinfecting and cleaning out the stables it is transformed into that effluent which we call pig slurry or pig manure.

The effluent is particularly difficult to handle and manage, as its dry material content varies from 1 to 7%. This is thus basically a liquid with a large amount of suspended particles. Traditionally, (apart from the direct application of the pig slurry on the land, to be used as a fertilizer due to the presence of nitrogen, phosphorus and potassium) different systems have been used for managing and treating that waste, almost all of them first based on separation processes, using different mechanical, physical, chemical systems or combination of these, followed by a biological treatment.

2.3 Methods

Determination of metals and other elements

For the elemental analysis, the samples were first filtered with a Whatman GF-C filter and then with a Sartorius 0.45 µm diameter cellulose acetate filter. Major and trace element contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).

Chemical Oxygen Demand (COD) and Total Kjeldhal Nitrogen (TKN) determinations¹⁶

To determine the chemical oxygen demand (COD), the dichromate reflux method was used, whereas the nitrogen content was determined using the macro-Kjeldahl method.

Ortho phosphate determination

The phosphate was determined using the ammonium molybdate spectrophotometric method (UNE-EN 1189 1996)¹⁷, which involves the prior filtration of the samples through a 0.45-µm diameter cellulose acetate filter (for this reason P was not determined in the AB samples).

Ammonium determination

The levels of ammonium ion in solution were assessed by using flow injection analysis (FIA) colorimetric methods.

3 RESULTS AND DISCUSSION

3.1 Preliminary study

As we commented before, the original leachate sample was diluted up to 10% using water from the urban supply system, so that this diluted leachate (AB) be the influent water to the zeolite adsorption treatment. The characterization of the so obtained diluted leachate sample is shown in Table 2.

Table 2. Influent water analysis (sample AB)

pH	5.23
COD/mg L ⁻¹	14630
BOD ₅ /mg L ⁻¹	10850
TKN/mg L ⁻¹	395
P-PO ₄ /μg L ⁻¹	

The AB sample was filtered through a GF/C glass fiber filter. The characteristics of the filtered leachate sample (ABF) are shown in Table 3:

Table 3. Influent filtered leachate (sample ABF)

pH	5.24
COD/mg L ⁻¹	12802
BOD ₅ /mg L ⁻¹	8850
TKN/mg L ⁻¹	246
P-PO ₄ /μg L ⁻¹	25000

As you can see, the BOD₅ of the influent water (AB) was substantially reduced after the filtration, reaching a reduction figure of 18%. In the same process the COD was reduced by 12%. A decrease of 38 % in the total nitrogen concentration was also observed after filtering the sample.

Stirred tank tests

After the treatment with the two zeolitic materials, A-IQE and CV-Z, samples 1 and 2 were obtained respectively; their characteristics are shown in Table 4.

Table 4. Zeolite adsorption treatment. Samples 1 and 2 analysis

	A-IQE	CV-Z
pH	8.17	8.11
COD/mg L ⁻¹	12385	11585
BOD ₅ /mg L ⁻¹		7900
TKN/mg L ⁻¹	162	106
P-PO ₄ /μg L ⁻¹	9866	2241

Column test

The analytical data of the sample (sample 3) obtained after the column test (CCV-Z) are shown in Table 5.

Table 5. Adsorption-filtration treatment. Column test

	CCV-Z
pH	8.50
COD/mg L ⁻¹	12000
BOD ₅ /mg L ⁻¹	5950
TKN/mg L ⁻¹	49
P-PO ₄ /μg L ⁻¹	1253

As we can see, there is no great effect on the COD reduction in any of the cases studied. With regard to the BOD, there is only an appreciable 33% reduction in the case of the column treatment. However, the treatment with zeolites removes a large quantity of N and P- PO₄, reaching N reduction percentages of 34%, 57% and 80% in the treatment with the A-IQE zeolite, that with the CV-Z zeolite and in the column, respectively. The results are even better with regard to the P-PO₄ elimination: 61% (A-IQE), 91% (CV-Z) and 95% (CCV-Z). These results are quite significant and show the potential of the CV-Z zeolite for the elimination of nitrogen and phosphorus from these leachates.

3.2 Zeolite adsorption treatment: Variables studied

Table 6. Influent water analysis (samples AB and ABF)

	AB	ABF
pH	5.1	5.1
COD/mg L ⁻¹	13570	12542
TKN/mg L ⁻¹	431	417
N-NH ₄ /mg L ⁻¹	222	
P-PO ₄ /μg L ⁻¹		13333

As we can see, this second water sample has quite a different pH from that of the sample used in the preliminary test, and their N and P contents are also different. There is more N and less P. We can also see that the ammoniacal form represents about half of the TKN. Although filtration also reduces the COD and TKN contents, the effect is not as noticeable as in the case of the first leachate sample.

Stirred tank test. Influence of the type of zeolite and zeolite dose

In Table 7 the results of the tests carried out to study the effect of the type of zeolite, comparing A-IQE and CV-Z, and the effect of different CV-Z doses (10, 30 and 50 g/L) are shown. In all the cases the water-zeolite samples were stirred for 30 min and then were decanted for 24 h.

Table 7. Influence of type of zeolite and zeolite dose

	ABF	A-IQE ₃₀₃₀₂₄	CV-Z ₁₀₃₀₂₄	CV-Z ₃₀₃₀₂₄	CV-Z ₅₀₃₀₂₄
pH	5.1	8.3	6.9	8.4	8.8
COD/mg L ⁻¹	12542	12336	11925	11952	11554
TKN/mg L ⁻¹	417	364	336	336	255
P-PO ₄ /μg L ⁻¹	13333	453	<100	416	<50

As can be observed, under the same conditions, the treatment with CV-Z yields a greater degree of depuration of the three parameters analyzed than the treatment with A-IQE. With regard to the amount of CV-Z zeolite, except in the case of P-PO₄, whose results do not allow us to draw any conclusions, it seems that there is a slight improvement in the elimination of COD and TKN as a result of increasing the amount.

Stirred tank test. Influence of the time of contact

In Table 8 the results of the tests carried out to study the effect of the zeolite-water time of contact were shown. Two variables have been dealt with: the mixing time (30 min or 2 hours) and the sedimentation (clarification) time (4 or 24 h). In all the cases the zeolite dose has been 30 g/L of NaP1-NA zeolite.

Table 8. Influence of time of contact

	ABF	CV-Z ₃₀₃₀₀₄	CV-Z ₃₀₃₀₂₄	CV-Z ₃₀₀₂₀₄	CV-Z ₃₀₀₂₂₄
pH	5.1	8.3	8.4	8.6	8.6
COD/mg L ⁻¹	12542	11925	11952	11446	11646
TKN/mg L ⁻¹	417	330	336	280	296
P-PO ₄ /μg L ⁻¹	13333	235	416	1347	227

The conclusions that can be drawn as regards the influence of the zeolite-water contact time on the efficiency of the depuration are the following:

- Neither an increase in the sedimentation time nor the agitation period improve depuration (rather, increasing contact time hinders depuration slightly).
- The results related to the influence of the contact time on the elimination of P-PO₄ are not conclusive (just as in the previous section).

Column test. Influence of the leachate flow rate

In Table 9 the results of the column tests (CCV-Z) carried out to study the effect of the leachate flow rate (50 and 100 mL/min) were shown along with those obtained in a stirred tank test (CV-Z₃₀₃₀₀₄) to serve as comparison. As in the previous column tests, 30 g of NaP1-NA zeolite were used and the volume collected was 1 L in order to maintain the same S/L proportion as in the stirred tank test.

Table 9. Influence of the column leachate flow rate

	ABF	CV-Z ₃₀₃₀₀₄	CCV-Z ₅₀	CCV-Z ₁₀₀
pH	5.1	8.3	8.7	8.6
COD/mg L ⁻¹	12542	11925	11245	11446
TKN/mg L ⁻¹	417	330	207	230
P-PO ₄ /μg L ⁻¹	13333	235	<40	<40

The results corresponding to the treatment with CV-Z in the column, especially when the leachate flow rate was lesser, were better than those obtained in the tests carried out in a stirred tank. These results contrast with those obtained by other authors who have found that, in general, the adsorption capacities for batch and column experiments did not correspond, but rather that the column tests yielded much lower adsorption capacities¹⁰. The elimination efficiency achieved by the best in-column treatment (CCV-Z₅₀) for the three parameters analyzed was: 10.3% (COD), 50.4% (TKN) y 100% (P-PO₄).

3.3 Second stage. Ammonia removal

Equilibrium experiments were conducted to study the effects of the zeolite dose on the ammonium adsorption of 5 different synthetic zeolites. The results show that the uptake of ammonium by zeolite increased with zeolite dose.

For the different types of zeolites tested, the maximum elimination percentages ranged from 16.7% to 45.0% in the case of the landfill leachate and from 32.2% to 43.4% in the case of the pig slurry. In general, the behavior of any given zeolite with regard to the elimination of N was always slightly superior in the case of the pig slurry samples, which had a greater concentration of ammonia N.

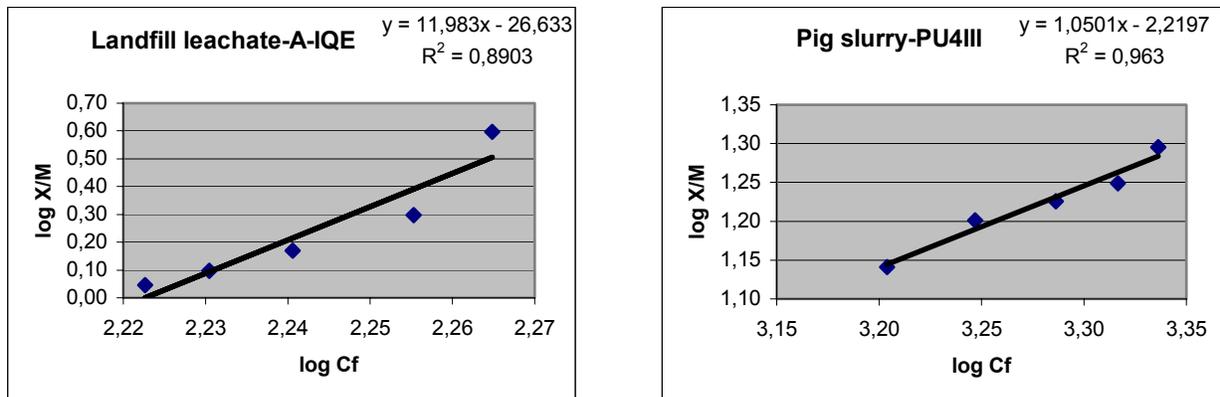


Figure 2. Freundlich isotherm graphs

Equilibrium uptake data found at room temperature were processed for fitting to both Freundlich and Langmuir adsorption isotherms. The constants in the Freundlich isotherm can be determined by plotting the ammonium concentration in the zeolite

(X/M) versus the ammonium equilibrium concentration in solution (C_f) in a double logarithmic paper. Adsorption of ammonium ions observed better the linear Freundlich isotherm (as is shown in Figure 2) than Langmuir isotherm, and also better in the case of landfill leachate than pig slurry samples, probably due to their high N-NH₄ content, although the presence of other species in the pig slurry, especially organic matter, could have also an influence on the uptake of ammonium ion¹⁸. However, other authors have found that Langmuir isotherm best describes the equilibrium of ammonia adsorption on a natural zeolite (clinoptilolite)^{10,18}.

	Landfill		Pig slurry		
		Dose (g/L)	N-NH ₄ C _f (mg/L)	Dose (g/L)	N-NH ₄ C _f (mg/L)
	1	0.0	222	0	2623.1
A-IQE	2	9.6	184	26	2115.8
	3	21.2	180	33	2087.3
	4	32.4	174	45	1993.1
	5	41.6	170	49	1972.4
	6	49.6	167	76	1777.5
X-IQE	7	12.0	194	26	2193.1
	8	20.4	192	35	2089.3
	9	33.6	189	41	1845.0
	10	43.6	189	52	1755.8
	11	50.0	185	74	1496.7
PU4II	12	9.2	170	26	2150.3
	13	20.4	154	24	2216.1
	14	32.0	150	38	1966.2
	15	38.0	132	60	1686.8
	16	51.2	134	79	1483.5
PU4III	17	9.8	184	23	2169.2
	18	20.0	181	31	2072.9
	19	33.2	170	41	1933.2
	20	40.0	160	54	1765.5
	21	47.6	157	74	1598.8
CV-Z	22	11.2	176		
	23	22.0	174		
	24	31.2	154		
	25	37.2	131		
	26	51.6	122		

Table 10. Results from the N-NH₄ elimination tests

3.4 Metals removal

With respect to the reduction of metals carried out by the zeolite adsorption treatment, it should be pointed out that the low initial concentrations of metals in the water did not permit an adequate assessment of the zeolite adsorption potential, and the values obtained are in this case not significant.

	Pig slurry	Landfill (AB)
Al	69.575	38.48
B	5.85	6.34
Ca	159.3	10876
Cr	0.7	
Cu	0.35	
Fe	14.55	297.8
K	4577.5	3718
Mg	160.625	672
Mn	4.15	15.32
Mo	9.575	
N-NH₄	2623.1	222
Na	1147.25	5016
S	70.2	884
Si	19.75	53.54
Zn	1.25	37

Table 11. Content of metals and other elements in the original samples (mg/L)

In the case of the landfill leachate, the potential elimination of the other metals was masked by the samples' high Ca content. In spite of this, maximum reductions of 82.5%, 24.3% and 60.5% were measured for Fe, Mn and Zn, respectively. With regard to the pig slurry sample, its metal contents were even lower than those of the landfill leachate. Perhaps for that reason nearly 100% of the Ca and Mg was eliminated in most cases as well as 90% of the Zn and 100% of the Mn and Mo. The Fe, however, was not appreciably eliminated.

4 SUMMARY AND CONCLUSIONS

The goal was to study the reduction of nitrogen, phosphorus, DQO, DBO and some metals as a result of treatment with synthetic zeolites. First, we studied the treatment of the leachate, comparing a commercial synthetic zeolite to one from an alkaline attack on coal fly ash, and tested different forms of contact (in a stirred tank and in a column) between the leachate and the alkaline attack zeolite. There were two parts to the study—a preliminary stage and an advanced stage—in order to try to define the variables that affect the adsorption process. None of the alternatives tested yielded a large COD reduction, but the TKN and P-PO₄ removal were quite effective. We found that the zeolitized fly ashes showed a better behavior than the synthetic zeolites tested,

which confirmed the observations of prior studies. Furthermore, the results from the column treatment, especially when there leachate flow rate was lesser, were better than those from the stirred tank treatment.

We also carried out a detailed study on the elimination of ammonia N from the leachate and the pig slurry, which has a very high N concentration (ten times more than the leachate), in order to see how the different forms of nitrogen behaved. We tried to design a model for the elimination of the ammonia N based on the study of the data adjustment from some of the most important adsorption isotherms (e.g. the Freundlich and Langmuir adsorption isotherms).

The results obtained are quite significant and show the potential of the zeolitized coal fly ashes for the elimination of nitrogen and phosphorus from different waste waters. This would, in turn, facilitate a subsequent biological treatment of them. The final goal of this project is to use the information obtained to design the best possible treatment system in the form of a pilot installation, which can be built and used within an existing MSW treatment plant.

REFERENCES

- [1] Moreno, N., Querol, X., Ayora, C., Fernández Pereira, C., and Janssen-Jurkovicova, M. *Environ. Sci. Technol.*, 2001, 35, p.3526.
- [2] Iyer, R.S. and Scott, J.A. *Resources Conservation and Recycling* 2001, 31, p. 217.
- [3] Graham, U., Robl, T.L., Groppo, J., and McCormick, C. J. In: *Proc. of the 1997 Int. Ash utilization symposium*, (Ed CAER), Lexington, KY, Oct 1997, pp 29-36.
- [4] Viraraghavan, T. and Ramakrishna, K.R. *Water Quality Res. J. Can.*, 1999, 34, p. 505.
- [5] Patnaik, S.N., Baisakh, P.C., and Patnaik, L.N. *Indian J. Environ. Prot.*, 1996, 16, p. 135.
- [6] Vandenbusch, M.B. *Resources, Conservation and Recycling*, 1992, 6, p. 95.
- [7] Kjeldsen, P., Barlaz, M.A., Rooker, A.P., Baun, A., Ledin, A., and Christensen, T.H. *Critical Reviews in Environmental Science and Technology*, 2002, 32(4), p. 297.
- [8] Lin, C.Y., Hesu, P.H., and Yang, D.H. *Journal of the Air and Waste Management Association* (1995), 2001, 51, p. 939.
- [9] Lee, J.H., Kim, D.S., Lee, S.O., and Shin, B.S. *Chawon Risaikring*, 1996, 5, p. 34, 1996 (Chemical Abstracts 127:194833, 1997).

[10] Liu, C.H. and Lo, K.V. Journal of Environmental Science and Health. Part A, 2001, 36, p. 1671.

[11] Liu, C.H. and Lo, K.V. Journal of Environmental Science and Health. Part B, 2001, 36, p. 667.

[12] Lee, H.S., Park, S.J., and Yoon, T.I. Process Biochemistry, 2002, 38, p. 81.

[13] Ahn, D.H., Chung, Y.C. and Chang, W.S. Journal of Environmental Science and Health. Part A, 2002, 37, p. 163.

[14] Otal, E., Pereira, C.F., Vilches, L.F., and Querol, X. In: Proceedings of the Waste Management and the Environment Conference. (Eds D. Almorza, C.A. Brebbia, D. Sales and V. Popov). WIT Press, Cadiz (Spain) 2002, pp. 141-150.

[15] Moreno, N., Querol, X., Plana, F., Andrés, J.M., Janssen, M., and Nugteren, H. J. Chem. Technol. Biotechnol., 2002, 77, p. 274.

[16] Greenberg, A.E., Rodhes Trussell, R. and Clesceri, L.S. (Eds) in Standard Methods for the Examination of Water and Wastewater, 17th Edition, A.P.H.A; A.W.W.W.A.; W.P.C.F., Washington, 1989.

[17] UNE Spanish Standards. UNE-EN 1189 1996. Phosphorus determination. Ammonium molybdate spectrophotometric method.

[18] Jorgensen, T.C. and Weatherley, L.R. Water Research, 2003, 37, p. 1723.