Ion exchange uptake of ammonium in wastewater from a Sewage Treatment Plant by zeolitic materials from fly ash

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ABSTRACT

The potential value of zeolitic materials (ZM) obtained from a hazardous waste, such as coal fly ash, for the retention of NH_4^+ present in liquid effluents from a Sewage Treatment Plant (STP) is studied. A wastewater sample was taken from an STP in Zaragoza (Spain) after conventional treatment at the Plant. The water was treated with different amounts of three ZM: NaP1 zeolite, K-F zeolite and K-Chabazite/K-Phillipsite zeolites all of them in powdered and granulated state. The wastewater was treated by two kinds of processes: continuous stirring batch experiments with powdered ZM, and fixed packed bed of granulated ZM in a column. The powdered materials reduced about 80% of NH_4^+ from wastewater, even in the presence of Ca^{2+}, which competes with NH_4^+ for the cation exchange sites in zeolites. Around 70% of NH_4^+ reduction was achieved with granulated materials. In both cases, moderate ZM/wastewater ratios had to be used to achieve those results, with K-zeolites slightly less effective in NH_4^+ retention.

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1. Introduction

Urban wastewaters usually contain a considerable amount of ammonium (NH_4^+), which is mostly removed using conventional methods such as activated sludge process, including flocculation and active carbon treatment. However, although the remaining NH_4^+ concentration after treatment is low (about 30–50 ppm), it becomes an environmental problem if discharged into a waterway with low water flow, as ammonium can encourage eutrophication of the waters receiving the discharge. This is potentially toxic for fish and other aquatic life, particularly if that water flows through a sensitive area, as was noted in some publications [1,2]. As the discharge of effluent waters containing ammonia and ammonium is coming under increasingly strict concentration limits discharge and the quality of water intended for human consumption as seen in the Directives from the Council of the European Union [3,4], the recommendation of American Committee on Water Quality [5] and discharge standards in some countries such as New Zealand [1], it will be necessary to comply with the requirements for wastewater treatment in a way that minimizes its impact on the environment. In some cases, it would be necessary to incorporate additional treatment, e.g. ion exchange with materials such as zeolites, given

that they may be effective agents in the process of reducing NH_4^+ concentration.

Zeolites are naturally occurring, hydrated aluminium-silicate minerals with cation exchange capacity and affinity for NH_4^+, as has been demonstrated in studies with natural zeolites, such as clinoptilolite, K-Chabazite or K-Phillipsite. This shows potential usefulness for removing this contaminant in wastewaters of different origins – urban, industrial or agricultural – as has been shown in different studies [1,2,6–10].

Over the last decade, intensive research has been focused on the use of coal fly ash for zeolite synthesis [11–14], and the application of the resulting ZM in the same way as natural zeolites, i.e. cation exchangers for of NH_4^+ and heavy metal removal, as reported by different authors [15–19]. However, in most of these studies, application was exclusively tested on synthetic solutions of those ions prepared in laboratories. Considering the complexity of the effluents to be treated in real cases, cation removal with zeolites that do not exhibit comparably high cation selectiveness could be limited when applied to real wastewater samples.

The present study deals with the application of three zeolitic materials (one Na- and two K-zeolites) obtained from coal fly ash, to the treatment of urban wastewater, after conventional treatment at a Sewage Treatment Plant (STP) and before discharge into the Ebro river (Zaragoza, Spain). The main objective of this work is to evaluate the effectiveness of those ZM as water purification agents in environmental protection through their ammonium exchange capacity. The influence of zeolite type, grain size and

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zeolite/wastewater ratio on the wastewater treatment has been studied.

2. Materials and methods

2.1. Zeolitic materials

Three ZM, each containing a NaP1 zeolite, a K–F zeolite, and a K-Phillipsite/K-Chabazite mixture, respectively, were synthesised from coarse and fine fractions of the by-product from manufacture of a lightweight aggregate (LA) made from coal fly ash agglomerated with lime. Synthesis was by means of alkali hydrothermal treatment using the same reaction conditions as previously described [20] and shown in Table 1. These ZM were used to evaluate their ability to remove NH_4^+ from urban wastewater. Treatment tests in batch process (shaking a fixed quantity of ZM with a fixed volume of wastewater) and column (flow-through) with the aforementioned wastewater were performed at room temperature (about 25 °C). Two different fractions of ZM presenting different particle sizes (d) were used: fine ZM (d < 0.2 mm) for batch experiments, and coarse ZM (0.8 mm ≥ d ≥ 0.2 mm) for column experiments. The size range for that last fraction of ZM has been proven to be suitable for work in laboratory as bed load in ion exchange columns. The size range of that fraction does not lead to a pressure deeping in stream due to partial plugging of the bed support in the column.

Cation exchange capacities (CEC) of coarse and fine zeolitic products were determined by NH_4^+ exchange. For CEC determinations of fine ZM, 50 ml of NH_4NO_3 solution, containing 0.35 eq NH_4^+/l, was mixed at room temperature with 0.5 g of each ZM. After continuous stirring for 30 min (this is the time required for NH_4^+ exchange equilibrium with the cited ZM to be achieved, as found in previous studies [20]), the mixture was filtered and the solid residue was washed with deionized water until remaining NH_4^+ was removed (test with Nessler's reagent was used) and dried at room temperature. After that, the exchanged NH_4^+ is extracted from the solid with 50 ml of a solution containing 0.35 eq/l of Na^+ ($NaNO_3$ for NaP1 zeolite) or K^+ (KNO_3 for K-zeolites). NH_4^+ concentration in the solution was determined by colourimetry ($\lambda = 410$ nm) using Nessler's method [21].

For determining the coarse ZM CEC, 50 ml of NH_4NO_3 solution containing 0.35 eq NH_4^+/l was passed at room temperature through 0.5 g of each ZM in a packed bed (equivalent to 1 cm bed height) in a glass column of 1 cm inner diameter. The feed was introduced using a peristaltic pump at volumetric flow of 0.35 ml/min. A low flow rate was chosen to ensure an adequate contact time for ZM-solution in order to achieve saturation in those conditions. After the 50 ml of ammonium salt were passed, the column was washed with 500 ml of deionized water to remove residual NH_4^+. The NH_4^+ in the ZM was then extracted by passing 50 ml of a solution containing 0.35 eq/l of Na^+ ($NaNO_3$) or K^+ (KNO_3) through the NH_4-ZM bed. Finally, the concentration of NH_4^+ in the solution was determined by the colourimetry method as previously described.

2.2. Wastewater sample from STP

The wastewater sample used in this study was obtained from "La Almozara" STP in Zaragoza (Spain) and it was taken after passing through the last system of treatment (secondary) and before discharging into the Ebro river. The concentrations of main cations and NH_4^+ in the wastewater were determined by ICP-OES and colourimetry, respectively [21].

Treatment experiments were carried out in two ways, using a batch process through the addition of fine ZM to the wastewater,

and through a continuous process, allowing the wastewater to flow through a fixed bed of coarse ZM.

Removal of NH_4^+ with ZM can be affected by presence of other cations in the wastewater (competition for cation exchange sites). Therefore, it is important to know the chemical characteristics of the wastewater before any attempt can be made to examine the capacity of zeolites to remove NH_4^+ from it. Final NH_4^+ concentration in the depurated wastewater was determined by colourimetry as referred previously [21].

2.3. Batch adsorption study

NH_4^+ uptake experiments were carried out by mixing 20 ml of waste solution with fine NaP1, K–F and K-Phillipsite/K-Chabazite materials with continuous stirring at room temperature for 30 min (time calculated previously as enough to complete cation exchange). In order to reduce NH_4^+ concentration as much as possible, each ZM was dosed considering different ratios of meq of exchangeable cation in ZM (S) to meq of cations in wastewater (L), with S/L = 0.5:1, 1:1, 2:1, 3:1 and 4:1. In this way, the ZM doses used in experiments were continuously increased until NH_4^+ concentration remained constant after treatment with two consecutive doses, those similar concentrations meaning that maximum NH_4^+ removal had been achieved. When cation exchange was considered to be finished, ZM was separated by filtration (pore of paper <0.45 μm) and NH_4^+ not retained on that material was determined in filtrate as has pointed out before.

2.4. Column study

As it has been noted before, NH_4^+ uptake experiments were carried out in a glass column with 1 cm inner diameter by allowing 50 ml of wastewater to flow through a packed bed of each coarse ZM (1 g ZM represents about 2 cm bed height) at room temperature, using a flow rate of 0.35 ml/min, which was deduced from previous studies to be the minimum flow needed to achieve the best cation exchange. Flows under 0.35 ml/min do not improve cation exchange. Only two ratios S/L were used, 1:1 and 2:1, in order to prevent decreased flow through the column. This phenomenon could occur if small amounts of zeolitic powder (≤0.2 mm) surrounding the coarse granules, but easily released, were to separate from the granule and become compacted onto the packed bed filter. This would hinder correct column operation. NH_4^+ content in the depurated wastewater was determined once it had left the column.

3. Results and discussion

3.1. Zeolitic materials

Values of CEC obtained for the two fractions of the ZM studied are shown in Table 1. Considering that repeatability for determination of CEC as described in Section 2.1 was ≤0.02 meq/g, according to experimental measurements carried out on different ZM in a previous work [20], differences in CEC showed in Table 1 can be considered meaningful. CEC for fine fractions of NaP1 and K–F materials being higher than that of coarse, suggest that fine fractions for those materials present higher content in zeolite. CEC for ZM are proportional to the concentration of zeolites with cation exchange properties present in ZM because they are the only component in ZM with capacity for cation exchange as it has been noted in a previous publication [20].

Table 1
Experimental conditions for synthesis of zeolitic materials and CEC of those materials

Zeolitic material	Temperature (°C)	Alkali solution	V_{as}/W_{sm}[a] ratio (ml/g)	Time (h)	CEC in fine ZM (meq/g)	CEC in coarse ZM (meq/g)
NaP1	150	0.5 M NaOH	10	72	1.31	0.99
K-F	150	3 M KOH	3.75	24	1.37	1.10
K-Phillipsite/K-Chabazite	200	1 M KOH	3.75	72	0.85	1.15

[a] V_{as}/W_{sm}: volume of alkali solution (V_{as})/weight of starting material (W_{sm}).

Table 2
Cation concentrations in wastewater after treatment at "La Almozara" Sewage Treatment Plant

Cation	Concentration (mg/l)
Na^+	110.0
NH_4^+	52.2
K^+	4.9
Ca^{2+}	157.6
Mg^{2+}	32.9
Sr^{2+}	2.3

3.2. Wastewater sample from STP

Concentrations of main cations in the wastewater (pH 7.7) after secondary treatment at the STP are given in Table 2. As it can be observed, the wastewater contained relatively high concentrations of NH_4^+ and Ca^{2+} on the day the sample was taken, with respect to annual average concentrations. This was due to seasonal fluctuations in the volume of water arriving at the STP. Nevertheless, concentration of NH_4^+ is usually high considering the origin of this cation through the degradation of nitrogen organic matters in wastewater after treatments in STP and concentration of Ca^{2+} is particularly high because all kind of waters in the Ebro river valley are rich in calcium due to the geological characteristics of that area.

The high Ca^{2+} concentration observed could be considered an impediment to NH_4^+ uptake owing to the foreseeable competition for cation exchange sites in the zeolites. Two factors could favour the preference for Ca^{2+} with regards to NH_4^+ in the cation exchange process: the higher concentration and the double charge. Similar behaviour could be expected for Mg^{2+} and Sr^{2+} although in those cases, competition will be lower given the scarce concentration of both cations in the wastewater. This phenomenon was already observed by the authors in a previous work [17] using synthetic NH_4^+, Ca^{2+} and Mg^{2+} solutions. In that study, it was confirmed that both Ca^{2+} and Mg^{2+} occupied a part of the exchange positions in the zeolite and reduced NH_4^+ retention.

In the present study, the competition of Ca for cation exchange sites could not be verified since Ca can be released by leaching of Ca-compounds present in ZM in a certain concentration (about 10% CaO) after retention experiments, so Ca in leachate will interfere in the calculus of real calcium exchanged measurements.

3.3. Batch adsorption retention

The results obtained in batch process for the NH_4^+ uptake by fine ZM using different doses (S/L = 0.5:1–4:1) of these materials, are shown in Table 3. Final pH, NH_4^+ concentrations in equilibrium after treatment, percentages of NH_4^+ retention and NH_4^+ exchanged (meq/g) are given for NaP1, K-F and K-Phillipsite/K-Chabazite ZM.

ZM tested have an alkaline reaction in water (residual alkalinity remaining in ZM after their preparation) so, as was expected, after treatment with those materials, pH rises (initial pH 7.7) in line with S/L ratio (increasing of S/L means that amount of ZM (S) increases while volume of wastewater (L) is maintained constant). The pH increases favour cation exchange because it is known that pH is one of the variable with more positive effect on that process (higher pH less H^+ compete against the other cations for the cation exchange sites). Nevertheless, differences in the increases of pH (Table 3) are not too high between the different S/L ratios for the three ZM. So, final pH of solutions is not hopped to have appreciable influence on the different results of NH_4^+ uptake.

Table 3
NH_4^+ uptake onto fine zeolitic materials through batch experiments

Zeolitic material and S/L ratio[a]	pH[b]	Concentration in equilibrium (mg NH_4^+/l)	NH_4^+ removed (%)	NH_4^+ exchanged (meq/g)	CEC utilized in NH_4^+ retention (%)	Ca^{2+} exchanged[c] (meq/g)
NaP1						
0.5:1	8.6	22.4	57	0.39	30	0.34
1:1	8.7	18.2	65	0.22	17	0.32
2:1	8.0	12.4	76	0.13	10	0.20
3:1	9.1	8.4	84	0.10	8	0.14
4:1	9.1	8.3	84	0.07	5	0.11
K-F						
0.5:1	8.6	25.3	51	0.37	27	0.41
1:1	8.7	16.8	68	0.25	18	0.40
2:1	9.2	12.7	76	0.14	10	0.24
3:1	9.4	11.8	77	0.09	7	0.11
K-Phillipsite/K-Chabazite						
0.5:1	8.6	26.2	50	0.22	26	0.29
1:1	8.4	17.8	66	0.15	18	0.28
2:1	8.7	13.5	74	0.08	9	0.20
3:1	8.9	10.1	81	0.06	7	0.16
4:1	9.1	9.5	82	0.05	6	0.12

[a] S/L: meq of exchangeable cation in zeolitic material (S)/meq of cations in wastewater (L).

[b] Initial pH (wastewater) = 7.7.

[c] Hypothetical Ca^{2+} exchanged considering only the final Ca concentration in equilibrium. Possible leached Ca from zeolitic material and subsequently exchanged could not be quantified.
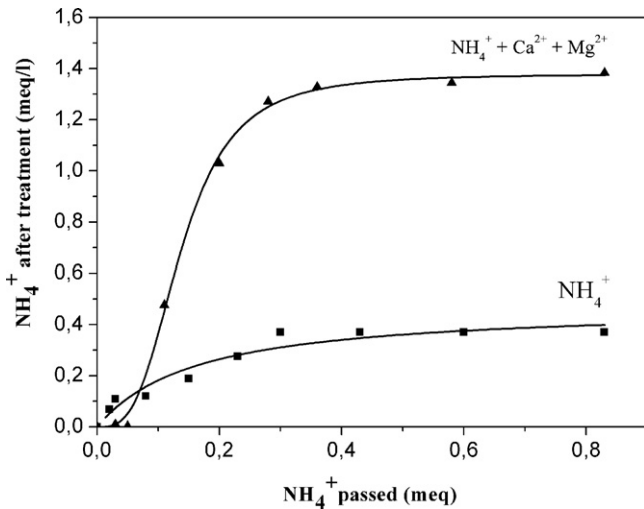
Fig. 1. Trends NH_4^+ saturation for ZM with NaP1 zeolite [17]. Variation of NH_4^+ meq flow-through, alone and in presence of Ca^{2+} and Mg^{2+}.

So then, level of NH_4^+ retention will be controlled by the S/L ratio, and, as can be seen in Table 3, NH_4^+ retention capacity increases in line with S/L owing to a higher availability of cation exchange sites through increases of amount of ZM for the same volume of wastewater. Results show similar behaviour for the three ZM for NH_4^+ retention (about 75% at S/L = 2:1), although NaP1 and K-Phillipsite/K-Chabazite materials exhibit a slightly higher NH_4^+ retention rate than K-F when higher S/L ratios (S/L = 3:1 and 4:1) are used. Despite retention percentages appearing high, it is important to take into account that to achieve approximately 80% retention, a considerable amount of ZM (S/L = 2:1, 3:1) is required. So then, to carry out NH_4^+ retention through only one batch process with the studied ZM, two choices could be chosen: reaching a medium removal of NH_4^+ (about 50% for S/L = 0.5:1) with a medium-low utilization of the CEC for exchanging NH_4^+ (30–26% CEC) or a high removal of NH_4^+ (about 80% for S/L = 3:1) with a low utilization of the CEC for exchanging NH_4^+ (about 7% CEC). In practice, the application of the present results to a large scale would have to involve probably several batches with a gradient in the profit of the exchange capacity of the ZM and a progressive increase in NH_4^+ retention.

The low CEC percentages utilized in NH_4^+ retention are related to the presence of Ca^{2+} in the solution to depurate. That fact has been previously checked in column tests [17] and competition of Ca^{2+} for exchange sites in zeolite versus NH_4^+ could be seen graphically (Fig. 1): in the absence of Ca^{2+} and Mg^{2+} in the solution, the residual concentration of NH_4^+ at the equilibrium was measured to be 0.4 meq/l. On the other hand, equilibrium concentration of NH_4^+

was increased to the level of 1.4 meq/l suggesting that Ca^{2+} and Mg^{2+} might be competing with NH_4^+ for the exchangeable sites on the zeolite. This was explained due to the presence of higher charges on Ca^{2+} and Mg^{2+} than NH_4^+. More, it was suggested that Ca^{2+} was predominant for the competition reactions over Mg^{2+} since former existed in higher concentration than the latter one in the solution (see Table 2).

In the present work, only an approach to Ca^{2+} competition can be made considering, as it has been noted before, that some amount of calcium present in ZM can be leached and subsequently exchanged. Assuming that situation, calcium concentrations in solution were determined after every retention batch test showing that achieved Ca levels were very similar for the three materials, about 130–120 mg Ca/l for S/L = 0.5:1 and about 65 mg Ca/l for S/L = 3:1 or 4:1. Hypothetical Ca^{2+} exchanged can be calculated from those results (Table 3) but emphasizing that calculated values will be slightly under the truth value.

Considering again results shown in Table 3 for NH_4^+ and Ca^{2+} retentions, it can be observed that NH_4^+ uptake is favoured at lower S/L ratio (0.5:1) in despite of Ca^{2+} competition due to the higher concentration of that cation and its double positive charge. When S/L ratios raise cation concentrations in equilibrium decrease and this leads to a reduction in the profit of the CEC in ZM because cation concentration and exchanged cation are in inverse relationship although that reduction seems to affect more to NH_4^+ exchange (meq/g).

So then, considering the above comments, higher S/L ratios would be necessary to use for obtaining high NH_4^+ retention capacities if only one batch reactor was used in the treatment process.

Nevertheless, NH_4^+ uptake rates achieved in present work are only slightly lower than those obtained with New Zealand clinoptilolite [9]. This, considering that their tests were carried out at similar S/L ratios to the highest used in the present study but with longer contact times (3 days) and Ca concentration about four times lower (40 mg Ca/l). So then, results obtained in the present work could be considered as enough satisfactory.

3.4. Column study

The results obtained in the NH_4^+ exchange in column for the coarse ZM using two doses of zeolitic products (S/L = 1:1, 2:1), are shown in Table 4. NH_4^+ concentrations in wastewater on leaving the column (mg/l), percentages for NH_4^+ retention, NH_4^+ exchanged (meq/g) and percentage of CEC utilized for that retention are given for NaP1, K-F and K-Phillipsite/K-Chabazite materials.

As can be observed in Table 4, retention efficacy in the coarse ZM is relatively high, about 70% for ratio S/L = 2:1, although, as with batch tests, K-F material showed a slightly lower value. CEC percentages utilized in NH_4^+ retention are similar to those obtained with

Table 4
NH_4^+ retention in coarse zeolitic materials through column experiments

Zeolitic material and S/L ratio[a]	Concentration at exit column (mg NH_4^+/l)	NH_4^+ removed (%)	NH_4^+ exchanged (meq/g)	CEC utilized in NH_4^+ retention (%)
NaP1				
1:1	17.4	67	0.18	18
2:1	15.0	71	0.10	10
K-F				
1:1	23.0	56	0.15	14
2:1	17.9	66	0.09	8
K-Phillipsite/K-Chabazite				
1:1	21.3	59	0.16	14
2:1	15.1	71	0.10	9

[a] S/L: the same meaning that footnote in Table 3.

Table 5
Operational conditions (S/L = 2:1) for batch and column treatments

Parameter	Batch	Column
Volume of effluent (ml)	50	50
Weight of MZ (g)	1.0–1.1	1.0–1.1
Bed height (cm)	–	2.0–2.2[a]
Treatment time (h)	0.5	2.4
NH$_4^+$ removed (%)	74–76	66–71

[a] Compaction of bed by gravity.

fine ZM in batch reactor at the same S/L ratio: the same percentage is obtained for MZ NaP1, slightly lower for MZ K-Phillipsite/K-Chabazite and lower for ZM K-F (CEC for coarse MZ are lower than fine MZ except for the third MZ, Table 1). Obviously, if 80% or upper NH$_4^+$ retention would be required in the column treatment it would be necessary to increase the height for the MZ bed (higher S/L ratio than 2:1). Therefore, it could be said that both fine and coarse ZM could be an option to be considered in the case where an additional treatment (tertiary treatment) was needed at Sewage Treatment Plant as the result of legal imperatives or environmental demands.

Operational conditions for the two kind of treatments studied in the present work are given in a summarized way in Table 5.

The use of discontinuous process (batch reactor) or continuous process (cation exchange column) would depend on the systems installed at the plant. On the other hand, both *NH$_4^+$ exchanged* and *CEC utilized in NH$_4^+$ retention* are generally very similar for any of the two procedures or slightly better for the batch reactor (see Tables 3 and 4, S/L = 1:1 and 2:1). For this reason, the choice of either procedure for wastewater treatment would not depend on the results of purification that can be achieved (very similar for both procedures) but the characteristics of the STP.

Continuous processes with fixed beds already exist for ammonium removal from urban sewage as described in Refs. [2,17,22]. However, in the case of "La Almozara" STP, wastewaters are treated in a pond system where a large amount of organic material with biochemical oxygen demand and suspended solids are removed. In this case, the tertiary treatment of waters with ZM could be carried out through incorporation into the same pond system.

Finally, it could be pointed out that reductions achieved in the present work for NH$_4^+$ concentration would let to fulfil European Directive 91/271/EEC in a hypothetical case of eutrophization of Ebro river in the point of the river bed where wastewater treated at STP is discharged. That case could be possible in future if trends in environmental affectations due to climate change are taken into account.

With regards to disposal of ZM spent in NH$_4^+$ uptake in wastewater, they could be added to culture soils as N-fertilizer without additional environmental problems. This would be possible because exchanged NH$_4^+$ is easily released through cation exchange and no leaching of dangerous cations can be expected for those ZM because they have been subjected to a strong alkaline leaching during their preparation (see Table 1) where any possible leaching of cations would have already occurred. Those strong chemical conditions in ZM preparation would contrast with the soft pH conditions in culture soils. Moreover, it is known that ZM from fly ash do not released dangerous metals but they are able to retain them even in acid conditions [12].

4. Conclusions

The results of the laboratory scale tests for the proposed application of the ZM from fly ash for the uptake of ammonium, based on the cation exchange capacity of zeolites, show significant removal rates for the three tested materials. The main conclusions extracted from this study may be summarized as follows:

- NH$_4^+$ uptake experiments with wastewater from STP gave high retention percentages (70–80%), even when considering that this cation coexists with high Ca^{2+} concentrations in wastewater. No important differences in those percentages were found between the ZM containing different type of zeolites (NaP1 zeolite or K-F zeolite or a K-Phillipsite/K-Chabazite mixture) and working in the same conditions. Small differences in retention percentages were obtained using continuous (column) or discontinuous (batch) processes, although high doses of ZM were needed to obtain the highest removal percentages (discontinuous process).
- Comparing the cation exchange sites in MZ used for NH$_4^+$ uptake (meq NH$_4^+$/g) it can be observed that they are similar for batch and column treatments.
- On the other hand, MZ NaP1 seems to be the material more favourable for NH$_4^+$ uptake at lower S/L ratios for both treatments.
- With regards to the competition of Ca^{2+} against NH$_4^+$ for the cation exchange sites, results suggest that competition is stronger as decrease cation concentrations in equilibrium (increasing S/L ratio).
- Given the behaviour of the ZM tested for NH$_4^+$ retention, they could be considered readily-available and low-cost sorbents for ammonium reduction in tertiary wastewater treatment if should this be required after conventional treatments in a wastewater treatment plant to fulfil European Directive 91/271/EEC.

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