Ammonium Ion Adsorption and Settleability Improvements Achieved in a Synthetic Zeolite-Amended Activated Sludge[*]

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Abstract Municipal wastewater treatment plants typically exhibits two classic problems: high ammonium concentration in water after conventional biological treatment and, in some cases, poor activated sludge sediment ability. Potential solutions to these problems were investigated by adding a synthetic zeolite obtained from coal fly ash to different steps of an activated sludge treatment. The experimental results for ammonium removal fit well with the theoretical adsorption isotherms of the Freundlich model and showed a maximum adsorption capacity of 13.72 mg g^{-1}. Utilisation of this kind of zeolite to improve activated sludge sediment ability is studied for the first time in this work. It is found that the addition of the zeolite (1 g L^{-1}) to an activated sludge with settling problems significantly enhanced its sediment and compact ability. This was confirmed by the Sludge Volume Index (SVI), which was reduced from 163 mL g^{-1} to 70 mL g^{-1}, the V_{60} value, which was reduced from 894 mL L^{-1} to 427 mL L^{-1}, and the zeta potential (ζ), which was reduced from -19.81 mV to -14.29 mV. The results indicate that the addition of this synthetic zeolite to activated sludge, as an additional waste management practice, has a positive impact on both ammonium removal and sludge settleability.

Keywords Low-cost sorbents, nitrogen, settleability, zeolite adsorption, zeta potential.

1 INTRODUCTION

Wastewater discharge from municipal wastewater treatment plants (WWTP) usually contains high concentrations of nitrogen and phosphorous that may lead to eutrophication, cause depletion of dissolved oxygen and can be potentially toxic for aquatic life. To prevent these problems, discharge concentration limits that are safe have been adopted in several countries, but achieving these low levels may be a challenge for some WWTP. The reason why secondary effluents from conventional WWTP have high nitrogen and phosphorus concentrations is well known, since the carbon-to-nitrogen and carbon-to-phosphorus ratios are higher in urban wastewater than in the equilibrated metabolism of biomass. To achieve an acceptable level of nutrients (nitrogen and phosphorus) in the secondary effluents of urban wastewater, numerous advanced methods (chemical and biological) have been developed.

An additional problem in WWTP is poor operation due to the low settling characteristics of the activated sludge. One reason for this is its charged colloidal structure (commonly in negative charge), which inhibits particle aggregation. In most cases, coagulation and flocculation of these colloidal suspensions allow breaking the colloidal structure and neutralization of the particle zeta potential, thus improving the settleability of the sludge. Moreover, sludge density depends mainly on the ratio of organic to inorganic material, as the inorganic fraction increases sludge density. The addition of inorganic ballasting agents in batch and/or continuous operation as a strategy to solve the problem has been tested [1-10], and it is concluded that the addition of mineral material improves activated sludge settling ability [3-10] and that sludge dewatering can be enhanced by adding the mineral material saturated with some cations (Ca or Na) [7].

For ammonium removal, natural zeolites, which are hydrated aluminium-silicate minerals with cation exchange capacity, have been widely used [11-14]. The material can be added at different stages of the wastewater treatment process or used in packed beds. An alternative to natural zeolites is the synthetic zeolites obtained from fly ash, a by-product of coal power plants, which has been used for sustainability purposes in a

number of applications, mainly because of their ion exchange and adsorption capacities. The zeolites are synthesized using the hydrothermal [15-22] or the fusion methods [23, 24]. The synthetic zeolite that has been investigated in this work (CV-Z) is mainly composed of NaP1 and low levels of analcime and chabazite zeolites as well as the fly ash remaining after the hydrothermal alkaline activation. The synthetic zeolite has a cation exchange capacity of 2.7 meq g^{-1}, equivalent to 60% zeolite content [25, 26]. CV-Z can be considered a low-cost adsorbent [27] when comparing the cost effectiveness of the treatment using the synthetic zeolite to a commercial adsorbent (Zeolite Type A). This material has previously been tested for the removal of contaminants in industrial wastewaters. Those studies show that the use of CV-Z does not significantly improve COD removal efficiency, but it is a promising material for nitrogen and phosphorus removal [25, 27, 28].

The aim of this research was to investigate the ammonium adsorption capacity of CV-Z in urban wastewater, which is a multi-component aqueous solution and some competitive adsorption problems could occur [29]. Another objective of this study is to examine the effect of CV-Z on the activated sludge settling and dewatering performance of the WWTP, which had not been studied, and to assess the feasibility of its application on activated sludge effluents to simultaneously solve or alleviate both problems.

2 EXPERIMENTAL

2.1 Adsorption studies

Urban wastewater was collected from the effluent of the primary settling tank of a WWTP in Seville (Spain). The sample was stored at 4 ˚C until use. CV-Z was obtained from the hydrothermal alkaline activation of coal fly ash from the Narcea Power Plant (Spain).

To elucidate the ammonium adsorption capacity of CV-Z, batch experiments at room temperature (20 °C) were performed in 200 mL volume flasks, using solutions that were prepared by dissolving 10, 25 and 50 mg L^{-1} of ammonium, as $(NH_4)_2HPO_4$, in wastewater. For each ammonium concentration, the influence of the adsorbent loading

on the ammonium removal was investigated using different CV-Z concentrations, from 1 to 4 mg L^{-1}. Control tests were carried out for all ammonium concentrations using blanks without CV-Z. The flasks were then mechanically shaken for 20 min at 150 r·min^{-1}. All tests were performed in duplicate. Ammonium concentrations in the filtered samples were determined using an Ammonium Selective Electrode (Crison Instruments).

To determine the NH$_4^+$ adsorption capacity of the synthetic zeolite, the Freundlich and Langmuir models were used. The amounts of NH$_4^+$ adsorbed onto CV-Z were calculated from the difference between the initial and the remaining ammonium concentrations in the solution. The amount of NH$_4^+$ adsorbed per gram of synthetic zeolite, X/m (mg g^{-1}) was given by $(C_o-C_e)V/m$, where X is the mass of ammonium adsorbed onto CV-Z (mg), m is the mass of CV-Z (g), C_0 is the initial ammonium concentration (mg L^{-1}), C_e is the equilibrium liquid phase ammonium concentration (mg L^{-1}) and V is the volume of solution (L).

The Freundlich model shows that the ratio of ammonium adsorbed to the adsorbent is a function of the equilibrium liquid phase solute concentration.

$$q_e = X/m = KC_e^{1/n} \qquad (1)$$

where, K (L g^{-1}) and n represent the Freundlich isotherm constants. The Freundlich coefficient K represents an indicator of adsorption capacity; $1/n$ indicates the adsorption intensity, while its reciprocal n represents the affinity factor for the Freundlich model.

The Langmuir isotherm is another useful and simple isotherm for describing both physical and chemical adsorption. It is a two parameter model.

$$q_e = X/m = Q_o b C_e /(1 + b C_e) \qquad (2)$$

where Q_0 is the Langmuir monomolecular layer capacity (mg g^{-1}) and b is the Langmuir isotherm constant.

2.2 Settling tests

Two different sludge samples collected from the same WWTP mentioned above, which differed in sedimentation qualities were used for the experiments. Batch settling

tests were performed to investigate the effect of CV-Z on sludge properties, such as sediment ability, monitored as settling sludge volume after 60 min (V_{60}), and SVI. Sludge was used within the first hour after collecting. Settling tests were carried out in a 500 mL settling vessel at room temperature (20 °C). The synthetic zeolite was added to the sludge as a dry powder at concentrations of 1, 2, and 3 g L^{-1}. For the blank tests, no zeolite was utilized. The suspensions formed with CV-Z and activated sludge were stirred in a Jar-Test (Selecta) for 15 min at 100 r·min^{-1} and then settled for 90 min. Total suspended solids (TSS), V_{60} and SVI were established according to the Standard Methods for the Examination of Water and Wastewater [30]. Total nitrogen (TN) content was determined using a Shimadzu TOC-V CPH/TOC-V CPN analyzer, with a 5.0% coefficient of variation. Samples were filtered through a 0.45 μm cellulose acetate filter before TN analysis. All the analyses were conducted in duplicate, from which the average was calculated. Solutions of CV-Z in distilled water or activated sludge were centrifuged at 4000 r·min^{-1} for 10 min and the supernatant was taken and used for the experimental ζ measurements. pH was adjusted with 0.1 mol L^{-1} H$_2$SO$_4$ or NaOH solutions. The equipment used, Zetaphoremeter IV (ZetaCompact CAD), has a microprocessor unit which determines the electrophoretic mobility of particles, each value being the mean of ten acquisition data. The ζ values were calculated from the electrophoretic mobility values, with the aid of the O'Brien conversion theory.

3. RESULTS AND DISCUSSION

3.1 Ammonium ion adsorption of the synthetic zeolite

The influence of adsorbent loading on ammonium removal has been investigated using different concentrations of (NH$_4$)$_2$HPO$_4$ dissolved in wastewater, which ranged from 10 to 50 g L^{-1}. For different initial ammonium concentrations C_0, the effect of the adsorbent dose on the variation of ammonium concentration at equilibrium C_e, is shown in Fig. 1. As reported by other authors [31], the ammonium adsorption efficiency increased with the increase in the adsorbent dose for a constant ammonium concentration. The effect of the adsorbent concentration is the strongest: at C_0 of 18.5 mg L^{-1}, C_e slightly

decreased from 12.2 mg L^{-1} to 7.5 mg L^{-1} as the adsorbent dose increased from 1 g L^{-1} to 4 g L^{-1}, while it decreased more evidently, from 48.6 mg L^{-1} to 27.3 mg L^{-1}, at C_0 62.3 mg L^{-1}.
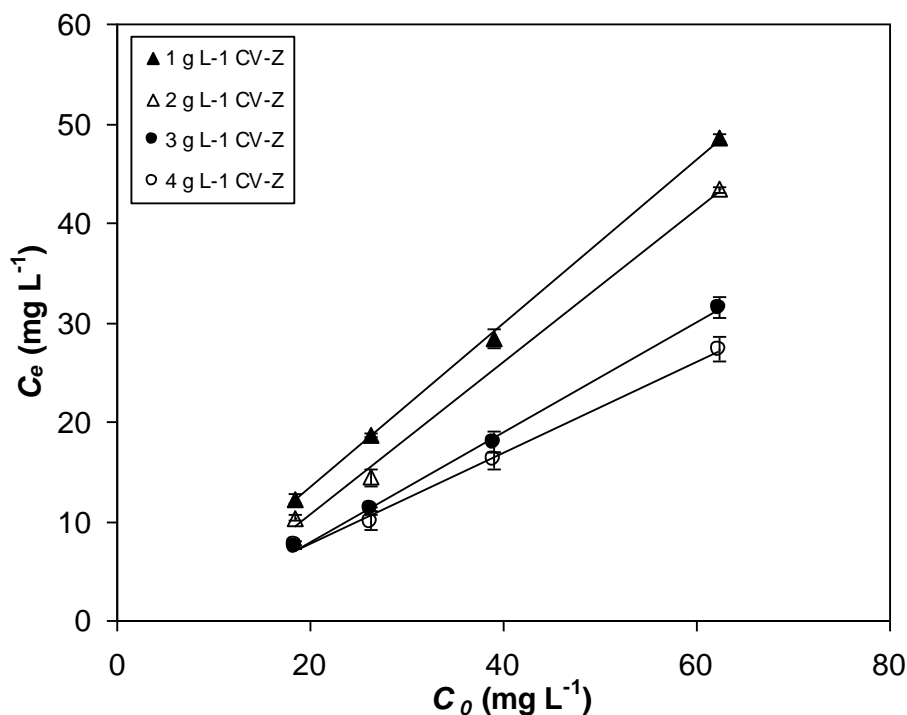

Figure 1 **Variation of equilibrium ammonium concentration (C_e) in relation to the initial ammonium (C_0) and adsorbent concentrations**

Data of ammonium adsorption to CV-Z were analyzed with the Freundlich and Langmuir models. Freundlich equilibrium isotherms at 20 °C for CV-Z range of 1 to 4 g L^{-1} and the coefficients calculated from the isotherms are shown in Fig. 2. This model fits experimental data adequately, giving R^2 values higher than 0.95. As the concentration of zeolite increases, $1/n$ (intensity of the reaction) increased. Under all the experimental conditions, n values are greater than unity (from 1.1416 to 1.8252), indicating that the ammonium ion is favourably adsorbed to the sorbent surface. It has been reported by other authors that n values between 1 and 10 represent beneficial adsorption [32-35]. As can be seen, the K coefficient decreases with an increase in CV-Z concentration. The maximum ammonium adsorption capacity of the zeolite (q_e) is observed to be 13.7 mg g^{-1} in the 50 mg L^{-1} of (NH$_4$)$_2$HPO$_4$ solution, for a CV-Z concentration of 1 g L^{-1} [Fig.2 (a)].
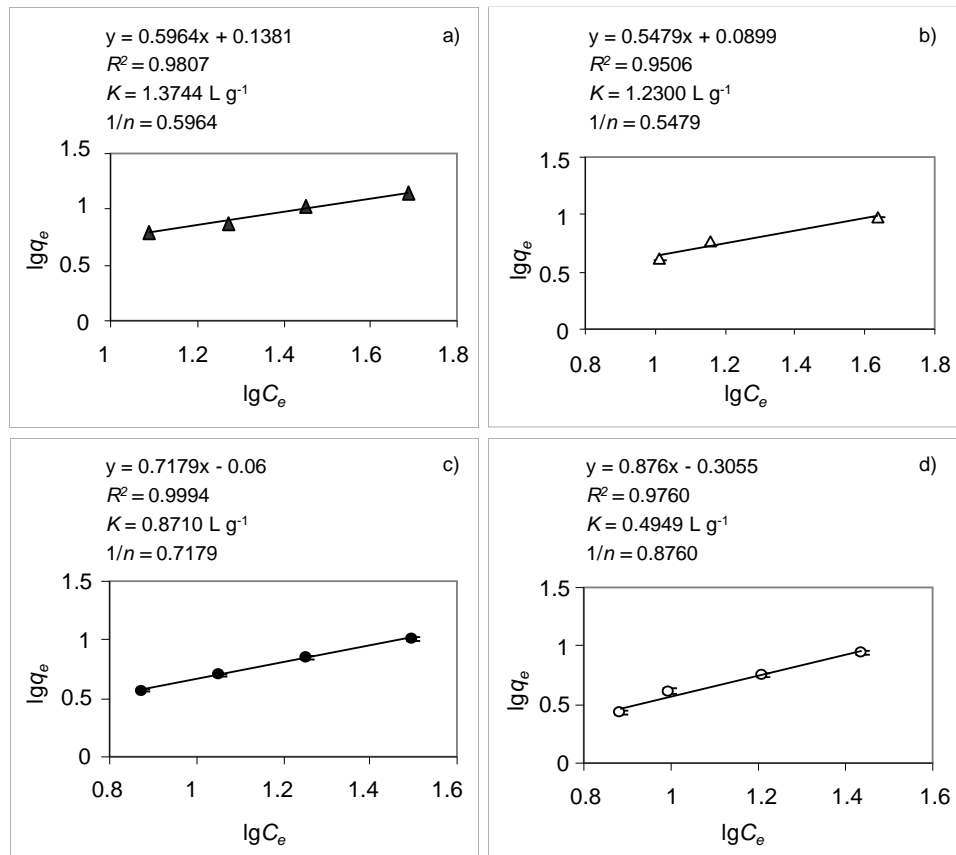
Figure 2 **Freundlich adsorption isotherm curves and adjustable parameters for different CV-Z concentrations at 20 °C** (error bars: standard deviations)

Langmuir equilibrium isotherms at 20 °C for CV-Z range of 1 g L^{-1} to 4 g L^{-1} solution are presented in Fig. 3. The linear form of the Langmuir isotherm fits experimental data adequately for 1, 2, and 3 g L^{-1} of CV-Z, giving R^2 values above 0.95. However, the R^2 value for 4 g L^{-1} is very poor (0.57). Langmuir constants (Q_0 and b) were calculated by least squares analysis. The maximum monomolecular layer capacity, $Q_0 = 40.8$ mg g^{-1}, is obtained with the highest zeolite concentration [Fig.3 (d)]. However, data from this condition fit the Langmuir model very poorly, and the estimated values are always found to be higher than the experimental ones.
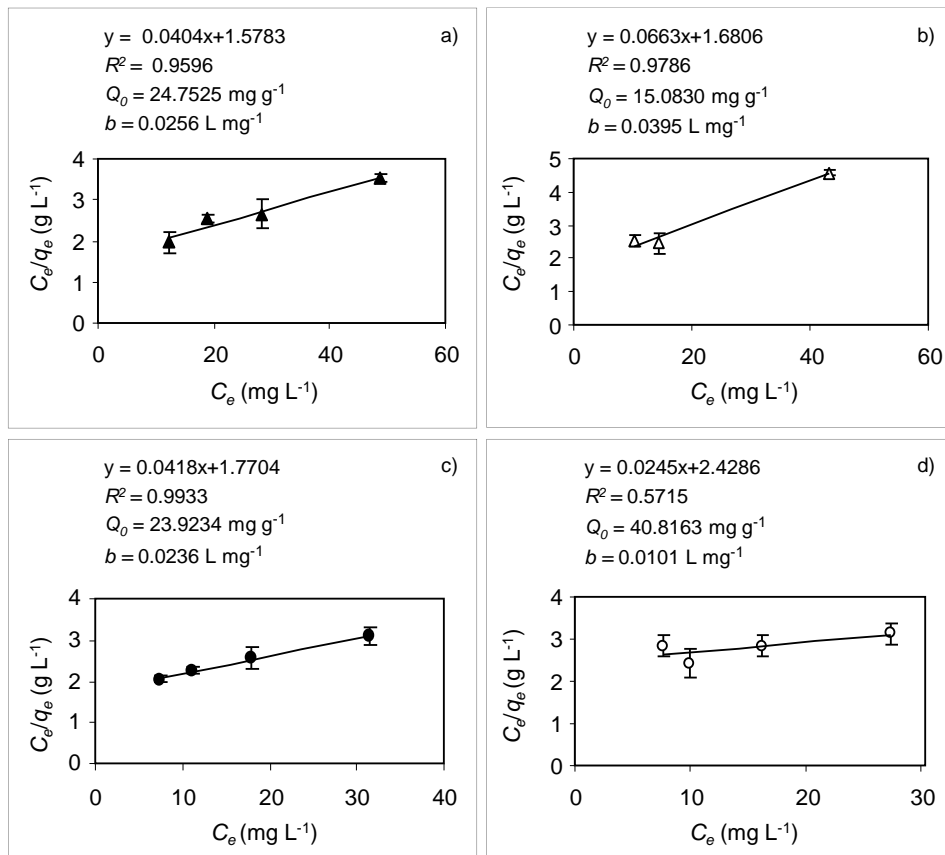
Figure 3 Langmuir adsorption isotherm curves and adjustable parameters for different CV-Z concentrations at 20 °C (error bars: standard deviations)

3.2 Settling tests

The effects of CV-Z concentration on the sludge settling properties were studied at three zeolite doses. During the settling tests, two samples of activated sludge with different settleability were evaluated: an activated sludge with "standard" settleability (AS1) and a sludge coming from the same WWTP but collected after an industrial discharge episode (AS2). Primary data of settleability, nitrogen removal and final pH after the zeolite treatments are shown in Table 1, and settleability curves are shown in Fig. 4. pH values of both types of sludge were increased due to the higher CV-Z dose, as CV-Z contained the remaining NaOH used in the zeolite synthesis.

Table 1 **Settling test parameters for aerobic sludge (AS1 and AS2) using three CV-Z zeolite loadings**

Test	pH	NH_4^+/mg L^{-1}	NH_4^+ removal/%	TN/mg L^{-1}	TN removal/%	TSS_0/mg L^{-1}	V60/mL L^{-1}	SVI/ml g^{-1})
AS1	7.5	22.9		-	-	3,950	110	28
AS1 + 1g L^{-1}	7.7	15.7	31	-	-	4,980	105	21
AS1 + 2g L^{-1}	8	10.4	55	-	-	5,930	100	17
AS1 + 3g L^{-1}	8.2	7.4	68	-	-	6,770	105	16
AS2	8	-	-	370		5,470	894	163
AS2 + 1g L^{-1}	8.3	-	-	260	30	6,075	427	70
AS2 + 2g L^{-1}	8.6	-	-	240	35	7,123	400	56
AS2 + 3g L^{-1}	8.8	-	-	210	43	8,140	480	59
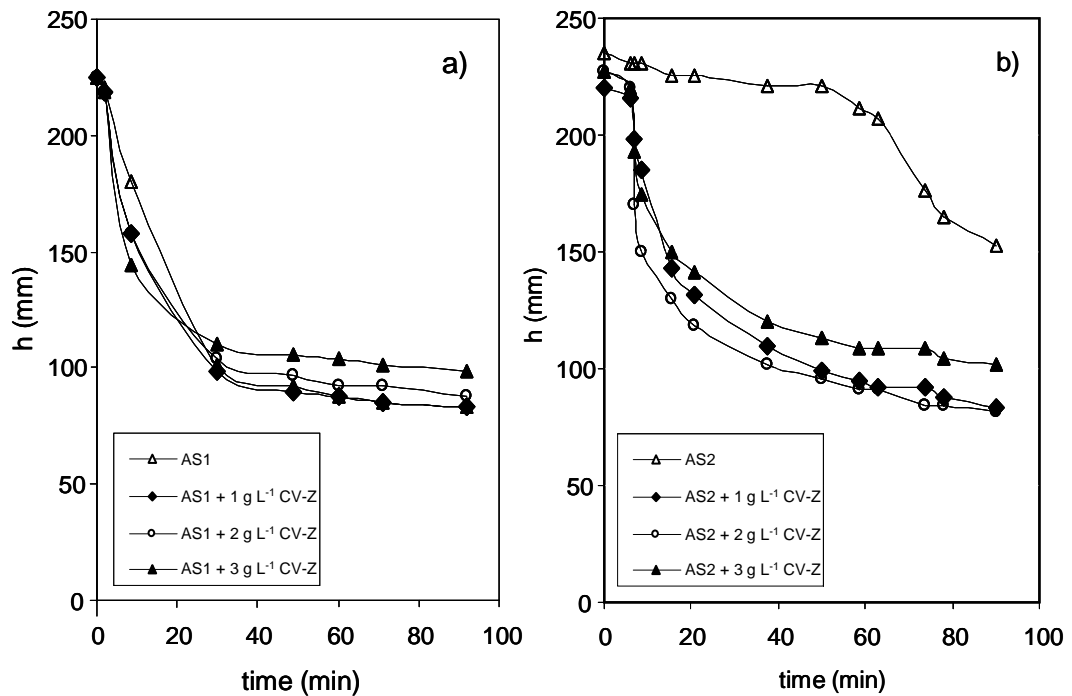
(a)   Activated Sludge 1   (b) Activated Sludge 2

Figure 4 **Height *vs.* time of activated sludge in settling experiments** (data:mean values of three measurements; standard deviations: below 3 mm)

Fig.4 (a) shows the standard settling curves obtained for the AS1 sludge. As previously reported [36], the settling curves show the four stages of induction, constant rate, falling rate and compression periods. The AS1 sludge settled properly by itself and settleability raw data (Table 1) indicate that the sludge settles to 1/10 of the original

volume in 60 min. The addition of zeolite does not improve settleability [Table 1, Fig.4 (a)]. In order to test zeolite performance in the AS1 sludge, ammonium removal was also tested. Increasing the CV-Z dose improves the ammonium removal significantly, reaching up to 70%. This removal efficiency is very similar to that obtained in treatments of the amended wastewater (Fig. 1).

The AS2 sludge [Fig.4 (b)] shows different behavior since settleability shows a 60 min lag period (the height of the sludge on the vessel only decreased 10% during the first 60 min) followed by a constant rate stage until 78 min, and finally by the falling rate and compression periods. Nevertheless, the sludge height after 90 min was still very high (152.7 mm), indicating its poor settleability. In the case of the AS2 sludge, the treatment with zeolite had an obvious effect on the sludge settleability. As shown in Table 1, CV-Z flocculation was effective regarding SVI reduction as the CV-Z loading was increased. This was most significant at zeolite dose of 1 g L^{-1}, which showed 57% SVI reduction. However, when the concentration increased two-fold, the SVI additionally reduced was just 9%, and no further reduction was found with a higher CV-Z dose. The improvement in settling observed for the zeolite amended AS2 is attributed to the fact that the volatile fraction diminishes by adding this inorganic material and also to the ballasting effect produced by CV-Z on the floc formed. Therefore, addition of synthetic zeolite may be an appropriate treatment to favor settleability of activated sludge.

In agreement with this, Fig. 4 shows that the lag phase disappeared even at the lowest zeolite dose tested, and no obvious improvement was observed with higher CV-Z doses. The sludge became compact, settled rapidly, and showed very similar settling kinetics to that of AS1. Therefore, attempts to operate at higher zeolite concentrations to improve efficiency are useless.

In addition, total nitrogen is generally the parameter to be controlled in the WWTP effluents since all nitrogen species contribute to the occurrence of eutrophication of surface waters. As shown in Table 1, in spite of the high nitrogen content of the waste water, CV-Z amendment of the sludges also achieved significant nitrogen reduction, yielding a maximum efficiency of 43%.

Similar concentrations of different ballasting agents have been used to obtain substantial settleability effects [1-10]. As previously discussed [4], although the amount of sorbent used may seem too high to make the process economically satisfactory in continuous operation, the added inorganic ballasting agent may be recycled along with the return sludge to the aeration tank.

The chemical composition and colloidal structure of solid particles in activated sludge may inhibit sludge settling ability and dewater ability, as in the case of AS2. To enhance sludge settling efficiency it is important to use additives that produce charge destabilization and favor the coagulation of the flocs. The ζ is the parameter that provides information about the particle charge. When the sludge charge is negative (the most common situation), the particles repel each other due to electrostatic interactions, this being one of the reasons for poor settling of the sludge [37-40]. Therefore, it is necessary to reduce the negative charges in an attempt to reach the neutral charge by increasing the ζ value.

Comparison of the ζ values of CV-Z suspensions in distilled water and activated sludge at different pH values is shown in Fig. 5. In both cases the ζ potential measured gaves lower values at basic pH. The ζ pattern for the CV-Z suspensions shows a C-type curve. On the other hand, the sludge curve shows that $°\zeta$ changes very little in the pH range of 4-8. Whith the AS2 treated with CV-Z (Fig. 6), the pH of the samples increased due to the CV-Z alkalinity, varying from 8 to 8.8. Results reflect the effect of CV-Z addition on ζ, which changes from -20 mV to -7 mV with the increase of CV-Z dose. These data support the theory that the use of CV-Z as a ballasting agent improves the sludge settling mechanism. A reason for this is the fact that a lot of inner silicon and aluminium active sites with positive charge might emerge on the surface after coal fly ash modification, as other authors have reported [41].
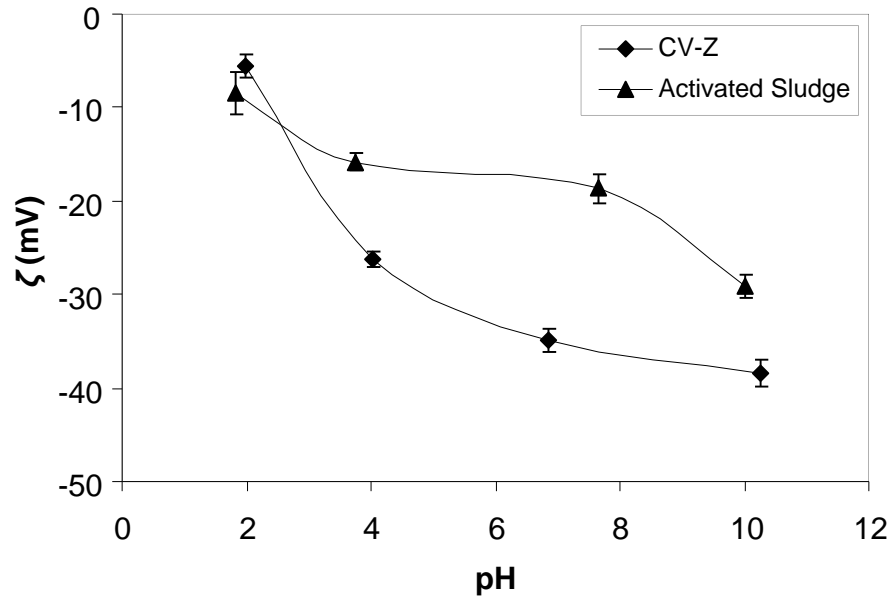
Figure 5 **Influence of pH on the zeta potential of CV-Z in distilled water solution and activated sludge** (error bars: standarddeviations)
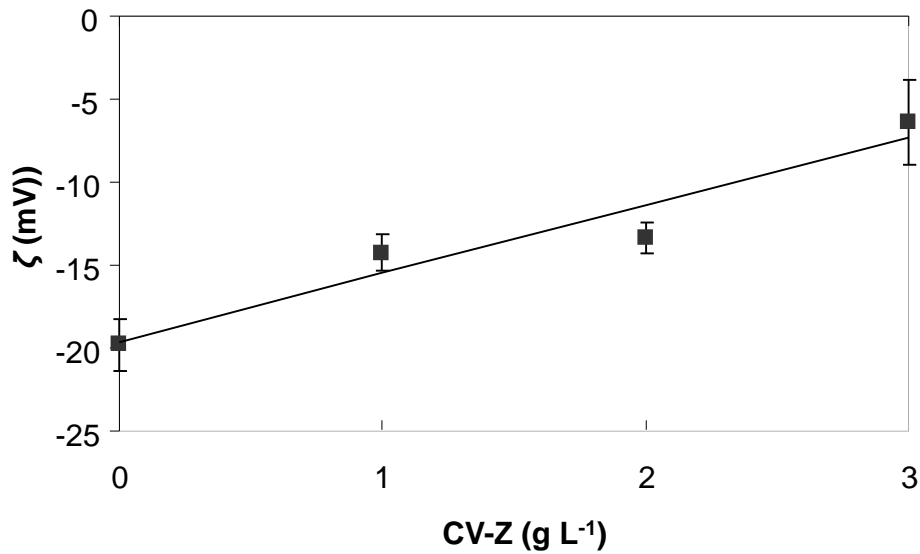

Figure 6 **Zeta potential vs. CV-Z concentration (g L-1)**

4 CONCLUSIONS

In this study, CV-Z was tested as sorbent material for the sorption of nitrogen, and as a ballasting agent to improve settleability of activated sludge from urban wastewaters.

The ammonium absorption equilibrium data obtained with synthetic water are successfully modelled by Freundlich and Langmuir isotherms and show that CV-Z was a suitable agent for the removal of ammonium, with a maximum capacity of 13.7 mg g^{-1}.

In activated sludge plants presenting poor sludge settling performance, the application of inorganic ballasting agents may considerably improve sludge settling characteristics. The application of CV-Z, which is used for the first time to solve sludge settleability problems, has demonstrated its ballasting properties in the solid/liquid separation of activated sludge. The tests performed with the poorly settled sludge present a faster settling and a decrease of the ζ even at the minimal CV-Z concentration used (1 g L^{-1}).

Besides its ballasting characteristics, the use of CV-Z has an added value, because this material can also remove nitrogen. At the minimal dose used to restore appropriate settleability (1 g L^{-1}), the total nitrogen content of the effluent water was reduced by 30%. The optimal dose to achieve a satisfactory economic and performance balance is probably not higher than 1 g of CV-Z per litre of sludge, which is an important consideration regarding sludge management and disposal. However, more tests should be conducted with a wider variety of sludge and additional experiments in continuous mode should be carried out to determine the optimum conditions more accurately.

Due to its high nitrogen absorption capability, the use of CV-Z may be appropriate even for well settled activated sludge which, has a high concentration of ammonium in the effluent water. However, zeolite treatment of the water effluent in packed beds may be more appropriate for ammonium removal than adding CV-Z directly to the activated sludge.

ACKNOWLEDGEMENTS

NOMENCLATURE

b	*Langmuir* isotherm constant
C_e	NH_4^+ equilibrium concentration, mg L^{-1}
C_0	NH_4^+ inlet concentration, mg L^{-1}
K	Freundlich isotherm constant, L g^{-1}
m	mass of solid (CV-Z), g
n	empirical constant in Freundlich isotherm
Q_0	Langmuir isotherm constant, mg g^{-1}
q_e	amount of NH_4^+ adsorbed per unit mass of solid (NH_4^+/CV-Z), mg g^{-1}
R	correlation coefficient
SVI	sludge volume index, mL g^{-1}
V_{60}	settling sludge volume after 60 min, mL
X	mass of ammonium adsorbed (mg)
ζ	Zeta potential, mV

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