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Ammonia removal from anaerobically treated piggery manure by ion exchange in columns packed with homoionic zeolite

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Abstract

Piggery manure digested in an anaerobic fixed bed reactor was treated by ion exchange for ammonia removal using potassic zeolite (K-Zeo), magnesic zeolite (Mg-Zeo), sodic zeolite (Na-Zeo) and calcic zeolite (Ca-Zeo). The best results were obtained with the use of Na-Zeo. The exchange K–NH_4 was affected by the low mobility of K in the zeolite structure. The exchanges Ca–NH_4 and Mg–NH_4 were affected by the high concentration of suspended solids and the viscosity of the influent, which led to a low mobility of these cations in the liquid phase. The effect of the flow rate was evaluated at bed heights of 6, 9, 18 and 27 cm for Na-Zeo. It was found that increasing the height improved the ammonia removal efficiency but the pressure drop was augmented. It was determined that the increase of the flow rate over 1.6 bed volumes per hour increased the dispersion coefficient and reduced the exchange capacity of the bed.

Keywords: Ammonia nitrogen removal; Ion exchange; Homoionic zeolite; Piggery manure

1. Introduction

The intensive use of the land for agriculture and animal breeding has led to an increase in the eutrophication of lakes, estuaries and rivers, and the contamination of underground water reservoirs, as a result of the presence of nitrogen, phosphorus and carbon compounds in effluents and run off, causing serious pollution problems that could directly affect human health. The continuous increase in the nutrient concentration in different sources of water has led to the introduction of strict regulations for the control of nitrogen and phosphorus disposal [1,2].

Many wastewater treatment systems do not allow the removal and recovery of nutrients, and final effluents are disposed of with nitrogen and phosphorus compounds [3–6]. Intensive aerobic treatment based on the utilization of activated sludge or oxidation ditch have the disadvantage that organic nitrogen is transformed to nitrate and a denitrification process is required with a considerable increase in the cost [7,8].

In contrast, anaerobic processes decompose organic nitrogen to ammonia, and orthophosphate is partially reduced [9–12]; these compounds could be further removed by the use of ion exchange. Kotter et al. [13] developed a system for ammonia nitrogen removal from wastewater, using natural zeolite. These authors obtained a maximum removal rate of 0.05 g NH_3 per gramme of zeolite. Mercier et al. [14] concluded that wastewater that contains high concentrations of ammonia in which biological nitrogen elimination would be too costly are more economically treated by ion exchange.

Sherman [15] presented a review of literature related to the use of the ion exchange process using natural and artificial zeolites for ammonia nitrogen removal from sewage, agricultural and industrial wastes, and concluded that ionic exchange is a very promising technology for ammonia nitrogen removal.

Jorgensen [16] studied the ion exchange process of two different wastes with zeolite-type clinoptilolite. He found that ion exchange was an attractive alternative to the nitrification–denitrification process; even the waste contains high concentrations of competitive ions such as calcium, magnesium and sodium.

Liberty and coworkers [17,18] studied the selective removal of phosphorus and nitrogen compounds from munic-

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ipal wastewater by ion exchange under different operational conditions, obtaining a considerable removal rate for both nutrients.

Borja and coworkers [19–21] demonstrated that the addition of natural zeolite to the anaerobic digestion process of cattle manure reduced the inhibitory effect of ammonia nitrogen accumulation caused by the organic nitrogen decomposition. These authors observed a reduction in the ammonia nitrogen concentration in the liquid phase, as a result of the ion exchange.

The results from the literature demonstrated the effect of ion exchange on anaerobically treated piggery waste using different homoionic zeolites, as well as the effects of the bed height and the volumetric flow rate.

2. Materials and methods

2.1. Characteristics of the waste

The piggery manure was transported to the laboratory in Havana, Cuba, from a nearby piggery farm and stored at 4 °C. The raw waste was prepared by adding the same proportion of water commonly used for piggery cleaning (20 l per kilogramme of manure).

The raw waste was screened using a 2 mm sieve to remove the coarse particles and the screened piggery manure was treated using an anaerobic fixed bed reactor (AFBR) operating at an organic volumetric loading rate with total chemical oxygen demand (COD) of 5 kg m^{-3} d^{-1}. The anaerobic effluent obtained was stored at 4 °C to be used in the ion exchange experiments.

The characteristics of the screened raw manure and the anaerobic effluent are summarized in Table 1.

Table 1
Characteristics of the screened manure and the effluent of the AFBR used in the experiment [a]

Parameter	Screened manure ($mg\ l^{-1}$)	Effluent of the AFBR ($mg\ l^{-1}$)
TCOD	12600	6350
TS	13900	8320
VS	9680	5580
TSS	4715	5910
VSS	4260	3300
PO_4^{-3}	800	115
Total phosphorus	1520	560
Ammonia nitrogen	540	600
Organic nitrogen	750	210
Alkalinity	6100	4330
pH	5.2	6.5

[a] Sample used in the experiment with less than 5% error.

2.2. Zeolite

The zeolite used in the experiments was obtained from the deposit at San Andres in the Province of Santiago de Cuba (see Table 2). This zeolite has been shown to be homoionic as follows: sodic (Na-Zeo), calcic (Ca-Zeo), potassic (K-Zeo) and magnesic (Mg-Zeo). All of these were transformed using stock samples of 100 g of zeolite with a particle size of 5 mm. The stock samples were treated with 1.6 l of 1.0 mol l^{-1} solutions of appropriate salts of cations (NaCl, $CaCl_2$, KCl and $MgCl_2$) at about 90 °C in a stirred vessel for about 2 h. This treatment was repeated twice to force the zeolite into the relevant homoionic form as far as possible. The samples treated in this way were washed with deionized water and subsequently dried at 50 °C [22].

Table 2
Chemical and phase compositions of natural zeolite

Chemical composition (%)		Phase composition (%)	
SiO_2	63.2	Clinoptilolite	40
Al_2O_3	12.45	Mordenite	35
Fe_2O_3	0.81	Montmorillonite	–
MgO	0.69	Others [b]	25
CaO	2.36		
Na_2O	1.2		
K_2O	2.31		
IW [a]	15.5		
Total	98.54		

[a] IW, ignition wastes.

[b] Others: calcite, feldespate and quartz.

2.3. Experimental procedure

Three experiments were carried out. In the first experiment, the performances of the different homoionic zeolites were compared to determine the zeolite with the best efficiency. For this experiment, four glass columns of internal diameter 3.26 cm and height 15 cm were employed. Each column was loaded with 91.7 g of homoionic zeolite with a Reynolds number in the range 0.128–0.319, depending on the particle size. The beds had a height of 11.5 cm and a volume of 96 cm^3. The waste was pumped in the upflow mode at a volumetric flow rate of 3.2 ml min^{-1}, which is equivalent to 2 bed volumes (BV) per hour, and a surface hydraulic loading of 5.5 m^3 m^{-2} d^{-1}. The experiment had a duration of 30 h and was carried out three times under the same conditions.

In the second experiment, the effects of the bed height on the ammonia nitrogen removal and on the pressure drop were studied using glass columns of internal diameter 4.53 cm and height 30 cm working in parallel. For this investigation, bed heights of 6 cm (column A), 9 cm (column B), 18 cm (column C) and 27 cm (column D) were evaluated at different volumetric upflow rates, surface hydraulic loadings and relative volumetric flow rates. Table 3 summarizes the operational conditions for each bed.

In the third experiment, the effect of the surface hydraulic loading on the flow pattern of the bed was evaluated at a bed height of 18 cm, using sodic zeolite, volumetric upflow rates

Table 3
Operational conditions at different bed heights

Volumetric flow ($ml\ h^{-1}$)	Surface hydraulic loading ($m^3\ m^{-2}\ d^{-1}$)	Relative volumetric flow rate ($BV\ h^{-1}$)			
		$h=6$ cm [a]	$h=9$ cm [a]	$h=18$ cm [a]	$h=27$ cm [a]
162	2.4	1.7	1.1	0.6	0.4
228	3.4	2.4	1.6	0.8	0.5
468	7.0	4.9	3.2	1.6	1.1
564	8.3	5.9	3.9	2.0	1.3
672	10.0	7.1	4.6	2.3	1.5
762	11.4	8.0	2.2	2.6	1.7
900	13.4	9.4	6.2	3.1	2.1

[a] *h*, bed height.

in the range 0.6–7.0 ml min^{-1} and relative volumetric flow rates in the range 2.7–15 BV h^{-1}.

2.4. Measurements and analytical techniques

In the first and second experiments, triplicate samples of effluents were taken each hour to determine the total COD, ammonia nitrogen, orthophosphate and pH by standard methods [23], and the pressure drop was determined using a mercury manometer.

In the third experiment, a saturated solution of ammonium chloride in water at 25 °C was used as a tracer in a column of exhausted sodic zeolite, and the system response was measured by determining the electrical conductivity in the effluents [23,24]. This experiment was carried out three times. All the experiments were carried out at a temperature in the range 30–35 °C.

3. Results and discussion

3.1. Comparison of homoionic zeolites

Table 4 reports the ionic composition of the samples of Na-Zeo, K-Zeo, Ca-Zeo, Mg-Zeo and untreated zeolite. The reported data clearly show that Na^+ and K^+ are selectively exchanged in this type of zeolite (San Andres deposit); i.e. the cationic composition of Na-Zeo involves 80% of Na^+, while it was 84% of K^+ for K-Zeo. For the bivalent cations Ca^{2+} and Mg^{2+}, the degree of exchange is lower at 50% of Ca^{2+} in Ca-Zeo and 70% of Mg^{2+} in Mg-Zeo, which agrees with the selectivity rules for ionic exchange in clinoptilolite zeolites [25].

Fig. 1 shows the concentration of ammonia nitrogen in the effluent as a function of the amount of waste treated, given in bed volumes (BV) for the different homoionic zeolites studied at an initial ammonia nitrogen concentration of 600 mg l^{-1}. As could be expected, the behaviour of the columns differed depending on the type of zeolite employed.

For 20 BV of waste treated (hour 10 of operation), the values of the efficiency of ammonia nitrogen removal were as follows: Na-Zeo, 91%; Ca-Zeo, 75%; K-Zeo, 62%; Mg-Zeo, 43.3%. This indicates significantly higher removal in the Na-Zeo bed.

For 40 BV of waste treated (hour 20 of operation), the removal efficiencies were 58.3% for Na-Zeo, 36.7% for Ca-Zeo, 33.3% for K-Zeo and 18.3% for Mg-Zeo, indicating that the efficiency of ammonia nitrogen removal of the bed packed with sodium zeolite was still considerable. For 60 BV of waste treated (30 h of operation), the removal efficiency of the Na-Zeo remained around 58%, that in the Ca-Zeo was around 45%, that in the K-Zeo was 25% and that in the Mg-Zeo was only 16.7%.

Obviously, the column packed with the homoionic sodic zeolite exhibited the best behaviour compared with the others. According to the experimental results obtained, the exchange capacity was in the order

$$Na-Zeo > Ca-Zeo > K-Zeo > Mg-Zeo$$

Jama and Yücel [22] have pointed out that K has a poor exchange capacity because this cation is located on the site of the crystalline structure of the zeolite with a very low mobility, where it is coordinated with six framework oxygen atoms and three molecules of water. Two sites are occupied by Na and Ca, with one coordinated by two framework oxygen atoms and five water molecules, and the other coordinated by three oxygen and five water molecules.

In the case of magnesium, this cation is located in a site coordinated by six water molecules, which theoretically give this cation a great facility for exchange. However, Mg and Ca exhibited lower mobility than Na in solution, because of

Table 4
Cationic composition of homoionic zeolites [a]

Sample	Na^+	Ca^{2+}	K^+	Mg^{2+}
Natural	4.6	16	15.6	8.5
Na-Zeo	36.8	2.0	11.7	–
Ca-Zeo	4.6	20	11.7	6.0
K-Zeo	4.6	–	66.4	1.2
Mg-Zeo	2.3	4.0	11.7	17.0

[a] The cationic composition is expressed in milligrammes of cation per gramme of zeolite.

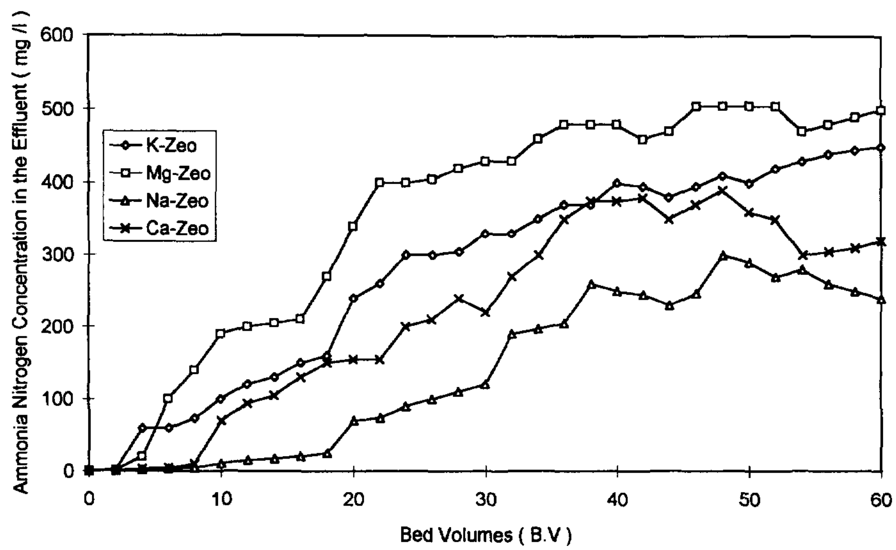

Fig. 1. Ammonia nitrogen concentration in the effluent as a function of the volumes of waste treated for different homoionic zeolites. Influent concentration, 600 mg l^{-1} N-NH$_4$.

the high concentration of suspended solids and viscosity of the waste, and because of the competition that Ca and Mg present in the liquid phase [16]. The total COD and orthophosphate concentration decreased with the ionic exchange, and maximum removal efficiencies in the ranges 15%–25% and 20%–35%, respectively, were obtained. However, differences among the homoionic zeolites studied could not be established with respect to the COD and orthophosphate.

Homoionic zeolites were found to have a buffer function and the effluent pH increased following treatment to values of 7.8, 7.6, 8.0 and 7.8 for K-Zeo, Mg-Zeo, Na-Zeo and Ca-Zeo respectively. It could be observed that the pH value appears to be a function of the amount of ammonia nitrogen removed and, consequently, of the amount of cation exchanged.

On considering the results obtained, the second experiment was carried out with sodium homoionic zeolite.

3.2. Effect of the flow rate and the bed height on the ammonia nitrogen removal

Fig. 2 presents the results at a bed height of 6 cm and with different hydraulic loadings applied. A typical exponential relationship appears to exist between the ammonia nitrogen concentration in the effluent and the volume of wastewater treated for different flow rates. The breakthrough curves

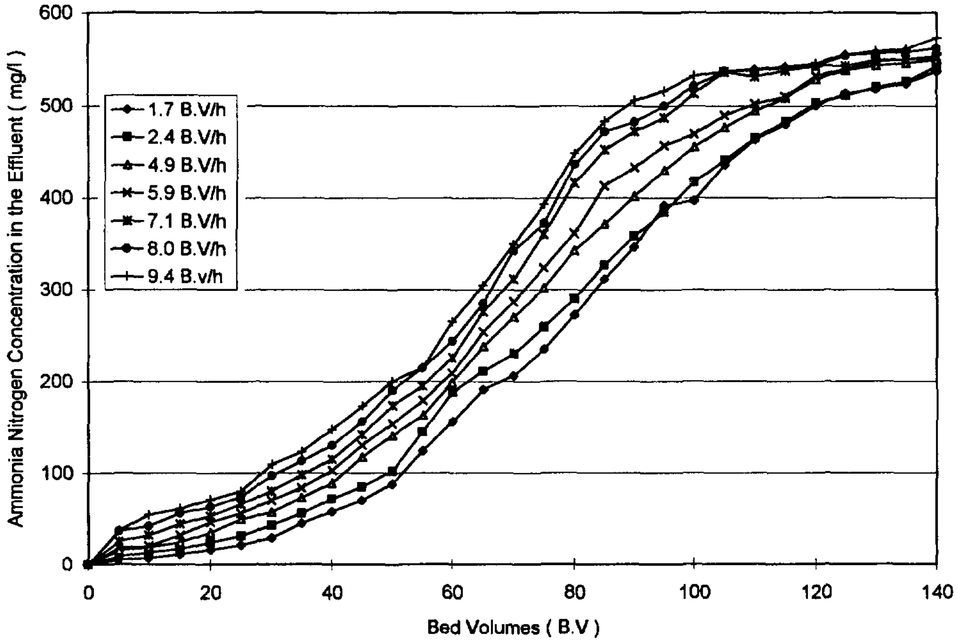

Fig. 2. Typical curves of ammonia nitrogen concentration in the effluent of column A (bed height, 6 cm) as a function of the volumes of waste treated for different relative volumetric flow rates. Influent concentration, 600 mg l^{-1}.

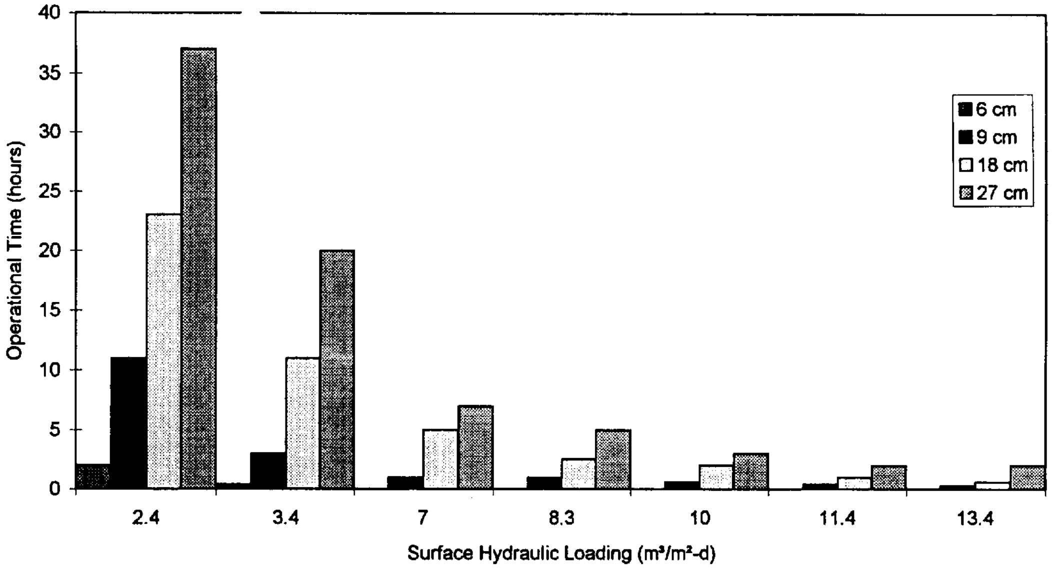

Fig. 3. Effect of the surface hydraulic loading rate on the operational time of the columns for different bed heights and an effluent ammonia nitrogen concentration of 2 mg l^{-1}.

obtained could be divided into three zones. There is an initial zone, where the ammonia concentration in the effluent was very low and increased slightly for BV < 40; an intermediate zone, where the ammonia nitrogen concentration in the effluent rapidly increased in the range 40–100 BV; and a final zone where the effluent concentration again slowly increased in line with the influent concentration for BV in the range 100–140.

The increase in the hydraulic loading rate determined the shape of the breakthrough curves, as can be seen in Fig. 2. At 40 BV, the highest ammonia concentration in the effluent corresponded to the maximum hydraulic loading rate applied. These results coincide with the reports of other authors [26,27], who claim that the shapes of the breakthrough curves depend on the flow rate.

The results obtained at bed heights of 9, 18 and 27 cm were similar to the results observed at 6 cm with similar hydraulic loading rates applied. Furthermore, the increase in bed height led to a reduction in the slope of the curves, which means higher removal efficiency as a result of the larger amount of zeolite in the columns.

Fig. 3 gives the operational capacities at different bed heights as a function of the surface hydraulic loading, to obtain an effluent with 2 mg l^{-1} of ammonia nitrogen (recommended value for final disposal). The figure shows that, at a bed height of 6 cm, the final disposal concentration could be obtained only at the minimum surface hydraulic loading during 3 h of operation; at a bed height of 9 cm, this was during 10 h of operation; and, at bed heights of 18 cm and 27 cm, this was during more than 20 h of operation.

Table 5
Results of the hydraulic tests [a]

Flow rate (ml min^{-1})	BV h^{-1}	D μl^{-1}	Linear velocity (cm min^{-1})	Re	Sh
0.6	2.7	0.09	3.06	0.09	0.148
0.8	3.8	0.10	4.31	0.13	0.150
1.2	7.8	0.13	8.84	0.15	0.152
2.0	9.4	0.20	10.66	0.16	0.153
4.0	11.2	0.26	12.69	0.40	0.162
6.0	12.7	0.34	14.39	0.61	0.167
7.0	15	0.45	17.00	0.71	0.170

[a] Mean values of three samples with less than 10% of error.

The results obtained show that an increase in the bed height led to an improvement in the ammonia nitrogen removal efficiency, probably as a result of greater removal of suspended solids which could affect the ion exchange. This fact could be demonstrated when ion exchange was carried out with filtrated and non-filtrated samples of wastewater with ammonia nitrogen concentrations of 420 mg l^{-1} and 456 mg l^{-1}, respectively, under the same operational conditions and for a removal efficiency of 90%. In the first case, the bed treated 2.66 l, while the bed lost its capacity when 0.54 l of influent were treated in the second case.

The increase in bed height had a marked effect in a better contact between the wastewater and ion exchanger, reducing the short circuiting which led to the improvement in the ammonia nitrogen removal efficiency.

A reduction in the relative volumetric flow rate also contributed to increasing the ammonia nitrogen removal efficiency. At low values of the Sherwood number (Sh), the adsorption and the ion exchange mechanisms are improved (see Table 5) [28].

The increase in bed height combined with a reduction in the relative volumetric flow rate gave the best results of ammonia nitrogen removal, but also led to the use of a greater volume of column, so increasing the cost of the process.

4. Effect of the bed height and the hydraulic loading on the pressure drop

The results obtained (Fig. 4) show an increase in the pressure drop with increasing bed height. The pressure drop was

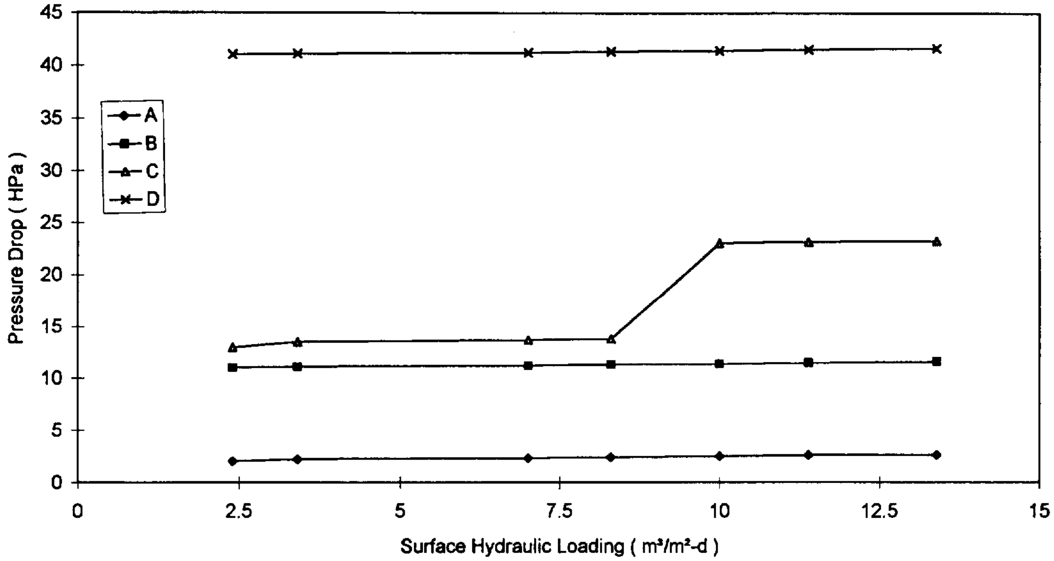

Fig. 4. Effect of the surface hydraulic loading rate and the bed height on the pressure drop.

about 2.0–2.6 hPa for a bed height of 6 cm, 11.0–11.6 hPa for a bed height of 9 cm, 13.0–23.2 hPa for a bed height of 18 cm and about 41.0–41.6 hPa for a bed height of 27 cm.

The increase in the surface hydraulic loading did not have an important effect on the pressure drop for the range of surface hydraulic loadings studied. However, at a bed height of 18 cm, the pressure drop abruptly increased for a hydraulic loading rate higher than 8.3 m^3 m^{-2} d^{-1}. This behaviour could probably be determined by short circuiting problems at values in the range 2.4–8.3 m^3 m^{-2} d^{-1}, because these conditions resulted in a very low increase in the pressure drop being observed when the bed height changed from 9 to 18 cm.

The best operational conditions were obtained for surface hydraulic loadings of up to 9 m^3 m^{-2} d^{-1} and bed heights of 9 and 18 cm (columns B and C respectively), which correspond to height:diameter ratios of 2 and 4 respectively. This meant that the pressure drops were lower than at a the height of 27 cm, leading to a reduction in the operational costs.

4.1. Hydraulic tests

Table 5 gives the results of the hydraulic tests for a bed height of 18 cm with increasing relative volumetric flow rates of 2.7–15 BV h^{-1}. The results show a laminar behaviour of the system, which operated as a plug-flow reactor with a dispersion number up to 0.2 for relative volumetric flow rates in the range 2.7–9.4 BV h^{-1}.

The values of Re remained in the range 0.09–0.15, which is favourable for ion exchange. The increase in the relative volumetric flow rate to values higher than 11.2 BV h^{-1} produced a significant increase in the dispersion coefficient that made the cationic exchange more difficult.

5. Conclusions

According to the experimental results obtained, sodium homoionic zeolite, followed by calcium homoionic zeolite, gave the best results for the removal of ammonia nitrogen in the treatment of anaerobically pretreated piggery manure.

An increase in the bed height combined with a decrease in the relative flow rate represented the most effective combination to obtain the highest ammonia nitrogen removal, but the hydraulic conditions of the process and the economical aspects must be considered.

Therefore, more appropriate operational conditions would be a bed height of 18 cm ($H/D=4$) and a relative flow rate of less than 7.8 BV h^{-1}.

The ion exchange was affected by the high concentration of suspended solids of the waste, mainly in the case of Mg-Zeo. Further experiments must be carried out to reduce the concentration of suspended solids of the influent, so increasing the exchange capacity of the system at high volumetric flow rates.

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