Ammonium recovery by ion exchange from effluents of anaerobic blackwater co-digestion and struvite precipitation reactors

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Abstract

In the field of resource-oriented sanitation systems, blackwater digestion has proven to be suitable for biogas production. As blackwater accounts for the majority of nitrogen and phosphorous in municipal wastewater, this study aims to investigate the potential for ammonium recovery from the effluent from blackwater digestors as well as struvite precipitation stages via sorption by clinoptilolite preceding desorption from the loaded clinoptilolite through ion exchange using either sodium chlorine or sodium sulphate solutions. It was established that the ratio between sodium ions in the regeneration solution and ammonium adsorbed had a significant effect on the ammonium recovery efficiency. Moreover both the regeneration solutions showed similar results. By increasing the ratio sodium ions to ammonium ions, a recovery efficiency of up to 98% was observed. The high recovery efficiencies from co-digested blackwater favours both ammonium recycling as fertilizer and energy balance in the wastewater treatment plant as aeration costs for the nitrification can be reduced.

Keywords

Sodium chlorine, sodium sulphate, clinoptilolite, nutrient recovery, source separated wastewater

INTRODUCTION

The aim of resource-oriented sanitation systems is to utilise the energy and nutrient content of wastewater (WW), thus closing nutrient and energy loops. The anaerobic treatment of blackwater may increase the energy yield of a municipal wastewater treatment plant (WWTP); however, remaining sludge liquors contain high nitrogen and phosphorus loads, which originate from the degradation of organic matter and may negatively shift the C:N ratio for denitrification. Therefore, ammonium and phosphorus recovery from sludge liquors arises as an alternative for reducing this effect, while enabling nutrient reuse as fertilizer and contributing to better energy efficiency of WWTPs, since biological nutrient removal in activated sludge tanks can be minimised. With regard to phosphorus recovery, struvite precipitation (Magnesium Ammonium Phosphate, MAP) has been suggested by many authors (Antakyali *et al.* 2013, Stolzenburg *et al.* 2015); however, most of the nitrogen load is not removed in form of struvite and therefore remains in effluents of MAP reactors. It is well-known that clinoptilolite is an excellent inorganic ion exchanger, as it consists of a three-dimensional lattice structure formed by AlO_4 and SiO_4 tetrahedra, both linked by a shared oxygen atom. These microporous arrangements form interconnected cages and channels wide enough to comprise water molecules and alkali ions (Englert and Rubio 2005). The ability of clinoptiliolite to exchange cations comes from the substitution of Al^{4+} by Si^{3+}, creating a negative charge, which has to be compensated by exchangeable cations such as Na^+, K^+, Ca^{2+} and Mg^{2+} (Weatherley and Miladinovic 2004). Beside alkali ions ammonium ions are also likely to be absorbed by clinoptilolite due to load balance (Alshameri *et al.* 2014a). According to Mazloomi and Jalali (2016) ammonium uptake is affected negatively by the presence of cations and anions following the order of preference $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ and $Cl^- > PO_4^{3-} > SO_4^{2-}$. Apart from these results the stability of clinoptilolite is questionable due to heavy metal adsorption, which is likely to limit its adsorption capacity permanently (Huang *et al.* 2015). Considerable research has been conducted with regard to characterising the properties of clinoptilolite with the aid of a binary ammonium competing ion system, where mainly the influences of temperature, pH and contact time were studied (Tosun 2012, Vassileva and Voikova 2009, Wang *et al.* 2007, Widiastuti *et al.* 2011). However, comparison of the literature data showed high variability due to the different clinoptilolite origins, although Malekian *et al.* (2011) reported an increase in performance with decreasing particle size for Iranian natural zeolite, which can be ascribed to shorter diffusion paths. Furthermore, removal of ammonium from municipal wastewater (Sarioglu 2005), landfill leachate (Halim *et al.* 2010, Karadag *et al.* 2008) and aquacultural production (Gendel and Lahav 2013, Zhou and Boyd 2014) have been thoroughly investigated in the literature.

As soon as the exchange capability for ammonium was exhausted, clinoptilolite was proposed to be used as a slow-release fertilizer in agriculture (Cyrus and Reddy 2011) or regenerated by using sodium chlorine, sodium carbonate, sodium bicarbonate and sodium hydroxide solutions (Du *et al.* 2005, Guaya *et al.* 2015, Karadag *et al.* 2008, Zhang *et al.* 2016).

Moreover, further regeneration practices have been investigated, such as chlorination by Huang *et al.* (2015), electrochemical chlorination by Gendel and Lahav (2013), acid treatment with HCl by Bolan *et al.* (2003) and simultaneous nitrification by immobilized bacteria in filter columns (Miladinovic and Weatherley 2008).

Nevertheless, in none of the considered methods was recovery of ammonium possible. Using the loaded clinoptilolite as slow-release fertiliser would require direct application onto the soil, making a recovery for reuse extremely complex. Further regeneration such as chlorination converts ammonium to nitrogen gas, which cannot be used as fertiliser, while acid treatment produces a solution with very low pH. In the case of the simultaneous nitrification by immobilized bacteria in filter columns ammonium is converted to nitrate, which is also a good fertiliser, but removes the benefit of a sole chemo-physical process.

From a review of literature, it is clear that sorption of ammonium on clinoptilolite is dependent upon different external factors e.g. initial concentration of ammonium, competing ions in the wastewater, contact time and particle size.

Ammonium desorption is a deeply studied process, but has mostly been in the context of ammonium regeneration in columns using fixed concentrations of sodium brine. Therefore, conclusions regarding the required ratio of exchange loaded ammonium ions to sodium ions cannot be drawn. Desorption from small particles has not been investigated thus far.

Therefore one of the primary goals of this study was to determine the ammonium load on small clinoptilolite particles from ammonium rich wastewaters with both low (effluent from co-digested blackwater) and high concentrations (effluent form a MAP reactor) of ammonium and competing ions as well as the relationship to contact time. Desorption from the loaded clinoptilolite with regard to sodium concentration and contact time was also investigated.

MATERIALS AND METHODS

Zeolite

The zeolite used as adsorbent for this study was purchased from Labradorit GmbH in Germany. It has a purity of > 90% clinoptilolite with traces of cristobalite, feldspar, mica, edisonite and quartz and was grinded to a particle size of <20 µm by the manufacturer. The mineralogical and chemical composition of the zeolite were provided by the manufacturer and are given in Table 1.

Table 1: Chemical composition (main parameters) in wt. % of the zeolite used in this study

SiO_2 [%]	Al_2O_3 [%]	K_2O [%]	CaO [%]	Fe_2O_3 [%]	MgO [%]	Na_2O [%]	TiO_2 [%]	Si/Al [-]
69,30 - 71,31	11,51 - 13,06	2,56 - 3,15	2,91 - 3,58	0,70 - 1,90	0,59 - 1,20	0,20 - 1,13	0,10 - 0,28	4,80 - 5,40

Filtrated effluents

For the investigations two different types of ammonium-rich WW where investigated: firstly effluents from a pilot-scale anaerobic CSTR reactor (effective volume: 630 L), operated with a mixture of primary and secondary sludge as well as blackwater, and secondly effluent from a MAP reactor which is rich in Magnesium and Sodium-ions, too.

Within the MAP reactor, sludge liquors had been processed for mainly phosphate recovery as struvite. Apart from minor amounts of ammonium precipitated as MAP, high concentrations of ammonium in the supernatant enabled further zeolite treatment.

The effluents were centrifuged (15 min at 4,000 rpm) and filtered by GE (597 ½), while the pH level was adjusted to 6 by addition of hydrochloric acid (1 M).

Additionally a synthetic ammonium solution was prepared from dried ammonium chloride dissolved in bi-distilled water without pH adjustment for reference analysis.

Table 2: Composition of used filtrated effluents (after pH adjustment)

	COD*	COD_{mf}	NH_4-N	TN_b	P_{tot}	PO_4-P	K^+	Na^+	Mg^{2+}	Ca^{2+}
					[mg L^{-1}]					
NH_4Cl	-	-	1077	-	-	-	-	-	-	-
CSTR	890 - 1512	370 - 1060	542 - 575	683 - 1020	49 - 197	19 - 49	204 - 255	280 - 285	25.3 - 38.5	109 - 119
MAP	5420	5400	1380	1447	1,24	-	167	2561	512	527

*filtered sample

Sorption

For sorption experiments (n = 8) equal volumes (200 mL) of each effluent were admixed with varying weight of dried unloaded clinoptilolite and stirred at 400 rpm under exclusion of air. After a contact time of 20 h clinoptilolite was removed by means of filters from GE (597 ½), so that ammonium was measured according to DIN 38406 (1983).

To determine of the required contact time 1.5 L of the different effluents were brought into contact with a specific dosage of clinoptilolite per mg ammonium (g/mg) and stirred. Samples of 10 mL were taken after different contact times (5 – 180 min) with a syringe and filtered using syringe nylon membrane filters with a pore size of 0.45 µm to interrupt the adsorption process. After filtration, the ammonium was measured.

Desorption

For desorption experiments, 2 g of dried and loaded clinoptilolite (Table 3) were admixed with various weighted amounts of solid sodium chlorine (n = 12) or sodium sulphate (n = 12) and 200 mL of distilled water. The amount of sodium varied in accordance with the ratio of Na^+ ions in solution to adsorbed NH_4^+ on clinoptilolite. After stirring at 400 rpm for the desired contact time, clinoptilolite was removed by the means of filters from GE (597 ½), thereby the ammonium was measured.

To determine the required contact time, a specific ratio of Na^+ ions to NH_4^+ ions loaded on the clinoptilolite of 30:1 was admixed with distilled water, loaded clinoptilolite and stirred. At varying contact times (5 – 180 min) 10 mL samples were taken by a syringe and filtered using syringe nylon membrane filters with a pore size of 0.45 µm to interrupt the desorption process. After filtration, the ammonium was measured.

Table 3: Provenance of ammonium and load of the clinoptilolite used in desorption experiments

Provenance	Ammonium load [mg g^{-1}]
NH_4Cl solution	14.6
CSTR effluent	9.8

MAP effluent	10.2

Calculations

The ammonium uptake at equilibrium state, q_{eq} [mg NH_4-N/g], onto clinoptilolite was calculated according to equation 1 where c_0 [mg/L] is the initial ammonia concentration, c_{eq} [mg/L] is the ammonia concentration in the filtered liquid phase at equilibrium state, V [L] is the batch volume and m [g] is the mass of clinoptilolite.

$$q_{eq} = \frac{(c_0 - c_{eq})V}{m} \tag{1}$$

To describe the data obtained from the Langmuir model, c_{eq}/q_{eq} vs. c_{eq} was plotted, where q_{eq} is the ammonia load at equilibrium, as basis for calculations of maximum uptake q_{max} [mg/L] and Langmuir constant K_L [L/ mg NH_4-N] according to equation (2).

$$\frac{c_{eq}}{q_{eq}} = \frac{1}{K_L q_{max}} + \frac{c_{eq}}{q_{max}} \tag{2}$$

The Langmuir constant K_L can be used to provide a testament to the affinity of the adsorbens and adsorbent, using equation (3) to calculate the dimensionless factor R_L.

$$R_L = \frac{1}{1 + K_L c_0} \tag{3}$$

There are four possibilities for R_L, illustrating the different affinities: $0<R_L<1$ for favourable adsorption, $R_L > 1$ for unfavourable adsorption, $R_L=1$ for linear adsorption and $R_L = 0$ for irreversible adsorption (Sun *et al.* 2013).

Due to reports from many authors stating that a pseudo-second-order model is suitable for describing adsorption kinetics of ammonium on clinoptilolite, calculations were undertaken using equation (4) (Alshameri *et al.* 2014a, Zhang *et al.* 2016).

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{4}$$

RESULTS AND DISCUSSION

Sorption isotherms

As shown in Figure 1, a similar decline in ammonium loading was achieved for all three solutions by increasing the dosage of g clinoptilolite per mg ammonium. With smaller zeolite dosages, loads close to 12 mg Ammonium per g clinoptilolite were reported, whereas higher clinoptilolite dosages yielded 2 mg g^{-1} ammonium loading (only CSTR effluent). At similar loadings, it can be inferred from that clinoptilolite loading is independent of the initial ammonium concentration, which contradicts reports made by Widiastuti *et al.* (2011), who stated that high ammonium concentrations in NH_4Cl-solution favour ammonium uptake on clinoptilolite.

In addition, similar ammonium loadings at equal clinoptilolite dosages were achieved with a synthetic ammonium chloride solution, while a slight difference between ammonium adsorption from the CSTR and MAP effluents was observed. This effect might be attributed to the presence of different ions dissolved in the effluent, particularly sodium and potassium (Table 2).

The fitted plots for the Langmuir model are represented in Figure 2 for the investigated effluents, while the corresponding parameters from the model are given in Table 4.

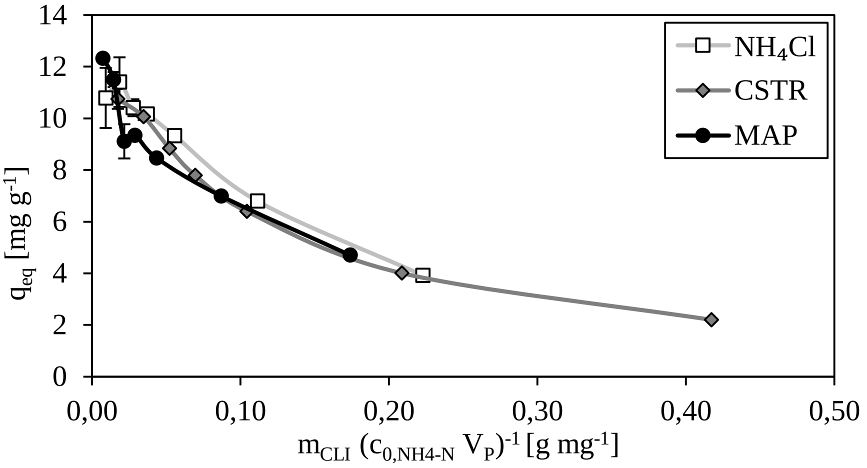

Figure 1: Equilibrium data for ammonium adsorbed on clinoptilolite from different effluents (MAP, c0 = 1380 mg/L; CSTR, c0 = 575 mg/L; NH4Cl, c0 = 1077 mg/L; every dot represents n = 3)

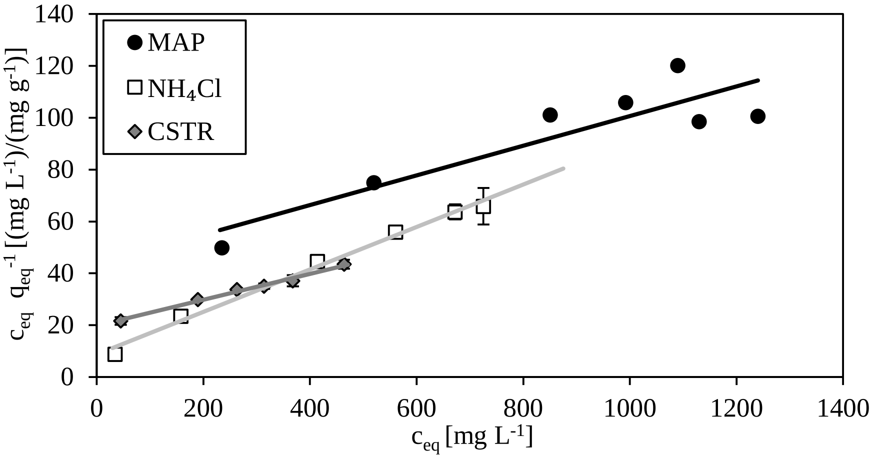

Figure 2: Langmuir plots for investigated effluents (MAP, c_0 = 1380 mg/L; CSTR, c_0 = 575 mg/L; NH4Cl, c_0 = 1077 mg/L; every dot represents n = 3)

Table 4: Constants for the Langmuir isotherm model and separation factor R_L for the investigated effluents

	Unit	NH_4Cl	MAP	CSTR
K_L	L mg NH_4-N^{-1}	0.0097	0.0013	0.0027
q_{max}	mg NH_4-N g^{-1}	12.18	17.41	19.48
r^2	-	0.977	0.783	0.977
R_L	-	0.087	0.353	0.396

The q_{max} values of the different effluents indicate a good adsorption of ammonium on clinoptilolite. Although MAP effluent has an ammonium concentration which is 2.4 times higher than of CSTR effluent, the difference in q_{max} appears to be minimal, whereas synthetic ammonium chloride solution, gave a 1.9 times higher ammonium concentration as compared to CSTR effluent yet achieved a smaller q_{max}. According to the Langmuir plot, the theoretical maximum adsorption of ammonium from synthetic NH_4Cl solution was 12.41 mg/g, however 17.41 mg/g and 19.48 mg/g were observed from the MAP and CSTR effluents respectively, indicating that either fewer competing ions in the effluents caused favourable ammonium uptake on clinoptilolite or uptake is supported by other chemical compounds found in the effluent of the CSTR but not in the MAP.

Furthermore, all the separation factors, R_L, of the examined effluents indicated a favourable sorption process of ammonium on clinoptilolite. The low separation factor for NH_4Cl causes a low desorption to be predicted whereas the separation factors for MAP and CSTR forecast that ammonium will desorb more easily.

The results fit well with the Langmuir isotherm sorption model furthermore the low separation factors, R_L, indicate a favourable sorption process of ammonium from the investigated effluents on clinoptilolite, despite competitive ions. It is indicated by both the parameters, q_{max} and K_L, that small particle clinoptilolite is a good adsorbent for ammonium from CSTR and MAP effluent.

Sorption kinetics

A kinetic study was conducted with a definite clinoptilolite ammonium ratio of 0.1 g mg^{-1} for MAP and NH_4Cl and 0.12 g mg^{-1} for CSTR (due to changed external boundaries) respectively.

According to Figure 3, a steady state was achieved after 60 minutes of contact time for NH4Cl and CSTR, while ammonium from MAP adsorbed even more rapidly. Within the first 5 minutes clinoptilolite adsorbed 50 % of ammonium from MAP, while 29 % from NH_4Cl and 32 % from CSTR were adsorbed in the same period. Before achieving a steady state a rapid increase of sorption can be reported for NH_4Cl and CSTR whereas MAP shows an almost linear increase with a small gradient.

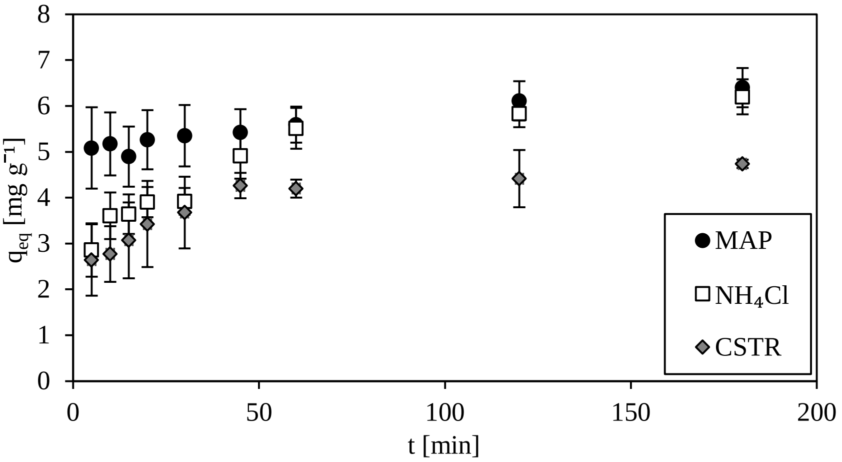

Figure 3: Ammonium load on clinoptilolite for investigated effluents (MAP, c_0 = 1380 mg/L; CSTR, c_0 = 542 mg/L; NH4Cl, c_0 = 1077 mg/L; every dot represents n = 3)

After contact time of 120 and 180 minutes a slight adsorption increase of 3 % and 7 % for NH_4Cl and CSTR was achieved, conversely MAP achieved a greater adsorption of 5 % and 8 %. Results by Huang *et al.* (2015) state an equilibrium after a contact time of 120 minutes for sorption from simulated swine wastewater on clinoptilolite.

MAP effluent reported faster adsorption in comparison to CSTR effluent. Although the sorption process quickly reaches the steady state (Figure 3), composition of the effluents in terms of competing ions and initial ammonium concentration is responsible for different adsorption speeds.

The results show that the kinetic of ammonium sorption is modelled well by a pseudo-second-order model, as demonstrated by a high correlation factor in Figure 4. Therefore it can be concluded that the kinetic model is suitable although varying concentration of competing ions in the investigated effluents are found.

Several authors reported pseudo-second-order models have good correspondence with sorption kinetics from leachate (Alshameri *et al.* 2014b), simulated swine wastewater (Huang *et al.* 2015), greywater (Widiastuti *et al.* 2011) and from sorbate solution in the presence of organic acids (Mazloomi and Jalali 2016).

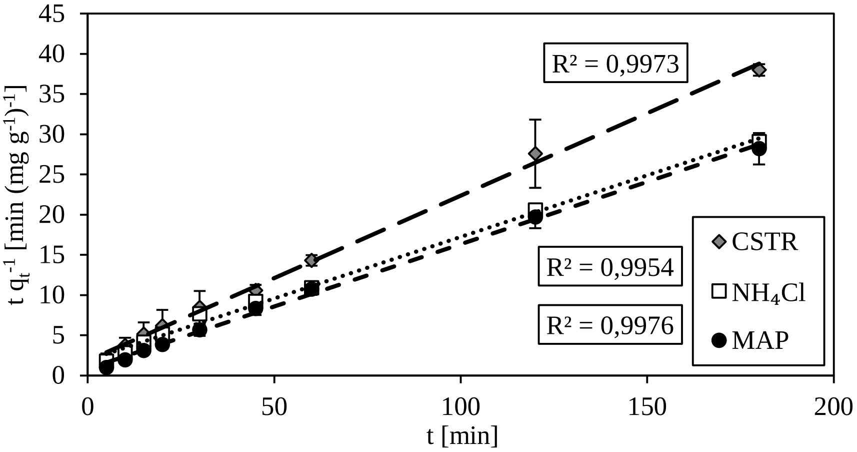

Figure 4: Pseudo second order model for investigated effluents (MAP, c_0 = 1380 mg/L; CSTR, c_0 = 542 mg/L; NH4Cl, c_0 = 1077 mg/L; every dot represents n = 3)

Desorption isotherms

As shown in Figure 5, a ratio of 30:1 of sodium to ammonium ions gave a regeneration of approximately 75 %, while a slightly higher regeneration of 77 % was observed for sodium from NaCl. The highest regeneration performance was achieved by ammonium from MAP loaded clinoptilolite with 96 %, while at the same ratio of 100:1, CSTR loaded clinoptilolite achieved 88 %. Error bars in the graph indicate a small variation of the results due to measurement errors. It can be concluded that neither clinoptilolite loading nor the provenance of the loaded ammonium affected regeneration efficiency.

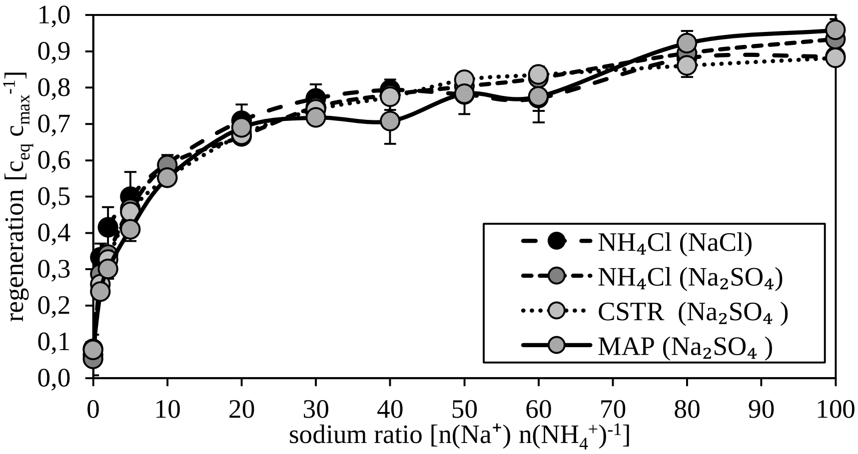

Figure 5: Regeneration of loaded clinoptilolite with different ratios of sodium per ammonium ions (every dot represents n = 3)

In addition, pH decreased from 7 to 6.5 with sodium ratio increase, eliminating the possibility of ammonium loss due to ammonia evaporation at high pH values. The pH shift was attributed to the sodium sulphate and sodium chloride dosage, which triggered an acidic pH when dissolved in water as well as uptake of H^+ ions by the clinoptilolite (Du *et al.* 2005).

Application of the Langmuir equation resulted in data given in Table 5. As mentioned in Table 4, the different separation factors, $R_{L,}$ of the sorption experiments showed a high affinity of ammonium from NH_4Cl to clinoptilolite, leading to less regeneration to occur at a relatively high q_{remain} compared to the regeneration of clinoptilolite loaded with ammonium from MAP or CSTR effluents.

Table 5: Constants for Langmuir isotherm model for the investigated effluents

Provenance (regeneration by)	Unit	NH_4Cl (NaCl)	NH_4Cl (Na_2SO_4)	MAP (Na_2SO_4)	CSTR (Na_2SO_4)
K_L	L mg NH4-N^{-1}	-0.022	-0.025	-0.032	-0.040
q_{remain}	mg NH4-N g^{-1}	1.52	1.52	0.81	1.19
r^2	-	0.6734	0.5655	0.4971	0.7558

Desorption kinetics

Desorption kinetics of ammonium from loaded clinoptilolite were undertaken with a fixed sodium to ammonia ratio of 30:1. The results of the desorption experiments can be found in Figure 6, where the ratio of dissolved ammonium, c_{eq}, to maximum ammonium concentration, c_{max}, is plotted against the contact time of the clinoptilolite with the sodium sulphate solution.

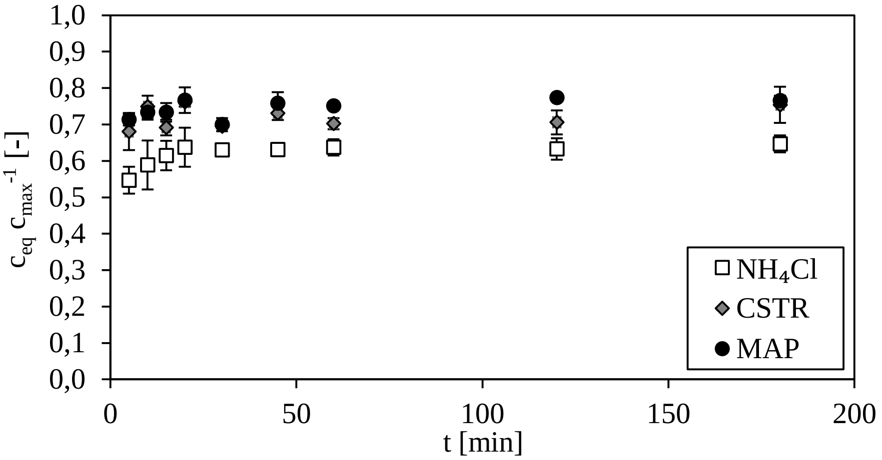

Figure 6: Equilibrium concentration of desorbed ammonium from loaded clinoptilolite in relation to desorption time (every dot represents n = 3)

All approaches showed that within the first 5 minutes that more than 50 % (NH_4Cl) to 70 % (CSTR, MAP) was desorbed (Figure 6). Although the initial loads were diverse for MAP and CSTR, a similar desorption behaviour was measured. The desorption equilibrium can be achieved for MAP and CSTR within 10 minutes of contact time while it takes 15 minutes for NH_4Cl. Finally, MAP and CSTR reach a similar desorption of 77 and 75 % after 180 minutes, whereas for NH_4Cl merely 65 % could be obtained. It is striking that the regeneration performance of NH_4Cl loaded clinoptilolite proved poor when compared to clinoptilolite loaded with ammonia from the effluents from the CSTR or MAP stage.

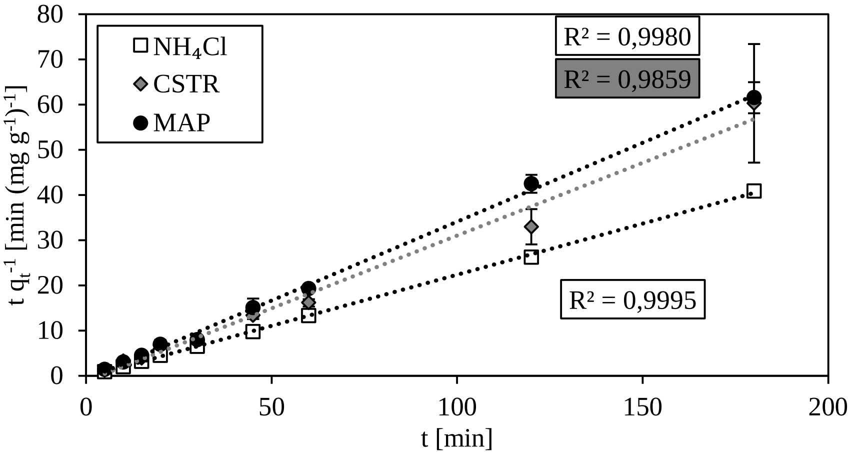

Figure 7: Pseudo second order model of desorbed ammonium from loaded clinoptilolite in relation to desorption time (every dot represents n = 3)

The desorption kinetic is like the adsorption kinetic described well by a pseudo-second-order model with linear plots as depicted in Figure 7. The results of this study demonstrated that ammonium desorption from loaded clinoptilolite is a rapid process with the following order of preference: NH_4Cl<CSTR<MAP.

CONCLUSIONS AND OUTLOOK

Clinoptilolite is suitable for ammonium removal by adsorption from both effluents, MAP and CSTR. Although twice as much ammonium was measured in the MAP effluent if compared to CSTR effluent, similar loadings were achieved. According to the Langmuir model, the calculated separation factor, R_L, sorption of ammonium is favoured. The results of the kinetic study implied a rapid sorption process, which was attributed to the small particle size and hence short diffusion routes for ammonium ions.

Sodium chlorine and sodium sulphate solutions proved to both be suitable for ammonium recovery. However, a higher ionic strength was required for recovering ammonium ions embedded in the clinoptilolite inner structure due to diffusion processes.

Regardless of ammonium load and provenance, desorption characteristics were comparable. Ammonium ions tend to occupy adsorption sites close to the clinoptilolite surface, which are regenerated first by sodium ions, resulting in a rapid desorption kinetic.

Further investigations regarding temperature-related recovery are necessary to provide more comprehensive information about the application of clinoptilolite for ammonium recovery. Additionally, investigations into increasing the ammonium concentrations in regeneration solutions by desorption and information about losses of clinoptilolite in a continuously operated process would be of relevance.

ACKNOWLEDGEMENT

The authors would like to thank the Federal Ministry of Education and Research (BMBF) of Germany for funding the research project TWIST ++.

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