

Removal of ammonium ions by laboratory-synthesized zeolite linde type A adsorption from water samples affected by mining activities in Ghana

Bright Kwakye-Awuah, Linus Kweku Labik, Isaac Nkrumah and Craig Williams

ABSTRACT

Ammonium ion adsorption by laboratory-synthesized zeolite (linde type A; LTA) was investigated in batch kinetics experiments. Synthesized zeolite LTA was characterized by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, thermogravimetric analysis, Fourier transform infrared spectroscopy and particle size analysis. Water samples were taken from the Nyam and Tano rivers in Ghana, and 0.8 g of zeolite was added to 100 ml portions of each sample. Portions of the samples were withdrawn every 30 min for 150 min and the concentration of ammonia in each sample was determined. The removal efficiency of zeolite LTA was evaluated by retrieving the zeolite from the water samples and adding to a fresh sample to repeat the process. Equilibrium data were fitted by Langmuir and Freundlich isotherms. Maximum adsorption capacities were 72.99 mg g^{-1} for samples from the River Nyam and 72.87 mg g^{-1} for samples from the River Tano. The equilibrium kinetic data were analysed using adsorption kinetic models: pseudo-first order and pseudo-second order kinetic models. Linear regression was used to estimate the adsorption and kinetic parameters. The results showed that the adsorption followed pseudo-second order kinetics and suggest that zeolite LTA is a good adsorbent for the removal of nitrogen ammonia from water.

Key words | adsorption, ammonium ions, characterization, synthesis, zeolite LTA

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INTRODUCTION

Ammonia (NH_3) is colourless gas that is highly soluble in water. In aqueous solutions, most (>90% below pH 8) of the ammonia is in the protonated form ammonium (NH_4^+) at equilibrium. Ammonia in the environment originates from both natural and anthropogenic sources. Nitrogen ammonia is found in wastewaters, leachates, condensates evolved during composting processes and effluents from mining wastewaters discharged into rivers (Tsuno *et al.* 1994; Sanchez *et al.* 1995; Booker *et al.* 1996; Nguyen & Tanner 1998; Kučić *et al.* 2013). Deleterious effects of this nitrogen ammonia include accelerated eutrophication of lakes, depletion of dissolved oxygen in receiving waters and toxicity to fish (Nguyen & Tanner 1998; Rahmani *et al.* 2004; Rahmani & Mahvi 2006). Some of the effects

of oral exposure of humans to high concentrations of ammonia and ammonium hydroxide include buccal, oesophageal and upper tracheal burns and oedema (Klein *et al.* 1985; Christesen 1995; Rosenbaum *et al.* 1998). Excess circulating levels of ammonia (hyperammonaemia) has been reported to cause serious neurological effects. Hyperammonaemia is a result either of inborn errors of the urea cycle enzymes or of liver toxicity caused by ingested toxins and viral infection (Felipo & Butterworth 2002). Ammonium ions may also contribute to the adverse effects of *Helicobacter pylori* on the stomach. *H. pylori* produces urease, which breaks down the urea normally present in the stomach into ammonia (Mégraud *et al.* 1992; Tsujii *et al.* 1992). It may also trigger the release of cysteine proteases in the stomach that

contribute to the development of gastric haemorrhagic mucosal lesions (Nagy *et al.* 1996). Neutrophils that migrate to the gastric mucosa in response to the presence of *H. pylori* may release hypochlorous acid, which can interact with NH_4^+ to produce the powerful cytotoxic oxidizing agent monochloramine (Murakami *et al.* 1995).

In recent years, ion exchange and adsorption have become the most efficient method of removing nitrogen from water and wastewater. This is because removal by biological nitrification–denitrification processes has been found to be slow in response to shock loads of ammonia (Lahav & Green 1998; Huang *et al.* 2010b). In addition, treatment of ammonium nitrogen in wastewater of low carbon content by a biological process requires an additional carbon source, adding to treatment costs (Booker *et al.* 1996; Karadag *et al.* 2006).

Zeolites are crystalline aluminosilicate inorganic materials whose framework structure consists of cavities or pores that are occupied by cations or water molecules (Occelli & Kessler 1997; Kwakye-Awuah 2008; Kwakye-Awuah *et al.* 2008). Although much research has been carried out on ammonia removal by zeolites, most of the zeolites used in such studies are of the natural type. Natural zeolites are relatively cheap compared to synthetic zeolites. However, synthetic zeolites are useful because of their controlled and known physico-chemical properties relative to natural zeolites (Mozgawa 2001). Furthermore, natural zeolites are mostly impure as they are mined from underlying rocks. The aim of this study was to investigate the adsorption potential of laboratory-synthesized zeolite (Linde type A; LTA) for the removal of ammonium from water samples from two rivers in Ghana: the Nyam and the Tano. The choice of these two rivers was strategic as they are closest to the effluent treatment sites of two major mining companies.

MATERIALS AND METHODS

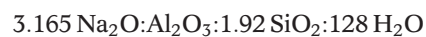
Materials and instrumentation

Sodium hydroxide, sodium aluminate and sodium metasilicate were purchased from Sigma Aldrich, UK. Water samples were collected from the River Nyam, in a suburb

of Obuasi, which is the river closest to the Anglo-Gold Ashanti mine site, and from the River Tano, which is the river closest to the Newmont Ghana Gold Ltd Ahafo mine site. Zeolite A was synthesized in the Water Research Laboratory, Kwame Nkrumah University of Science and Technology (KNUST), Ghana, and characterized in the School of Applied Sciences, Wolverhampton University, UK. Distilled water was obtained from the Water Research laboratory, KNUST. Whatman filters No. 45 were purchased from Sigma Aldrich, UK. A Wagtech 7100 Photometer was obtained from the General Chemistry Laboratory, Institute of Renewable Natural Resources, KNUST.

Synthesis and characterization of zeolite LTA

Zeolite A was synthesized according to method described by Kwakye-Awuah *et al.* (2008) with some modifications. The batch composition for the synthesis was



Eighty millilitres of distilled water was mixed with 0.723 g NaOH in a plastic beaker. The mixture was stirred continuously until the sodium hydroxide was completely dissolved. Half of the resulting sodium hydroxide solution was mixed with 8.258 g of sodium aluminate and half with 15.48 g of sodium metasilicate; both mixtures were stirred to obtain homogenous suspensions. The two suspensions were then mixed together and again stirred until a homogenous gel was formed. The gel was transferred into polytetrafluoroethylene (PTFE) bottles which were capped, then the bottles were put in a pre-heated electric oven at 100 °C for 4 h. The bottles were then removed and the reaction quenched immediately by running tap water over the bottles. The crystallized samples were filtered and washed copiously with distilled water until the pH of the filtrate was 9. The filtered samples were then dried in an electric oven at 100 °C for 12 h after which they were transferred into plastic containers and stored in a cupboard.

Characterization of zeolite LTA

The zeolite was characterized using scanning electron microscopy (SEM), X-ray diffractometry (XRD),

energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and particle size analysis. The surface morphology and the chemical composition were analysed by SEM and EDX using a Zeiss EVO 50 scanning electron microscope (Zeiss, UK). The EDX spectrophotometer was attached to the SEM microscope. The phase purity of the zeolite LTA was analysed with a Philips PW 1710 X-ray diffractometer (PANalytical UK Ltd, Cambridge). The chemical structure was examined by FTIR analysis using a Mattson FTIR spectroscope (Thermo, Cambridge, UK) and the particle size distribution was analysed with a Mastersizer long bed 2000 analyser.

Adsorption and kinetic studies

The batch technique was utilized to monitor the effect of contact time on ion exchange. One hundred millilitre water samples (100 ml) were measured into conical flasks and 0.8 g of zeolite was added to each sample. The flasks were placed on a rotary shaker at an average speed of 200 rpm at room temperature. Portions of the samples were withdrawn from the flasks at 30, 60, 90, 120 and 150 min and filtered using Whatman filter No. 45 to obtain clear solutions and also retrieve the zeolite. The concentrations of ammonium ion in the samples before and after zeolite addition were measured by using a Wagtech 7100 Photometer. The photometer measured the amount of ammonium nitrogen present in the sample and the result was multiplied by 1.2 to obtain the amount of ammonia present in the sample. Ten millilitres of the sample was put into a glass cruet and Palintest Ammonia Tablets Nos 1 and 2 were added, crushed and stirred until dissolved. The solution was allowed to stand for 10 min and then placed into the photometer. Readings were taken at room temperature and the procedure was repeated three times to obtain an average concentration.

Repeated retrieval and reuse of zeolite LTA

The extent to which zeolite LTA persisted in its adsorption activity was investigated according to the method given by Kwakye-Awuah *et al.* (2008) with some modifications. Zeolite LTA was retrieved after 150 h by centrifugation

(6,900 × g, 6 min). The retrieved zeolite was washed copiously (five times) with de-ionized water and air-dried in a fume cupboard and then dried at 50 °C in an electric oven for 3 h. The retrieved zeolite was weighed and added to a fresh water sample with the same zeolite mass:water volume ratio, and adsorption activity was investigated as before.

RESULTS AND DISCUSSION

Characterization of zeolite

SEM micrographs showed that LTA was highly crystalline and confirmed phase purity and uniform particle morphology morphology (Figure 1).

The XRD analysis of the zeolite (Figure 2) was validated by the literature. The XRD patterns of the synthesized zeolite did not have a flat base as in some studies (Treacy & Higgins 2001; Kwakye-Awuah 2008). The first three peaks appeared at 6.8, 12.2 and 14.8°, in agreement with Treacy *et al.* (2001); no impurity phases were seen.

The FTIR spectrum of zeolite LTA is given in Figure 3. Peaks occurred at wave numbers 1,700, 997, 744, 674, 553 and 432 cm⁻¹. According to Aronne *et al.* (1997) and Sitarz *et al.* (2001), the peak at 997 cm⁻¹ is attributed to the overlapping of the asymmetric vibrations of Si-O (bridging) and Si-O (non-bridging). The peak at 744 cm⁻¹

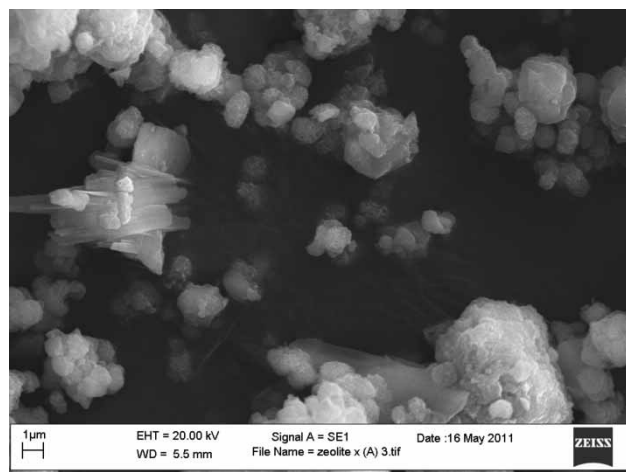


Figure 1 | SEM micrograph of zeolite LTA.

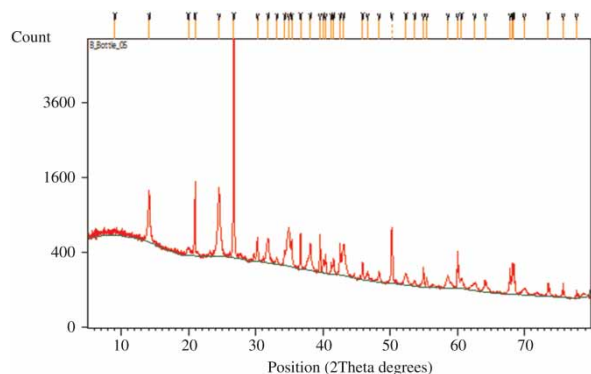


Figure 2 | XRD spectrum of zeolite LTA.

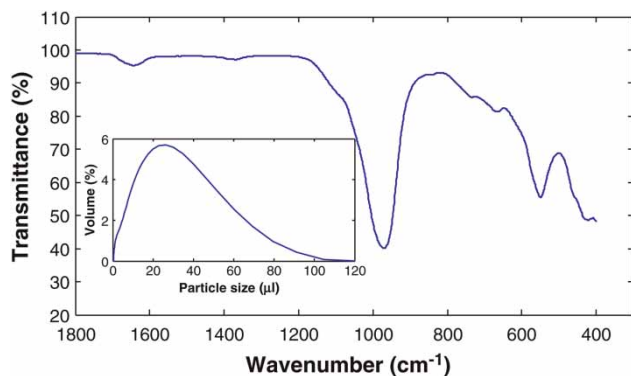


Figure 3 | FTIR spectrum and (inset) particle size distribution of zeolite LTA powder.

is assigned to the symmetric stretching of the external T–O linkages (Mozgawa 2001; Sitarz *et al.* 2001). Vibrations associated with double rings (D6R) that connect the sodalite cages occurred at 553 cm^{-1} whilst the band at 432 cm^{-1} is assigned to the vibrations due to the bending of the T–O

tetrahedra (Mozgawa 2001; Kwakye-Awuah 2008; Kwakye-Awuah *et al.* 2008). Our findings are in agreement with Ojha *et al.* (2004), who stated that the two most intense bands of zeolites usually occur at $860\text{--}1,230\text{ cm}^{-1}$ and $420\text{--}500\text{ cm}^{-1}$. The particle size distribution obtained is shown in Figure 3 (inset). Most particles were in the size range of $2\text{--}60\text{ }\mu\text{m}$ with a modal size of $22\text{ }\mu\text{m}$.

Figure 4(a) shows a TGA curve for the synthesized zeolite LTA. Loss of water from the zeolite did not affect its thermal stability. Figure 4(b) represents the elemental composition of the synthesized zeolite. The main elements present in the zeolite were aluminium, silicon and sodium. The peak for oxygen coincides with that of iron; this overlap occurs because of the closeness of the energy levels of the backscattered electrons emitted by the two elements.

Removal of ammonia and adsorption isotherms

For each treatment type, the removal of ammonium ions by zeolite LTA was initially a fast process with 85% of the removal being achieved within the first 60 min (Figure 5). Thereafter, with increase in contact time the rate of removal slowed down (with the exception of first addition treatment when the rate slowed down after 90 min). After 120 min the rate was almost negligible. This trend of removal may be attributed to the rapid utilization of readily available adsorbing sites in the zeolite LTA resulting in the fast diffusion and attainment of the equilibrium (Donghui *et al.* 2003; Wen *et al.* 2006; Kućić *et al.* 2013). After approximately 120 min of adsorption, sorption equilibrium begins to establish leading to the reduction in the removal rate. The trend

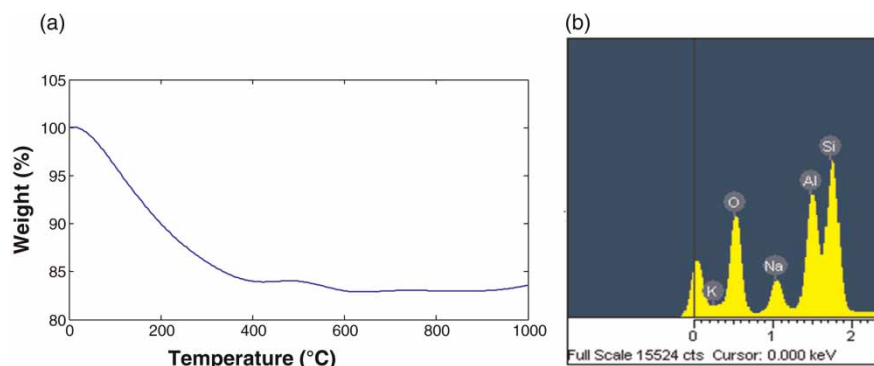


Figure 4 | (a) TGA curve obtained and (b) EDX spectrum of the zeolite LTA.

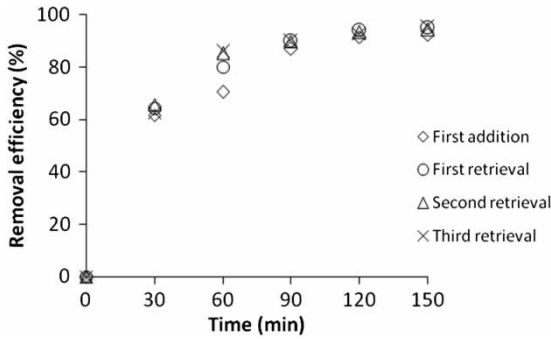


Figure 5 | Removal of ammonium in River Nyam water at different contact times. Dose of zeolite LTA dose was 8 g/L, pH = 9 and initial ammonium concentration = 3.625–3.635 mg/l. Similar results were obtained for River Tano water (data not shown).

of removal rate was similar in all cases after regeneration and application of the zeolite to fresh water samples.

The adsorption equilibrium data were analysed using the Langmuir and Freundlich isotherm models. The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface. This implies that all adsorbing sites are equivalent and adsorption on an active site is independent of whether or not an adjacent site is occupied. Mathematically, the model is given by the equation (Donghui *et al.* 2003; Jafarpour *et al.* 2010):

$$q_e = \left(\frac{Mk_L}{1 + k_L C_e} \right) \quad (1)$$

where C_e (mg/L) is the equilibrium concentration, q_e (mg/g) is the amount of ammonium ion adsorbed at equilibrium, M (mg/g) and k_L (L/mg) are the maximum adsorption capacity and Langmuir constants, respectively.

The linearized form can be expressed as:

$$q_e = \left(\frac{Mk_L}{1 + k_L C_e} \right) \quad (2)$$

The linear plot of Langmuir isotherm is shown in Figure 6. The values of M and k_L are calculated from the slope and intercept of the plot of C_e/q_e and C_e . Table 1 ((a), (b)) shows that the maximum amount of ammonium ion adsorbed at equilibrium was 72.99 (mg/g) for the River Nyam water and 72.87 (mg/g) for the River Tano water. The amount adsorbed after regeneration of zeolite LTA and

when added to fresh samples gave similar results in all treatments for both rivers.

The Freundlich isotherm assumes a multilayer adsorption with interactions between ions and is expressed as (Huang *et al.* 2010a)

$$q_e = k_F C_e^{1/n} \quad (3)$$

where q_e (mg/g) is the amount of ammonium ion adsorbed at equilibrium, k_F (measure of adsorption capacity) and $1/n$ (measure of adsorption intensity) are Freundlich constants. Taking natural logs on both sides of (3), we obtain

$$\ln q_e = \ln k_F + (1/n) \ln C_e \quad (4)$$

Values of C_e and k_F are calculated from a plot (Figure 7) of $\ln q_e$ against $\ln C_e$ and are given in Table 1 ((a), (b)). The Freundlich model yields a better fit ($R^2 = 0.900 - 0.980$) than the Langmuir model ($R^2 = 0.948 - 0.966$). In addition a value of $1/n$ between 0 and 1 indicates a favourable adsorption. Since the values of $1/n$ obtained in this study for all treatments in both rivers were less than 1 it follows that the Freundlich adsorption conditions were favourable. The repeated retrieval and reuse of zeolite LTA showed that it continued in its adsorption activity (Figures 6–9).

Kinetic studies

To understand the adsorption mechanism of ammonium ion uptake onto the zeolite at time t , the pseudo-first and second-order kinetic models were used. The pseudo-first-order kinetic model is given by the equation (Kučić *et al.* 2012)

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (5)$$

Integrating (5) from $t = 0$ to $t = t$ and from $q_t = 0$ to $q_t = q_t$ we obtain

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of ammonium ion adsorbed at equilibrium and at time t and k_1 (1/min) is the

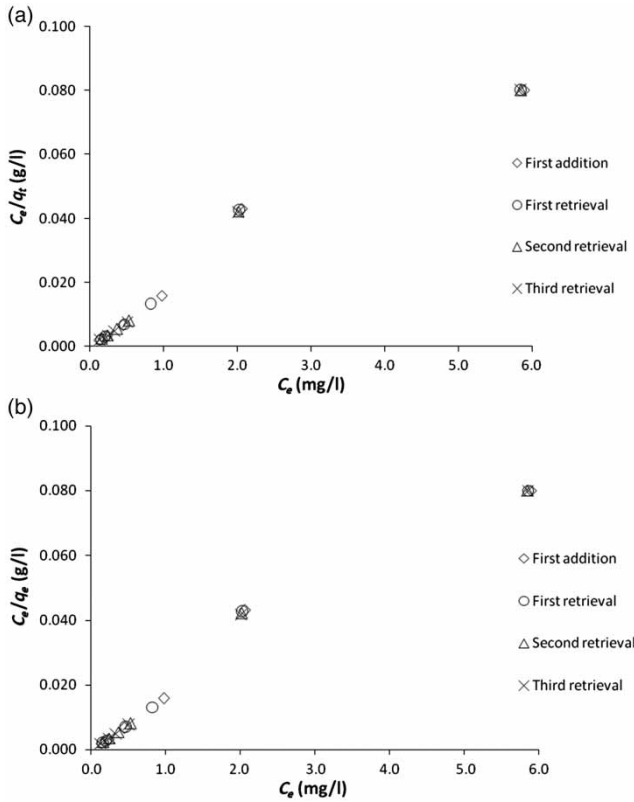


Figure 6 | Langmuir isotherms of ammonium adsorption on zeolite LTA for each treatment in (a) River Nyam water and (b) River Tano water obtained in batch experiments.

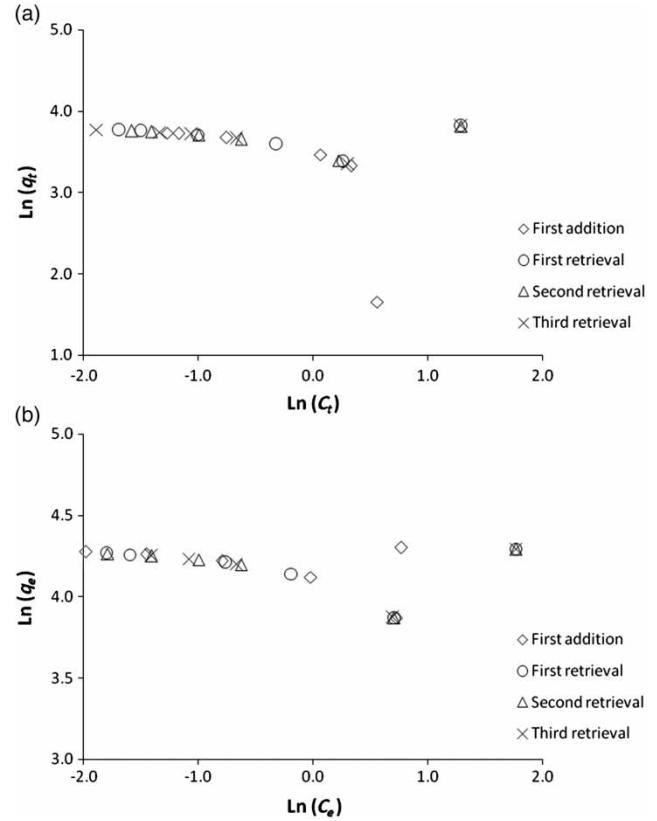


Figure 7 | Freundlich isotherms of ammonium adsorption on zeolite LTA for each treatment in (a) River Nyam water and (b) River Tano water obtained in batch experiments.

Table 1 | Isotherm equation coefficients extracted from the linearized curves in Figures 6 and 7 for (a) River Nyam water and (b) River Tano water

Treatment	Langmuir parameter			Freundlich parameter		
	M (mg/g)	k_L (l/mg)	R^2	k_F (mg/g)	n	R^2
River Nyam water						
First addition	72.993	4.893	0.963	62.797	29.754	0.935
First retrieval	72.464	5.308	0.964	64.136	28.736	0.910
Second retrieval	71.942	6.043	0.966	64.703	29.155	0.980
Third retrieval	71.942	6.318	0.967	64.780	28.818	0.980
River Tano water						
First addition	11.455	4.269	0.930	19.834	30.836	0.928
First retrieval	11.377	6.500	0.957	38.648	34.014	0.915
Second retrieval	71.942	7.655	0.964	39.146	50.505	0.900
Third retrieval	71.942	7.226	0.948	38.749	30.488	0.979

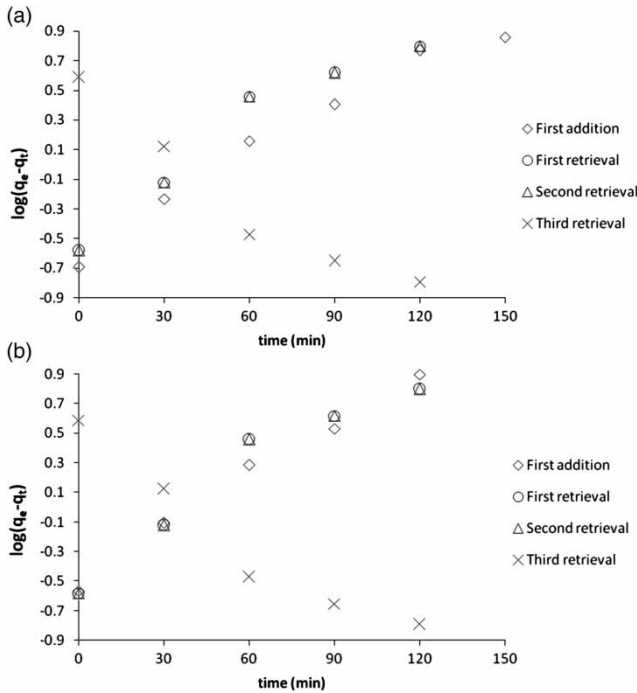


Figure 8 | Pseudo-first-order kinetic plots of ammonium adsorption on zeolite LTA in (a) River Nyam water and (b) River Tano water obtained in batch experiments.

pseudo-first-order rate constant. The values of q_e and k_1 were calculated from the slope and intercept of a plot (Figure 8) of $\ln(q_e - q_t)$ against t . Table 2 ((a), (b)) shows that the experimental value obtained for q_e is far greater than that obtained from calculation. Furthermore, the R^2 value obtained suggests that the experimental data did not fit the pseudo-first-order kinetic model. The pseudo-second-order kinetic model is given by the expression (Kučić *et al.* 2012, 2013)

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2 \quad (7)$$

Integrating from $t = 0$ to $t = t$ and from $q_t = 0$ to $q_t = q_t$ we obtain

$$q_t = \frac{t}{1/(k_2 q_e^2) + t/q_e} \quad (8)$$

where, again, q_e (mg/g) and q_t (mg/g) are the amount of ammonium ion adsorbed at equilibrium and at time t and k_2 (1/min) is the pseudo-first-order rate constant. The values of q_e and k_1 were calculated from the slope and

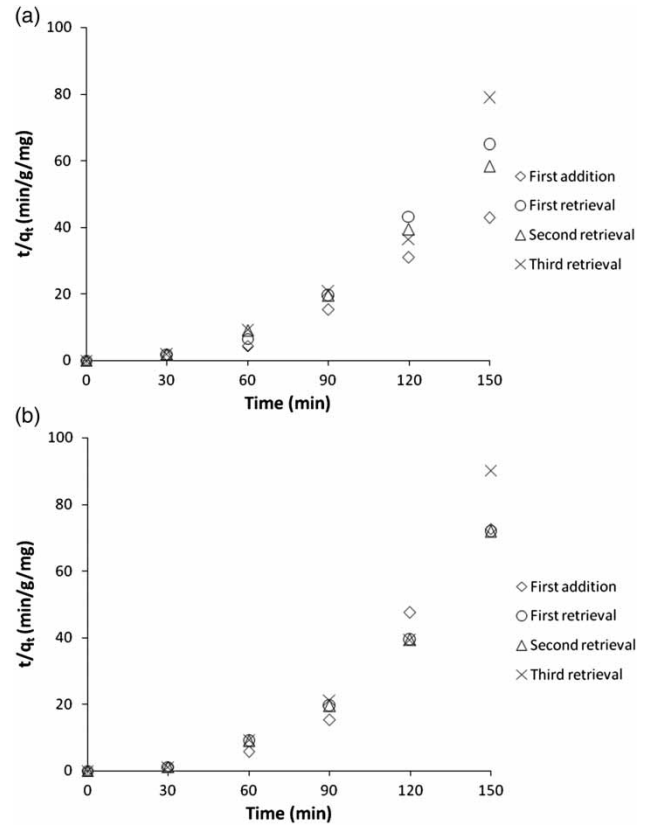


Figure 9 | Pseudo-second-order kinetic plots of ammonium adsorption on zeolite LTA in (a) River Nyam water and (b) River Tano water obtained in batch experiments.

intercept of a plot (Figure 9) of t/q_t against t . Results obtained are shown in Table 2 ((a), (b)). As can be seen from Table 2 ((a), (b)), the R^2 values obtained showed high correlation. Furthermore, the experimental and theoretical values of q_e and q_t are in good agreement. It therefore follows that pseudo-second-order kinetics predominate over pseudo-first-order kinetics. Thus the rate limiting step is likely to be chemical sorption, involving forces due to the sharing of or exchange of electrons between the adsorbent and the adsorbate.

Health implications of the presence of ammonia in relation to

The need to treat contaminated water bodies is very urgent because many farmers depend on a good water supply for their activities and also because of the increasing demand for potable water in urban and rural areas. Although ammonia levels in groundwater are usually below 0.2 mg/l,

Table 2 | Kinetic equations coefficients extracted from the linearized curves in Figures 8 and 9 for (a) River Nyam water and (b) River Tano water

Treatment	Pseudo-first-order				Pseudo-second-order			
	k_1 (L/min)	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	R^2	k_2 (L/min)	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	R^2
River Nyam water								
First addition	0.173	19.894	0.377	0.846	0.019	19.894	12.819	0.970
First retrieval	0.080	19.142	0.403	0.867	0.019	19.142	11.109	0.924
Second retrieval	0.079	19.138	0.367	0.867	0.019	19.138	11.109	0.924
Third retrieval	0.080	19.938	0.392	0.808	0.021	19.938	14.331	0.934
River Tano water								
First addition	0.017	14.869	0.377	0.948	0.012	14.869	6.451	0.910
First retrieval	0.020	13.404	0.403	0.959	0.019	13.404	10.274	0.890
Second retrieval	0.019	12.969	0.367	0.919	0.019	12.969	8.238	0.916
Third retrieval	0.020	13.046	0.392	0.944	0.125	13.046	11.890	0.833

ammonia may be present in drinking water as a result of disinfection with chloramines. Furthermore, cement mortar used for coating the insides of water pipes may release considerable amounts of ammonia into drinking water and compromise chlorine disinfection (Wendlandt 1988). For communities affected by mining activities, ammonia levels in both underground and surface waters may even be higher. Mining involves the extraction of rock that contains valuable materials or minerals, such as coal, diamonds, gold, platinum, vanadium and copper. This rock is abstracted by means of both opencast and underground blasting. Blasting to access the mineral ore typically involves the use of ammonia-based explosives. Metallurgical extraction of minerals from the rock typically involves the use of nitrate-based acids, such as aqua regia (Yashina & Nesterova 1992). Both these activities lead to increased concentrations of nitrates in groundwater resources as the nitrogen cycle flows between ammonia under reducing (or acidic) conditions, and nitrite under oxidizing conditions (Moore & Luoma 1990). High levels of ammonia on slimes dams (which are used to retain mining waste) are oxidized as the water from the slimes dam leaches into the groundwater, where it occur as high levels of nitrate. If present at high levels in water sources, the ammonia may interfere with removal processes of other heavy metals that are deleterious to human health since too much oxygen is consumed by nitrification. In addition, the presence of the ammonium cation in raw water may result in drinking water containing

nitrite as the result of catalytic action (Reichert & Lochtmann 1984) or the accidental colonization of filters by ammonium-oxidizing bacteria. High levels of nitrate are particularly harmful to human health, and can cause blue-baby syndrome, kidney failure and cancer. Irrespective of the mining method, one of the biggest and most long-term impacts of mining activities is on water resources. Using zeolite LTA is promising means of removing nitrogen ammonia from water sources by adsorption of the ammonium ion.

CONCLUSIONS

From the results obtained and their evaluation, it can be concluded that zeolite LTA is a good adsorbent for removing ammonium ions from aqueous solutions. The removal percentage was between 92.2 and 95.8% in the various treatments stages. Langmuir and Freundlich isotherms were both demonstrated to provide good fit for the sorption of ammonium ions onto zeolite LTA. The adsorption capacity of zeolite LTA was found to be 72.99 and 72.46 mg/g for first addition and first retrieval and 71.94 for second and third retrieval processes for water samples from the River Nyam. An adsorption capacity of 72.87 and 72.39 for first addition and first retrieval and 71.94 for second and third retrieval processes were obtained for water samples from the River Tano. Kinetics studies suggest that ammonium adsorption

on zeolite LTA could be better described by the pseudo-second-order model with the parameters better estimated by the linear method.

REFERENCES

- Aronne, A., Esposito, S. & Pernice, P. 1997 FTIR and DTA study of lanthanum aluminosilicate glasses. *Mater. Chem. Phys.* **51**, 163–168.
- Booker, N. A., Cooney, E. L. & Priestly, A. J. 1996 Ammonia removal from sewage using natural Australian zeolite. *Water Sci. Technol.* **34**, 17–24.
- Christesen, H. B. 1995 Prediction of complications following caustic ingestion in adults. *Clin. Otolaryngol.* **20**, 272–278.
- Donghui, W., Tang, X.-y. & Qianru, M. 2003 Research on the adsorption capacity for ammonia of natural zeolite. *Res. Environ. Sci.* **16**, 31–34.
- Felipo, V. & Butterworth, R. F. 2002 Neurobiology of ammonia. *Prog. Neurobiol.* **67**, 259–279.
- Huang, H., Xiao, X., Yan, B. & Yang, L. 2010a Ammonium removal from aqueous solutions by using Chinese natural (Chende) zeolite as adsorbent. *J. Hazard. Mater.* **175**, 247–252.
- Huang, H., Xiao, X., Yang, L. & Yan, B. 2010b Recovery of nitrogen from saponification wastewater by struvite precipitation. *Water Sci. Technol.* **61** (11), 2741–2748.
- Jafarpour, M. M., Foolad, A., Mansouri, M. K., Nikbakhsh, Z. & Saeedzade, H. 2010 Ammonia Removal from Nitrogenous Industrial Waste Water using Iranian Natural Zeolite of Clinoptilolite Type. World Academy of Science, Engineering and Technology 14th International Oil, Gas and Petrochemical Congress.
- Karadag, D., Koc, Y., Turan, M. & Armagan, B. 2006 Removal of ammonium ion from aqueous solution using Turkish clinoptilolite. *J. Hazard. Mater.* **136**, 604–609.
- Klein, J., Olson, K. R. & McKinney, H. E. 1985 Caustic injury from household ammonia. *Am. J. Emerg. Med.* **3**, 320.
- Kučić, D., Markić, M. & Briski, M. 2012 Ammonium adsorption on natural zeolite (clinoptilolite): adsorption isotherms and kinetics modeling. *Holistic Approach Environ.* **2**, 14–158.
- Kučić, D., Osi, I., Marija Vuković, M. & Briski, F. 2013 Sorption kinetics studies of ammonium from aqueous solution on different inorganic and organic media. *Act. Chim. Slov.* **60**, 109–119.
- Kwakye-Awuah, B. 2008 Production of Silver-Loaded Zeolites and Investigation of their Antimicrobial Activity. PhD Thesis, University of Wolverhampton, UK.
- Kwakye-Awuah, B., Williams, D., Kenward, M. A. & Radecka, I. 2008 Antimicrobial action and efficiency of silver-loaded zeolite X. *J. Appl. Microbiol.* **104**, 1615–1624.
- Lahav, O. & Green, M. 1998 Ammonium removal using ion exchange and biological regeneration. *Water Res.* **32**, 2019–2028.
- Mégraud, F., Neman-Simha, V. & Brugmann, D. 1992 Further evidence of the toxic effect of ammonia produced by *Helicobacter pylori* urease on human epithelial cells. *Inf. Immun.* **60**, 1858–1863.
- Moore, J. N. & Luoma, S. N. 1990 Hazardous wastes from large-scale metal extraction. *Env. Sci. Technol.* **24**, 1278–1285.
- Mozgawa, W. 2001 The relation between structure and vibrational spectra of natural zeolites. *J. Mol. Struct.* **596**, 129–137.
- Murakami, M., Asagoe, K., Dekigai, H., Kusaka, S., Saita, H. & Kita, T. 1995 Products of neutrophil metabolism increase ammonia-induced gastric mucosal damage. *Digest Dis. Sci.* **40**, 268–273.
- Nagy, L., Kusstatscher, S., Hauschka, P. V. & Szabo, S. 1996 Role of cysteine proteases and protease inhibitors in gastric mucosal damage induced by ethanol or ammonia in the rat. *J. Clin. Invest.* **98**, 1047–1054.
- Nguyen, M. L. & Tanner, C. C. 1998 Ammonium removal from wastewaters using natural New Zealand zeolites. *New Zealand. J. Agric. Res.* **41**, 427–446.
- Ocelli, M. I. & Kessler, H. (eds) 1997 *Synthesis of Porous Materials: Zeolites, Clays and Nanostructures*. CRC Press, New York.
- Ojha, K., Pradhan, N. C. & Samanta, A. N. 2004 Zeolite from fly ash: synthesis and characterization. *Bull. Mater. Sci.* **27**, 555–564.
- Rahmani, A. R. & Mahvi, A. H. 2006 Use of ion exchange for removal of ammonium: A biological regeneration of zeolite. *Global NEST J.* **8**, 146–150.
- Rahmani, A. R., Mahvi, A. H., Mesdaghinia, A. R. & Nasser, S. 2004 Investigation of ammonia removal from polluted waters by clinoptilolite zeolite. *Int. J. Environ. Sci. Technol.* **1**, 125–133.
- Reichert, J. & Lochtmann, S. 1984 Auftreten von Nitrit in Wasserversorgungssystemen (Occurrence of nitrite in water distribution systems). *Gas- und Wasserfach, Wasser-Abwasser* **125**, 442–446.
- Rosenbaum, A. M., Walner, D. L., Dunham, M. E. & Holinger, L. D. 1998 Ammonia capsule ingestion causing upper aerodigestive tract injury. *Otolaryngol. Head Neck Surg.* **119**, 678–680.
- Sanchez, E., Milan, Z., Borja, R., Weiland, P. & Rodriguez, X. 1995 Piggery waste treatment by anaerobic digestion and nutrient removal by ionic exchange. *Resour. Conserv. Recycl.* **15**, 235–244.
- Sitarz, M., Handke, M. & Mozgawa, W. 2001 FTIR studies of the cyclosilicate-like structures. *J. Mol. Struct.* **596**, 185–189.
- Treacy, M. M. J. & Higgins, J. B. 2001 *Collection of Simulated XRD Powder Patterns for Zeolites*. Elsevier, Amsterdam.
- Tsuji, M., Kawano, S. & Tsuji, S. 1992 Ammonia: a possible promoter in *Helicobacter pylori*-related gastric carcinogenesis. *Canc. Lett.* **65**, 15–18.

- Tsuno, H., Nishimura, F. & Somiya, I. 1994 Removal of ammonium nitrogen in bio-zeolite reactor. *J. Hydraul. Coast. Environ. Eng.* **503**, 159–166.
- Wen, D., Ho, Y.-S. & Tang, X. 2006 [Comparative sorption kinetics of ammonium onto zeolite](#). *J. Hazard. Mater.* **133**, 252–256.
- Wendlandt, E. 1988 Ammonium/Ammoniakals Ursache für Wiederverkeimungen in Trinkwasserleitungen. (Ammonium/ammonia as cause of bacterial regrowth in drinking-water pipes). *Gas- und Wasserfach, Wasser-Abwasser* **129**, 567–571 (in German).
- Yashina, G. M. & Nesterova, S. V. 1992 [Possible methods for preliminary opening up of minerals to accelerate complex extraction of metals from balanced ores](#). *J. Mining Sci.* **28**, 299–306.

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