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# Microwave-assisted synthesis of coal fly ash-based zeolites for removal of ammonium from urine

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Zeolites synthesized from biomass waste materials offer a great opportunity in the sustainable utilization of the waste. In this work, energy-efficient processes (*i.e.* microwave and ultrasound irradiation) were used to synthesize pure phase sodalite (zeolite) from coal fly ash obtained from a power plant in South Africa. The pure-phase sodalite was obtained with a comparatively higher surface area ( $16 \text{ m}^2 \text{ g}^{-1}$ ) and cation exchange capacity (2.92 meq. g<sup>-1</sup>) with 40 min total reaction time. The removal of ammonium from urine was carried out using (i) the coal fly ash-derived sodalite, (ii) raw coal fly ash and (iii) a commercially available natural zeolite (clinoptilolite). The pure phase sodalite exhibited the highest removal efficiency of about 82% and 73% in synthetic and real hydrolyzed urine respectively. The adsorption process followed the pseudo second-order kinetic model and the Freundlich adsorption isotherm, indicating that the adsorption process occurred on a heterogeneous surface.

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## Introduction

Urine is the most nutrient-rich part of domestic wastewater, even though it constitutes only 1% of the total wastewater volume.1 It contains essential nutrients such as nitrogen (N) in the form of ammonium  $(NH_4^+)$ , phosphorus (P) and potassium (K) which can be recovered and used to make fertilizer.<sup>2</sup> If these nutrients are not recovered and find their way to the water bodies, they lead to eutrophication which is harmful to aquatic life.3 In developing countries, where most communities do not have access to proper sanitation, waste disposal and management is a challenge. The waste is disposed into rivers that are often used for drinking purposes, rendering the water not safe for consumption and a major cause of waterborne diseases. However, the urine in the wastewater could be separated prior to discharge into water sources and converted to useful fertilizer for agricultural applicants. For instance, schools in the rural communities of South Africa and many other African countries use source separate toilets (especially male toilets) which would make urine collection for the recovery and recycling of nutrients possible.<sup>2</sup>

The recovery of K-struvite (KMgPO<sub>4</sub>·6H<sub>2</sub>O) fertilizer from urine is of great interest because potassium is overlooked in the recovery of valuable nutrients even though it forms an essential part in NPK fertilizers.<sup>4</sup> The natural source of K (potash) is presumed to run out in the near decades, thus calling for alternative sources of K such as urine, to be explored. To recover K-struvite, nitrogen (N) in the form of the ammonium (NH<sub>4</sub><sup>+</sup>) needs to be removed. This is because magnesium–ammonium–phosphate (MAP) also referred to as ammonium struvite (NH<sub>4</sub>MgPO<sub>4</sub>·6H<sub>2</sub>O) is readily formed during the precipitation process<sup>5</sup> and so it interferes with the magnesium–potassium–phosphate (MPP) precipitation. As such, the ammonium must be removed from urine, to favor the precipitation of K-struvite.

Conventional methods for the removal of ammonium from aqueous solutions have been studied using air stripping,<sup>6</sup> biological nitrification–denitrification<sup>7</sup> and ion-exchange.<sup>8</sup> Air stripping and ion exchange have been shown to be the technologies with the highest ammonia removal in urine (Table 1). The removal percentage is around 97% and these technologies can have higher ammonia removal even up to 100% with optimum conditions. Among the various methods, ionexchange remains the most widely used due to its simplicity, environmental friendliness and low cost practicability.<sup>9</sup> Additionally, zeolites have been explored as low-cost materials for wastewater treatment. Clinoptilolite, among other natural zeolites, has demonstrated high cation exchange capacity and selectivity for the ammonium ion.<sup>10</sup> It has been used to treat water with high ammonium concentration such as greywater.<sup>9</sup>

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#### Paper

Owing to their low-cost, high selectivity at low temperatures and environmental friendliness of releasing non-toxic exchangeable cations such as Na<sup>+</sup>, Ca<sup>+</sup> and Mg<sup>+</sup>, natural zeolites receive greater interest compared to synthetic cation exchange materials such organic resins.<sup>11</sup>

Zeolite materials occur either naturally or are synthesized from waste materials such as coal fly ash. Although coal fly ash is regarded as waste, it has a high content of valuable Si and Al and can be used as a precursor for the synthesis of zeolite.<sup>19–22</sup> Zeolites synthesized from coal fly ash have shown high cation exchange capacity and selectivity compared to natural zeolites.<sup>23,24</sup> As a result, they have gained more attention as adsorbents and catalysts in water treatment. Most studies on the synthesis of zeolites from coal fly ash have reported the use of fusion and hydrothermal methods which are energy intensive,<sup>25–28</sup> hence they are not environmentally friendly nor economically viable.

Microwave and ultrasound energies provide a viable alternative for zeolite synthesis since these methods consume less energy and reduce the reaction time. Microwave irradiation increases the rate of a chemical reaction and gives a rapid homogeneous heating of the reaction solution, leading to a more abundant nucleation.20 The mechanism of energy transfer due to microwave irradiation and ultrasound irradiation is different from that of conventional heating. The chemical effects of ultrasound originate from acoustic cavitation and collapsing of generated micro-bubbles in liquid medium, which leads to a micro-mixing effect. This phenomenon increases the secondary nucleation rates and enhances mass transfer that eventually increases crystal growth rates.29 Belviso et al., found that ultrasound irradiation accelerates the dissolution of the Na silicate and aluminosilicate formed with NaOH pre-fusion. This resulted in Al-Si supersaturation, which produced higher nucleation rate of crystalline phases to be involved in zeolite synthesis.30

The focus of this study was to develop green synthesis approach for synthesis of valuable zeolitic materials from coal fly ash using a microwave-assisted method. The zeolites were used for the removal of ammonium from urine. The influence of various parameters such as adsorbent dosage, contact time and pH on the performance of the adsorbents were studied. Adsorption isotherms and kinetics were also studied to better understand the mechanisms and rates of adsorption.

# Methods

#### Materials

Sodium hydroxide (97%), sodium aluminate (90%), calcium chloride (90%), potassium chloride (99.5%), hydrogen potassium phosphate (99.5%), and urea (99.4%) were purchased from Sigma Aldrich (Darmstadt, Germany). Hydrochloric acid (35%), magnesium chloride (99.99%), sodium chloride (99.6%), sodium sulfate (99.2), trisodium citric acid (99.2%), sodium oxalate (99.99%) and ammonium chloride (99.99%) were purchased from VWR prolab chemicals (Pennsylvania, USA). Creatine (98%) was purchased from Alfa Aesar (Massachusetts, USA). Clinoptilolite was received from Pratley Perlite Mining Company (Gauteng, South Africa), coal fly ash was supplied by Duvha Thermal Power Plant (Mpumalanga, South Africa). All chemicals were AR grade and used as received without any further purification.

# Experimental

#### Zeolite preparation

The zeolites were synthesized using coal fly ash using a unique process of combining microwaves and ultrasound. Typically, 20 g of raw coal fly ash and 5 g of NaOH were transferred into a conical flask and mixed with 125 ml of distilled water. The resulting slurry was subjected to microwave irradiation for 20 min at a constant temperature (100 °C) using Sineo UWave-1000 microwave with the power set at 300 W. Thereafter, it was filtered and the obtained clear extract and solid materials were separated. Subsequently, 28 ml of the prepared NaAlO<sub>2</sub> solution was added to the clear extract (filtrate) to adjust the Si/Al ratio, in order to improve crystallization of zeolite phases.31 To achieve crystallization, the extract solution was irradiated at 600 W for 20 min with ultrasound using the same microwave instrument. In a separate (reverse method) experiment, ultrasound irradiation followed by microwave irradiation was performed. In this method, the solution obtained was not filtered and the Si/Al ratio in the slurry was adjusted using the same NaAlO<sub>2</sub>

Table 1 Teenhologies of anim			
Technology	Approach	Removal efficiency (%)	Ref.
Air-stripping	Stripping column having a 1 m diameter and 2.5 m packing height	97	12
Ion-exchange/adsorption	Natural zeolite material (clinoptilolite)	97	13
Nitrification-denitrification	Membrane bioreactor	90	14
Gas separation membrane	60 membrane surface area/reactor volume ratio, at 35 °C feed temperature with 350 L m <sup><math>-2</math></sup> h <sup><math>-1</math></sup> acid and in 8 h' hydraulic retention time	85	15
Forward osmosis and membrane distillation	Fresh urine (ammonia removed as urea)	55	16
Electrochemical oxidation	Thermally decomposed iridium oxide film anode	40	17
Bioelectrochemical system	Microbial fuel cell (MFC) and a microbial electrolysis cell (MEC)	30	18

Table 1 Technologies of ammonia removal from uring

solution. Solution crystallization was performed as above. The products were centrifuged and the separated crystals (zeolites) obtained were dried in an oven at 100  $^\circ$ C for 24 h.

The elemental composition, crystallinity, morphology, and specific surface area of the coal fly ash and as-synthesized zeolites were characterized using X-ray fluorescence (XRF, NEX CG Rigaku), X-ray diffraction spectroscopy (XRD, Rigaku 124 Ultimate IV X-ray diffractometer), scanning electron microscopy (SEM, JEOL STM-IT300) and Brunauer–Emmett–Teller (BET, 3Flex surface area analyser) respectively. Cation exchange capacity was determined using a procedure adopted from Musyoka *et al.*<sup>32</sup> The concentrations of exchangeable cations (Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>) in the final solution were determined by using 930 Compact IC Flex Metrohm ion chromatography.

#### Preparation of synthetic urine

Synthetic human urine (similar to that of a normal healthy adult) is characterized by 11 solutes in concentration. However, synthetic urine is free from organic macromolecules (matrix), pyrophosphates and unspecified substances that can potentially enhance or inhibit the nutrient recovery.<sup>2</sup> To prepare synthetic urine for use in this study, a desired mass of each salt was weighed and added into a volumetric flask and dissolve with distilled water. The salts were stirred until complete dissolution was attained. The concentrations of the solutes constituting the synthetic urine are presented in Table 2. The salt concentrations presented in Table 2 are based on measured

Table 2	Composition	of synthetic	urine prepared	l in this study
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Salt	Formula	Concentration $(mg L^{-1})$
Suit	Tormulu	(IIIS L )
Calcium chloride	$CaCl_2 \cdot 2H_2O$	650
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	650
Sodium chloride	NaCl	4600
Sodium sulfate	$Na_2SO_4$	2300
Trisodium citric acid	$C_6H_5O_7 \cdot 2H_2O \cdot 3Na$	650
Sodium oxalate	$Na_2$ -(COO) <sub>2</sub>	20
Hydrogen potassium	KH <sub>2</sub> PO <sub>4</sub>	4200
phosphate		
Potassium chloride	KCl	1600
Ammonia chloride	NH <sub>4</sub> Cl	1000
Urea	NH <sub>2</sub> CONH <sub>2</sub>	25 000
Creatine	$C_4H_7N_3O$	1100

masses and are thus theoretical. The actual concentration of the ions of interest measured using ion chromatography are presented in Table 5.

#### Preparation of hydrolyzed urine

Fresh urine was collected from source separate male toilets at Ghent University (Belgium) and upon storage in plastic bottles, it was biologically hydrolyzed by urease bacteria. The urea was hence converted to ammonium ions according to eqn (1).

$$NH_2(CO)NH_2 + 3H_2O \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^- + OH^-$$
 (1)

#### Analytical methods

The concentrations of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and NH<sub>4</sub><sup>+</sup> present in synthetic urine and hydrolyzed urine before and after adsorption were determined using a 930 Compact IC Flex Metrohm ion chromatography. The solution pH was determined using Hanna ISE pH meter.

#### Batch ammonium adsorption

The batch experiments for adsorption of the synthetic and hydrolyzed urea were conducted using clinoptilolite, coal fly ash and the as-synthesized zeolites. 25 mL of synthetic or hydrolyzed urine were transferred into conical flasks containing a desired mass of the adsorbent. The mixture was stirred on an Edmund Buhler sm-30 thermostatic shaker at room temperature for a specific period. The effect of adsorbent dose (0.2–1 g), contact time (10–120 min) and pH (2–10) were studied. To determine the rate of adsorption of ammonium on the zeolites, the kinetic studies were performed using the pseudo first order and pseudo second order models. Furthermore, Langmuir and Freundlich isotherms were conducted to understand the mechanism of ammonium adsorption onto zeolites.

The amount of ammonium ion removal capacity per unit mass of the adsorbent (q) and percentage ammonium removal were calculated using eqn (2) and (3) respectively.

$$q = \frac{(C_0 - C_e)V}{m} \tag{2}$$

% Removal efficiency = 
$$\frac{C_0 - C_e}{C_0} \times 100$$
 (3)

 Table 3
 The nomenclature of the parameters and constants used in the study

Parameter	Description	Constant	Description
$ \begin{array}{c} C_0 \\ C_e \\ V \\ m \\ q_e \\ q_t \\ t \end{array} $	Initial concentration (mg $l^{-1}$ ) Ammonium ions concentration at equilibrium (mg $l^{-1}$ ) Sorbent volume (ml) Mass of absorbent (mg) Amount of ammonium ions adsorbed at equilibrium (mg $g^{-1}$ ) Amount of ammonium ions adsorbed at a given time (mg $g^{-1}$ ) Time (min)	$K_1$ $K_2$ $q_{\rm max}$ $K_L$ $K_F$ $1/n$ $R^2$	Rate constant of pseudo $1^{st}$ order $(min^{-1})$ Rate constant of pseudo $2^{nd}$ order $(g mg^{-1} min^{-1})$ Maximum uptake of ammonium ion exchange $(mg l^{-1})$ Langmuir constant $(l mg^{-1})$ Freundlich constant $(l mg^{-1})$ Heterogeneity factor Coefficient of determination

Table 4X-ray fluorescence results of South African coal fly ashillustrating the major elements

Compound	Mass%
SiO <sub>2</sub>	46.9
$Al_2O_3$	31.3
FeO	4.98
CaO	4.33
Fe <sub>2</sub> O <sub>3</sub>	2.96
TiO <sub>2</sub>	1.54
K <sub>2</sub> O	0.72
MgO	0.60
$P_2O_5$	0.47
SO <sub>3</sub>	0.40
SrO	0.12
BaO	0.11
$V_2O_5$	0.06
MnO	0.03
Cr <sub>2</sub> O <sub>3</sub>	0.03
Co <sub>2</sub> O <sub>3</sub>	0.01
Y <sub>2</sub> O <sub>3</sub>	0.01
Loss on ignition	4.89
Total	99.46
Si/Al	1.50

The pseudo first order (eqn (4)) and pseudo second order (eqn (5)) are presented.

$$\log(q_{\rm e} - q_t) = \log q_{\rm e} - K_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$
(5)

The linear form equation of Langmuir isotherm is represented by eqn (6).

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{q_{\rm max}K_{\rm L}} + \frac{C_{\rm e}}{q_{\rm max}} \tag{6}$$

The  $q_{\text{max}}$  and  $K_{\text{L}}$  were calculated from the slope and intercept from the graph  $C_{\text{e}}$  versus  $C_{\text{e}}/q_{\text{e}}$ .

The linear form of Freundlich isotherm is represented by:<sup>3</sup>

$$\log q_{\rm e} = \log K_{\rm F} + \frac{1}{n} \log C_{\rm e} \tag{7}$$

The summarized nomenclature of the parameters and constants used in the current study is provided in Table 3.

## Results and discussion

#### Elemental composition of the zeolites

The raw coal fly ash was classified as Class F because the sum of  $SiO_2$ ,  $Al_2O_3$  and FeO was greater than 70% (Table 4). This elemental composition is typical of coal fly ash obtained from the combustion of South African bituminous coal.<sup>33</sup> The Si/Al ratio was found to be 1.50. This ratio is important because it governs the type of zeolite that can be synthesized from the coal fly ash.

In Fig. 1, XRD and SEM images of clinoptilolite (Fig. 1a), coal fly ash (Fig. 1b), products obtained using the microwaveultrasound method (Fig. 1c) and products obtained using the ultrasound-microwave (reverse) methods (Fig. 1d) are presented. The SEM analysis showed irregular shaped particles of clinoptilolite (Fig. 1a), while raw fly ash showed smooth spherical particles due to the glassy crystals that covered the surface (Fig. 1b). The dominant crystal phases for clinoptilolite were clinoptilolite and albite (Fig. 1a). While fly ash had mullite and quartz as its dominant crystal phases as shown by the XRD profile (Fig. 1b). The morphology and crystal structure of coal fly ash was transformed significantly by microwave and ultrasound irradiations. Pure phase sodalite phases were formed when the microwave-ultrasound irradiation method was used (Fig. 1c). Some spherical flower-like structures that are associated with sodalite were observed.

The 'reverse method' gave mixed phase sodalite with impurities of coal fly ash phases (Fig. 1d). Sodalite crystals forming on top of the coal fly ash particles were observed. This is because the slurry was not filtered and hence coal fly ash crystals were still present in the final sodalite product.

# Surface area and cation exchange capacity analysis of coal fly ash and its products

The surface area and the cation exchange capacity of the raw coal fly ash were 1.2 m<sup>2</sup> g<sup>-1</sup> and 0.29 meq. g<sup>-1</sup> respectively (Table 5). These low values indicated that the raw coal fly ash would have a low ammonium uptake. A significant improvement in the surface area and cation exchange capacity was recorded upon zeolitization. The mixed phase sodalite had a surface area of 7.8  $m^2 g^{-1}$  and cation exchange capacity of 1.18 meq.  $g^{-1}$ . Furthermore, the pure phase sodalite showed a higher surface area (16  $m^2 g^{-1}$ ) and cation exchange capacity (2.92 meq.  $g^{-1}$ ). The surface area of pure phase sodalite was comparable to that of clinoptilolite Table 5. For this reason, the pure phase sodalite and clinoptilolite were expected to show higher ammonium ion uptake. In this study, the ammonium ion removal efficiency of the synthesized zeolites was compared with that of a natural zeolite (clinoptilolite), which is known for high cation exchange capacity and selectivity towards ammonium in aqueous solutions. The clinoptilolite used in this study was characterized by surface area and cation exchange capacity of 18 m<sup>2</sup> g<sup>-1</sup> and 2.13 meq. g<sup>-1</sup> respectively.

#### Zeta potential of coal fly ash and its products

The zeta potential of the raw coal fly ash, clinoptilolite, and the synthesized zeolites was carried out with the sole purpose of elucidating the effect of pH on the adsorption of ammonium ions from urine and the results are presented on Fig. 2. It is worth noting that, at the surface of aluminosilicates, the anionic groups present are silicates ( $O-SiO_2^-$ ) and aluminates ( $O-AIO^-$ ). These functional groups are negatively charged. However, they are pH dependent and can undergo protonation or deprotonation as a function of pH.<sup>34</sup> The isoelectric point (IEP) (*i.e.* pH of neutral charge) of coal fly ash, clinoptilolite,



Fig. 1 XRD plots and SEM images of (a) clinoptilolite, (b) raw coal fly ash, and its synthesized products (c) sodalite and (d) pure phase sodalite (Clp = clinoptilolite, Ab = albite, M = mullite, Q = quartz, S = sodalite).

mixed phase sodalite (MS) and pure phase sodalite (S) was determined as 4.7, 7.9, 6.3 and 6.8 respectively. The negative charge of all the materials increased rapidly with an increase in

Table 5	Surface	area, pore	e volume	and cation	ו exchange	capacity of
clinoptile	olite, raw	coal fly a	sh and sy	nthesized	zeolitic pro	ducts

Material	BET surface area $(m^2 g^{-1})$	Pore volume $(m^3 g^{-1})$	$\begin{array}{c} { m CEC} \ ({ m meq}. \\ { m g}^{-1} \end{array}$
Coal fly ash	1 1965	0.001109	0.29
Clinoptilolite	17.8972	0.029877	2.13
Mixed sodalite	7.8100	0.018864	1.18
Sodalite	15.5000	0.034826	2.92

pH beyond the IEP. The negative charge of the zeolites has a direct impact on the adsorption of the positively charged ions. Specifically, the positively charged ions are attracted to the negatively charged surface of the zeolites, *i.e.* a process known as an electrostatic interaction.

# Removal of ammonia from synthetic urine and hydrolyzed urine

The concentration of ammonium and selected ions before and after adsorption is presented in Table 6. A higher removal of  $NH_4^+$  compared with the other cations (K<sup>+</sup>, Na<sup>+</sup> and Ca<sup>2+</sup>) in both synthetic and hydrolyzed urine was observed. This was due to the high concentration of  $NH_4^+$  which subsequently ensured greater driving force for adsorption.<sup>35</sup> The  $Mg^{2+}$  ions were not

 Table 6
 Characterization of synthetic and hydrolyzed urine before and after adsorption<sup>a</sup>

Parameters		Synthetic urine after adsorption				Hydrolyzed urine after adsorption				
	Synthetic urine before adsorption	CFA	MS	Clin	Sod	Hydrolyzed urine before adsorption	CFA	MS	Clin	Sod
$NH_4^+ - N (mg l^{-1})$	215.2	131.1	87.41	51.24	39.01	723.5	476.1	415.3	225.6	215.7
$Ca^{2+}$ (mg l <sup>-1</sup> )	28.12	30.62	33.20	54.33	48.07	93.01	88.02	96.77	103.0	118.2
$K^{+}$ (mg l <sup>-1</sup> )	153.3	150.3	149.0	115.3	120.4	213.4	210.5	186.3	160.3	181.4
Mg <sup>2+</sup>	ND	8.323	20.10	66.63	4.114	ND	11.07	22.06	65.55	57.06
$Na^+$ (mg l <sup>-1</sup> )	92	86.22	112.8	103.7	126.0	127.6	120.9	136.4	160.8	203.2

<sup>*a*</sup> ND: not detected; CFA: coal fly ash, MS: mixed sodalite, Clin: clinoptilolite, Sod: sodalite.

#### Paper



Fig. 2 pH vs. zeta potential of raw coal fly ash, clinoptilolite, mixed-phase sodalite and pure phase sodalite.

detected from both synthetic urine and hydrolyzed urine due to the dilution effect. However, Mg2+ ions were detected after adsorption. Furthermore, when adsorption was carried out using mixed sodalite, pure sodalite and clinoptilolite, the concentration of Na<sup>+</sup> and Ca<sup>2+</sup> ions was increased. Notably, zeolites consist of weakly bound cations which are likely to be exchanged with cations in solution.<sup>36</sup> This suggests that Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> ions present in the zeolites were exchanged with NH<sub>4</sub><sup>+</sup> ions in solution. The synthetic zeolites were alkali-treated with NaOH leading to an increase in concentration of Na<sup>+</sup> ions. These ions enable ionic exchange with NH4<sup>+</sup> from urine. Lu et al., also noted that Al<sup>3+</sup> has stronger affinity with zeolite compared to Na<sup>+</sup>, synthetic zeolite (Na<sup>+</sup> modified zeolite) demonstrated higher ion exchange capacity compared to natural zeolite for ammonium adsorption.37 It is worth noting that ionic exchange capacity between divalent ions (Mg<sup>2+</sup> and  $Ca^{2+}$ ) and  $NH_4^+$  ions from an exchange surface is lower than the exchange between two monovalent cations such as Na<sup>+</sup> ions.<sup>35</sup> This explains the high ammonium ion removal efficiency by sodalite due to the high amount of monovalent Na<sup>+</sup> ions induced by NaOH treatment. Nonetheless, the concentration of K<sup>+</sup> ions in solution was reduced after adsorption indicating possible re-adsorption by the adsorbents due to its strong affinity to zeolites.38 On the other hand, coal fly ash

demonstrated minimal cation exchange due to its low cation exchange capacity and therefore displayed the lowest ammonium ion removal (Table 6). Ion-exchange was not the only controlling mechanism during the adsorption process. This is because the major ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) released from the adsorbents to the solution were not equivalent to the NH<sub>4</sub><sup>+</sup> ions adsorbed. It is therefore believed that molecular adsorption was involved in the removal of NH<sub>4</sub><sup>+</sup> ion from the urine samples.

#### Effect of adsorbent dosage

To study the effect of adsorbent dosage, experiments were carried out at a neutral pH of 7 for 30 min at room temperature (25 °C), while dosage was varied from 0.2-1 g. Fig. 3 shows the effect of adsorbent dosage on the removal ammonium from synthetic and hydrolyzed urine. Raw coal fly ash, clinoptilolite and coal fly ash-derived zeolitic products were evaluated as adsorbents. A proportional increase in ammonium removal with an increase in adsorbent dosage was observed in all cases. This increase in ammonium uptake was attributed to the increased number of exchangeable and active adsorption sites.9 Xu et al., also observed an increase in ammonia removal efficiency from 2% to 55% with an increase in zeolite adsorbent dosage of 4 g  $l^{-1}$  to 10 g  $l^{-1}$  respectively.<sup>39</sup> It is worth noting that understanding the effect of adsorbent dosage facilitate the determination of the most effective amount of adsorbent for a given volume of urine. Due to its porous nature, high cation exchange capacity and surface area (Table 5), sodalite presented the highest ammonium removal efficiency from synthetic urine (82%) and hydrolyzed urine (73%). The porosity and cation exchange capacity of sodalite were improved during microwave treatment which subsequently led to the high uptake of the ammonium ions from solution. Likewise, clinoptilolite showed high ammonium removal efficiencies of up to 78% from synthetic urine and 70% from hydrolyzed urine due to its high cation exchange capacity and ammonium ion selectivity. On the other hand, the mixed phase sodalite adsorbent showed low removal efficiencies due to its low crystallinity and the presence of coal fly ash phases (Fig. 1c). This was as a result of its low



Fig. 3 Effect of adsorbent dosage on the removal of ammonium from (a) synthetic urine and (b) hydrolyzed urine.



Fig. 4 Effect of contact time on the removal of ammonium from (a) synthetic urine and (b) hydrolyzed urine.

cation exchange capacity and surface area a raw coal fly-ash demonstrated the lowest removal efficiency (Table 5). Comparably, the removal efficiency was reduced when hydrolyzed urine was used instead of synthetic urine. This phenomenon was attributed to the presence of organic macromolecules (matrix) and pyrophosphates in hydrolyzed urine.<sup>2</sup> These macromolecules are believed to hinder the diffusion of ammonium ions to active adsorption sites of the adsorbent. The findings of this study were relatively comparable to the results reported by (Zhang *et al.*).<sup>23</sup>

#### Effect of contact time

The effect of contact time was performed at constant pH of 7, absorbent dosage of 1 g at room temperature of 25 °C, while contact time was varied from 10–120 min. Fig. 4 presents the effect of contact time on the removal of ammonium from synthetic and hydrolyzed urine using coal fly ash, clinoptilolite and the synthesized zeolitic products. The percentage removal of ammonium ion increased with an increase in contact time. Notably, a rapid ammonium removal occurred from 10 min to 30 min. This was attributed to high solute gradient and abundant vacant adsorbent sites at the beginning of experiment leading to high driving force for ammonium ions to diffuse to

the exchangeable sites. Previous studies has shown that ammonium uptake by zeolites is a fast process and it can attain equilibrium in short times (e.g. 10-15 min).25 This is similar to results reported by Xue et al., where 66% of ammonia was removed after 5 min of contact time. However, only 5% increase in removal efficiency was observed after 1440 min.40 Beyond 30 min, the rate of ammonium removal proceeded at a slower rate until equilibrium was attained at 60 min. This observation was explained by the saturation of active adsorption sites.9 All other adsorbents attained equilibrium at 60 min except sodalite which attained equilibrium at 30 min for synthetic urine. However, sodalite desorbed ammonium back to solution beyond 60 min of agitation. This observation was due to that sodalite is a cation exchange material. The framework cations (*i.e.*  $Na^+$ ,  $Ca^{2+}$ ) that exchanged with  $NH_4^+$  ions can readily exchange back to attain a neutral state. Nonetheless, the  $NH_4^+$ percentage removal by coal fly ash did not reduce after equilibrium due to its low cation exchange capacity.

#### Effect of pH

The effect of pH studied at optimum conditions of 1 g adsorbent dosage, 60 min contact time at room temperature (25  $^{\circ}$ C), while varying the pH between 2–10. According to the zeta potential



Fig. 5 Effect of pH on the removal of ammonium from (a) synthetic urine and (b) hydrolyzed urine.

#### Paper

results, the adsorbents became more negatively charged at higher pH values. The negative surface charge was desired for the removal of ammonium from urine. Following the zeta potential results, the adsorption of ammonium ions on various adsorbents was carried out at the pH range of 2-10 and the results are presented on Fig. 5. The removal efficiency increased from the acidic pH (i.e. pH 2) to neutral pH of 7. A further increase in pH (8-10) led to a decrease in ammonium adsorption. Remarkably, the zeta potential results showed that the zeolites became negatively at the higher pH values (*i.e.* pH > IEP) (Fig. 2). In acid medium, the low removal efficiency was attributed to the positive surface charge resulting in the repulsive forces between the adsorbent surface and positively charged NH4<sup>+</sup> ions. This decrease in ammonia removal at low pH was also reported by Liu et al., and it was attributed to the dissolution or collapse of the zeolite structure at pH levels below 4.41 Likewise, Hermassi et al., reported a similar trend where the optimum pH for ammonium removal was between pH 4 and 8.5.42 An increase in pH beyond the characteristic optimal values affects the adsorption properties of the zeolites and exchanging ions, leading to a decrease in adsorption capacity.43 The NH<sub>4</sub><sup>+</sup> ions were converted to NH<sub>3</sub> at higher pH values leading to a decrease ion exchange capacity with the zeolitic materials.44 Likewise, different forms of ammonia in solution affects the surface charge of the adsorbent as well as the degree

of ionization and speciation of the adsorbate.<sup>45</sup> Therefore, a neutral pH (*i.e.* pH 7) was optimal for removal of ammonium ions from urine. These findings were in agreement with the previously reported study.<sup>46</sup> Sun *et al.*, also observed high selectivity of ammonium ions on an aluminosilicate adsorbent at pH 7 and an optimum removal efficiency of 99% was recorded.<sup>47</sup>

#### Adsorption kinetics

Adsorption kinetics are crucial as they provide information about the reaction pathways.<sup>48</sup> The exchange of ammonium ions on coal fly ash, clinoptilolite and the synthesized zeolitic products was modeled using pseudo first order and pseudo second order kinetics. The rate constants were calculated from the slope and intercept of the graph (Fig. 6). The *R*<sup>2</sup> values of the linearized plots were used to determine the kinetic model that best fits the adsorption of ammonium onto the zeolites.

Based on the  $R^2$  values, the adsorption of ammonium on all adsorbents followed pseudo-second-order kinetics with coefficient of determination ( $R^2 > 0.99$ ) higher than those of the pseudo-first-order kinetics ( $R^2 < 0.96$ ) (Table 7). The same results were observed by Xin *et al.*, where the removal of ammonia from aqueous solution using a zeolite adsorbent was reported to follow a pseudo-second-order kinetics with 0.9973 coefficient of determination.<sup>49</sup> The pseudo second order



Fig. 6 First order kinetics for (a) synthetic urine and (b) hydrolyzed urine and second order kinetics (c) synthetic urine (d) hydrolyzed urine.

Table 7 Rate constants and correlation coefficients for the studied kinetics models

Synthetic urine				Hydrolyzed urine				
Material	$K_1$ (min <sup>-1</sup> )	$q_{\rm e}  ({ m mg g}^{-1})$	$R^2$	Material	$K_1$ (min <sup>-1</sup> )	$q_{\rm e} ({\rm mg~g^{-1}})$	$R^2$	
Coal fly ash	3.638	0.020	0.91568	Coal fly ash	2.458	0.391	0.27644	
Mixed sodalite	3.684	0.011	0.96674	Mixed sodalite	2.458	0.391	0.27644	
Clinoptilolite	3.556	0.016	0.90264	Clinoptilolite	2.786	0.005	0.60286	
Sodalite	1.799	0.010	0.8629	Sodalite	2.458	0.391	0.27644	
Pseudo second or	rder							
Synthetic urine				Hydrolyzed urine				
Material	$K_2 (\mathrm{mg g}^{-1} \mathrm{min}^{-1})$	$q_{\rm e} ({ m mg g}^{-1})$	$R^2$	Material	$K_2 (\mathrm{mg g}^{-1} \mathrm{min}^{-1})$	$q_{\rm e} ({\rm mg~g}^{-1})$	$R^2$	
Coal fly ash	0.809	2.679	0.99962	Coal fly ash	0.081	8.159	0.99962	
Mixed sodalite	0.306	4.006	0.9983	Mixed sodalite	0.907	15.48	0.9991	
Clinoptilolite	0.628	4.948	0.99956	Clinoptilolite	0.0448	10.33	0.99989	
Sadalita	0.402	5 524	0.00974	Sodalite	0.897	16.03	0 99924	

suggests that the adsorption rate was governed by chemical adsorption mechanism.<sup>50</sup> Therefore, the ammonium adsorption process was affected by the chemical properties of the zeolite and urine leading to an ion exchange being the rate-

determining step and subsequently resulting in longer periods for ammonium uptake.<sup>23</sup> The adsorption capacity  $(q_e)$  was highest for sodalite which agreed with the high ammonium removal efficiency obtained compared to the other adsorbents.



Fig. 7 Langmuir isotherm for (a) synthetic urine and (b) hydrolyzed urine; and Freundlich isotherm for (c) synthetic urine and (d) hydrolyzed urine.

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#### Table 8 The constants and correlation coefficients for the isotherm models

Synthetic urine					Hydrolyzed urine				
Material	$q_{ m max} ( m mg \  m g^{-1})$	K (L	$mg^{-1}$	$R^2$	Material	$q_{\max} \left( \text{mg g}^{-1} \right)$	K (L mg <sup>-1</sup> )	$R^2$	
Coal fly ash	4.132	6.05	$5  imes 10^{-4}$	0.81452	Coal fly ash	N/A	N/A	N/A	
Mixed sodalite	0.362	0.19	)1	0.5365	Mixed sodalite	N/A	N/A	N/A	
Clinoptilolite	3.116	0.01	.5	0.9409	Clinoptilolite	N/A	N/A	N/A	
Sodalite	0.912	0.01	.1	0.8207	Sodalite	N/A	N/A	N/A	
Freundlich									
Synthetic urine					Hydrolyzed urine				
Material	$K_{\rm F} \left( { m mg g}^{-1}  ight) \left( { m mg L}^{-1}  ight)$	$^{-1})^{1/n}$	1/ <i>n</i>	$R^2$	Material	$K_{\rm F}  ({ m mg g}^{-1})  ({ m mg L}^{-1})^{1/n}$	1/ <i>n</i>	$R^2$	
Coal fly ash	0.36		0.33	0.9962	Coal fly ash	0.016	0.13	0.9995	
Mixed sodalite	0.44		0.62	0.9886	Mixed sodalite	0.087	0.25	0.997	
Clinoptilolite	1.12		0.35	0.9876	Clinoptilolite	0.56	0.18	0996	
Sodalite	1.89		0.29	0.9433	Sodalite	0.93	0.22	0.991	

The increase in  $q_e$  with an increase in initial ammonium concentration, was higher for hydrolyzed urine compared to synthetic urine. This was due to the existence of equilibrium between the liquid phase concentration (urine) and the adsorption capacity of the zeolite. An increase in the initial ammonium ion concentration resulted in the equilibrium shifting towards a higher adsorption capacity region.<sup>51</sup> The  $q_e$  values for the pseudo second order were closer to the experimental values, showing that pseudo second order was the best fitting adsorption kinetics.

#### Adsorption isotherms

Adsorption isotherms are important because they provide adsorption mechanism for the interaction between the adsorbent and the adsorbate.52 The Langmuir and Freundlich isotherms were used models to study the adsorption mechanism of ammonium on coal fly ash, clinoptilolite and the synthesized zeolite products. The Langmuir isotherm assumes that adsorption occurs at specific homogeneous sites within the adsorbent, meaning the adsorbate forms monolayer onto the surface of the adsorbent.53 Moreover, Freundlich isotherms describes the formation of the multiple layers on the surface of the adsorbent.<sup>48</sup> The constants were calculated from the slope and intercept of the graph (Fig. 7). The Langmuir constants for adsorption of ammonium on zeolites were in the range of 0.00061 to 0.19 L  $g^{-1}$  while those of the Freundlich isotherm ranged between 0.13 and 1.89 mg  $g^{-1}$ . The coefficient of determination  $(R^2)$  demonstrated a better fit on the linear plots of Freundlich isotherm model as opposed to those of Langmuir (Table 8); suggesting that the adsorption of ammonium onto zeolites followed the Freundlich isotherm. He et al., found ammonia adsorption on synthesized zeolites to favor Freundlich isotherm, which is in agreement with the results obtained in this study. The findings suggested a non-uniform

distribution of adsorption energy over the surface of the zeolite adsorbent.<sup>54</sup> Similarly, the heterogeneity factor 1/n was between 0–1 suggesting that the adsorption process was favorable.

## Conclusions

Greener energy efficient processes involving microwave and ultrasound irradiation were developed to synthesize sodalite zeolite materials from coal fly ash biomass waste. It was observed that raw coal fly is not an effective adsorbent for ammonium in solution and urine. Pure phase sodalite with relatively high surface area ( $16 \text{ m}^2 \text{ g}^{-1}$ ) and CEC (2.92 meq.  $\text{g}^{-1}$ ) exhibited higher ammonium removal efficiency (up 82%) compared to natural zeolite (clinoptilolite). The adsorption process followed the Freundlich isotherm and the pseudo  $2^{nd}$ order kinetic model. The coal fly ash derived zeolites offer a great opportunity in environmental remediation as low-cost adsorbent.

# Conflicts of interest

There are no conflicts to declare.

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