Enhanced removal of nitrate from water using amine-grafted agricultural wastes

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Abstract

Adsorption using low-cost adsorbents is a favourable water treatment method for the removal of water contaminants. In this study the enhanced removal of nitrate, a contaminant at elevated concentration affecting human health and causing eutrophication of water, was tested using chemically modified agricultural wastes as adsorbents. Batch and fixed-bed adsorption studies were performed on corn cob and coconut copra that were surface modified by amine-grafting to increase the surface positive charges. The Langmuir nitrate adsorption capacities (mg N/g) were 49.9 and 59.0 for the amine-grafted (AG) corn cob and coconut copra, respectively at pH 6.5 and ionic strength 1×10^{-3} M NaCl. These values are higher than those of many commercially available anion exchange resins. Fixed-bed (15-cm height) adsorption capacities (mg N/g) calculated from the breakthrough curves were 15.3 and 18.6 for AG corn cob and AG coconut copra, respectively, for an influent nitrate concentration 20 mg N/L at a flow velocity 5 m/h. Nitrate adsorption decreased in the presence of sulphate, phosphate and chloride, with sulphate being the most competitive anion. The Thomas model fitted well to the fixed-bed adsorption data from four repeated adsorption/desorption cycles. Plug-flow model fitted well to the data from only the first cycle.

Keywords

Nitrate; Water treatment; Agricultural wastes adsorbents; Adsorption models

1. Introduction

The high intake of nitrate from water by humans can cause several health problems such as vomiting, hypertension, diarrhea, respiratory tract infections, spontaneous abortions and ‘blue baby’ syndrome or methemoglobinemia (Fewtrell, 2004). In order to prevent these health hazards, permissible levels of nitrate in water have been recommended in many countries. The maximum nitrate limit for drinking water established by the World Health Organization is 50 mg/L (11.3 mg N/L) (WHO, 2011) and Australia's maximum nitrate limit is 50 mg/L for infants up to 3 months old, and 100 mg/L for adults and children over the age of 3 months (NHMRC, 2011). Apart from such health issues, the high concentration of nitrate in water bodies such as rivers and lakes can cause environmental problems such as eutrophication (Camargo and Alonso, 2006).

Nitrate is a highly soluble ion and stable in water. Thus traditional water treatment methods such as lime softening and filtration are difficult to use for the removal of nitrate from water. Several nitrate removal technologies such as electro-dialysis, reverse osmosis, adsorption and chemical and biological methods have been used in water treatment (Bhatnagar and Sillanpää, 2011 and Loganathan et al., 2013). Of these, some methods (electro-dialysis, reverse osmosis) have high operational cost (Bhatnagar and Sillanpää, 2011). Biological denitrification method requires specific microorganisms and the treated water needs a post treatment due to the presence of germs and metabolic substances (Kapoor and Viraraghavan, 1997 and Samatya et al., 2006). Furthermore the process is slow and requires maintenance of optimum conditions such as temperature which are difficult. On the other hand, adsorption is an attractive method because of its cost-effectiveness, simplicity of design and ease of operation with minimal waste production (Bae et al., 2002). However, the efficiency of this method depends on the type of adsorbent used.

Agricultural wastes have been investigated as adsorbents for the removal of contaminants from waste water (Loganathan et al., 2013). Agricultural wastes are widely available at low cost with no disposal problems and therefore their use incurs low operational expense. In previous studies a number of agricultural wastes such as rice hull, sugarcane bagasse, coconut shells, wheat straw and almond shell have been tested for the removal of nitrate from water. Another advantage of using agricultural wastes as adsorbent is that when they are fully saturated with nitrate and cannot be used further for the removal of nitrate the nitrate-rich wastes can be disposed to agricultural lands to supply nitrate as fertiliser.

One of the disadvantages of using agricultural wastes in removing nitrate is that they have low adsorption capacities. However, if they are chemically or physically modified they can prove to be good adsorbents (Loganathan et al., 2013). Various methods of modification such as protonation (Chatterjee et al., 2009), metal impregnation (Kalaruban et al., 2016) and amine-grafting (Orlando et al., 2002a and Orlando et al., 2002b) have been used to increase the nitrate adsorption capacity of adsorbents. Of these, the amine grafting method is a highly efficient method for agricultural wastes where the amine groups possessing positive charges can increase the adsorption of negatively charged nitrate (Bhatnagar and Sillanpää, 2011 and Loganathan et al., 2013). For example, Orlando et al. (2002a) reported that grafting amine groups onto lignocellulosic agricultural wastes such as *Moringa oleifera* husk, rice husk, sugarcane bagasse, and pine bark resulted in high Langmuir nitrate adsorption capacities of 63–74 mg NO_3^-/g. They stated that these increased adsorption capacities as a result of amine-grafting was approximately equal to that of the commercial anion exchanger, Amberlite IRA-900. Most studies on the use of agricultural wastes for nitrate removal were tested in static batch adsorption experiments (Bhatnagar and Sillanpää, 2011 and Loganathan et al., 2013), yet only a few have been tested using dynamic fixed-bed adsorption experiment (Xing et al., 2011 and Xu et al., 2012). Findings from fixed-bed experiments are more relevant to real operating systems in treatment plants.

The main objectives of the research were to: (i) study the efficiency of nitrate removal from synthetic water using amine-grafted (AG) corn cob and coconut copra in batch and fixed-bed adsorption experiments; (ii) model the batch equilibrium, batch kinetics and fixed-bed data on nitrate removal; (iii) study the effect of co-existing anions at different concentrations on the adsorption of nitrate; and (iv) investigate desorption of nitrate from the adsorbents and the regeneration of adsorbents for multiple reuse. The new aspect of the study is to test the nitrate adsorption behaviour of amine-grafted agricultural wastes in column mode dynamic system consisting of many repeated adsorption/desorption cycles which have more practical application. Further the mathematical modelling of the dynamic system used in this study has not been dealt previously for agricultural wastes. Though amine-grafting to increase the nitrate adsorption capacity is not new, previous studies on this subject were conducted mainly in static batch mode and only two studies on fixed-bed system (Xing et al., 2011 and Xu et al., 2012). However, these two column studies neither tried to model the adsorption behaviour nor considered complementary ions effects on nitrate as in our study. Corn cob was selected as an agricultural waste as corn is one of the largest grain crops cultivated in many parts of the world with an annual worldwide production of about 520×10^9 kg (Ioannidou et al., 2009) and corn cob waste is available in large quantities. Coconut is one of the main palm trees cultivated throughout the tropical world to produce copra which is used to make vegetable oil (Bhatnagar et al., 2010). Large quantities of copra waste are available from the total annual coconut production of about 50 million tonnes in various countries.

2. Materials and methods

2.1. Materials

Fresh corns were obtained from Paddy's Market in Sydney, New South Wales, Australia, and waste corn cobs were separated from the corn kernels. The corn cobs were cut into small pieces, washed with distilled water and heated for 24 h at 100 °C inside an oven. Then they were ground and sieved to a size of 300–600 μm.

Fresh coconuts were also obtained from the same market and each coconut was cut into two pieces. The coconut kernels were scraped manually from these pieces and milk extracted by hand-squeezing as much as possible. The residue was kept in an oven at 100 °C for 48 h. The dried material known as copra was ground and sieved to 300–600 μm.

2.2. Material modification

Samples of the corn cob and coconut copra (300–600 μm) were surface modified by amine grafting using Orlando et al.'s method (Orlando et al., 2002b). In this method, 20 g corn cob or coconut copra were reacted with 200 mL of epichlorohydrin in 240 mL *N*, *N*-dimethyl formamide (DMF) at 100 °C for 1 h. Pyridine (80 mL) was added to the solution and stirred for 1 h at 100 °C. Amine groups were then introduced by adding 200 mL of 50% dimethylamine solution. The mixture was stirred for 3 h at 100 °C and washed with 2 L

0.1 M NaOH, 0.1 M HCl and 2 L diluted ethanol (ethanol: water volume ratio = 1:1). Finally, it was washed with a large volume of 0.1 M NaCl and heated at 100 °C for 24 h.

2.3. Feed solutions

Feed solution containing nitrate was prepared for the batch experiments by dissolving ANALAR grade KNO_3 in Milli-Q water to obtain a concentration of 20 mg N/L. Ionic strength and pH of the solution were maintained at 1×10^{-3} M NaCl and 6.5, respectively. For the ion competition studies, ANALAR grade KH_2PO_4, Na_2SO_4 and NaCl were added to the nitrate solution to produce the required concentrations of phosphate, sulphate and chloride. For fixed-bed adsorption studies tap water was used instead of Milli-Q water to prepare the feed solution at a concentration of 20 mg N/L at pH of 6.5–7.5. Tap water was used because large volumes of solution for these studies were required. All experiments were conducted in synthetic solutions containing a fixed nitrate concentration and a range of complementary ions concentrations to obtain basic information on the suitability of the AG products in the adsorptive removal of nitrate. Phosphate, sulphate and chloride ions were selected for the study as they are common anions present in ground and surface waters (Akan et al., 2012, Shah and Trivedi, 2011 and Somasundaram et al., 1993). The concentrations used were in the ranges of ions generally present in these contaminated waters.

2.4. Nitrate analysis

Nitrate concentration was measured using an ion chromatograph (Model 790 personal IC) equipped with an auto sampler and conductivity cell detector. The ion chromatograph was cleaned before the analysis by the mobile phase solutions containing Na_2CO_3 and $NaHCO_3$ followed by diluted sulphuric acid and Milli-Q water.

2.5. Adsorbent characterisation

Samples of dried corn cob, coconut copra, AG corn cob and AG coconut copra were analysed using Zeiss supra 55VP field emission model scanning electron microscope in conjunction with energy dispersion spectrometry operated at 15 kv to determine the elemental composition. The materials' BET surface area and pore size distribution were determined using a Micrometrics 3 Flex surface characterisation analyser at 77 K. The total nitrogen and carbon were measured using a Leco TruSpec CN instrument.

Zeta potential measurement was done to characterise the surface electrical potential of the adsorbents. Unmodified and AG corn cob and coconut copra were suspended in Milli-Q water at a dosage of 1 mg/L and pH adjusted to various values in the 3–8 range using diluted HCl and NaOH solutions. The flasks were shaken at 120 rpm in a flat shaker for 3 h and then the zeta potential was measured on the suspensions using a Zetasizer nano instrument (Nano ZS Zen 3600, Malvern, UK). The measurements were conducted on three replicates and the means and standard errors were calculated.

2.6. Batch adsorption experiments

Nitrate adsorption by the AG and unmodified corn cob and coconut copra was determined using equilibrium and kinetics adsorption experiments at room temperature (24 ± 1 °C). All experiments were conducted in duplicate and the means and standard errors of the data of duplicate samples were calculated.

2.6.1. Equilibrium adsorption

Equilibrium adsorption experiments were conducted by adding different amounts of adsorbent (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 g/L) to 100 mL solutions containing a nitrate concentration of 20 mg N/L and ionic strength of 1×10^{-3} M NaCl at pH 6.5 and agitating the suspensions at a speed of 120 rpm in a flat shaker for 24 h. At the end of this period, the suspensions were filtered using filters with 1.2 μm size openings and analysed using an ion chromatograph analyser. The amount of nitrate adsorption was calculated by subtracting the amount of nitrate in solution after adsorption from the amount of nitrate in solution before adsorption.

2.6.2. Adsorption kinetics

Adsorption kinetics experiments were conducted by adding an adsorbent dose of 1 g/L to a solution containing a nitrate concentration of 20 mg N/L at an ionic strength of 1×10^{-3} M NaCl and pH 6.5 and agitating the samples at a speed of 120 rpm for different time intervals. At the end of the different shaking periods, the samples were filtered and the filtrates were analysed for nitrate. The amount of nitrate adsorbed was calculated as before.

2.7. Effect of pH on nitrate adsorption

The experiment on the effect of pH on nitrate adsorption was carried out using the same procedure as described for equilibrium adsorption. The initial nitrate concentration was the same as before but only one adsorbent dose of 0.5 g/L and initial pHs of 3, 4, 5, 6, 7, 8 and 9 were used. The pH was adjusted by adding diluted HCl or NaOH. The final pHs were measured and these values were used to determine the relationship of pH and amount adsorbed.

2.8. Complementary ions effect

Studies on the complementary ions effect were done using different concentrations of sulphate (20, 30, 50, and 70 mg S/L), phosphate (0.5, 1, 5, 10 and 30 mg P/L) and chloride (20, 30, 50 and 70 mg Cl/L) with a fixed dose of adsorbent (1 g/L) and a constant concentration of nitrate (20 mg N/L) at pH 6.5. These three ions were selected for the study as they are common anions present in ground and surface waters (Akan et al., 2012, Shah and Trivedi, 2011 and Somasundaram et al., 1993). The concentrations used were in the ranges of ions generally present in contaminated ground and wastewaters.

2.9. Fixed-bed adsorption studies

Fixed-bed column adsorption experiments were performed using 2 cm internal diameter acrylic glass columns packed with 20 g of modified and unmodified corn cob and coconut copra to a height of 15 cm. Influent solution containing nitrate at a concentration of 20 mg N/L was passed through the columns at a filtration velocity of 5 m/h (26.6 mL/min). A peristaltic pump was used for pumping the feed water in the up-flow mode through the column. The effluent solutions were collected on an hourly basis and nitrate was examined as before.

The maximum amount of nitrate adsorption (mg) onto the fixed-bed is defined by the equation given below (Nur et al., 2015),

$$q_{total} = \frac{Q}{1000}\int_{t=0}^{t-total} C_{ad}.dt \qquad (1)$$

where, C_{ad} is the adsorbed nitrate concentration ($C_{ad} = C_0 - C_t$) mg N/L and Q is the flow velocity (L/min). q_{total} is equal to the area under the plot of C_{ad} vs time and was calculated manually from the breakthrough curves using Microsoft Excel spreadsheet. The maximum adsorption capacity was calculated by dividing the maximum adsorption of nitrate by the amount of adsorbent used in the column.

2.10. Adsorption models

The batch and fixed-bed adsorption data were analysed using the adsorption models presented in Table 1. The procedures for the use of all the models, except the Elovich model and the axially dispersed plug-flow model, have been described in detail elsewhere (Kalaruban et al., 2016, Kim et al., 2015 and Nur et al., 2014). The procedure for the use of Elovich model was described by Riahi et al. (2013). The axially dispersed plug-flow model is described below.

Table 1. Adsorption models.

Experiment	Models	Equation	Parameters
Batch equilibrium	Langmuir	$q_e = \frac{q_m b C_e}{1+bC_e}$	q_m, b
	Freundlich	$q_e = K_f {C_e}^{1/n}$	K_f, n
	Sips	$q_e = \frac{q_m b C_e^{1/n}}{1+bC_e^{1/n}}$	q_m, b, n
Batch kinetics	Pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	k_1,q_e
	Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	k_2, q_e

Column kinetics	Elovich model	$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$	α, β
	Thomas model	$\ln(\frac{c_0}{c_t} - 1) = \frac{k_{Th} q_0 M}{Q} - k_{Th} c_0 t$	q_0, k_{Th}
	Axially dispersed plug-flow model	$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} - \frac{1-\varepsilon_b}{\varepsilon_b} \rho_p \frac{\partial q}{\partial t}$ Initial and boundary conditions $0 < z < L;\ t = 0;\ c = 0$ $z = 0;\ t > 0\ D_L \frac{\partial c}{\partial z}\|_{z=0} = -v(c\|_{z=0^-} - c\|$ $z = L;\ t > 0\ \frac{\partial c}{\partial z}\|_{z=L} = 0$	DL

*C_e = equilibrium concentration of nitrate (mg N/L), q_e = amount of nitrate adsorbed per unit mass of adsorbent (mg N/g), q_m = maximum amount of nitrate adsorbed per unit mass of adsorbent (mg N/g), b = Langmuir and Sips affinity constant (L/mg), K_f = Freundlich constant (mg/g)(L/mg)$^{1/n}$, n = Freundlich and Sips constant, q_t = amount of nitrate adsorbed at time t(h), (mg N/g), k_1 = rate constant of pseudo-first order (1/h), k_2 = rate constant of pseudo-second order (g/mg h), α = initial adsorption rate (mg/g min), β = related to extent of surface coverage and activation energy for chemisorption (g/mg), k_{Th} = Thomas rate constant (mL/min mg), q_o = equilibrium nitrate uptake per g of adsorbent (mg N/g), c_0 = inlet nitrate concentration (mg N/L), c_t = outlet nitrate concentration at time t (mg N/L), M = mass of adsorbent (g), Q = filtration velocity (mL/min), t = filtration time (min), D_L = axial dispersion coefficient (m^2/s), c = nitrate concentration in the liquid phase (mg N/L), q = nitrate concentration in the solid phase (mg N/L), ϵB = bed porosity, ρp = bulk density (kg/m^3), v = fluid velocity (m/s) and z = bed depth (m).

The axially dispersed plug-flow model parameters, axial dispersion coefficient, D_L and film mass transfer coefficient, k_f were calculated using empirical correlations given byChung and Wen (1968) (Eq. 2), Wakao and Funazkri (1978) and Luna et al. (2011) (Eq.3), respectively. In addition, the diffusion coefficient (D_s) of the homogeneous surface diffusion model (HSDM) was determined by matching the simulation results with the data obtained in experimental adsorption breakthrough curve. In order to numerically solve the axially dispersed plug-flow and the HSDM equations, in this work, Nelder-Mead simplex method (Nelder and Mead, 1965), orthogonal collocation method (OCM) (Villadsen and Stewart, 1967) and double variable ordinary equation (DVODE) program were used.

$$\frac{D_L \rho}{\mu} = \frac{R_e}{0.2 + 0.11\ R_e^{0.48}} \tag{2}$$

$$Sh = 2.0 + 1.1\ Sc^{1/3} Re^{0.6} = \frac{k_f d_p}{D_m} \tag{3}$$

where, ρ is the solution density (kg/m^3), μ is the fluid viscosity (kg/m·s), *Re* is the Reynold's number, *Sh* is the Sherwood number, *Sc* is the Schmidt number, d_p is the particle diameter (m), and D_m is the aqueous-phase diffusivity (m^2/s).

3. Results and discussion

3.1. Characteristics of adsorbents

3.1.1. Chemical composition and surface area

The EDS data showed that the N content increased in the coconut copra and corn cobs after the amine modification (Table 2). The Cl percentage also increased because the AG materials were finally washed with large amounts of NaCl to remove the excess acid and alkali used in the preparation of these materials. The Cl^- ions in the NaCl would have adsorbed onto the positive charges on the amine groups by electrostatic attraction.

Table 2. Elemental composition of adsorbents as determined by EDS and chemical combustion methods and nitrate adsorption on the adsorbents.

Adsorbent	**EDS**		**Leco chemical combustion**	**Batch adsorption**
	Nitrogen (mg/g)	Chlorine (mg/g)	Nitrogen (mg/g)	Nitrogen (mg/g)
Corn cob	94.0	0	10.3	–
AG corn cob before adsorption	141.0	93	52.6	–
AG corn cob after adsorption	163.5	39	83.7	–
N adsorbed	22.5	–	31.1	34
Coconut copra	61.0	0	11.5	–
AG coconut copra before adsorption	113.0	70	57.8	–
AG coconut copra after adsorption	168.0	24	89.8	–
N adsorbed	55.0	–	32.0	39

The total N contents of the materials estimated by chemical combustion method were much lower than those estimated by EDS. This is probably because EDS measures only the surface layer of a few micro meters of the adsorbents (Yao et al., 2011), whereas the combustion method measured the whole particle elemental composition. However, the increase in N content following amine grafting in the materials is approximately the same in the two methods. Xu et al. (2010) reported virtually the same amount of N increased (32 mg/g) after amine grafting of wheat straw using the method used in the present study.

The BET surface areas were 10.3 m^2/g and 9.8 m^2/g for the corn cob and AG corn cob, respectively, and 8.1 m^2/g and 7.1 m^2/g for the coconut copra and AG coconut copra, respectively.

3.1.2. Zeta potential

The unmodified corn cob and unmodified coconut copra both had a zero point of charge (ZPC) of approximately pH 3.0 whereas the AG corn cob and AG coconut copra had ZPC greater than pH 8.5 (Fig. 1). This shows that amine grafting of the adsorbents has changed the surface charges on the adsorbent from negative to positive in the entire pH range of 3 to 8.5, which is favourable for nitrate adsorption by electrostatic forces. This is in agreement with the results of Deng et al. (2013) who found that the amine modification of rice husk increased the ZPC from pH 2.7 to 8.5, suggesting that the net surface charge was positive up to pH 8.5. Xing et al. (2011) also reported that amine grafting changed the surface charge from negative to positive in wheat straw in the pH range of 2 to 9.

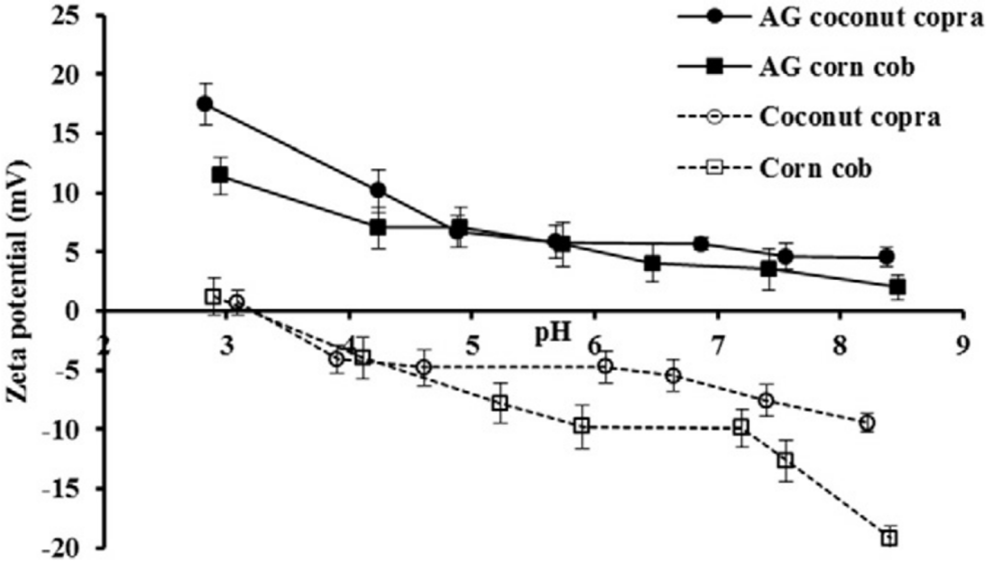


Fig. 1. Effect of pH on the zeta potential at the adsorbent/solution interface for corn cob, AG corn cob, coconut copra, and AG coconut copra. Vertical bars on the graphs represent standard errors of means of the data points.

3.2. Batch adsorption studies

3.2.1. Effect of pH

The effect of pH on nitrate adsorption showed that for the AG materials there was no significant change in the percent adsorption in the pH range from 3 to 9. The percentage adsorbed increased from 42% to 49% as the pH increased for the AG coconut copra and 37% to 45% for the AG corn cob. For the unmodified corn cob and the unmodified coconut copra, percentage adsorbed increased from 3% to 8% and 3% to 9%, respectively. The much higher adsorption capacity of the AG materials is due to the positive surface charges produced by the amine groups (Fig. 1). The unmodified materials showed a very low percentage of adsorption because of net negative surface charges on the adsorbent surface.

3.2.2. Adsorption isotherms

The nitrate removal efficiencies of the AG adsorbents were much higher than those of the unmodified adsorbents (Fig. 2). Langmuir, Freundlich and Sips models were used to model the experiment data. The data fitted satisfactorily to all the three models (Table 3). The Langmuir maximum adsorption capacities for the AG coconut copra and AG corn cob were 59.0 mg N/g and 49.9 mg N/g, respectively. The maximum adsorption capacities obtained for AG coconut copra and AG corn cob are higher than the corresponding values reported by others for amine grafted wheat straw, moringa hull, lauan sawdust, coconut husk, rice husk, pine bark and sugarcane bagasse (11–17 mg N/g; Orlando et al., 2002a and Xu et al., 2010). They are also higher than those reported for commercially available anion exchange resins such as Dowex 21K XLT (27.6 mg N/g) (Kalaruban et al., 2016), Purolite A520 E (33 mg N/g) (Nur et al., 2015) and NDP-2 (39.3 mg N/g), Purolite A 300 (33.3 mg N/g) and D201 (39.2 mg N/g) (Song et al., 2012). The corresponding values obtained from the Sips model were 67.4 mg N/g and 59.2 mg N/g, respectively. Nitrate adsorption on the unmodified adsorbents failed to fit the models.

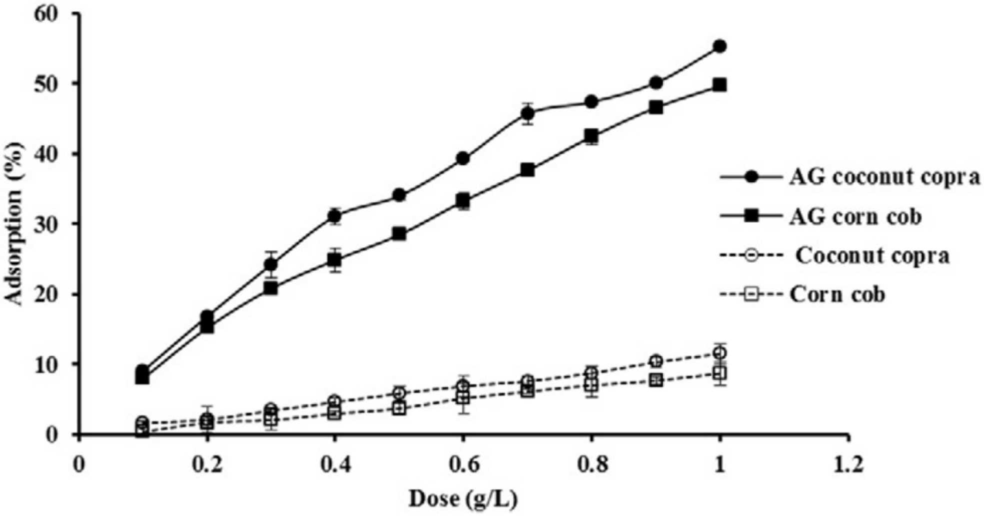


Fig. 2. Effect of adsorbent dose on the removal of nitrate at pH 6.5 (initial nitrate concentration 20 mg N/L). Vertical bars on the graphs represent standard errors of means of the data points.

Table 3. Model parameters for the adsorption of nitrate.

Model	Parameters	AG corncob	AG coconut copra
Langmuir	q_m (mg N/g)	49.9	59.2
	b (L/mg)	0.02	0.02
	R^2	0.8769	0.9606
Freundlich	k_f (mg/g)(L/mg)$^{1/n}$	1.24	2.07
	n	1.15	1.33
	R^2	0.9041	0.9615
Sips	q_m (mg N/g)	59.2	67.4
	b (L/mg)	0.01	0.02
	n	1.09	0.96
	R^2	0.8938	0.9610

Fig. 3 illustrates that nitrate removal efficiency drastically fell in the presence of sulphate ion and moderately decreased in the presence of phosphate and chloride ions. The adsorption occurred through the electrostatic attraction between positive surface charges on the adsorbent and negative charges on the anions by outer sphere surface complexation (non-specific adsorption) (Loganathan et al., 2014 and Oladoja and Helmreich, 2014). Sulphate has two valance charges, and therefore it has a tendency to adsorb stronger than chloride which has one charge and phosphate which has predominantly one-charged species ($H_2PO_4^-$) and some two-charged species (HPO_4^{2-}) at pH 6.5 of the study. At pH 6.5 > 80% phosphate is in the form of $H_2PO_4^-$ and the rest is in the form of HPO_4^{2-} (Pan et al., 2009). The differences in the magnitude of charges in the anions have also been used by Oladoja and Ahmad (2013) to explain the differences in the competitiveness of the anions for the adsorption of Cr(VI) on binary metal oxides. Because the chloride ion has one negative charge like nitrate its competition with nitrate was significant only at high concentrations especially in corn cob. The reason for the reduced competition of the chloride at concentrations similar to nitrate is that its hydration energy is higher than that of nitrate, and lower hydration energy favours adsorption (Song et al., 2012). Phosphate's competition with nitrate was the lowest because of its low concentrations in terms of moles/L. For example, only at L5 (30 mg P/L) is its competitiveness equal to that of chloride at L1 (20 mg Cl/L), where the concentrations (moles/L) of the two ions are nearly equal. The extent of complementary ions competition with nitrate may vary according to wastewater conditions and the concentration of complementary ions.

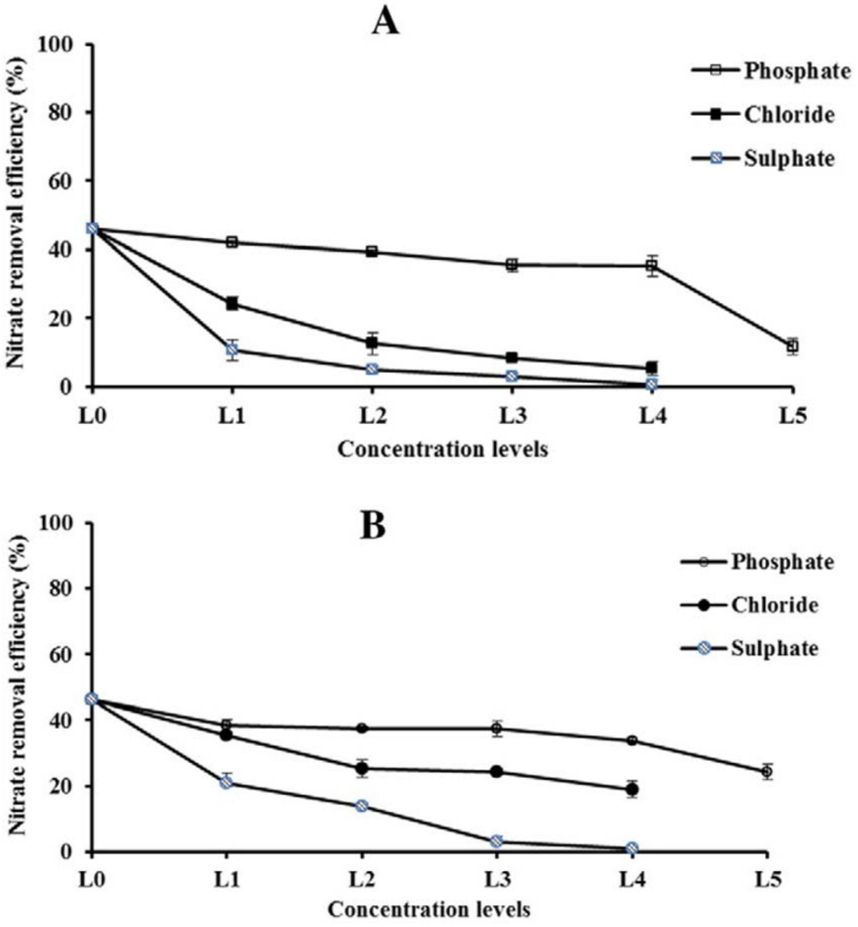
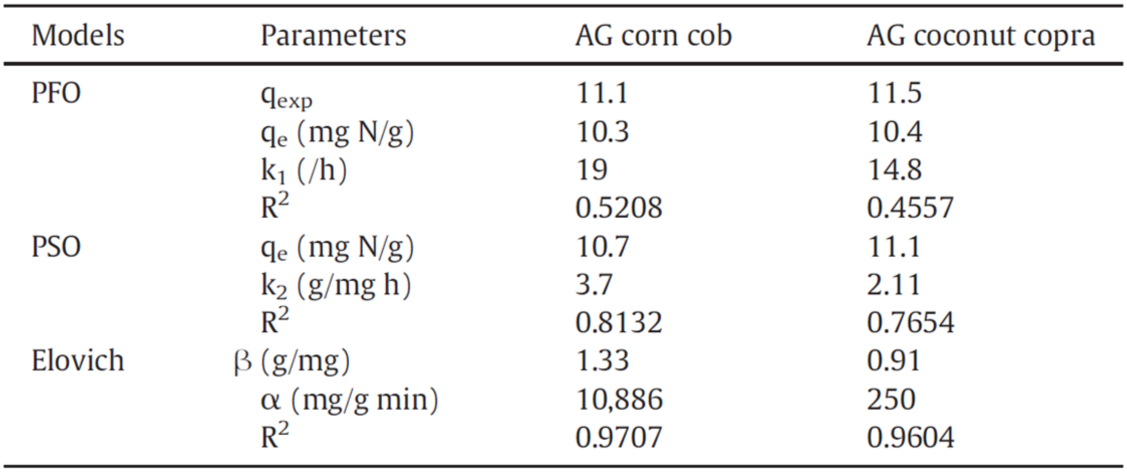


Fig. 3. Effect of complementary ions on the removal of nitrate by (A) AG corn cob, and (B) AG coconut copra (initial nitrate concentration 20 mg N/L). L1, L2, L3, and L4 for sulphate chloride and sulphate are 20, 30, 50, and 70 mg Cl or S/L. For phosphate L1, L2, L3, L4, and L5 represent 0.5, 1, 5, 10, and 30 mg P/L. Vertical bars on the graphs represent standard errors of means of the data points.

3.3. Adsorption kinetics

The study on the adsorption kinetics was conducted to predict the rate of nitrate removal by the adsorbents. The data was fitted to pseudo-first order, pseudo-second order and Elovich models and the values for the model parameters are given in Table 4. Of the three models, the Elovich model fitted the data well for both the AG adsorbents ($R^2 = 0.96–0.97$), whereas the PFO and PSO models' fits to data were poor ($R^2 = 0.46–0.81$). The reason for the good fit of data to Elovich model is that this model is applicable to kinetics of adsorption of solutes on heterogeneous surfaces with variation of adsorption energies (Özacar and Şengil, 2005 and Riahi et al., 2013). The surfaces of the agricultural wastes being heterogeneous (Riahi et al., 2013), this model was found to describe the adsorption kinetics very well.

Table 4. Batch adsorption kinetic parameters for the pseudo-first order (PFO) and pseudo-second order (PSO) models fit to the adsorption of nitrate on AG corn cob and AG coconut copra.



Models	Parameters	AG corn cob	AG coconut copra
PFO	q_{exp}	11.1	11.5
	q_e (mg N/g)	10.3	10.4
	k_1 (/h)	19	14.8
	R^2	0.5208	0.4557
PSO	q_e (mg N/g)	10.7	11.1
	k_2 (g/mg h)	3.7	2.11
	R^2	0.8132	0.7654
Elovich	β (g/mg)	1.33	0.91
	α (mg/g min)	10,886	250
	R^2	0.9707	0.9604

3.4. Fixed-bed adsorption experiment

3.4.1. Nitrate adsorption with and without complementary ions

Synthetic solutions were used for this study as in the case of the batch studies. However, the concentrations of nitrate and the complementary ions, phosphate and sulphate used were similar to those generally found in contaminated ground and wastewaters as stated earlier in this paper. The breakthrough curves for the nitrate adsorption on AG and unmodified corncob and coconut copra at the influent concentration of 20 mg N/L are given in Fig. 4. The breakthrough curves for the unmodified adsorbents reached the adsorption saturation level faster (2 h and 3 h for the corn cob and coconut copra, respectively) than the curves for the AG adsorbents (12 h and 14 h for AG corn cob and AG coconut copra, respectively). This is due to the higher number of adsorption sites in the AG materials compared to the unmodified materials as explained under batch studies results.

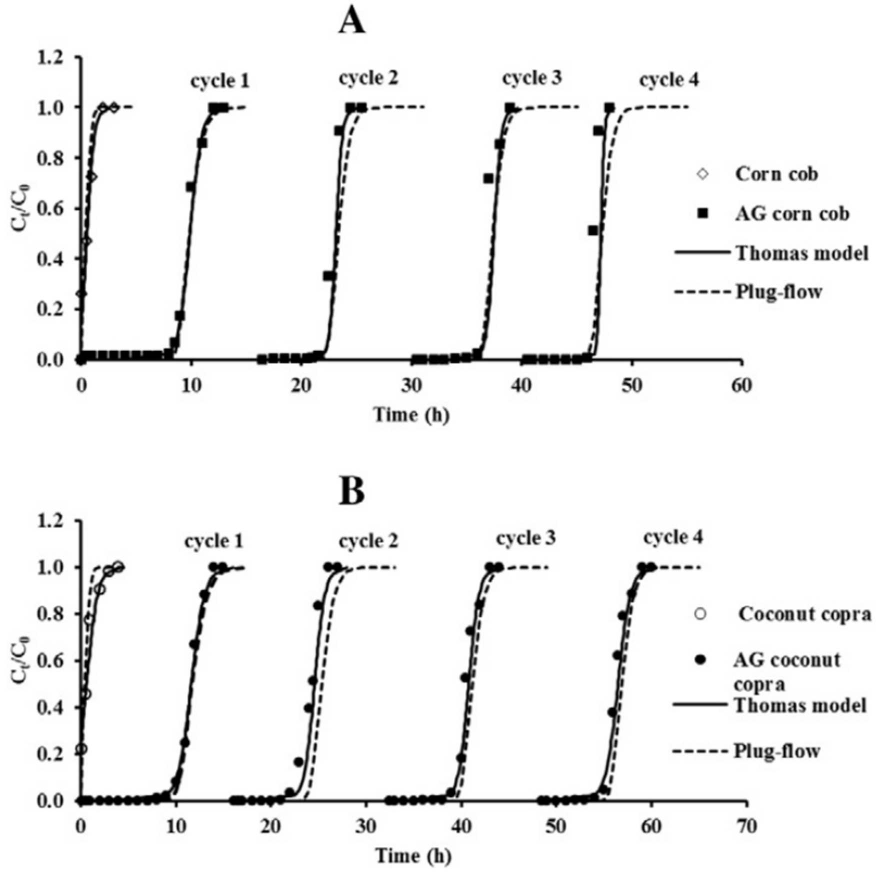


Fig. 4. Breakthrough curves for nitrate adsorption on AG (for 4 adsorption/desorption cycles) and unmodified (A) corn cob and (B) coconut copra (nitrate only in influent solution.

The adsorption capacities were calculated from the breakthrough curves manually (Eq.1) and are shown in Table 5. Consistent with the batch adsorption results, the fixed-bed adsorption capacities for the AG adsorbents were very much higher than the unmodified adsorbents. While the AG corn cob adsorption capacity up to the saturation time of 12 h (400 bed volumes; bed volume = flow velocity (m/h) ∗ time (h)/bed height (m)) was 15.3 mg N/g, the unmodified corn cob up to the saturation time of 2 h (66 bed volume) was 0.6 mg N/g. The AG coconut copra adsorption capacity was a little higher than that of the AG corn cob and was 18.6 mg N/g up to 14 h (460 bed volume) and 0.9 mg N/g for up to 3 h (100 bed volume) for the unmodified coconut copra. The fixed-bed adsorption capacities were lower than the batch Langmuir adsorption capacities, because in the batch experiments, adsorption reached equilibrium and Langmuir model predicted the maximum adsorption capacity at high nitrate concentration unlike in the fixed-bed experiment, where adsorption capacity was measured at a lower concentration of 20 mg N/L. Another reason for the lower nitrate adsorption capacity in the column experiment is the use of tap water in this experiment where the presence of chloride (30 mg/L) may have competed with nitrate for adsorption. In the batch experiment Milli-Q water with negligible concentrations of anions was used.

Table 5. Nitrate adsorption capacity of AG and unmodified corn cob and coconut copra and percentage of nitrate desorbed for different adsorption/desorption cycles.a

Adsorbents	Feed concentration	Number of adsorption-desorption cycles	Adsorption bed volumes[a]	Adsorption capacity (mg N/g)	Amount of N adsorbed (mg)	Amount of N desorbed (mg)	% Desorbed	Desorption bed volumes[a]	Desorption % at half the bed volumes[a]
Corn cob	**20mgN/L**	**1**	**66**	**0.6**	**11**	**10**	**83.9**	**16**	**72**
AG corn cob	**20mgN/L**	**1**	**400**	**15.3**	**307**	**305**	**99.9**	**40**	**78**
		2	**300**	**11.3**	**227**	**224**	**99.2**	**35**	**84**
		3	**300**	**10.7**	**215**	**215**	**99.9**	**35**	**86**
		4	**300**	**10.7**	**213**	**212**	**99.6**	**35**	**86**
	20mgN/L+5mgP/L	**1**	**315**	**12.7**	**255**	**242**	**95.1**	**33**	**81**
	20mgN/L+50mgS/L	**1**	**132**	**3.9**	**79**	**70**	**88.9**	**25**	**83**
Coconut copra	**20mgN/L**	**1**	**100**	**0.9**	**17**	**15**	**84.6**	**16**	**74**
AG coconut copra	**20mgN/L**	**1**	**460**	**18.6**	**372**	**366**	**98.3**	**40**	**76**
		2	**360**	**12.9**	**259**	**251**	**96.9**	**40**	**80**
		3	**360**	**12.5**	**251**	**250**	**99.8**	**40**	**84**
		4	**360**	**11.6**	**232**	**231**	**99.3**	**40**	**84**
	20mgN/L+5mgP/L	**1**	**365**	**14.1**	**282**	**274**	**97.2**	**33**	**79**
	20mgN/L+50mgS/L	**1**	**165**	**5.7**	**114**	**107**	**93.8**	**25**	**82**

a Bed volume = Flow velocity (m/h) ∗ time (h)/bed height (m).

In the presence of complementary ions the complete breakthrough occurred at 1 h, 5 h and 8 h for the N + S, N + P and N feed, respectively, for the AG corn cob and 3 h, 6 h and 9 h for the AG coconut copra. The results showed that, when the complementary ions are present in the water less time was needed to reach saturation in the fixed-bed due to reduction in the nitrate's adsorption capacity. The sulphate ion competed most with nitrate adsorption resulting in a significant reduction in nitrate adsorption capacity as observed in batch studies. This is because it has more negative charges.

3.4.2. Nitrate desorption and adsorbent regeneration

The regeneration of the adsorbents was carried out by leaching the adsorbed nitrate from the fixed-bed by 1 M KCl solution at a flow rate of 26.6 mL/min to desorb the nitrate from the adsorbents and determine whether the adsorbents can be reused. Results showed that the high concentration of chloride ions displaced the nitrate from the adsorption sites. Four adsorption-desorption cycles were conducted for the influent solution containing nitrate alone

(Fig. 4). 97–100% of the adsorbed nitrate was desorbed during the adsorption-desorption cycles for the AG corn cob and AG coconut copra adsorbents (Table 5). The number of bed volumes of 1 M KCl required for desorption of nitrate was 35–40 compared to the number of bed volumes required for adsorption of 300–460 (Table 5). This means the desorbed solution was about 10 times concentrated than the influent nitrate concentration. When the volume of the desorbing KCl solution was reduced to half (16 bed volumes), the amount of nitrate desorbed was still high at 76–86% (Table 5). Thus the cost of the desorbing reagent can be cut down by half with only 20–30% reduction in desorption. Chloride concentration in the desorbed solution is also cut down by half which may cause less or no damage to crops if the desorbed solution is used as nitrate fertiliser. The nitrate adsorption capacity dropped by approximately 30% in the second cycle and then marginally decreased thereafter for each cycle for both the adsorbents. Thus, the AG corn cob and coconut copra can be reused several times by maintaining good adsorption capacity for nitrate adsorption, reducing operational costs. Alternatively, the used bio adsorbents can be used as fertiliser. The nitrate in the desorbed solution can be used in fertigation to supply nitrogen to plants. The K in the desorbed solution will also benefit plants.

3.4.3. Fixed-bed column modelling

To properly design the adsorption process, one needs to clearly understand the relationship between the adsorption equilibrium, intra particle diffusion and hydrodynamic condition of the fixed-bed column. In this work, the axially dispersed plug-flow model with several correlation parameters were used to predict the fixed-bed column behaviour. In addition, the Freundlich isotherm parameters (Table 3) were used to explain the adsorption equilibrium at solid/liquid interfaces.

The main parameters controlling the fixed-bed adsorption characteristics are axial dispersion and the external film mass transfer coefficients. Regarding axial dispersion, the adsorption front axially increases due to flow in the inter particle voids. It is derived from the contribution of the molecular diffusion and dispersion caused by the fluid flow. The adsorbate diffuses from the bulk liquid phase to the stagnant boundary layer of the adsorbent external surface which is referred to as the film mass transfer. The axially dispersion coefficient (D_L) parameter values determined using equation 2 were 3.5×10^{-6} and 3.4×10^{-6} m/s for the AG corn cob and AG coconut copra, respectively, for the first adsorption/desorption cycle. The film mass transfer coefficient (k_f) values were obtained using equation 3. These values were 4.3×10^{-3} and 2.2×10^{-3} m/s for the AG corn cob and AG coconut copra, respectively, for the first adsorption-desorption cycle. The surface diffusion coefficient (D_S) was determined by matching the simulation values with the experimental adsorption values obtained from the breakthrough curve. The D_s values for the corn cob and AG corn cob were 1.96×10^{-9} and 1.64×10^{-10} m^2/s, respectively, and 1.58×10^{-9} and 1.28×10^{-10} m^2/s for the coconut copra and AG coconut copra, respectively, for the first adsorption/desorption cycle.

To predict the adsorption breakthrough curves for the 2nd to the 4th adsorption/desorption cycles, the assumption was further taken that the parameter values are the same for all the cycles, even though adsorption capacity of the AG materials for the 2nd to 4th cycles decreased around 20–30% of the 1st cycle. The model parameters D_s, k_f and D_L depend on the influent concentration and/or filtration velocity which are the same for all the cycles. Therefore the assumption that the parameter values are same for all the cycles is reasonable.

As shown in Fig. 4, the axially dispersed plug-flow model reasonably fitted the adsorption breakthrough curve patterns, even though some deviations were observed for the 2nd to 4th cycles, probably because the adsorption capacity decreased from the values of the first cycle and the ratio of the adsorption capacity decrease was utilised in the model prediction. In comparison to this finding, our recent study on nitrate adsorption by Fe-coated Dowex ion exchange resin showed that the adsorption capacity remained nearly the same during three adsorption/desorption cycles and plug-flow model satisfactorily fitted to the data of all the three cycles (Kalaruban et al., 2016).

The empirical Thomas model was also used to predict the fixed-bed experimental results. The model equation and the parameter values are given in Table 1 and Table 6, respectively. This model fit to the data was better than that of axially dispersed plug-flow model, especially for the second cycle onwards. The Thomas model adsorption capacities (q_0) agreed well with the adsorption capacities, calculated manually from the breakthrough curve (Table 6).

Table 6. Thomas model parameters for the adsorption of nitrate ion in fixed-bed containing corn cob, coconut copra, AG corn cob and AG coconut copra for different adsorption-desorption cycles.

Models	**Parameters**	**Corn cob**	**AG corn cob**				**Coconut copra**	**AG coconut copra**			
		1st cycle	1st cycle	2nd cycle	3rd cycle	4th cycle	1st cycle	1st cycle	2nd cycle	3rd cycle	4th cycle
Thomas model	k_{TH} (ml/minmg)	2.58	1.59	2.84	2.46	5.15	1.45	1.19	1.53	1.54	1.28
	q_0 (mgN/g)	0.83	15.4	10.34	10.88	10.41	0.95	18.12	12.76	13.71	13.2
	R_2	0.974	0.9825	0.9624	0.9623	0.9669	0.9921	0.9786	0.9832	0.9584	0.9717

4. Conclusions

Amine-grafted (AG) biosorbents such as corn cob and coconut copra are very effective in removing nitrate from water. They have adsorption capacities many times higher than those of the respective unmodified materials. The Langmuir maximum adsorption capacities (mg N/g) of AG corn cob (50) and coconut copra (59) are also higher than many of the other amine-grafted biosorbents (11–17) and commercially available ion exchange resins (28–39) reported in literature. They are attractive low-cost biosorbents that can be used in many countries, especially in rural areas where large quantities of these wastes are produced. The used adsorbents can be directly applied to lands as nitrate fertilisers and the desorbed nitrate solution containing K can be used in fertigation to supply nutrients (N and K) to plants. Mathematical models developed for fixed-bed column mode adsorption behaviour can be successfully used in designing full-scale treatment plant. It is recommended that this study with synthetic solutions be extended to real ground and surface waters contaminated with nitrate.

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