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

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## HIGHLIGHTS

- Ground coconut copra and corn cob particles surfaces are readily amine-grafted.
- Amine-grafting reversed the particles' surface charge from negative to positive.
- Amine-grafting of the waste particles increased nitrate adsorption capacity.
- Nitrate adsorption capacity reduced by co-ions;
  sulphate > chloride > phosphate.
- Fixed-bed nitrate adsorption data fitted well to Thomas and plug-flow models.

## GRAPHICAL ABSTRACT
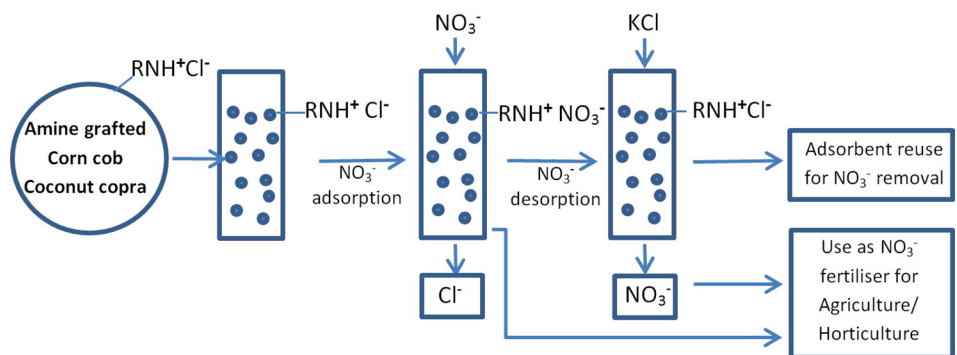
## ABSTRACT

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 $1 \times 10^{-3}$ 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.

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## 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; 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; 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,b) 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; 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; Loganathan et al., 2013), yet only a few have been tested using dynamic fixed-bed adsorption experiment (Xing et al., 2011; 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; 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 $520 \times 10^9$ 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 $1 \times 10^{-3}$ 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