NITRATE REMOVAL FROM WATER USING SURFACE-MODIFIED ADSORBENTS

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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DEDICATION

To My Lovely Parents

JOURNAL PAPERS

Kalaruban, M., Loganathan, P., Shim, W., Kandasamy, J., Naidu, G., Nguyen, T.V., Vigneswaran, S., 2016. Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidised-bed adsorption studies. Separation and Purification Technology. 158, 62-70.

Kalaruban, M., Loganathan, P., Shim, W., Kandasamy, J., Ngo, H., Vigneswaran, S., 2016. Enhanced removal of nitrate from water using amine-grafted agricultural wastes. Science of the Total Environment. 565, 503-510.

Johir, M.A.H., Nguyen, T.V., Kalaruban M., Prahan, M., Ngo, H., Shim, W., Vigneswaran , S., 2016. Removal of phosphorus by a high rate membrane adsorption hybrid system. Bio Resource Technology. 201, 365-369.

Kalaruban, M., Loganathan, P., Kandasamy, J., Vigneswaran, S., 2017. Submerged membrane adsorption hybrid system using four adsorbents in removing nitrate from water. Environmental Science and Pollution Research, 1-8.

Kalaruban, M., Loganathan, P., Kandasamy, J., Vigneswaran, S., Enhanced removal of nitrate in an integrated electrochemical- adsorption system (Submitted to Separation and Purification Technology).

CONFERENCE PAPERS AND PRESENTATION

Kalaruban, M., Loganathan, P., Shim, W., Kandasamy, J., Naidu, G., Nguyen, T.V., Vigneswaran, S. 2014. Nitrate removal from water by adsorption to amine grafted agricultural wastes and Dowex. CRC Communication Conference, Adealide, South Australia, 10^{th}- 13^{th} September, 2014.

Kalaruban, M., Loganathan, P., Kandasamy, J., Vigneswaran, S., 2016. Submerged membrane adsorption hybrid system using four adsorbents in removing nitrate from water. 5^{th} IWA regional conference on Membrane Technology, Kunming, China, 22^{nd} - 24^{th} August, 2016.

Kalaruban, M., Loganathan, P., Shim, W., Kandasamy, J., Ngo, H., Vigneswaran, S., 2016. Enhanced removal of nitrate from water using surface modified agricultural wastes. International Conference on Water : From Pollution to Purification (ICW 2016), Kerala, India, 12^{th}-15^{th} December 2016.

AWARDS & SCHOLARSHIPS

Won the second prize of “Best Poster Presentation Award” in the 5^{th} IWA regional conference on Membrane Technology, Kunming, China.

Higher Degree Research publication award

CRC Care postgraduate scholarship, Sydney, Australia (2014 – 2017)

International Research Scholarship – University of Technology Sydney (2013 -2017)

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NOMENCLATURE/ABBREVIATION

AG = amine grafted

Al^0 = Zero valent aluminium

Cl^- = chloride

ClO^- = hypochlorite

ClO_4^- = perchlorates

C_e = equilibrium concentration of nitrate-N (mg /L) equilibrium

COD = chemical oxygen demand

D_L = the axial dispersion coefficient (m^2/s)

Dm = aqueous phase diffusivity (m^2/s)

Ds = the surface diffusion coefficient (m^2/s)

Dowex 21K XLT = strong base anion exchange resin composed of Styrene-DVB

dS/m = desiSiemens per meter

Fe^0 = zero valent iron

Fe^{3+} = iron (III)

$FeCl_3.6\ H_2O$ = Iron(III) chloride hexahydrate

FTIR = Fourier transform infrared spectroscopy

H_2PO_4 = dihydrogen phosphate ion

HCl = hydrochloric acid

HCO_3^- = bicarbonate

HSDM = Homogeneous surface diffusion model

HNO_3 = Nitric acid

kf = the external mass transfer coefficient (m/s)

K_F = Freundlich constants (mg/g)

KNO_3 = Potassium nitrate

KH_2PO_4 = Monopotassium phosphate

KCl = Potassium chloride

K_L = Constant related to the affinity of the binding sites (L/mg)

LDHs = layered double hydroxides

M = mass of dry adsorbent (g)

MBR = membrane bioreactor

mg N/L = milligram nitrogen per litre

mg NO_3^- / L = mg nitrate per litre

mg N/g = milligram nitrogen per gram

mg P/L = milligram phosphorus per litre

mg PO_4^{3-} / g = mg phosphate per gram

mg P/g = milligram phosphorus per gram

mg SO_4^{2-} / g = mg sulphate per gram

mg S/g = milligram sulphur per gram

Mg^0 = zero-valent magnesium

N = nitrogen

N_2 = nitrogen gas

NaCl = sodium chloride

NaOH = sodium hydroxide

Na_2SO_4 = sodium sulphate

Na_2CO_3= sodium carbonate

$NaHCO_3$ = sodium bicarbonate

NH_3 = ammonia

NO = nitric oxide

N_2O = dinitrogen monoxide

NO_3^- = nitrate

NO_2^- = nitrite

$(NH_4)_2SO_4$ = ammonium sulphate

No = saturation adsorbate concentration (mg/L)

n = Freundlich constant

P = phosphorus

PE = population equivalent

pH = measure of the acidity or basicity of an aqueous solution

PZC = point of zero charge

Q = flow rate (cm^3/s)

Q_e = amount of nitrate adsorbed per unit mass of adsorbent (mg N/g)

Q_{max} = maximum amount of the nitrate-N adsorbed per unit weight of the adsorbent (mg/g)

r = radial distance from the centre of adsorbent particle (m)

RO = reverse osmosis

rpm = revolutions per minute

SEM = Scanning electron microscopy

SMAHS = submerged membrane adsorption hybrid system

SO_4^{2-} = sulphate

XRD = X-ray diffraction

ZVI = Zero-valent iron

ABSTRACT

Elevated concentrations of nitrate in surface and ground waters can cause eutrophication of natural water bodies, and in drinking water they can pose a threat to human health, especially to infants by causing 'blue baby' syndrome. Adsorption technology is an attractive method to remove nitrate from water compared to other technologies in terms of simplicity, cost, design, operation and maintenance, and effectiveness.

An anion exchange resin known as Dowex 21K XLT was surface modified by incorporating Fe (Dowex-Fe) to increase the surface positive charges and tested for removing nitrate. The batch adsorption data at pH 6.5 fitted well to the Langmuir model with maximum adsorption capacities of 27.6 mg N/g, and 75.3 mg N/g for Dowex and Dowex-Fe resins, respectively. The fluidised-bed adsorption capacities were 18.6 mg N/g and 31.4 mg N/g at a feed concentration of 20 mg N/L and filtration velocity of 5 m/h for Dowex and Dowex-Fe, respectively. Low-cost agricultural wastes, specifically corn cob and coconut copra were also surface modified but by amine-grafting to increase the surface positive charges. The Langmuir nitrate adsorption capacities (mg N/g) were 49.9 and 59.2 for the amine-grafted (AG) corn cob and AG coconut copra, respectively, at pH 6.5. Fixed-bed adsorption capacities were 15.3 mg N/g and 18.6 mg N/g at the same feed concentration and flow velocity as in the Dowex study for AG corn cob and AG coconut copra, respectively. In both batch and column experiments, nitrate adsorption declined in the presence of sulphate, phosphate and chloride, with sulphate being the most competitive anion. More than 95% of adsorbed nitrate was desorbed by 1 M KCl in all adsorption/desorption cycles and the adsorbents were successfully regenerated in each cycle with little reduction in adsorption capacity.

A submerged membrane (microfiltration) adsorption hybrid system (SMAHS) was utilised for the continuous removal of nitrate. The volume of water treated to maintain the nitrate concentration below the WHO limit of 11.3 mg N/L and the amount of nitrate adsorbed per gram of adsorbent for all four flux (2.5, 5, 10 and 15 L/m^2h) tested were in the order Dowex-Fe > Dowex > AG coconut copra > AG corn cob. A rise in flux increased the volume of water treated and the amount of nitrate adsorbed. The exhausted agricultural waste adsorbents in both the column and SMAHS trials can be directly applied to lands as nitrate fertilisers, while the desorbed nitrate solution containing K can be used in fertigation to supply nutrients (N and K) to plants.

An electrochemical-adsorption system was investigated to remove nitrate simultaneously using the adsorption and electrochemical methods. In this system four adsorbents were added inside an anode stainless steel box where the Cu plate served as the cathode. It was found that nitrate removal was higher in a short period of time and the cost was low. The optimum nitrate removal scenario for the integrated system was at pH 7, 1 A, and 31 V for a distance of 1 cm apart between the electrodes. Nitrate removal in the integrated system is approximately the sum of the removals derived from the individual processes. The innovative feature of this study is the integration of an electrochemical system with the adsorption process where the adsorbents are kept intact with the anode.

The different methods undertaken in the four nitrate removal studies can't be compared and each method has advantages and disadvantages in terms of nitrate removal efficiency, cost, raw water quality and removal efficiency of other pollutants. However, if the raw water contains only nitrate the column method is best compared to other methods. It is recommended that the encouraging results obtained in our laboratory scale studies be tested in series of cells connected to each other for continuous removal of nitrate. It is also recommended that these experiments are conducted at pilot plant scale, which is closer to practical conditions.