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# **Submerged membrane adsorption hybrid system using four adsorbents to remove nitrate from water**

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## **Abstract**

Nitrate contamination of ground and surface waters causes environmental pollution and human health problems in many parts of the world. This study tests the nitrate removal efficiencies of two ion exchange resins (Dowex 21k XLT and iron modified Dowex 21k XLT (Dowex-Fe)), and two chemically modified bio-adsorbents (amine grafted corn cob (AG corn cob) and amine grafted coconut copra (AG coconut copra)) using a dynamic adsorption treatment system. A submerged membrane (microfiltration) adsorption hybrid system (SMAHS) was used for the continuous removal of nitrate with a minimal amount of adsorbents. The efficiency of membrane filtration flux and replacement rate of adsorbent were studied to determine suitable operating conditions to maintain the effluent nitrate concentration below the WHO drinking standard limit of 11.3 mg N/L. The volume of water treated and the amount of nitrate adsorbed per gram of adsorbent for all four flux tested were in the order Dowex-Fe > Dowex > AG coconut copra > AG corn cob. The volumes of water treated (L/g adsorbent) were 0.91 and 1.85 and the amount of nitrate removed (mg N/g adsorbent) were 9.8 and 22.2 for AG corn cob and Dowex-Fe, respectively at a flux of 15 L/m<sup>2</sup>h.

**Key words:** Bio-adsorbents; Ion exchange resin; Membrane filtration/adsorption system; Nitrate removal; Transmembrane pressure

**Highlights:**

- > SMAHS treatment of polluted water continuously maintained  $\text{NO}_3^-$  below WHO limit.
- >  $\text{NO}_3^-$  adsorption capacity: Dowex-Fe > Dowex > coconut copra/amine > corn cob/amine
- > Treated water volume was in the same order as the adsorption capacity.
- > Transmembrane pressure increased with flux and was highest for bio-adsorbents.

**Introduction**

Nitrate concentrations in ground and surface waters in many parts of the world exceed the World Health Organization (WHO) drinking standard limit of 11.3 mg N/L (WHO 2011). Elevated concentrations of nitrate can seriously affect people's health, for example cause methemoglobinemia. It can also damage the environment such as causing eutrophication (Camargo and Alonso 2006; Fewtrell 2004). Several treatment technologies are being used to remove nitrate, for instance electro-dialysis, reverse osmosis, adsorption and chemical and biological methods. Of these electro-dialysis and reverse osmosis have very high operational costs (Bhatnagar and Sillanpää 2011; Loganathan et al. 2013). The biological denitrification method has some disadvantages. Mainly, the process is slow and requires specific microorganisms and post-treatment to remove the germs and metabolic substances produced during the process (Kapoor and Viraraghavan 1997; Samatya et al. 2006).

Adsorption is a simple, effective and low cost method. Adsorption combined with membrane filtration is a currently developing water treatment process. Membrane filtration with micro-filter and ultra-filter systems require considerably less energy and it also has the

advantages such as producing high quantities of good quality water with controllable membrane fouling, and incurring low capital and operational costs. Although the micro filter membrane fails to remove nitrate, it can remove colloids, macro molecules, micro particles, microorganisms. It also separates the adsorbent particles from the water stream (Guo et al. 2005).

The benefits of this submerged membrane adsorption hybrid system (SMAHS) is that the adsorbent particle size can be small so that high adsorption capacities are achieved. This is in contrast to the commonly used column mode of adsorption where very small sized adsorbents reduce the flow rate and require more energy to pump the feed water. Furthermore, the fine particles can clog the filter beds in columns causing increased pressure heads. This clogging problem is significantly reduced in SMAHS, because the particles are kept in suspension by pumping air into the system. The adsorbent particles in this system provide mechanical scouring on the membrane surface and remove deposits from the membrane. Consequently there is less membrane fouling and the operational time increases (Johir et al. 2011; Johir et al. 2013).

Most previous SMAHS studies have mainly focused on the removal of metals (Bryjak et al. 2008), phosphate (Johir et al. 2016), colour and reactive dyes (Lee et al. 2006), and organic micropollutants (Shanmuganathan et al. 2015a). To our knowledge, no studies have yet reported on nitrate removal using SMAHS. The length of treatment time varied in these SMAHS studies with some experiments conducted on a short-term (6 h) (Shanmuganathan et al. 2015a) and long-term period (14 days) basis with partial replacement of adsorbents (Shanmuganathan et al. 2015b). The partial replacement of adsorbent helps to prevent cake formation on the membrane surface, resulting in reduced transmembrane pressure (Smith and Vigneswaran 2009) as well as providing fresh adsorption sites for the removal of additional nitrate.

The SMAHS performance depends on the adsorbent's capacity to remove pollutants, adsorbent dose, reactor configuration, operation condition such as water flux and feed water characteristics (Vigneswaran et al. 2003). High flux of water reduces operation costs due to large amounts of water being treated in a short period of time. However, because the hydraulic retention time is short the removal efficiency of pollutants can decrease with increasing flux. Also, the high flux can cause the rate of fouling on the membrane to increase. However, applying aeration to the adsorbent suspension keeps the adsorbent particles dispersed in the reactor and helps to reduce the solid deposition on the membrane surface by the air scouring effect.

The adsorbents used in this study were ion exchange resin Dowex 21K XLT, iron-modified Dowex (Dowex-Fe), and modified bio-adsorbents, specifically amine-grafted (AG) corn cob and AG coconut copra. These adsorbents have proved to be suitable for nitrate removal in our previous research using batch and column modes experiments (Kalaruban et al. 2016a, b).

The objectives of the research were to: (i) compare the nitrate adsorption performance of the ion exchange resin, Dowex, iron-coated Dowex (Dowex- Fe), amine grafted (AG) corn cob and AG coconut copra in a SMAHS with frequent adsorbent replacement under four filtration flux; and (ii) determine the volume of water that can be treated to produce high quality water (nitrate concentration below the recommended WHO limit). This research is new because hitherto no SMAHS experiment under continuous operation with small amounts of adsorbent replacement has been reported for removing nitrate from water.

## **Experimental**

### **Materials**

#### *Feed solution*

The feed solution was prepared using tap water spiked with nitrate for the water to have a concentration of 20 mg N/L. ANALAR grade KNO<sub>3</sub> was used to prepare the synthetic water and the pH of the solution was maintained at 6.5-7.5. This solution was used for all experiments to ensure that the influent nitrate concentration remained constant.

#### *Adsorbents*

The anion exchange resin Dowex 21K XLT, iron-modified Dowex 21k XLT (Dowex-Fe), AG corn cob and AG coconut copra served as adsorbents. Dowex is a commercially available anion exchange resin produced by DOW Chemical Pte Ltd, USA and contains ammonium functional group and chloride as counter ion. The method of Fe modification of Dowex has been described elsewhere (Kalaruban et al. 2016a). The methods of amine grafting of coconut copra and corn cob have also been documented elsewhere (Kalaruban et al. 2016 b). Characteristics of these adsorbents were also described in other studies (Kalaruban et al. 2016a, b). They are summarized in Table 1.

#### *Membrane characteristics*

A hollow fibre membrane with the specifications of 0.1 µm nominal pore size and 0.1 m<sup>2</sup> surface area was used. It consists of hydrophilic modified poly acrylic nitrile (PAN) type membrane with 1.1 mm inner and 2.1 mm outer diameter. This product was manufactured by Mann+Hummel Ultra –Flo Pty Ltd, Singapore.

## **Methodology**

### *Submerged membrane adsorption hybrid system (SMAHS)*

The experiments were carried out in a dynamic system with a continuous mode operation which can be applied in a real-practical process. The membrane was submerged into the reactor and the adsorbents were added to the water. The adsorbent performance was evaluated in terms of volume of treated water and the amount of nitrate adsorption. Fig. 1 is a schematic diagram of the SMAHS. The water volume was maintained at 4 L in the reactor. A peristaltic pump was used to feed the influent to the reactor and periodically remove effluent from the tank at a controlled flux. The effect of filtration flux was studied by varying the flux at 2.5, 5, 10 and 15 L/m<sup>2</sup>h. 10 g adsorbent was initially added to the reactor and 2 g of adsorbent was replaced each time when the effluent reached the WHO nitrate concentration limit of 11.3 mg N/L. This was done by removing a measured volume of suspension, filtering the adsorbent contained in it and adding fresh adsorbent equal to the weight of adsorbent removed from the filtered water. The transmembrane pressure (TMP) was continuously measured using a pressure transducer (PTX 1400 Druck Industrial Pressure Sensor, Druck Limited, UK). Air was pumped at a rate of 3.5 L/min to keep the adsorbent particles in suspension. The membrane was cleaned using 0.4% NaOCl before commencing each experiment.

### *Analytical method*

Nitrate concentration was measured using an ion chromatograph (Model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. Before the analysis commenced the ion chromatograph was cleaned utilizing the mobile phase solutions containing Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>. This was followed by diluted sulphuric acid and Milli-Q water.

## Results and discussion

### Nitrate adsorption

Nitrate adsorption capacities of the four adsorbents for all the flux conditions in the SMAHS (Table 2) were much lower than the Langmuir adsorption maxima for the respective adsorbents obtained in a previous batch study (Table 1). The adsorption capacities obtained in a previous column study were also lower than those in the batch study (Table 1). The reason for the lower adsorption capacities in SMAHS and column studies is the higher mass transfer limitations in these studies. The higher mass transfer limitations are due to the lower concentration gradient between the nitrate in solution and the solid surface as well as the shorter contact time between the nitrate and the adsorbent. The intense agitation in the batch study resulted in longer and closer contacts. Furthermore, the Langmuir adsorption capacity represents the maximum adsorption capacity which was calculated at a much higher nitrate concentration than the concentrations used in the SMAHS and column studies. However, the mass transfer limitation in the column study can be reduced by either increasing the feed nitrate concentration or reducing the flow rate of the solution as reported for phosphate adsorption on Zr-loaded okra (Nguyen et al. (2015) and nitrate adsorption onto an ion exchange resin (Nur et al. 2015).

The nitrate removal efficiency in the SMAHS was in the order Dowex-Fe > Dowex > AG coconut copra > AG corn cob for all the flux conditions (Table 2; Fig. 2). This order is slightly different from the Langmuir maximum adsorption capacities determined in batch experiments where the order was Dowex-Fe > AG coconut copra > AG corn cob > Dowex (Table 1). However, the adsorption capacities determined in column experiments had the same order as in the SMAHS experiments (last column of Table 1). The reason for Dowex having higher adsorption capacity than the bio-adsorbents in SMAHS and column experiments is that chloride in tap water used in these experiments might have competed with nitrate for adsorption in the case of bio-adsorbents. In the batch experiment, Milli-Q water



was used and consequently no chloride was present to compete with nitrate. The tap water contained 30 mg /L concentration of chloride ions. The co-ions effect studies revealed that the efficiency of removing nitrate declined considerably in the presence of chloride for bio-adsorbents but only slightly for Dowex (Fig. 3). Although the phosphate concentration in tap water was also high (13 mg P/L) it did not reduce the efficiency in removing nitrate much for all the adsorbents (Fig. 3). Kalaruban et al. (2016a, b) also reported that phosphate had low affinity for these adsorbents. Sulphate which competed with nitrate in those studies had low concentration in tap water (0.04 mg S/L) and therefore it might not have affected nitrate adsorption in the present study.

The amount of nitrate adsorption increased with flux for all the adsorbents (Fig. 4).

Mass balance of nitrate during the experimental period showed that increase of flux increased the amount of nitrate removed mainly because at increased flux, the amount of nitrate that entered the reactor per unit time increased (Table 2). Because both the nitrate input and removal increased at approximately similar rates, the percentage removal remained nearly the same. The rate of nitrate removal also increased with flux (Table 2). This is due to higher mass transfer of nitrate at higher flux as a result of more nitrate ions contacting the adsorption sites per unit time, though the retention time decreased with increased flux. Retention times of nitrate were 16, 8, 4, and 2.7 h at 2.5, 5, 10, and 15 L/m<sup>2</sup>h. The fact that nitrate adsorption increased with flux shows that retention time is less important compared to the total amount of nitrate flowing through the reactor, and therefore the latter is the overall factor controlling the adsorption.

### **Volume of treated water**

The volume of water treated to reduce the nitrate concentration below the WHO standard limit per mass of adsorbent was calculated using Microsoft Excel spreadsheet and presented in Table 2 (6<sup>th</sup> column of Table 2). The volume of water treated per mass of adsorbent

increased with flux for all the adsorbents (Fig. 4). This is because at increased flux the volume of water that entered the reactor per unit time increased. The increased amounts of nitrate that entered the reactor, were increasingly removed by the adsorbents and in this way the WHO nitrate limit of 11.3 mg N/L was maintained. The volume of water treated per mass of adsorbent at any flux was in the order, Dowex-Fe > Dowex > AG coconut copra > AG corn cob. This order was the same as that for nitrate adsorption (Table 2 and Fig. 4).

### **Adsorbent replacement**

During the experiment, when the effluent reached the WHO standard concentration of 11.3 mg N/L, 20% (2 g) adsorbent was replaced (i.e. 0.5 g/L of adsorbent in the 4L tank volume). Various amounts of adsorbent replacements were earlier tried and 0.5 g/L was found to be the best, considering the efficiency of nitrate removal, cost effectiveness and practicability of replacement frequency. Immediately after the replacement the effluent nitrate concentration fell to a low level due to adsorption on the newly added adsorbent and then increased with time as before (Fig. 2). The replacement interval of an adsorbent depended on the adsorption capacity of the adsorbent; it was more frequent for the adsorbent with poorer adsorption capacity. It was also shorter for the higher flux conditions because the adsorbents treated a larger volume of water in a shorter period of time by adsorbing a larger amount of nitrate. In accordance with these observations the replacement interval declined when the adsorption capacity of the adsorbents also decreased (Dowex-Fe > Dowex > AG coconut copra > AG corn cob). Thus, the number of replacement cycles for the adsorbents followed the reverse order. According to these observations, the decrement of effluent concentration soon after adsorbent replacement was higher in lower flux conditions and for the adsorbent having higher adsorption capacity.

### **Transmembrane pressure (TMP)**

The transmembrane pressure (TMP) rose with the increasing flux for all adsorbents (Fig. 5). When the flux increased, the membrane treated more water and the rate of fouling increased. The TMP of membrane with bio-adsorbents in suspension was higher than ion exchange resins because of higher specific volumes of bio-adsorbents. The specific volumes were  $1.1\text{m}^3/\text{kg}$  and  $0.9\text{ m}^3/\text{kg}$  for bio-adsorbents and ion exchange resins, respectively. Consequently the bio-adsorbents might have blocked the membrane surface more than the ion exchange resins and thereby increased the TMP. Also, the very fine particles produced during the grinding of the bio-adsorbents would have deposited in between adjacent membranes to cause this blockage. This deposition was noticed during the experiments.

### **Comparison of SMAHS and column-mode nitrate removals**

SMAHS and Column-mode adsorption processes are dynamic and continuous treatment systems which are more relevant to real-water treatment process than the static batch system of treatment. Therefore, these two systems are compared in this section. Table 3 presents the nitrate adsorption performance and volume of water treated to meet the WHO drinking water limit of  $11.3\text{ mg N/L}$  in SMAHS and data obtained in a previous study (Kalaruban et al. 2016a, b) using column experiments for an influent nitrate concentration of  $20\text{ mg N/L}$  and flow rate of  $1.5\text{-}1.6\text{ L/h}$ . As the data for the column experiment was available only for the flow rate of  $1.6\text{ L/h}$  ( $27\text{ mL/min}$ ) the comparison was made only for this flow rate (against the SMAHS flux of  $15\text{ L/m}^2\text{h}$ ). The data showed that there was no significant difference in volume of water treated or the amount of nitrate adsorption between the two experiments for all adsorbents (Table 3). This could be due to two opposing factors influencing the processes. Mass transfer of nitrate is expected to be greater in SMAHS due to better contact of solution nitrate with the adsorbent because of agitation of the suspension by aeration. However, because the concentration gradient was lower at most of the time ( $4\text{-}11\text{ mg N/L}$  solution

concentration, Fig. 2) compared to column filtration (more fresh solution of 20 mg N/L), mass transfer would be lower in SMAHS.

The advantage of the SMAHS is that the medium is in suspension unlike in column mode of treatment. Also, very fine sized adsorbents with higher surface area can be used in this system. This is not possible in a column experiment due to the column clogging problem. In this study, adsorbents with 300-600  $\mu\text{m}$  diameter were used to compare the results with those from column experiments. However, use of adsorbents of finer size ( $< 300 \mu\text{m}$ ) will lead to higher nitrate removal due to higher surface area. Another advantage of SMAHS is that simultaneous removal of colloids, microorganisms and suspended solids can be achieved.

The material cost for the removal of 1000 mg of nitrate as N was 2.52, 3.81, 0.72 and 0.96 USD for Dowex-Fe, Dowex, AG coconut copra and AG corn cob, respectively. These costs were calculated using the market prices of the ion exchange resin and chemicals used to modify the adsorbents, and assuming coconut copra and corn cob have no cost. The only bio-adsorbent-related cost is that of amine-grafting reagents which are used to modify these adsorbents. If finer-sized adsorbents are used, the material cost would have further been reduced because a finer size can produce higher adsorption capacity. The bio-adsorbents used are agricultural wastes, which can be applied after their use to agricultural lands to provide nitrate for increasing crop production. This beneficial outcome can solve problems associated with the cost of chemicals used to modify the bio-adsorbents.

## **Conclusions**

The SMAHS with 20% adsorbent replacement at appropriate times during the treatment process proved to be highly effective in the continuous removal of nitrate from water, and nitrate concentration was maintained below the WHO limit of 11.3 mg N/L. In terms of volume of water treated and the amount of nitrate removed per unit mass of adsorbent, Dowex-Fe recorded the best performance out of the four adsorbents which included two

chemically modified bio-adsorbents. These results agree with those reported in previous column studies (Kalaruban et al. 2016a, b). However, when considering the cost of adsorbents, bio-adsorbents may constitute a better choice, especially when implementing the technology in developing countries. Another advantage of bio-adsorbents is that the exhausted adsorbents can be directly applied to agricultural lands as nitrate fertilisers. SMAHS has the advantage of continuous treatment operation. It also leads to simultaneous removal of colloids, suspended solids and microorganisms that are present in the water.

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### **References**

- Bhatnagar A, Sillanpää M (2011) A review of emerging adsorbents for nitrate removal from water. *Chem Eng J* 168: 493-504.
- Bryjak M, Wolska J, Kabay N (2008) Removal of boron from seawater by adsorption–membrane hybrid process: implementation and challenges. *Desalination* 223: 57-62.
- Camargo JA, Alonso Á (2006) Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. *Environ Int* 32: 831-849.
- Fewtrell L (2004) Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion. *Environ Health Perspect* 1371-1374.
- Guo W, Shim W, Vigneswaran S, Ngo H (2005) Effect of operating parameters in a submerged membrane adsorption hybrid system: experiments and mathematical modeling. *J Membr Sci* 247: 65-74.

- Johir M, Aryal R, Vigneswaran S, Kandasamy J, Grasmick A (2011) Influence of supporting media in suspension on membrane fouling reduction in submerged membrane bioreactor (SMBR). *J Membr Sci* 374: 121-128.
- Johir M, Nguyen TT, Mahatheva K, Pradhan M, Ngo HH, Guo W, Vigneswaran S (2016) Removal of phosphorus by a high rate membrane adsorption hybrid system. *Bioresour Technol* 201: 365-369.
- Johir M, Shanmuganathan S, Vigneswaran S, Kandasamy J (2013) Performance of submerged membrane bioreactor (SMBR) with and without the addition of the different particle sizes of GAC as suspended medium. *Bioresour Technol* 141: 13-18.
- Kalaruban M, Loganathan P, Shim W, Kandasamy J, Naidu G, Nguyen TV, Vigneswaran S (2016a) Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidised-bed adsorption studies. *Sep Purif Technol* 158: 62-70.
- Kalaruban M, Loganathan P, Shim W, Kandasamy J, Ngo H, Vigneswaran S (2016b) Enhanced removal of nitrate from water using amine-grafted agricultural wastes. *Sci Total Environ* 565: 503-510.
- Kapoor A, Viraraghavan T (1997) Nitrate removal from drinking water - review. *J Environ Eng* 123: 371-380.
- Lee JW, Choi SP, Thiruvengatachari R, Shim WG, Moon H (2006) Submerged microfiltration membrane coupled with alum coagulation/powdered activated carbon adsorption for complete decolorization of reactive dyes. *Water Res* 40: 435-444.
- Loganathan P, Vigneswaran S, Kandasamy J (2013) Enhanced removal of nitrate from water using surface modification of adsorbents – a review. *J Environ Manage* 131: 363-374.

- Nguyen TAH, Ngo HH, Guo WS, Pham TQ, Li FM, Nguyen TV, Bui XT (2015) Adsorption of phosphate from aqueous solutions and sewage using zirconium loaded okra (ZLO): Fixed-bed column study. *Sci Total Environ* 523: 40-49.
- Nur T, Shim WG, Loganathan P, Vigneswaran S, Kandasamy J (2015) Nitrate removal using Purolite A520E ion exchange resin: Batch and fixed-bed column adsorption modelling. *Inter J Environ Sci Technol* 12: 1311-1320.
- Samatya S, Kabay N, Yüksel Ü, Arda M, Yüksel M (2006) Removal of nitrate from aqueous solution by nitrate selective ion exchange resins. *React Funct Polym* 66: 1206-1214.
- Shanmuganathan S, Nguyen TV, Jeong S, Kandasamy J, Vigneswaran S (2015a) Submerged membrane – (GAC) adsorption hybrid system in reverse osmosis concentrate treatment. *Sep Purif Technol* 146: 8-14.
- Shanmuganathan S, Johir MA, Nguyen TV, Kandasamy J, Vigneswaran S (2015b) Experimental evaluation of microfiltration–granular activated carbon (MF–GAC)/nano filter hybrid system in high quality water reuse. *J Membr Sci* 476: 1-9.
- Smith P, Vigneswaran S (2009) Effect of backwash and powder activated carbon (PAC) addition on performance of side stream membrane filtration system (SSMFS) on treatment of biological treatment effluent. *Desalin Water Treat* 11: 46-51.
- Vigneswaran S, Chaudhary D, Ngo H, Shim W, Moon H (2003) Application of a PAC-membrane hybrid system for removal of organics from secondary sewage effluent: experiments and modelling. *Sep Sci Technol* 38: 2183-2199.
- WHO (2011) Guidelines for Drinking-water Quality. fourth ed. World Health Organization, Geneva, Switzerland.

### **Figure captions**

**Fig. 1** A schematic diagram of the submerged membrane adsorption hybrid system used

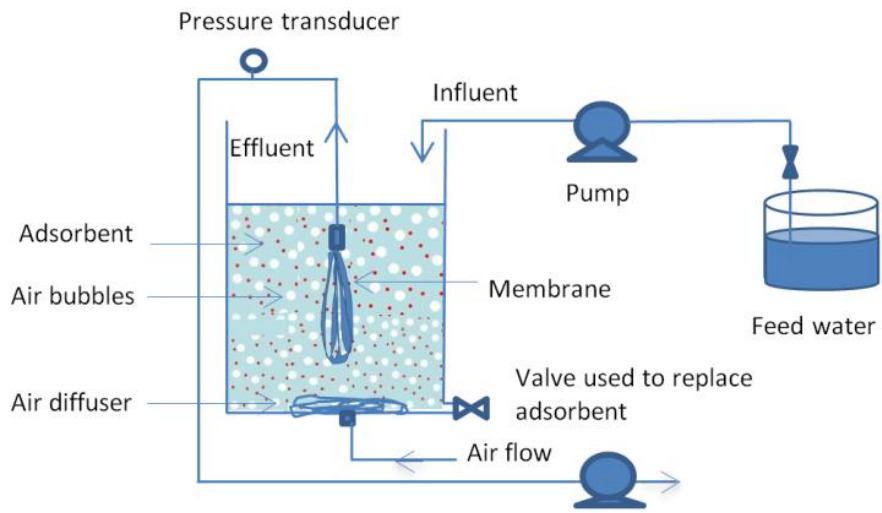
**Fig. 2** Comparison of adsorbents' performance in maintaining nitrate concentration in water for four flux filtration rates (adsorbent amount of 0.5 g/L of tank volume was replaced when N concentration exceeded the WHO limit of 11.3 mg N/L)

**Fig. 3** Effect of chloride and phosphate ions on nitrate removal efficiency

**Fig. 4** Effect of flux on nitrate adsorption (closed symbols) and volume of water treated (open symbols)

**Fig. 5** Transmembrane pressure (TMP) build-up with time for different flux and adsorbents





**Fig. 1**

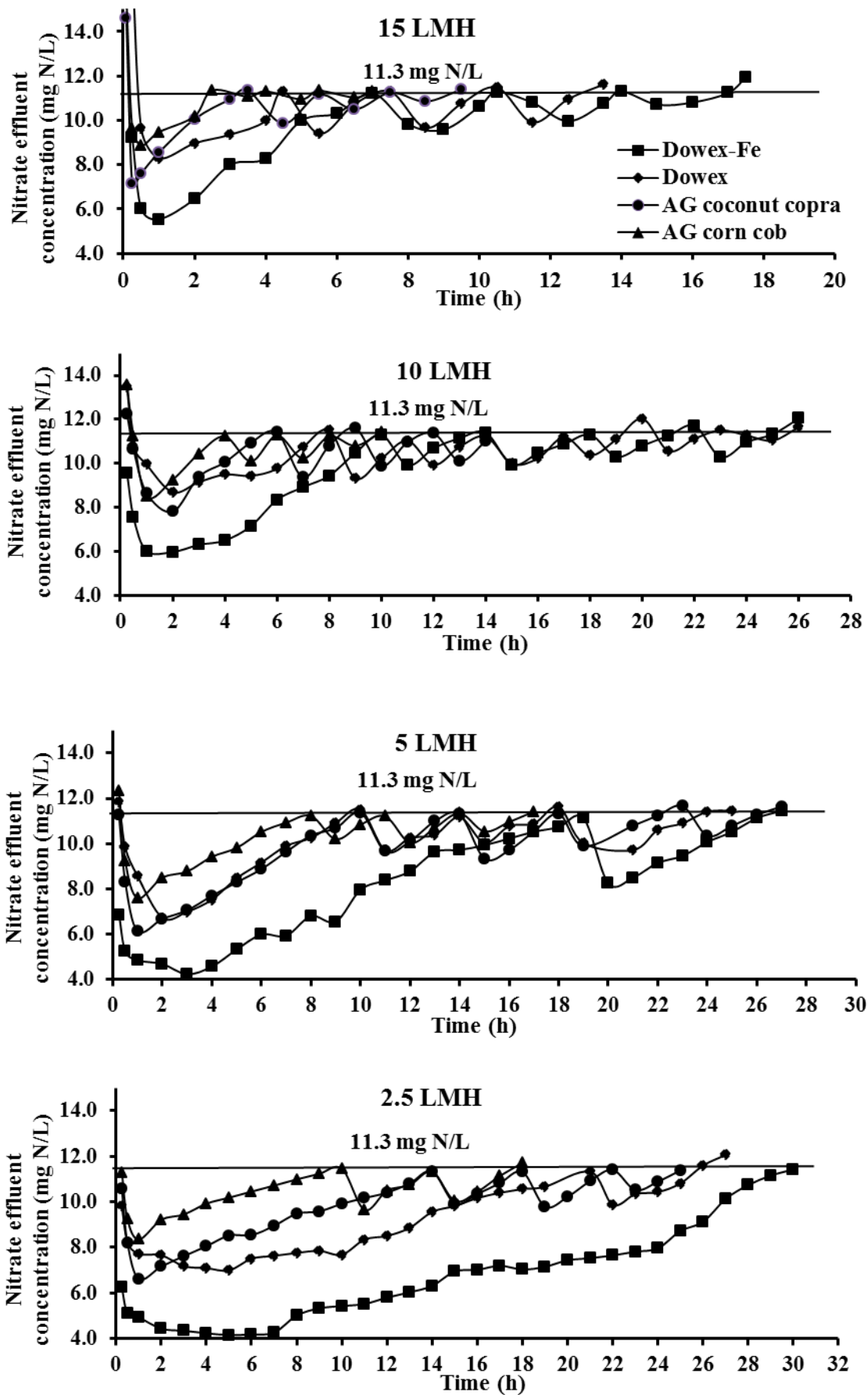


Fig. 2

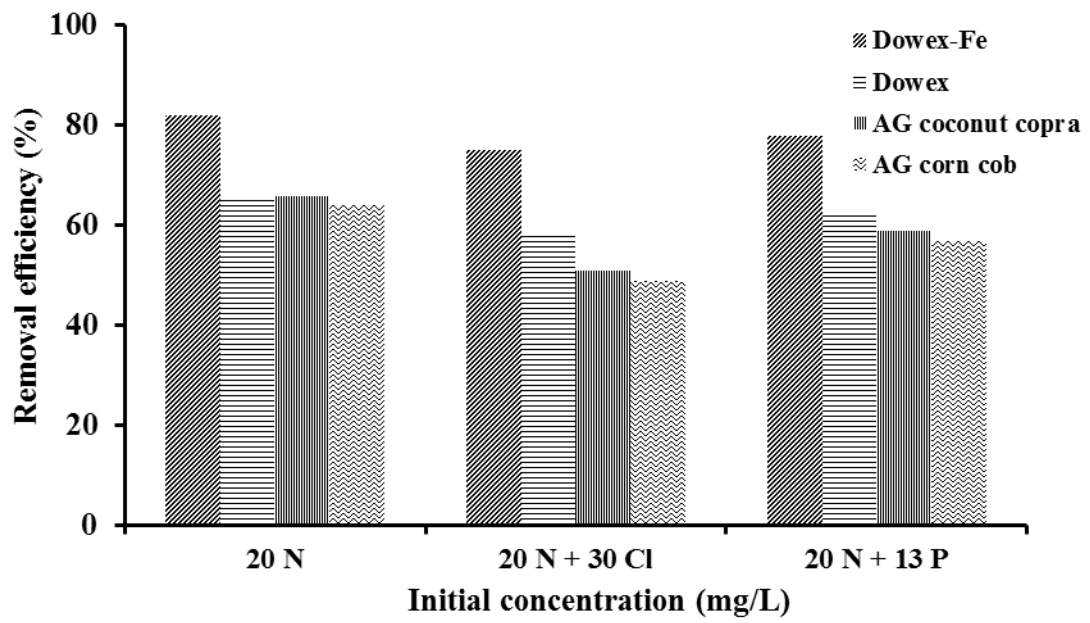


Fig. 3

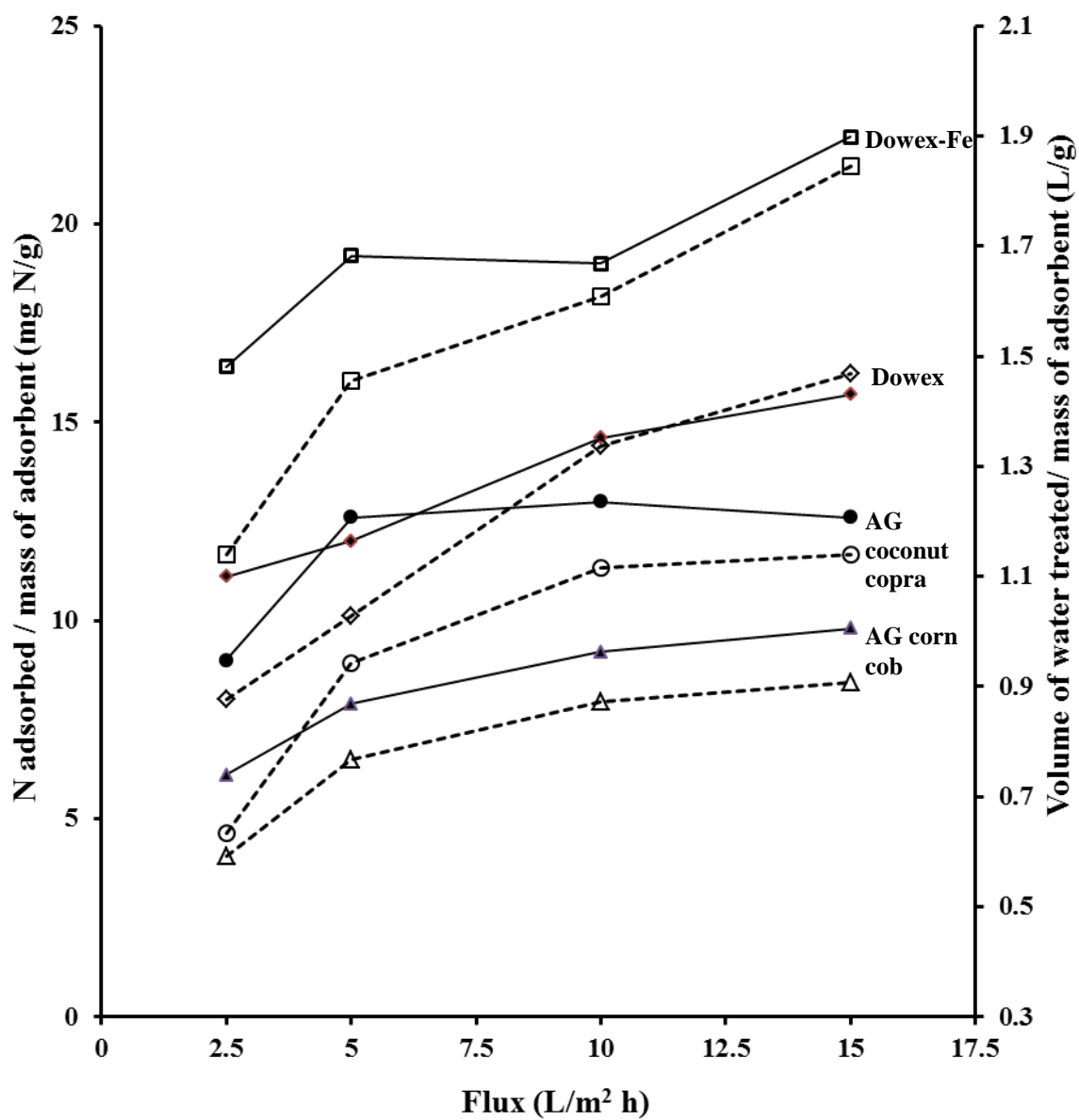


Fig. 4

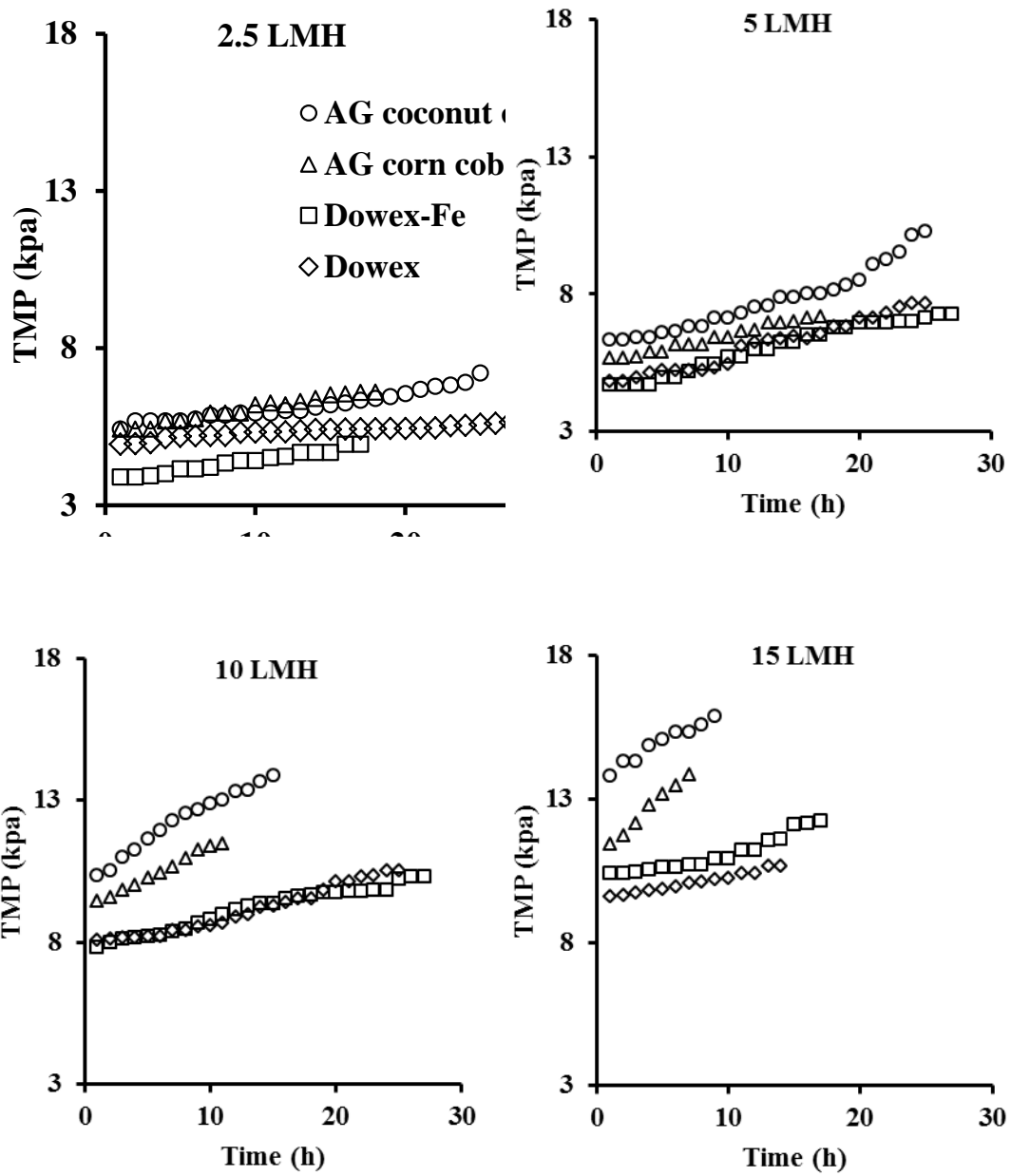


Fig. 5

**Table 1**

Characteristics of the adsorbents (Kalaruban et al. 2016a, b).

Adsorbent	Particle size ( $\mu\text{m}$ )	Zero point of charge pH	Langmuir adsorption capacity (mg N/g)	Column adsorption capacity* (mg N/g)
Dowex-Fe	300-1200	-	75.3	31.4
Dowex	300-1200	-	27.6	18.6
AG coconut copra	300-600	> 8.5	50.2	18.6
AG corn cob	300-600	> 8.5	49.9	15.3

\*Nitrate initial concentration 20 mg N/L; Flow velocity 5 m/h, Initial dry bed height 15 cm. Adsorption capacity calculated at column saturation (complete breakthrough of nitrate).

**Table 2** Nitrate removal performance and volume of water treated for the four adsorbents at four different flux.

Flux (L/m <sup>2</sup> h)	Adsorbent	Total time (h)	Total Volume (L)	Nitrate inlet (mg)	Nitrate outlet (mg)	Total amount of adsorbent used (g)	Nitrate adsorbed/mass of adsorbent (mg N/g)	Total amount adsorbed (mg)	Rate of removal (mg N/h)	Rate of removal/g of adsorbent (mg N/h g)	% removal
15	Dowex-Fe	17.5	29.5	590	235	16	22.2	355	20	1.27	60
	Dowex	13.5	23.5	470	219	16	15.7	251	19	1.16	53
	AG coconut copra	9.5	18.2	364	154	16	13.1	210	22	1.38	58
	AG corn cob	7.0	14.5	290	133	16	9.8	157	22	1.40	54
10	Dowex-Fe	26	28.9	607	265	18	19.0	342	13	0.73	56
	Dowex	26	29.0	609	288	22	14.6	321	12	0.56	53
	AG coconut copra	14	17.9	376	168	16	13.0	208	15	0.93	55
	AG corn cob	10	23.5	494	346	16	9.2	147	15	0.92	30
5	Dowex-Fe	27	17.4	365	135	12	19.2	230	9	0.71	63
	Dowex	25	16.5	347	155	16	12.0	192	8	0.48	55
	AG coconut copra	27	16.9	355	128	18	12.6	227	8	0.47	64
	AG corn cob	17	12.2	256	130	16	7.9	126	7	0.46	49
2.5	Dowex-Fe	30	11.4	239	75	10	16.4	164	5	0.55	69
	Dowex	27	10.5	221	87	12	11.1	133	5	0.41	60
	AG coconut copra	25	10.1	212	68	16	9.0	144	6	0.36	68
	AG corn cob	18	8.3	174	89	14	6.1	85	5	0.34	49

\* Reactor volume 4L \*\* Each replacement was 0.5 g/L when N concentration exceeded the WHO standard limit of 11.3 mg N/L

**Table 3**

Comparison of volume of water treated (nitrate concentration < 11.3 mg N/L) and nitrate adsorption between SMAHS and column-based system for similar flow rates (SMAHS 25 mL/min, column 27 mL/min) and influent nitrate concentration (20 mg N/L).

Adsorbent	SMAHS		Column*	
	Nitrate adsorbed/ mass of adsorbent (mg N/g)	Volume of water treated per mass of adsorbent (L/g)	Nitrate adsorbed/ mass of adsorbent (mg N/g)	Volume of water treated per mass of adsorbent (L/g)
Dowex-Fe	22.2	1.85	26.7	1.96
Dowex	15.7	1.47	15.4	1.14
AG coconut copra	13.1	1.14	18.0	0.92
AG corn cob	9.8	0.91	15.0	0.76

\*Kalaruban et al. 2016a, b