Mathematical Modelling of Nitrate Removal from Water Using a Submerged Membrane Adsorption Hybrid System with Four Adsorbents

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Abstract: Excessive concentrations of nitrate in ground water are known to cause human health hazards. A submerged membrane adsorption hybrid system that includes a microfilter membrane and four different adsorbents (Dowex 21K XLT ion exchange resin (Dowex), Fe-coated Dowex, amine-grafted (AG) corn cob and AG coconut copra) operated at four different fluxes was used to continuously remove nitrate. The experimental data obtained in this study was simulated mathematically with a homogeneous surface diffusion model that incorporated membrane packing density and membrane correlation coefficient, and applied the concept of continuous flow stirred tank reactor. The model fit with experimental data was good. The surface diffusion coefficient was constant for all adsorbents and for all fluxes. The mass transfer coefficient increased with flux for all adsorbents and generally increased with the adsorption capacity of the adsorbents.

Keywords: nitrate in water; submerged membrane adsorption hybrid system; adsorption; modelling adsorption; ion exchange resin

1. Introduction

Nitrate contamination in ground water causes human health problems (methemoglobinemia, kidney failure, vomiting, diarea) [1,2]. Among the several nitrate removal technologies available, adsorption is the most promising in terms of cost and efficiency, as measured by the percentage of nitrate removal, simplicity of design, operation and maintenance and minimising waste production. Experiments in the adsorption process are usually undertaken in a batch operation mode or a column operation mode. The column operation mode is a dynamic and continuous operation process which can be easily related to actual water treatment plants. However, very small size adsorbents which have higher adsorption capacities (due to higher surface area and availability of more adsorption sites) cannot be used in column mode due to the head loss. Furthermore, micro-particles and suspended solids, if present in the influent water, usually clog the column and reduce operating performance.

The submerged membrane adsorption hybrid system (SMAHS) is an alternative dynamic adsorption system developed during the last two decades to obtain high quality effluent water. In this process, microfiltration (MF) or ultrafiltration (UF) membranes coupled with adsorption technology are used to treat the water. Although the MF or UF do not remove the nitrate, they can remove suspended solids, colloids, micro-organisms and micro-particles from water. The adsorbents are retained in the reactor [3,4] and kept continuously in suspension via aeration to facilitate increased

adsorption of pollutants. The integrated adsorption and membrane filtration system offers several advantages. Here the adsorbents kept in suspension by the aeration reduce membrane fouling by abrasion and membrane scouring. Consequently, the membrane's operation time and total usable life span increases, which in turn helps to minimise operation and maintenance costs. In addition, this reduces the frequency of membrane cleaning and the membrane cleaning requires smaller amounts of chemicals.

Another advantage is, unlike in column mode of operation, smaller size adsorbents can be used in SMAHS for higher removal of pollutants and this has been proved in past studies [5,6]. Johir et al. [5] studied the effect of three particle sizes of granular activated carbon (GAC) on scouring of membrane and dissolved organic carbon removal in SMAHS. They found that the scouring effect was highest for intermediate particle size but DOC removal by adsorption on to GAC was highest for the smallest particle size. The difference in the particle effects were explained by particle settling in the suspension adsorption capacity.

Most previous SMAHS studies have mainly focused on the removal of metals [7,8], phosphate [9], colour and reactive dyes [10], and organic micropollutants [11]. Relatively recently, nitrate removal using the SMAHS was reported [12]. The data obtained in the study of Kalaruban et al. [12] was not mathematically modelled. Models have the advantage of simulating the performance of SMAHS at other experimental conditions without expending the time and expense of physical experiments. The model will be helpful to optimise the operating conditions which is important in ground water treatment. The application of mathematical model for SMAHS has not been reported for nitrate. However, a model has been applied for organics removal in the literature [6,13].

The objectives of this study were to: (i) compare 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 under four filtration flux; and (ii) simulate the experimental data with a mathematical model. This research is new because to date, in literature, there has been no mathematical model shown to be able to simulate experimental data of nitrate removal from influent water using SMAHS with different adsorbents under different flux conditions.

2. Experimental

2.1. Materials

2.1.1. Feed Solution

Synthetic nitrate solution at a concentration of 20 mg N/L was prepared using Analar grade KNO_3 (Sigma Aldrich, St. Louis, MO, USA) and tap water. The pH of the solution was kept in a range between 6.5 and 7.5. The same type of solution was used for all experiments to ensure that the influent nitrate concentration remained constant. The tap water contained 30 mg/L of chloride, 1 mg P/L of phosphate and 0.04 mg S/L of sulphate.

2.1.2. Adsorbents

Four adsorbents, such as anion exchange resin Dowex 21K XLT, iron-modified Dowex 21K XLT (Dowex-Fe), AG corn cob and AG coconut copra, were used. Dowex is a commercially available anion exchange resin produced by DOW Chemical Pte Ltd., (Dow Chemical Co., Pevely, MO, USA) and contains ammonium functional group and chloride as counter ion. Dowex was modified by adding $FeCl_3.6H_2O$ (Sigma Aldrich, St. Louis, MO, USA) and NaOH solution (Sigma Aldrich, St. Louis, MO, USA). The method of Fe modification of Dowex has been described elsewhere [14]. The Fe content of the product is 0.4% by weight. The agricultural wastes, corn cob and coconut copra were dried, ground and sieved to 300–600 μm. Then they were amine-grafted using epichlorohydrin (Sigma Aldrich, St. Louis, MO, USA), *N,N*-dimethyl formamide (Sigma Aldrich, St. Louis, MO, USA), pyridine (Sigma Aldrich, St. Louis, MO, USA) and dimethylamine solution (Sigma Aldrich, St. Louis,

MO, USA). The method of amine grafting has been documented elsewhere [15]. Table 1 summarises the characteristics of these adsorbents.

Table 1. Characteristics of the adsorbents [14,15].

Adsorbent	Particle Size (μm)	Zero Point of Charge pH **	Langmuir Adsorption Capacity (mg N/g)	Column Adsorption Capacity * (mg N/g)
Dowex-Fe	300–1200	>8	75.3	31.4
Dowex	300–1200	>8	27.6	18.6
Amine grafted coconut copra	300–600	>8.5	50.2	18.6
Amine grafted 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); ** Zero point of charge pH is the pH at which net surface charge on the adsorbents was zero.

2.1.3. Membrane Characteristics

A hollow fibre membrane with a specification of 0.1 μm nominal pore size and 0.1 m^2 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 is manufactured by Mann+Hummel Ultra–Flo Pty Ltd., Singapore.

2.2. Methodology

2.2.1. Submerged Membrane Adsorption Hybrid System (SMAHS)

Figure 1 is a schematic diagram of the SMAHS. The experiments were carried out in a dynamic system which can be readily applied in a real treatment process. The volume of water in the reactor was maintained at 4 L. The adsorbent was added to the water in the reactor and the membrane was submerged into the reactor. The adsorbent performance was evaluated in terms of volume of treated water and the amount of nitrate adsorbed. A peristaltic pump (Extech Equipment Pty Ltd., Boronia, VIC, Australia) was used to feed the influent containing 20 mg N/L to the reactor and periodically remove effluent from the tank at a controlled flux. The effect of filtration flux was studied by conducting experiments at a flux of 2.5, 5, 10 and 15 L/m^2 h. 10 g adsorbent was added to the reactor and the treatment was continued until the concentration of nitrate in the effluent reached the WHO prescribed nitrate concentration limit of 11.3 mg N/L [16]. 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 (Sigma Aldrich, St. Louis, MO, USA) before commencing each experiment. Experiments were conducted with each of the four adsorbents.
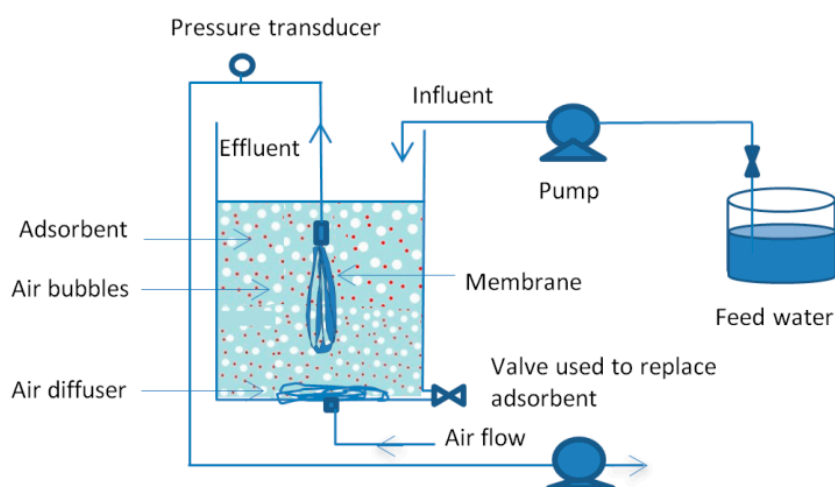
Figure 1. Submerged membrane adsorption hybrid system.

2.2.2. Analytical Method

Nitrate concentration was measured using an ion chromatograph (Model 790 Personal IC, Metrohm, Gladesville, NSW, Australia) equipped with an autosampler and conductivity cell detector. Before commencing an analysis, the ion chromatograph was cleaned with mobile phase solutions containing Na_2CO_3 (Sigma Aldrich, St. Louis, MO, USA) and $NaHCO_3$ (Sigma Aldrich, St. Louis, MO, USA). This was followed by cleaning with diluted sulphuric acid (Sigma Aldrich, St. Louis, MO, USA) and Milli-Q water (University of Technology Sydney, NSW, Australia).

2.2.3. Mathematical Modelling of the Results of SMAHS

The homogeneous surface diffusion model (HSDM) was used to study the adsorption kinetics process which comprises 3 steps: (i) the adsorbate diffuses through a stagnant liquid film layer surrounding the adsorbent particle; (ii) the adsorbate adsorbs from the liquid phase onto the outer surface of the adsorbent; and (iii) the adsorbate diffuses along the inner surface of the adsorbent particles until it reaches its adsorption site. A detailed description of the model was reported elsewhere [17,18]. The model equations are:

$$\frac{\partial q_{td}}{\partial t} = D_s \left(\frac{\partial^2 q_{td}}{\partial r^2} + \frac{2}{r} \frac{\partial q_{td}}{\partial r} \right) \tag{1}$$

Initial and boundary conditions for the process are given in Equations (2)–(4):

$$t = 0; \, q_{td} = 0 \tag{2}$$

$$r = 0; \, \frac{\partial q_{td}}{\partial r} = 0 \tag{3}$$

$$r = r_p; \, D_s \rho_p \frac{\partial q_{td}}{\partial r} = k_f(C - C_s) \tag{4}$$

where, D_s = surface diffusion coefficient (m^2/s) which is the rate of diffusion of nitrate along the surface of the adsorbent particle, q_{td} = nitrate-N concentration in the solid phase (mg/L), C = nitrate-N concentration in the liquid phase (mg/L), C_s = liquid phase nitrate concentration at the adsorbent surface (mg N/L), r = radial distance from the centre of adsorbent particle (m), k_f = external mass transfer coefficient (m/s), and ρ_p = particle density (kg/m^3).

The mass balance of the nitrate in bulk solution in the membrane reactor was calculated using Equation (5). This model was developed using the concept of a continuous flow stirred tank reactor (CSTR) and by incorporating membrane packing density (A_M/V_M) and membrane correlation coefficient (MCC) into the adsorption model [3,13].

$$\frac{dC_b}{dt} = \frac{Q}{V}(C_0 - C_b) - \frac{M}{V}\frac{dq}{dt} - \frac{A_M}{V_M} MCC \, C_b \tag{5}$$

where C_b is the nitrate concentration in the bulk phase in the reactor (mg N/L); Q is the flow rate (m^3/s); V is the volume of the bulk solution in the reactor (m^3); C_0 is the nitrate concentration in the feeding tank (mg N/L); M is the mass of the adsorbent used (g); A_M is the surface area of the membrane (m^2); V_M is the volume of membrane (m^3); MCC is the membrane correlation coefficient. The term [(M/V) (dq/dt)] denotes the adsorption of nitrate onto the adsorbent in suspension, and [(A_M/V_M) MCC C_b] represents the adsorption onto the adsorbents layer deposited onto membrane surface. The first two terms on the right-hand side of Equation (5) represent adsorption. Once the particles are adsorbed, the adsorbent (together with nitrate) is retained by the membranes which is represented by the third term of the equation on the right-hand side. The retention and possible further adsorption on the membrane are assumed to be proportional to the packing density (A_m/V_m). Here, the packing density is the area of membrane in a unit volume of the membrane module. The proportionality is

represented by a surrogate parameter of membrane correlation coefficient (MCC). More details are given in the paper of Guo et al. [3]. A higher value of MCC indicates a more efficient removal of adsorbate and adsorbent which contained the adsorbate by the membrane [13]. The latter part of the equation ((A_M/V_M) MCC C_b) can be neglected because of the negligible amount of nitrate adsorbed on the membrane surface compared to that adsorbed by the adsorbents.

In order to numerically solve the SMAHS model equations, the orthogonal collocation method [19], ordinary differential equations (ODEs) and double variable ordinary equation (DVODE) were used. The surface diffusion coefficient (D_s) depends on the influent concentration of nitrate. The Ds value was taken from previous [14] batch experimental data (HSDM) and used for the SMAHS simulation in this study. The external mass transfer co-efficient (k_f) value depends on the air flow rate used to keep the adsorbents in a suspension mode and was determined from the SMAHS data by simulation. Here, the Nelder-Mead simplex method [20] was used to minimise the differences between the experimental value and the prediction values as a function of time.

3. Results and Discussion

The SMAHS experimental results showed that the amount of nitrate removed and the volume of water treated per gram of adsorbent increased with flux (Table 2). This is mainly due to the increased amount of nitrate that entered the reactor per unit time, though at higher flux the contact time of solution with the adsorbent (retention time) was low and hence tended to produce reduced adsorption. Because of the decreased amount of nitrate that entered the rector per unit time at lower flux, the adsorption capacity decreased at lower flux. However, the reduction in adsorption capacity is less than 15% from 15 to 2.5 L/m^2 h. The performance of adsorbents was compared in terms of adsorption capacity and the volume of water treated per gram of adsorbent.

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

Flux (L/m^2 h)	Adsorbent	Volume of Water Treated (L)	Nitrate Adsorbed/Mass of Adsorbent (mg N/g)
15	Dowex-Fe	14.5	19.2
	Dowex	10.8	12.8
	AG coconut copra	9.3	12.2
	AG corn cob	7.8	9.0
10	Dowex-Fe	13.8	18.6
	Dowex	11.8	12.7
	AG coconut copra	9.9	11.8
	AG corn cob	7.9	8.8
5	Dowex-Fe	13.2	18.1
	Dowex	8.9	11.5
	AG coconut copra	8.9	11.7
	AG corn cob	7.9	8.8
2.5	Dowex-Fe	11.4	16.4
	Dowex	8.9	11.2
	AG coconut copra	7.4	9.8
	AG corn cob	6.5	7.7

Figure 2 shows the changes of effluent concentration with time. The Dowex-Fe performed the best out of the four adsorbents. The experiments were conducted till the effluent reached the WHO limit of 11.3 mg N/L and the duration was higher for Dowex-Fe for all flux. The Dowex-Fe reached the WHO limit in 30 h for low flux (2.5 LMH) whereas the concentration exceeded the limit in 10 h for AG corn cob. At high flux, Dowex-Fe reached the WHO limit in 7 h and AG corn cob reached it in 2.5 h. These results show that the operation time until the WHO limit is reached depends on the adsorption capacity of the adsorbents and the flux.

Table 2 shows that the performance was in the order Dowex-Fe > Dowex $\geq$ AG coconut copra > AG corn cob. This order agreed with the adsorption capacity order obtained from a column mode study [14,15] but not with the Langmuir adsorption capacities obtained from a batch mode study (Table 1). The continuous column study used the same influent nitrate concentration of 20 mg N/L as in the SMAHS study whereas the Langmuir adsorption capacities in the static batch study were the maximum adsorption capacities calculated at very high equilibrium concentrations. These differences can explain the reason for the similarities/differences observed in the order of adsorbent performance observed in SMAHS continuous mode and batch mode studies.

The SMAHS model fit to the experimental data is satisfactory (Figure 2) as evident from the high correlation (R^2) values (Table 3). Deviation of some experimental data points from the model values were noticed at the lowest flux (2.5 L/m^2 h) for AG coconut copra and AG corn cob (Figure 3). The correlation coefficients (R^2) were also low for AG corn cob (0.735) and AG coconut copra (0.744) at this flux. This may be due to the low mass transfer that occurred at low flux. Also, the corn cob and coconut copra are natural materials which were modified by amine grafting. This may not have uniform adsorption sites. On the other hand, Dowex is a commercial product which has beeb more uniformly studied and thus it gave rise to a higher correlation coefficient.
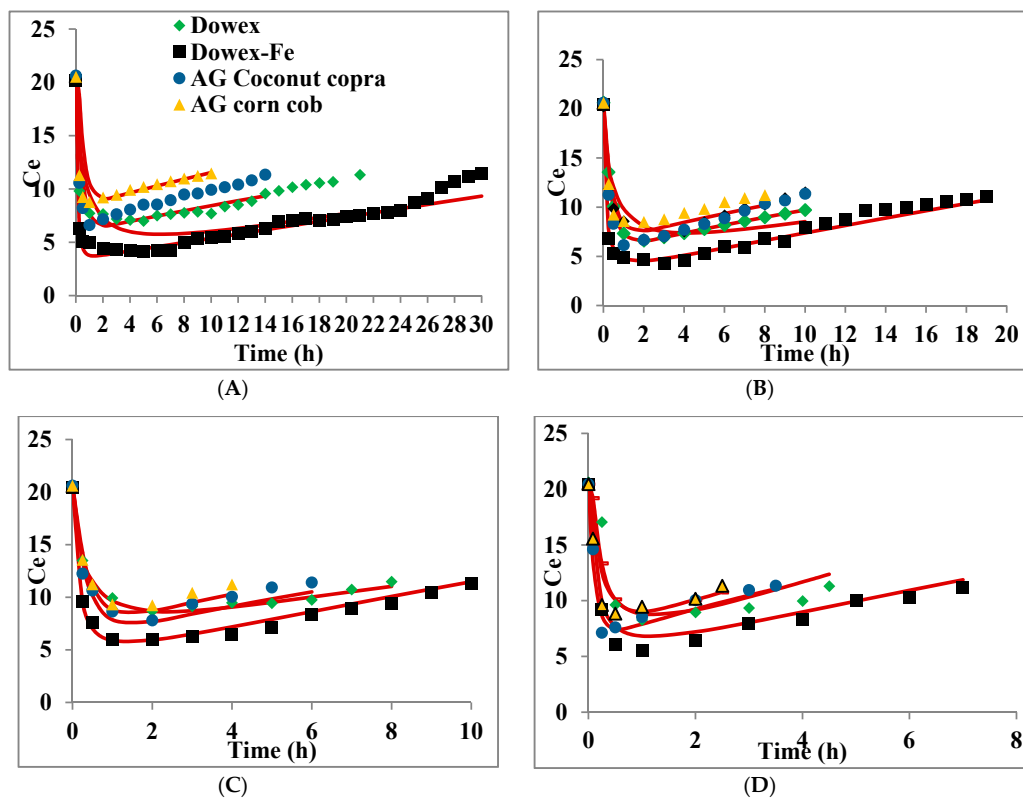
Figure 2. Model prediction of nitrate removal for four adsorbents at various flux of (**A**) 2.5 L/m^2 h; (**B**) 5 L/m^2 h; (**C**) 10 L/m^2 h and (**D**) 15 L/m^2 h. Data points are experimental data and lines are model simulations.

The model parameters are given in Table 3. The Ds values were virtually the same for all four flux for each adsorbent. This was due to the constant concentration of nitrate used in all experiments. The k_f values increased with flux for all the adsorbents due to a higher mass transfer that occurs at high flux, when more nitrate entered the reactor per unit time. k_f values also increased with adsorption capacity (Dowex-Fe > Dowex > AG coconut copra > AG corn cob, Table 2). A higher mass transfer at the adsorbent surface provides a higher sink for the adsorbate. MCC was found to increase with

flux, a result also found for organics removal by powdered activated carbon in SMAHS [13]. This is probably due to more nitrate entering the reactor per unit time at higher flux.
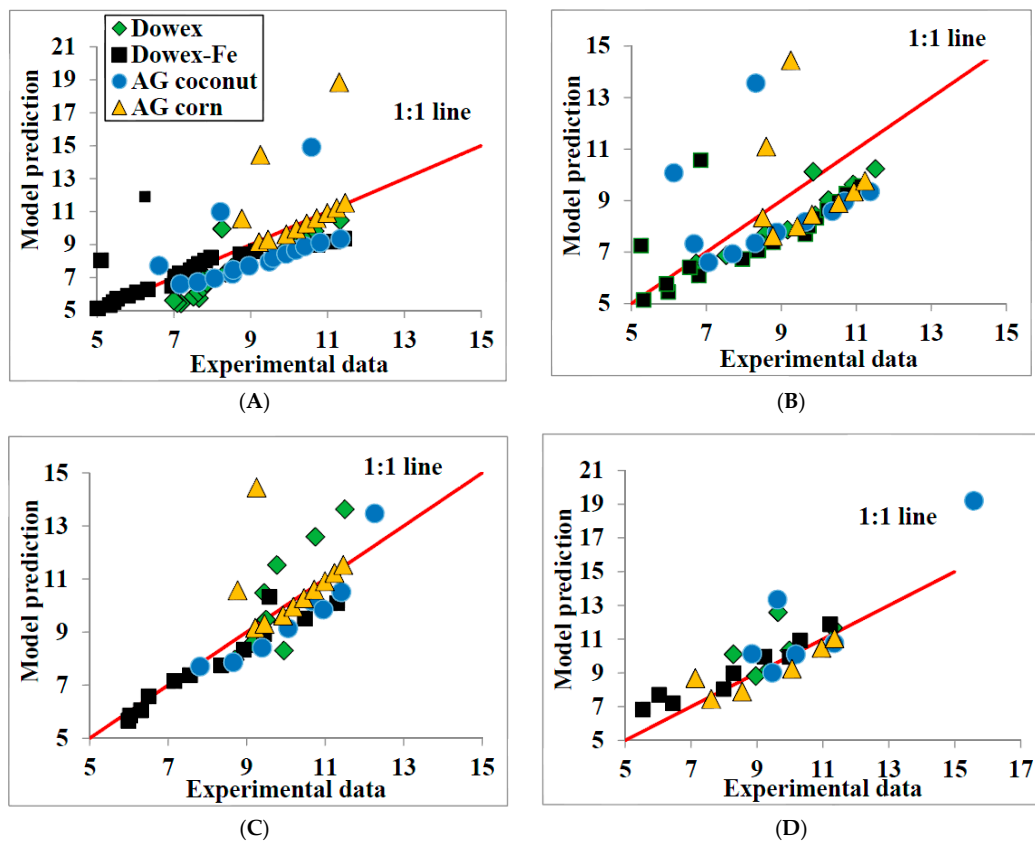
Figure 3. Comparison of model prediction and experimental data of effluent nitrate concentration (mg N/L) for the four adsorbents at the different filtration flux of (**A**) 2.5 L/m^2 h; (**B**) 5 L/m^2 h; (**C**) 10 L/m^2 h and (**D**) 15 L/m^2 h.

Table 3. The modelling parameters of submerged membrane adsorption hybrid system (SMAHS) at different flux for four adsorbents. MCC: membrane correlation coefficient.

Adsorbents	Parameters	Filtration Flux			
		2.5 L/m^2 h	5 L/m^2 h	10 L/m^2 h	15 L/m^2 h
Dowex-Fe	D_s (m^2/s)	3.3×10^{-12}	3.3×10^{-12}	3.3×10^{-12}	3.3×10^{-12}
	k_f (m/s)	2.0×10^{-4}	2.0×10^{-4}	2.3×10^{-4}	3.9×10^{-4}
	MCC (m/s)	1.1×10^{-12}	1.3×10^{-12}	1.4×10^{-12}	2.0×10^{-12}
	R^2	0.852	0.854	0.976	0.956
Dowex	D_s (m^2/s)	1.7×10^{-12}	1.7×10^{-12}	1.7×10^{-12}	1.7×10^{-12}
	k_f (m/s)	8.8×10^{-5}	9.1×10^{-5}	11.7×10^{-5}	15.4×10^{-5}
	MCC (m/s)	1.2×10^{-12}	1.5×10^{-12}	1.6×10^{-12}	1.9×10^{-12}
	R^2	0.829	0.904	0.851	0.839
AG coconut copra	D_s (m^2/s)	1.6×10^{-11}	1.6×10^{-11}	1.6×10^{-11}	1.6×10^{-11}
	k_f (m/s)	3.5×10^{-5}	3.6×10^{-5}	3.7×10^{-5}	6.4×10^{-5}
	MCC (m/s)	9.1×10^{-14}	1.0×10^{-13}	1.3×10^{-13}	1.4×10^{-13}
	R^2	0.744	0.904	0.970	0.964
AG corn cob	D_s (m^2/s)	4.3×10^{-11}	4.3×10^{-11}	4.3×10^{-11}	4.3×10^{-11}
	k_f (m/s)	2.7×10^{-5}	2.9×10^{-5}	3.0×10^{-5}	12×10^{-5}
	MCC (m/s)	9.3×10^{-14}	1.3×10^{-13}	1.3×10^{-13}	1.9×10^{-13}
	R^2	0.735	0.888	0.945	0.860

4. Conclusions

The performance of four adsorbents in terms of volume of water treated and the amount of nitrate removed in a SMAHS were in the order Dowex-Fe > Dowex > AG coconut copra > AG corn cob. Agricultural wastes, coconut copra and corn cob are mostly locally available materials and are the preferred adsorbents in terms of cost, especially in developing countries. The study showed that the amount of nitrate adsorbed and volume of water treated to maintain low nitrate concentration were higher for higher flux. A mathematical model incorporating membrane packing density and membrane correlation (MCC) coefficient in the homogeneous surface diffusion model applying the concept of CSTR reactor, demonstrated a good fit with the experimental data of nitrate removal in SMAHS. The application of the findings of this study to practical conditions may vary depending on the water quality, amount of water need/day, adsorption capacity of the adsorbent, its cost and availability. Furthermore, this study was a short-term study and needs to be extended with long-term experiments, and with repeated replacements of the exhausted adsorbents to obtain more information on practical applications.

Author Contributions: Author Contributions: Conceived and designed the experiments: Jaya Kandasamy, Kalaruban Mahatheva and Saravanamuthu Vigneswaran. Experiments conducted: Mahatheva Kalaruban. Analysed the data and wrote the paper: Mahatheva Kalaruban, Paripurnanda Loganathan and Saravanamuthu Vigneswaran. Modelling: Saravanamuthu Vigneswaran, Jaya Kandasamy, Wang Geun Shim, and Mahatheva Kalaruban. All authors read and approved the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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