

Enhanced removal of nitrate in an integrated electrochemical-adsorption system

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Abstract

The electrochemical (EC) method of removing pollutants in water is a widely used process in water and wastewater treatment. An EC-adsorption integrated system was investigated to test whether the simultaneous removal of nitrate by the two processes would be better than removal utilising the individual EC and adsorption methods. In the integrated system, an adsorbent (ion exchange resin - Dowex 21k XLT) was placed inside a stainless steel box that served as an anode with a Cu plate as cathode. In an experiment using 2 L nitrate solution containing 20 mg N/L and 2 g adsorbent the rate of nitrate removal in the integrated system was initially fast with 35% removed in 30 min, though slowing down later. The rate of removal increased with increasing current, voltage and pH up to 7 but decreased as the distance between the electrodes also increased. The optimum nitrate removal of 67% was obtained at pH 7, 1 A, and 31 V for a distance of 1 cm between the electrodes after 180 min. The amount

of nitrate removed fell when sulphate was present in the integrated system due to sulphate competing with nitrate for adsorption. Concentration of ammonium produced by nitrate reduction in the EC system was reduced in the presence of adsorbent. Nitrate removal in the integrated system is approximately equal to the sum of the removals in the two individual processes.

Key words: Nitrate, electrochemical treatment, adsorption, electrodes, ion exchange resin

Highlights

- Stainless steel box with adsorbent acted as anode in an electrochemical (EC) cell.
- Nitrate removal: combined EC-adsorption system \approx adsorption system + EC system.
- Nitrate removal was highest at pH 7, 1 cm electrodes-apart, 1 A, and 30 V.

1. Introduction

The electrochemical (EC) method is a widely used process for water and wastewater treatment. It is an environmentally friendly treatment technology for removing nitrate and a wide range of pollutants with less sludge production and less use of chemicals [1,2]. In this treatment method, nitrate ions are converted to N_2 gas at the cathode as the major product and released into the environment [3]. Other pollutants such as ammonia [4], oil [5], dye [6], heavy metals [7], viruses [8], E-Coli [9], turbidity [10], phosphate [11], and fluoride [12] can also be removed from water through this method. This technology is fairly inexpensive to operate and the cost can be further reduced if renewable energy sources are employed. Although this method has several advantages, it also has some disadvantages such as metal oxide formation on the cathode and the need to regularly replace sacrificial electrodes.

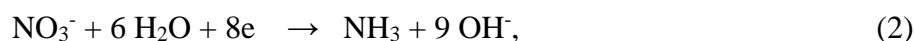
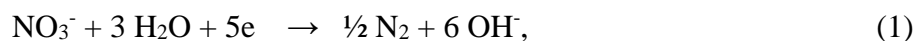
The EC process has been used at several locations for ground water nitrate treatment [13]. Electro-reduction of nitrate has been studied over the last few decades using electrodes of

metals such as Ni, Fe, Al, Zn, Au, Pt, Pd, Ag, Cu, Ru, and Rh [14-19]. Of these metals, Cu emerged as the best cathode for reducing nitrate [14, 19]. A stainless steel plate has been employed in previous studies for the removal of nitrite [10], nitrate [20] and ammonia [21]. In the nitrite removal study, stainless steel served as both the cathode and anode electrodes while in the studies on ammonium and nitrate removal it was used only as the cathode and other metals such as conductive diamond and TiO₂ were used as anode.

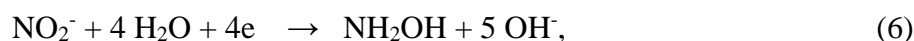
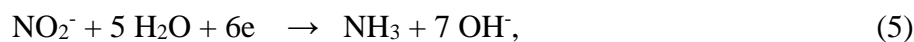
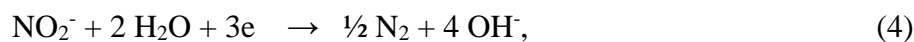
Although the nitrate decomposes to harmless nitrogen gas as the main product at the cathode, low concentrations of some by-products such as ammonia and nitrite may also be produced in the solution [22]. Consequently, the ammonia is oxidised to nitrogen gas at the anode [23]. If chloride ions are present in the water they are also oxidised at the anode as chlorine gas, which dissolves in water to produce hypochlorite. The hypochlorite reacts with the ammonia/ammonium ions to produce nitrogen gas [3]. In the study by Li et al. [23] nitrite or ammonia was not detected in the final solution due to the presence of chloride ions.

The possible reactions at the cathode are as follows [23,24]:

Nitrate reduction to N₂, NH₃, NO₂⁻



Nitrite reduction to N₂, NH₃, NH₂OH

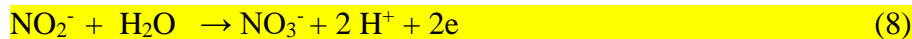


Hydrogen evolution is the main parasitic cathodic reaction (equation 7) [24]



The possible reactions at the anode are [25]:

Oxidation of NO_2^- and NH_3 to NO_3^- and N_2



Oxygen evolution is the main anodic reaction (equation 10) [24]



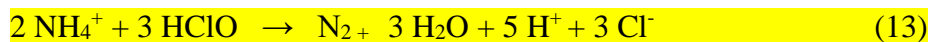
The following is a possible reaction at the anode when Cl^- ions are present in the water:



The Cl_2 produced according to equation 11 immediately reacts with water to form hypochlorite

(HClO) (equation 12) which would react with ammonia to produce nitrogen gas (equation 13)

[22,23]. This would reduce the concentration of NH_4^+ produced by the EC reduction of NO_3^- .



Despite the fact that several studies have reported the removal of nitrate using EC technology [24-27], only one analysis investigated the removal of nitrate using an integrated EC-adsorption system. In that study, a carbon anode electrode was coated with a nitrate selective BHP55 ion exchange resin and used for nitrate and chloride removal [28]. The nitrate and chloride removals were 19 and 15 mmol/m² from solutions containing 2 mM and 5 mM chloride, respectively. However, the relative contribution of resin adsorption and EC in nitrate removal was not reported. Coating the electrode with the adsorbent may not produce its full potential of removing nitrate because parts of the electrode and adsorbent may not be available to actively remove nitrate. Instead of coating the electrode with the adsorbent, the adsorbent can be retained in suspension near the electrode inside a box to produce the full potential of the adsorbent and the electrode in removing nitrate. The study reported in this paper is based on having a stainless steel electrode box as the anode with the box containing an adsorbent. The main objectives of the research were to: (i) study the efficiency in removing nitrate using the

integrated EC-adsorption system and compare the removal with the same technologies when they are used separately; and (ii) investigate the effects of operating conditions such as pH, voltage, current, and distance between electrodes on the removal of nitrate with and without the presence of co-ions sulphate and phosphate.

2. Experimental details

2.1. Materials and methods

An anion exchange resin Dowex 21k XLT was used in this integrated system. In the EC system, Cu plate and stainless steel sieve box were used as cathode and anode electrode, respectively. The dimensions of the Cu plate were 11 cm x 6 cm x 0.5 cm and the dimensions of the submerged part of the plate inside the solution were 9 cm x 6 cm x 0.5 cm. A stainless steel (304) sieve with an aperture size of 0.25 mm was employed to make the electrode box. The dimensions of the submerged part of the box inside the solution were 9 cm x 6 cm x 2 cm. A feed solution containing nitrate was prepared by dissolving ANALAR grade KNO_3 in tap water to obtain a concentration of 20 mg N/L. Tap water had chloride, sulphate and phosphate concentrations of 30 mg Cl/L, 1.1 mg S/L and 1 mg P/L, respectively. For the ion competition studies, ANALAR grade KH_2PO_4 and Na_2SO_4 were added to the nitrate solution to produce the required concentrations of phosphate and sulphate.

In each experiment, 2 g adsorbent was packed inside the stainless steel sieve box (anode electrode) and immersed in a 2 L solution in parallel with the Cu plate (Fig. 1). The EC and adsorption experiments were conducted individually using the same conditions to compare the advantage of the integrated system over the individual systems. A magnetic stirrer rotating at a speed of 120 rpm was used at the bottom of the container to keep the adsorbent in suspension and to maintain the solution at a uniform concentration. A Powertech MP 3086 model AC to DC converter provided direct current to the EC system. The voltage/current was measured in

the converter. The performance of the EC and the integrated systems were studied in terms of nitrate removal at different distances between the electrodes (0.5, 1, 2 and 3 cm), voltage (15, 20, 25, and 30 V), current (0.2, 0.5, 0.7, and 1 A) and pH (3, 5, 7, 9, and 11). All the experiments were conducted at the room temperature of 25-27⁰ C.

2.2. Chemical analysis

Nitrate, phosphate, and sulphate concentrations were analysed by an ion chromatograph (Model 790 Personal IC) equipped with an auto sampler and a conductivity cell detector. The ion chromatograph was cleaned before the analysis using a mobile phase solution (Na₂CO₃, NaHCO₃), diluted sulphuric acid and Milli-Q water. Ammonium ion concentration was measured using a HACH DR 3900 test kit. The solutions' pH was measured using an HQ40d portable pH meter. The dissolved Fe ions concentration was measured using a Microwave Plasma-Atomic Emmison Spectrometer (Agilent 4100 MP-AES).

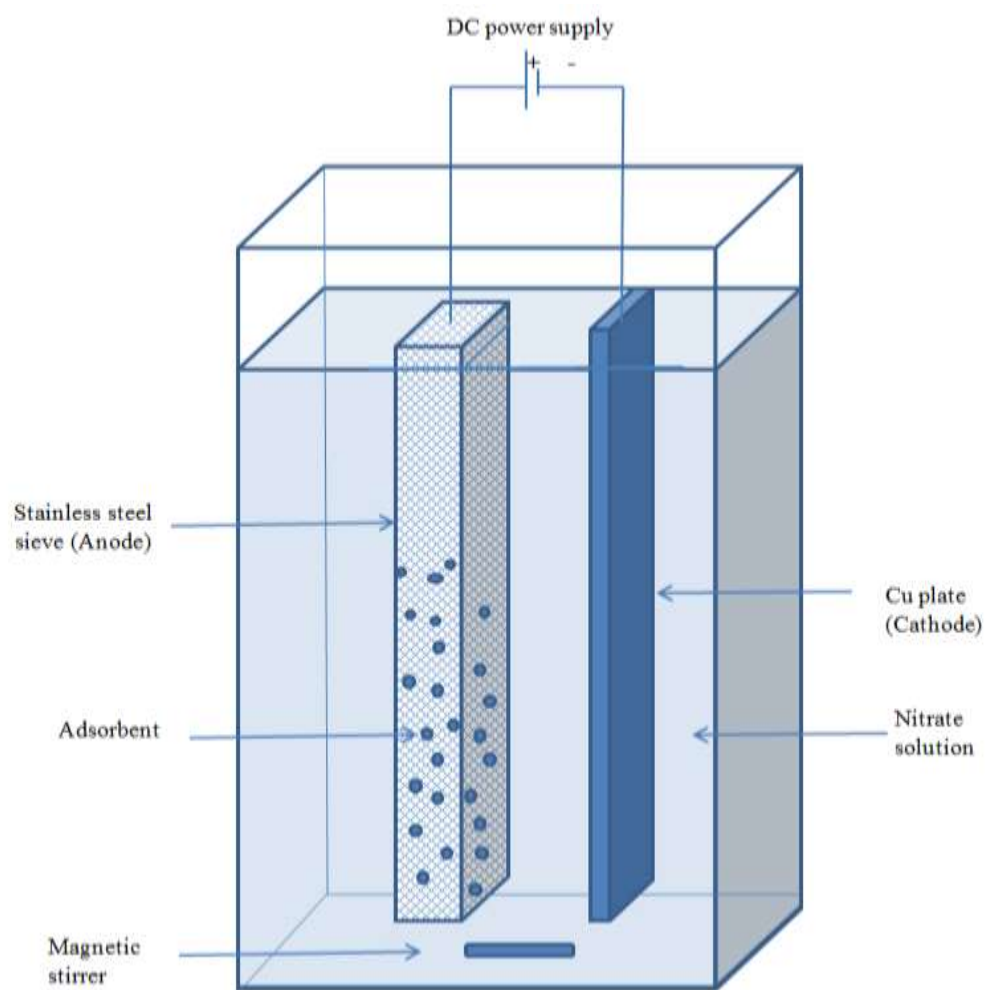


Fig. 1. Integrated EC-adsorption system

3. Results and discussion

3.1. Effect of distance between electrodes

The current decreased from 1.3 A to 0.2 A as the distance between the electrodes increased at a constant voltage of 30 V. The nitrate removal increased when the distance between the electrodes for both the EC system and integrated system shortened (Fig. 2). The reason for this is that when the gap between electrodes narrows, the resistance between the electrodes reduced and the current increased [29]. Thus, the rate of nitrate reduction at the cathode increased and reduced forms of nitrogen species were produced (Eq 1 - Eq 7). In the integrated system, in addition to the reduction of nitrate at the cathode, the nitrate that moved to the anode was adsorbed on to the adsorbents.

Some of the nitrates in the solution were reduced to ammonia at the cathode (Eq 2) However, the chloride in the solution which originated from the tap water used in the experiment was oxidised to hypochlorite and the hypochlorite oxidised the ammonium in the solution to nitrogen gas (Eq 11, 12, and 13). The percentage of nitrate removed in the integrated system was almost equal to the sum of the removals in the adsorption and EC system. The highest removal efficiency of 68% was achieved at 0.5 cm distance between electrodes distance and this was only marginally higher than that at 1 cm electrode distance (67%). However, the power consumption (voltage x current x time) for the 0.5 cm electrodes distance (1.3 A x 30 V x 3 h) was higher (0.12 kWh) than that for 1 cm electrodes distance (1 A x 30 V x 3 h = 0.09 kWh). Therefore, to avoid the higher cost due to increased power consumption the remaining experiments were conducted using 1 cm electrode distance.

The ammonium concentration in the final solution increased with distance between the electrodes for the EC (0.12 to 0.64 mg/L) and integrated (0.01 to 0.25 mg/L)

systems. The increase in ammonium concentration was due to only a limited amount of hypochlorite being available in the solution to oxidise ammonium. Hypochlorite limitation was due to the low current values at large distances between electrodes; the low current values were not enough to oxidise the chloride to hypochlorite. This explanation is consistent with the results documented by Vanlangendonck et al. [21] where decreased current reduced the ammonium oxidation rate.

It is interesting to note that the amount of ammonium ion in solution was lower in the integrated system than in the EC system. This is probably due to the chloride released from the adsorbents during nitrate adsorption [30, 31] in addition to the chloride present in tap water. The higher concentration of chloride in the system would have produced a larger concentration of hypochlorite, which oxidised greater amounts of ammonium ions resulting in lower ammonium concentration in solution (Eq 11, 12 and 13).

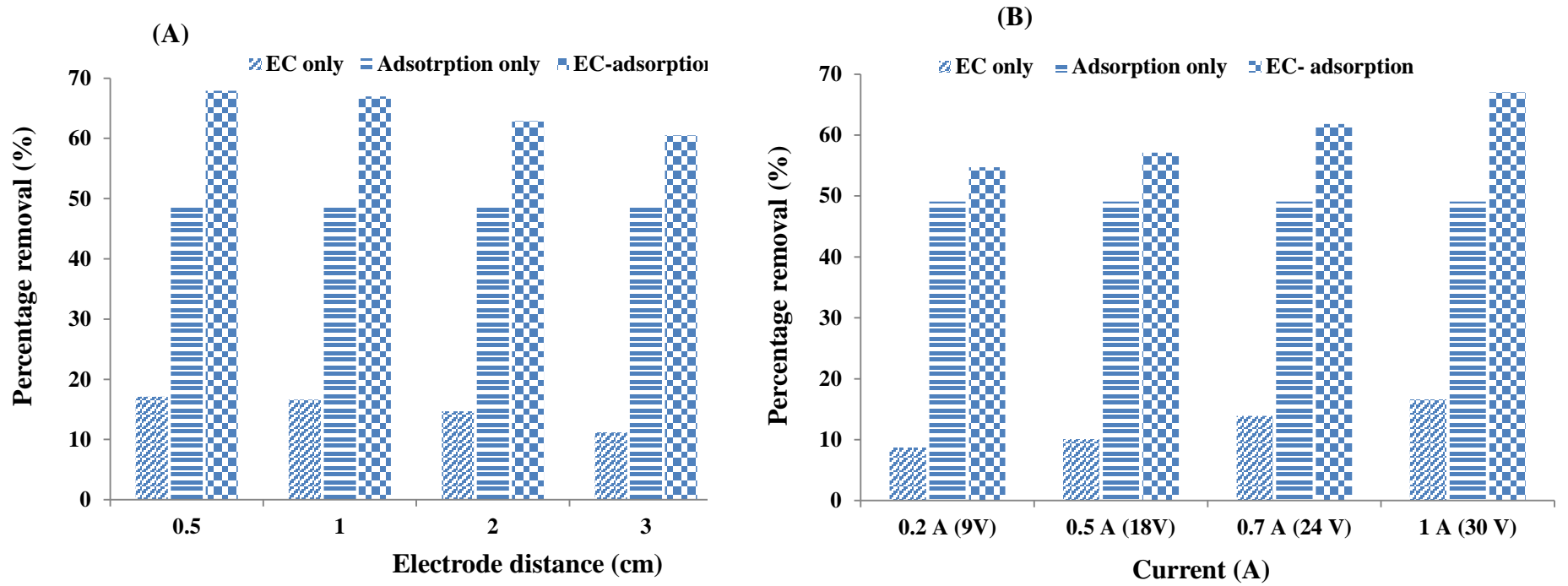


Fig. 2. Percentage of nitrate removal with (A) increasing distance between electrodes and (B) increasing current (volume of solution- 2 L, amount of adsorbent 2 g and initial nitrate concentration 20 mg N/L).

3.2. Effect of current

The effect of current on nitrate removal was investigated using the current values of 0.2, 0.5, 0.7 and 1 A with 1 cm distance between the electrodes at pH 7. The voltages increased automatically while increasing the current and the values were 9, 18, 24 and 30 V for the current values of 0.2, 0.5, 0.7 and 1 A, respectively. The percentages of nitrate removal increased with current for the EC and integrated systems (Fig. 2). The increased current would have enhanced the oxidation-reduction reaction rate at the electrodes [21]. Therefore, at higher current, a larger percentage of nitrate was converted to N₂ or NH₃ gas/NH₄⁺ (Eq 1-6) resulting in reduced nitrate concentration in the solution [26].

The economics of the nitrate removal process should also be considered. The total power consumption (current x voltage x time) rose with the increase in current and they were 0.005, 0.027, 0.050, and 0.090 kWh for the current of 0.2, 0.5, 0.7 and 1 A for 3 h operation, respectively. For the EC system, the percentage of nitrate removed for the lowest current of 0.2 A and the highest current of 1 A were 8.7% and 16.6% (3.44 and 6.34 mg), respectively. These values correspond to 8.7% and 16.6% nitrate removals. The cost of removing 1000 mg N was calculated in proportion to the cost of removing the amount of nitrate in the experiment. The costs for the highest and lowest currents were A\$4.26 and A\$0.48, respectively, for the removal of 1000 mg N (cost = current x voltage x operation time x A\$0.3/kWh [32] for EC and A\$50/kg [33] for ion exchange resin). This calculation did not include labour and equipment costs. In the integrated system most of the nitrate removal occurred due to adsorption. Also, the adsorbent cost is much higher than the cost of electricity in the integrated system. Therefore, although the EC cost was much higher at the higher current, the total cost of the integrated system was almost equal for both the current values in the integrated system values; they were A\$5.14 and A\$5.03 for 1 A and 0.2 A, respectively. In the integrated system, the amount of nitrate removal

was 12% higher for the highest current (1 A) compared to the lowest current (0.2 A) (Fig. 2).

The ammonium concentration in the solution declined when the current increased, probably due to the elevated rate of hypochlorite formation by the oxidation of chloride in the solution (Eq 11 and 12). This would have reacted with ammonia/ammonium ions to release nitrogen gas (Eq 13).

3.3. Effect of pH

The effect of pH on nitrate removal was investigated at pHs of 3, 5, 7, 9 and 11 with 1 cm distance between the electrodes, 1 A and 25-30 V; results are presented in Fig. 3. To adjust the pH, diluted hydrochloric acid (HCl) and diluted sodium hydroxide (NaOH) were used, and therefore the ionic concentration would have increased in the solution at low and high pHs, increasing the conductivity of the solution.

The removal of nitrate by Dowex was slightly high at low pH due to the protonation of the Dowex surface and above 7 it decreased due to the repulsion of nitrate ions by the negatively charged surface of Dowex and competition from increased OH^- concentration for adsorption. In the EC system, less nitrate was removed compared to the adsorption system but was nearly the same at all pH levels. The integrated system percentage of nitrate removal was equal to the sum of adsorption and EC systems percentages removal for pH 7- 11; it was, however, lower than the sum for pH less than 7. This may be due to the competition from OH^- produced at low pH, as a result of increased hydrogen evolution at the cathode, with nitrate for adsorption on Dowex (Eq 7). Li et al. [34] also reported that hydrogen evolution increased with decreasing pH resulting in the release of more OH^- ions in the EC system which comprised the Fe cathode and Ti/IrO₂-Pt anode. The optimum pH for nitrate removal in the integrated system was pH 7.

The ammonium ion concentration in the solution after 3 h was in the range of 0.1-0.5 mg/L for the EC system and 0.01-0.05 mg/L for the integrated system for all pHs. The low ammonium ion concentration in the integrated system is probably due to the release of chloride from Dowex during nitrate adsorption and the released chloride being converted to hypochlorite, which oxidised the ammonium (Eq 13).

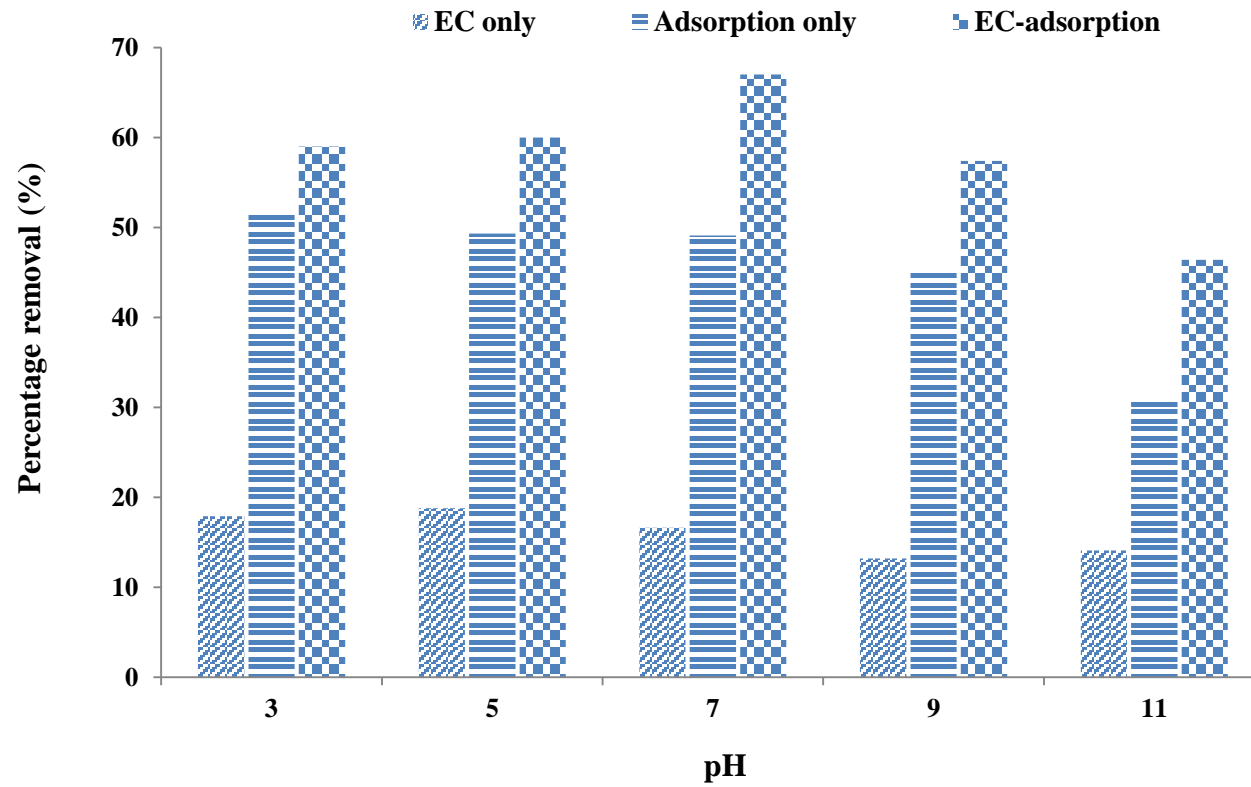


Fig. 3. Percentage of nitrate removed with change of pH (volume of solution- 2 L, amount of adsorbent 2 g and initial nitrate concentration 20 mg N/L).

3.4. Effect of time

The study on the kinetics of nitrate removal was conducted at the optimum conditions of nitrate removal of pH 7, 1 cm distance between the electrodes, 1 A and 30 V. The cumulative nitrate removal increased with time in all the three systems (Fig. 4). In the EC system, the nitrate removal was faster at the start but very much slowed down after 1 h, probably due to the decrease in cathode activity of the Cu electrode with time. Paidar et al. [24] reported that though Cu cathode material has high electrocatalytic activity for nitrate reduction, it can get deteriorated by cathode polarisation. In their experiment on EC reduction of nitrate using Cu cathode, nitrate reduction markedly slowed down after three hours compared to the treatment with Cu addition where nitrate reduction was much higher. According to them, activation of the Cu electrode can be achieved by adding Cu salts to the solution which produces fresh Cu deposition on the cathode. On the other hand, Filimonov and Shcherbakov [35] attributed the increase of nitrate reduction caused by Cu salt addition to cuprous ions that form as an intermediate product in the course of electrochemical reduction of cupric cations. The cuprous ions were reported to have acted as a catalyst in the nitrate reduction.

Li et al. [23] also reported that nitrate reduction rate drastically reduced three hours after commencement of their EC experiment on nitrate reduction using Cu/Zn electrode. In both the studies of Li et al. [23] and Paidar et al. [24], the decrease in activity of the Cu electrode was considered to be mainly due to the formation of CuH or CuH₂ on the surface of the Cu electrode. Pérez-Gallent et al. [36] also attributed the deactivation of Cu electrode during nitrate reduction as due to hydrogen adsorption. In the study of Li et al. [23], the colour of the Cu/Zn cathode changed to silvery white resulting in passivation of the electrode. This was reported to have caused by the selective dissolution of Cu during electrolysis.

In the adsorption system, the number of vacant adsorption sites decreased with increased time resulting in a reduced rate of adsorption (Fig. 4) [30]. In the integrated system, both the electrode passivation and reduction in adsorption sites occurred with increased time causing a reduced nitrate removal rate (Fig. 4). The integrated system percentage removal was almost equal to the sum of the individual batch adsorption and EC system at all sampling times. The ammonium ion concentration was measured at every 1 h interval and it was observed that, for the EC system, it increased continuously and reached 0.26 mg/L at 3 h. For the integrated system it remained almost the same in the 0.01-0.02 mg/L range. The lower ammonium concentration in the integrated system might be due to the conversion of chloride ions released from the adsorbent during nitrate adsorption (by ion exchange process) to hypochlorite (equation 12), which reacted with ammonia/ammonium ions to produce nitrogen gas (equation 13). In the EC system, there was no adsorbent to release chloride ions into solution by exchanging with nitrate in solution and therefore the ammonium/ammonia was not much lost as nitrogen gas as in the integrated system.

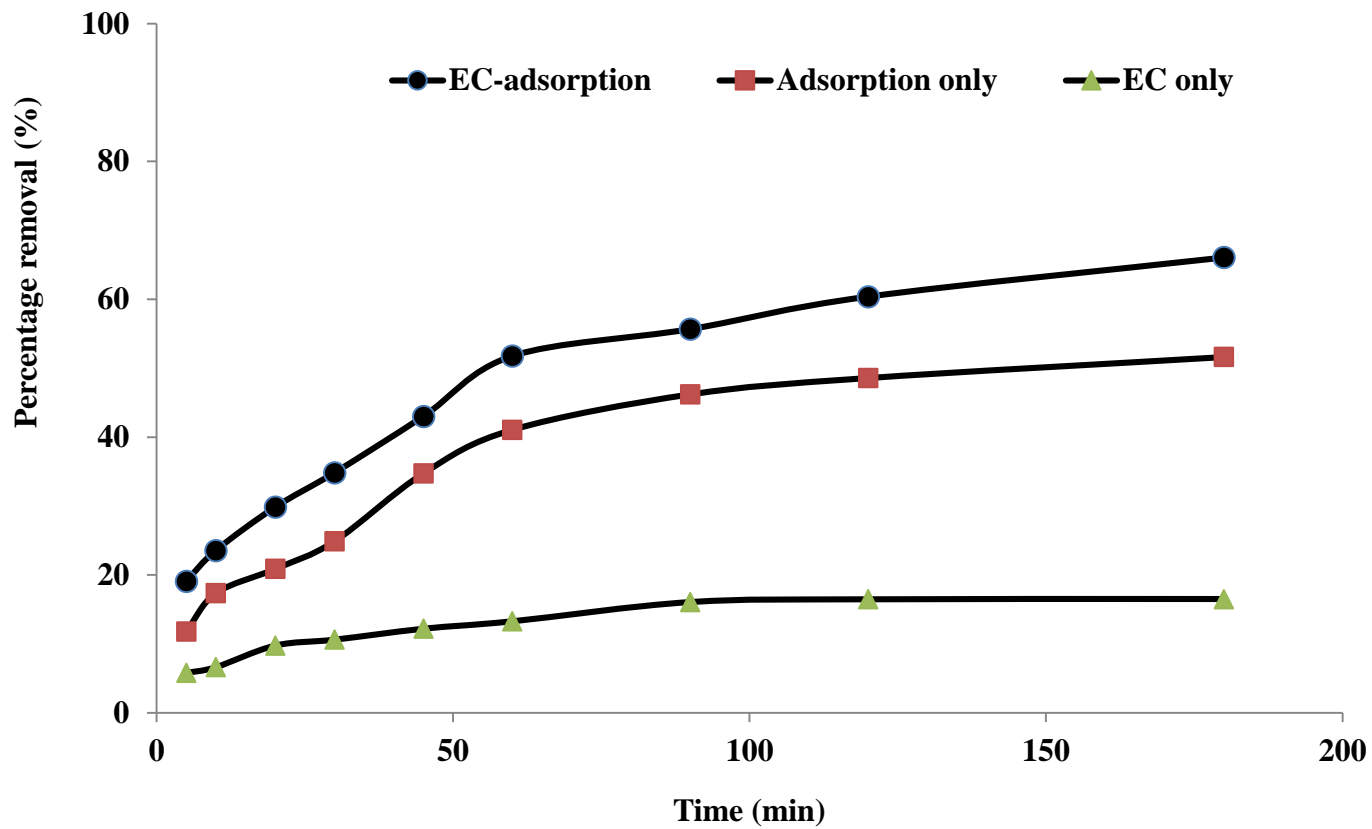


Fig. 4. Percentage removal of nitrate over time for the three nitrate removal systems (volume of solution- 2 L, amount of adsorbent 2 g and initial nitrate concentration 20 mg N/L)

3.5. Effect of complementary ions

3.5.1. Effect of phosphate

Phosphate's effect on nitrate removal was conducted with 20 mg N/L and 5 mg P/L at pH 7 and with the conditions of 1 A, and 28 V; the results are presented in Fig. 5.

A smaller concentration of phosphate than nitrate was used in the experiment to mimic the concentration differences of these ions normally found in surface and ground water. The nitrate removal percentage fell slightly in the presence of phosphate ions for all three systems. The previous batch and column adsorption experimental results also revealed that nitrate removal was reduced slightly in the presence of phosphate due to competition between the higher valent phosphate with lower valent nitrate for adsorption. The reduction in nitrate removal in the EC system may be because of electrode passivation from phosphate adsorbing on the anode or precipitating as FePO_4 on the anode surface. A significant amount of Fe ions was found in the solution during the EC process due to the dissolution of the stainless steel sieve anode. The concentration of Fe ions in the solution was found to be 1.25 mg/L after 3 h. The oxidation of Fe^{2+} ions occurs above pH 5 and therefore this oxidation is highly likely at the experimental pH of 7 [37]. Lacasa et al. [38] reported that in their EC system, Fe^{2+} ions were rapidly oxidised to Fe^{3+} ions. Assuming that the measured Fe concentrations were that of Fe^{3+} and converting the Fe ions concentrations in mg/L to mol/L unit, a calculation was made to determine whether precipitation of FePO_4 occurred using the measured Fe (2.23×10^{-5} M) and P (1.6×10^{-4} M) concentrations. The calculation showed that $[\text{Fe}^{3+}] [\text{PO}_4^{3-}] = 3.59 \times 10^{-9}$. However, the solubility product of the FePO_4 at 25 °C is 1.3×10^{-22} [39]. Therefore, $[\text{Fe}^{3+}] [\text{PO}_4^{3-}]$ in the experimental solution was $> K_{sp}$ which demonstrates that the phosphate was likely to have precipitated in the experiment as FePO_4 in the solution or on the electrode's surface.

Phosphate removal by EC was more than double that when using adsorption whereas nitrate removal was four times higher in adsorption than EC (Fig. 5). This difference between nitrate and phosphate removals supports the reasoning that phosphate was removed by precipitation, assisted by the EC process where Fe dissolved from the electrode reacted with phosphate.

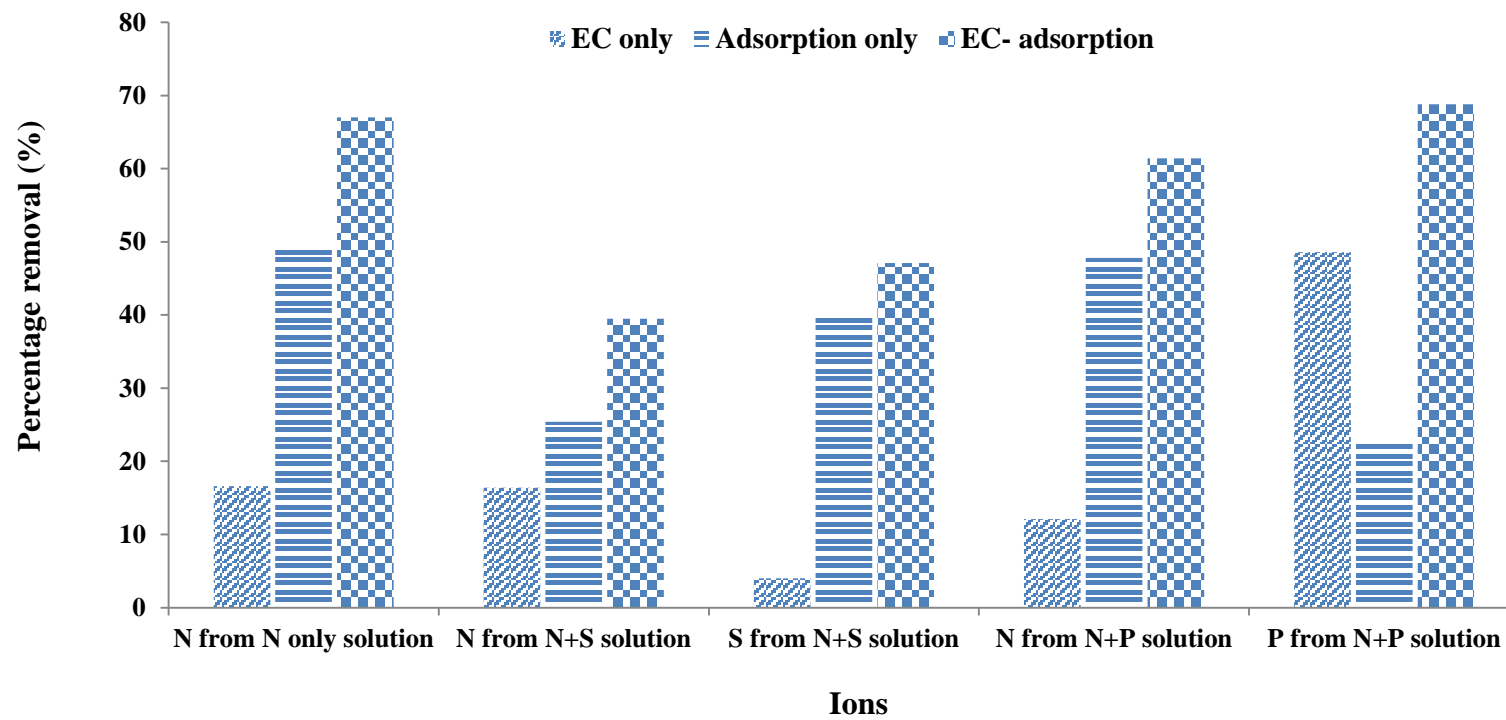


Fig. 5. Percentages of nitrate, phosphate and sulphate removed from solutions containing N only solution (20 mg N/L), N+P solution (20 mg N/L + 5 mg P/L) and N+S solution (20 mg N/L +50 mg S/L). Volume of solution = 2 L, amount of adsorbent = 2 g.

3.5.2. *Effect of sulphate*

Sulphate's effect on nitrate removal was investigated in the presence of 50 mg S/L and 20 mg N/L at pH 7. The current was maintained at 1 A and the voltage fell from 30 V to 20 V due to the increased concentration of ions, as a result of adding high concentration of sulphate ions (Fig. 5). The increased ionic concentration decreased the resistance between the electrodes and elevated the electrical conductivity of the solution (conductivity 755 $\mu\text{S}/\text{cm}$ compared to 427 $\mu\text{S}/\text{cm}$ without adding sulphate); therefore, the voltage decreased. However, the nitrate removal was not influenced by the addition of sulphate ions in the EC system. On the other hand, adding sulphate reduced the removal of nitrate in the adsorption system and integrated system. The reduction in nitrate removal is probably due to the competition of sulphate with nitrate for adsorption. The previous batch and column adsorption studies indicated that sulphate ion intensively competed with nitrate due to its higher valence (two negative charges) than nitrate (one negative charge) ions [30]. A much higher percentage of sulphate than nitrate was adsorbed by the resin supporting the contention that sulphate competed with nitrate for adsorption (Fig. 5). The percentage of nitrate removed in the integrated system is approximately equal to the sum of the nitrate removed in the adsorption and EC systems.

3.5.3. Effect of phosphate and sulphate

The phosphate and sulphate ions' competition with nitrate was tested in the presence of 5 mg P/L phosphate and 50 mg S/L sulphate. This solution contained 20 mg N/L of nitrate with the following conditions: 1 cm between electrodes, 1 A and 18 V (Fig. 6) at pH 7. In the presence of these co-ions the EC system's nitrate removal efficiency was not affected. However, the percentage of nitrate removed by adsorption on Dowex was reduced by these co-ions especially by the sulphate (compared to removals in the presence of P and S (Fig. 5). Consistent with this data the sulphate adsorption was many times higher than phosphate adsorption (Fig. 6). The phosphate removal was higher in this N+P+S solution (Fig. 6) compared to the N+P solution (Fig. 5). This may be due to the increase in iron concentration in the solution when sulphate was present. The iron concentration rose from 1.25 mg/L to 8 mg/L when the sulphate ion was added to the N+P solution. The phosphate ions formed FePO_4 precipitate in solution/or surface precipitation at the surface of the stainless steel electrode as discussed in sub-section 3.5.1. The reason for the higher Fe concentration in the N+P+S solution was due to higher electrical conductivity produced by the higher N+P+S ion concentration (conductivity 793 $\mu\text{S}/\text{cm}$ for N+P+S compared to 465 $\mu\text{S}/\text{cm}$ for N+P). Unlike phosphate, sulphate does not form a precipitate with iron and therefore no notable change occurred in the sulphate removal for this solution compared to the N+S solution.

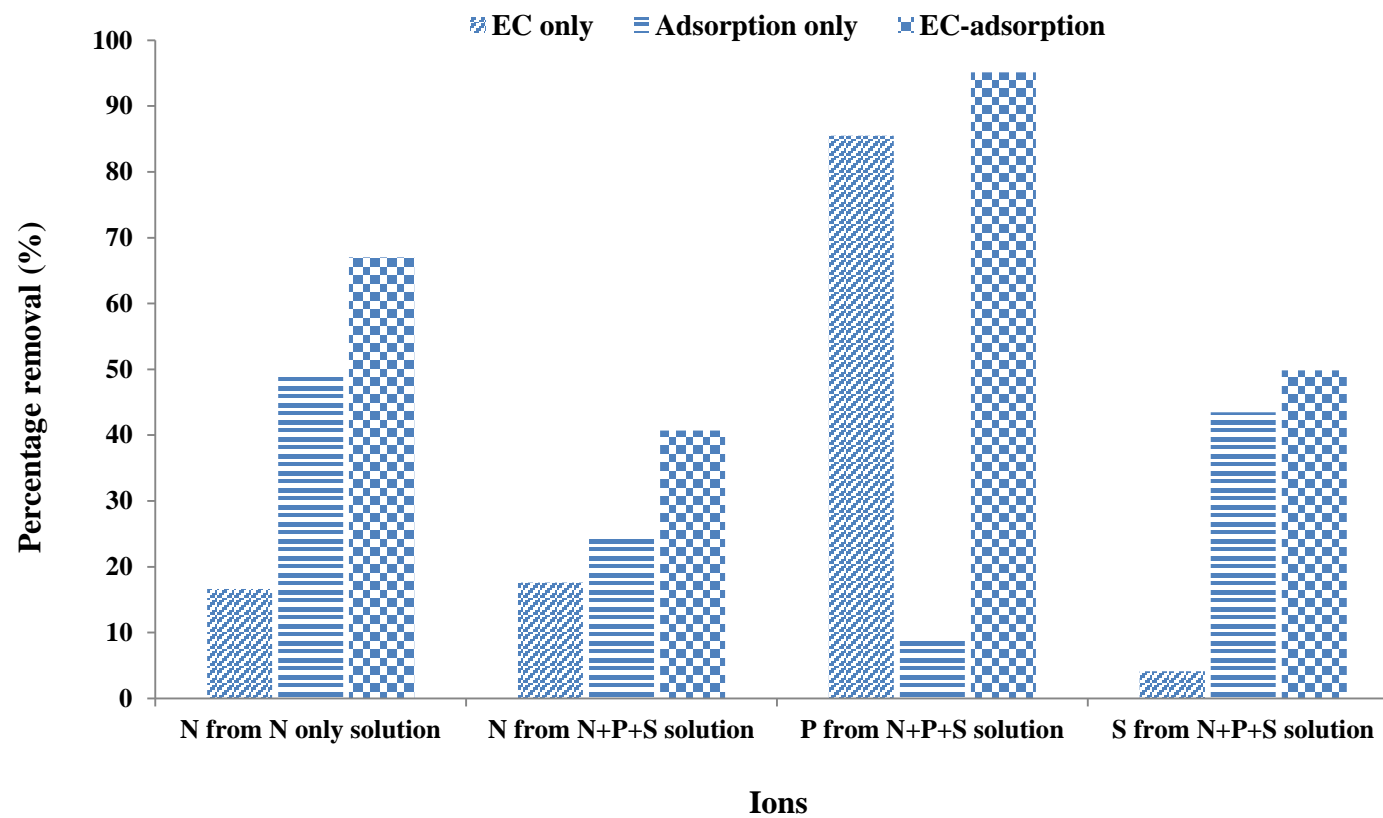


Fig. 6. Percentage of nitrate, phosphate and sulphate removed from the solution containing nitrate (20 mg N/L), phosphate (5 mg P/L) and sulphate (50 mg S/L) (N+P+S solution) and nitrate only (20 mg N/L) (N only solution).

1.3.6. Cost calculation

Cost is an important factor in the water treatment process. Removing more pollutants at lower cost is preferred. Approximate cost calculations were made for the EC, adsorption and integrated (EC-adsorption) systems separately using the results obtained in the experiments. The cost of electricity in the EC system was assumed to be A\$0.30 for 1 kWh [32] and that of Dowex was A\$50/ kg [33]. The costs of removing 1000 mg N from the nitrate solution were calculated and found to be A\$4.3, A\$5.5, and A\$5.1 for EC, adsorption, and EC-adsorption, respectively (Table 1). The EC system's N removal efficiency was low compared to the adsorption system but the cost to remove 1000 mg N was also less in the EC system. However, the cost in the adsorption system can be reduced if the resin is regenerated and repeatedly used. Alternatively, low-cost adsorbents such as surface modified agricultural wastes can be used to reduce the cost of the adsorption system and still maintain the high nitrate removal efficiency [31]. Similarly, the integrated system cost can be reduced if the resin is regenerated or low-cost adsorbents are utilised. The costs for removing 1000 mg N as nitrate in the presence of sulphate and phosphate were A\$2.7, A\$10.4, and A\$8.3 for EC, adsorption, and ES-adsorption systems, respectively. By adding these co-ions, the current could be maintained at the same value of 1 A at a lower voltage in the EC system, and therefore less power would be consumed and this reduced the cost of the EC system.

Conversely, in the adsorption system the presence of phosphate and sulphate reduced nitrate adsorption and therefore the cost to remove 1000 mg N increased. In the case of the EC-adsorption system, the cost of EC partly decreased while that of adsorption increased much more than the cost fell in the EC part of the EC-adsorption system. A cost calculation was done for the removal of 1000 mg N in order to compare the processes, though it is difficult to remove 1000 mg N by the EC method using a single EC cell (one cathode/one anode). Multiple cells are required to achieve this amount of removal and doing so will increase the operational costs.

This suggests that an adsorbent needs to be added to the EC system (integrated EC-adsorption system) to achieve the highest removal of nitrate in a shorter period of time. The simple cost calculation made here demonstrated that the integrated system of removing nitrate could be a cost-effective process.

Table 1

Cost calculation for (A) EC system (B) adsorption system and (C) EC- adsorption system (1 kWh = A\$0.30; 1 kg Dowex = A\$50)

(A)

Experiments	Current (A)	Voltage (V)	Time (h)	W	kWh	Cost (A\$)	N removed (mg)	Cost for 1000 mg N removal (A\$)
N only	1	30	30	3	0.09	0.027	6.34	4.3
N+P+S	1	18	18	3	0.054	0.016	6.08	2.7

(B)

Experiments	Adsorbent used (g)	Adsorbent cost (A\$)	N removed (mg N)	Cost for 1000 mg N removal
N only	2	0.1	18.12	5.5
N+P+S	2	0.1	9.62	10.4

(C)

Experiments	EC cost (A\$)	Adsorbent cost (A\$)	Cost (A\$)	N removed (mg N)	Cost for 1000 mg N removal
N only	0.027	0.1	0.13	24.72	5.1
N+P+S	0.016	0.1	0.12	14.06	8.3

4. Conclusions

The integrated EC-adsorption system removed more nitrate compared to the adsorption and EC systems when they were operated separately. Of the four distances (0.5 cm, 1 cm, 2 cm and 3 cm) between the electrodes, 1 cm was found to be the most cost-effective. The optimum nitrate removal (67% from solution containing 20 mg N/L) was achieved for the integrated system at pH 7 with the conditions where electrodes were 1 cm apart at 1 A, 30 V and 30 °C for Dowex. There was no significant change in nitrate removal efficiency in the EC system and integrated system in the presence of sulphate and phosphate. Ammonium ions were found in the EC system due to the reduction of nitrate at the cathode. However, their concentration was lower in the integrated system due to the release of Cl^- ions from the adsorbents by ion exchange with nitrate. The Cl^- ions would have oxidised to Cl_2/OCl^- which reduced NH_4^+ to N_2 . The integrated system can be operated over the long-term by adding larger amounts of adsorbents initially and later frequently to the stainless steel electrode box. This study was conducted with a single cell (one cathode and one anode) to demonstrate the suitability of the integrated system for nitrate removal. It is recommended that future studies use multiple cells connected in series to continuously and more efficiently remove nitrate.

Acknowledgement

This study was financially supported by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) (project number 4.1.17-13/14).

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