CHAPTER 3: MATERIALS AND METHODOLOGY

In this chapter, the experimental and analytical techniques used for the study are described. This chapter is divided into three sections: (1) Chemical and material sources; (2) Analytical methods for determination of NO_3-N, NO_2-N, and NH_3-N; (3) Experimental protocols for ECR of nitrate.

3.1 Chemicals and Material Sources

The analytical standard grade of sodium sulphate (Na_2SO_4), ammonia solution (NH_4OH, 25% w/w), sodium borohydride ($NaBH_4$), silver nitrate ($AgNO_3$), oxalic acid ($C_2H_2O_4$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), zinc sulphate ($ZnSO_4$), copper sulphate ($CuSO_4.7H_2O$), cadmium sulphate ($CdSO_4.5H_2O$), manganese sulphate ($MnSO_4$), nickel sulphate ($NiSO_4$), and ruthenium chloride ($RuCl_3$) were all acquired from LOBA Chemie Pvt. Ltd., India. A free sample of polyvinyl alcohol (PVA) gel beads was provided by Sujal Solutions, India. Potassium nitrate (KNO_3) was acquired from Ranbaxy, India, which was used to prepare a synthetic nitrate solution. Plates of titanium (Ti), stainless steel (SS), and copper (Cu) were bought from Sachin Steel Centre, India. Super Steel Traders in India provided the iron (Fe) plate. The cation exchange membrane (CMI-7000S) was purchased from Membrane International Inc., USA.

3.2 Analysis method of NO_3-N, NO_2-N, NH_3-N and N_2-N

3.2.1 Experiments with Ag-PVA beads

For experiments in which Ag-PVA beads were used for nitrate reduction, the Standard Methods (22nd Edition) were used for the determination of nitrate (APHA Method 4-115), nitrite (APHA Method 4-112), and ammonia (APHA Method 4-108). To determine the concentrations of NO_2-N and NH_3-N, standard calibration plots (Figure 2) were prepared ($R^2>0.98$) and referred to. All samples were diluted 10 times.

In nitrate analysis, nitrite interferes as it is formed during the process of nitrate reduction. As in APHA Method 4-115, nitrite also absorbs light at 220 and 275 nm, which is used to measure residual nitrate. A separate calibration plot of nitrite concentration v/s absorbance at 220 and 275 nm was made to determine the net absorbance owing to nitrate. The nitrite content was first assessed for a sample at a certain time point of response using APHA Method 4-112. The calibration plot of nitrite concentration v/s absorbance at 220 and 275 nm was used to determine the corresponding absorbances at 220 and 275 nm for this nitrite concentration. These absorbances (i.e., total absorbance of nitrate and nitrite) were deducted from those obtained for the sample to get the net absorbance due to nitrate alone. Annexure 1 describes the sample calculation.

The N mass balance calculation method was used to determine the concentration of N_2 wherein gaseous-N is calculated by subtracting the concentrations of NO_3-N, NO_2-N, and NH_3-N from the total nitrogen (TN) at any given reaction time point. The N mass balance method has been employed in several research papers demonstrating reduction of nitrate (Bosko et al., 2014; Yao et al., 2021; Z. Zhang et al., 2016; X. Zhao et al., 2021).

3.2.2 Experiments with AgMPs

For the ECR of nitrate using AgMPs, nitrate was determined by a colorimetric technique named the chromotropic acid method (West & Ramachandran, 1966). A calibration plot for NO_3-N was prepared at the absorbance of 412nm. 15 seconds before the scheduled sampling time, stirring was stopped to allow AgMPs to settle. Then samples were collected from the reactor (electrolytic cell in case of undivided cell and cathode compartment in case of divided cell) and diluted five times for the analysis of nitrate and ten times for the analysis of nitrite and ammonia. For nitrate analysis, a urea solution was prepared including urea and sodium sulphite to avoid nitrite interference in nitrate analysis. Chromotropic acid was prepared by dissolving 0.1gm in 100mL of concentrated sulphuric acid (H_2SO_4). For nitrate analysis, a total volume of 1.2mL of five times diluted sample was prepared and then 1 drop of urea solution, 0.6mL of chromotropic acid reagent and 1.8mL of concentrated H_2SO_4 were added and allowed to develop colour and cool down for 30min. After 30min, absorbance was noted at 412nm.

Nitrite-N, ammonia-N, and N_2-N concentrations were determined as described earlier in section 3.2.2.

3.2.3 Experiments with Ti/Co_3O_4

Analytical methods similar to that used in AgMPs experiments were used for the detection of nitrate, nitrite, ammonia, and N_2-N. For NO_3-N, a calibration plot was prepared at an absorbance of 412 nm and the procedure was explained earlier in the 3.2.2 section. To measure nitrate, nitrite and ammonia, samples were obtained at the appropriate periods and diluted 5 times for nitrate and 10 times for nitrite and ammonia. 2mL sample was collected every 15min and centrifuged for 1min to settle the precipitates formed while the reaction. After that, samples were diluted and examined. Nitrite-N, ammonia-N, and N_2-N concentrations were determined as described earlier in section 3.2.2.

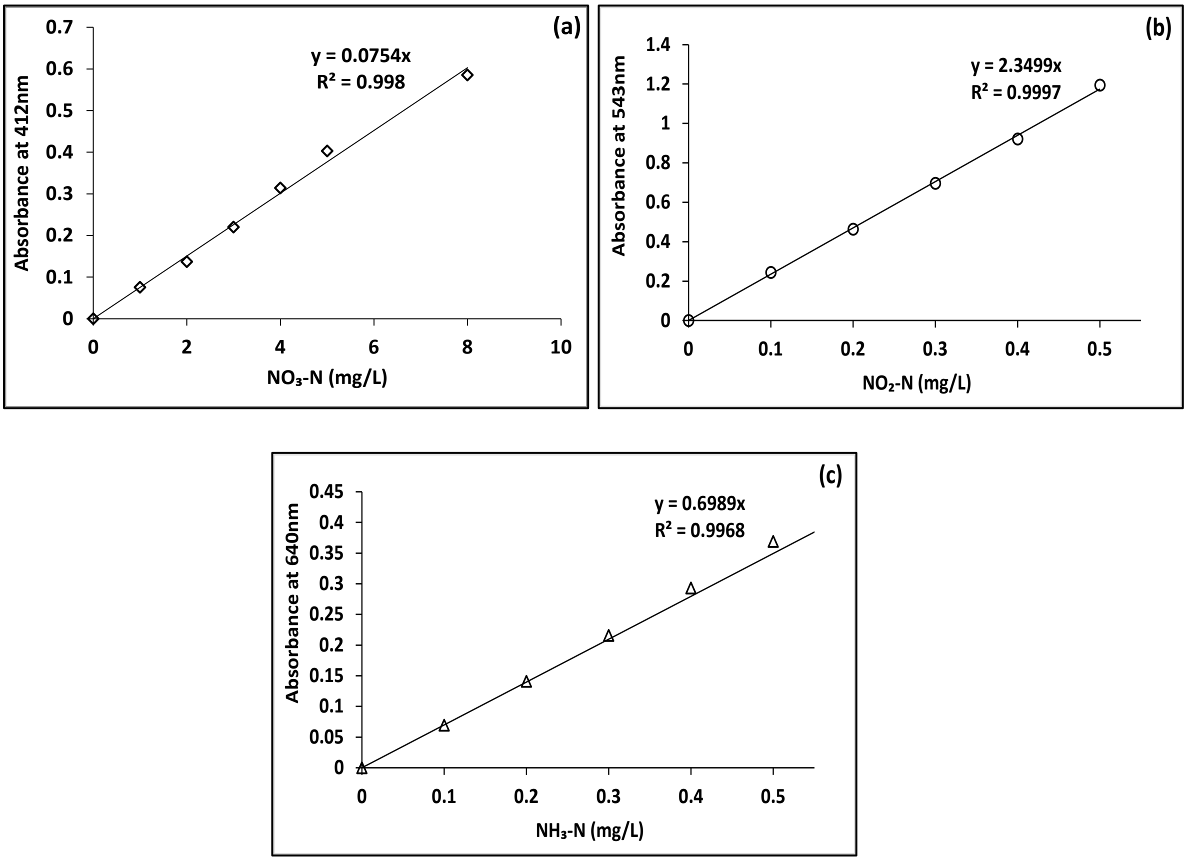

Figure 1 : Calibration plot of NO_3-N (a), NO_2-N (b) and NH_3-N (c)

3.3 Experimental Work

3.3.1 Preparation of catalyst and mixed metal oxide (MMO) electrode

3.3.1.1 Preparation of Ag-PVA beads

4mM, 8mM, and 10mM solutions were prepared by adding 0.101g, 0.136g, and 0.169g of $AgNO_3$ to 100mL of deionized (DI) water, respectively. NH_4OH solution was used to bring the pH of the solution to around 8 as the initial pH of $AgNO_3$ solution was 5.2-5.4. Separately, a 100 mL solution of $NaBH_4$ was prepared, with a molar concentration that was four times that of the $AgNO_3$ solution. 30mL of fresh PVA beads (about 730 beads, 3–4 mm in diameter) shown in Figure 4 were added to $AgNO_3$ solution and stirred at 60° C until the entire solution was absorbed by the beads. Then the beads were added to the $NaBH_4$ solution and vigorously mixed for 1-2 minutes in the $NaBH_4$ solution. Ag-PVA beads' concentration of Ag was thought to be stoichiometric since the entire solution was absorbed in the beads. The beads became brownish because sodium borohydride reduces silver. Following multiple rounds of washing with distilled water, the beads were then placed in deionized water for storage until they were needed in experiments. The morphological study of Ag-PVA beads was conducted by SEM and EDAX analyses.

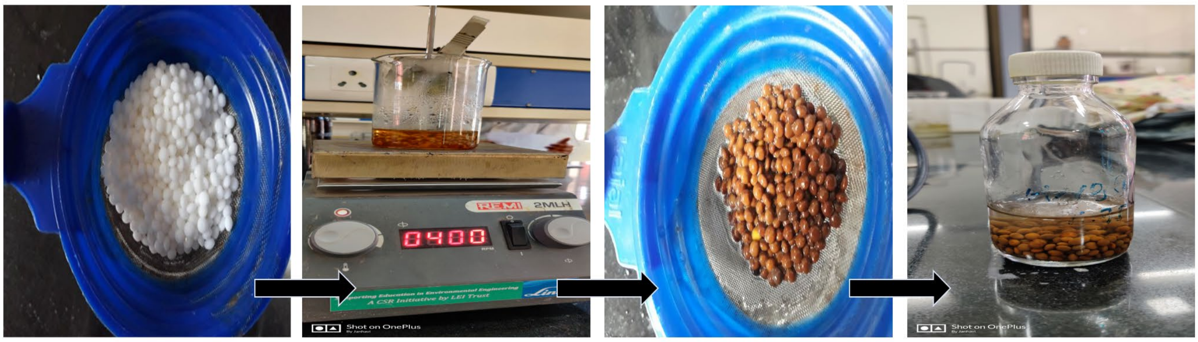

Figure 2: Preparation of Ag-PVA beads

3.3.1.2 Preparation of Ag-MPs

Figure 5 shows preparation of AgMPs via a method outlined in Popli & Patel, 2017, and Song et al., 2009. Typically, deionized (DI) water was used to prepare 100 mL of various $AgNO_3$ concentrations (4 mM, 6 mM, 8 mM, 10 mM, 14 mM, and 20.8 mM). Separately, 100 mL of $NaBH_4$ solutions were prepared with four times as much $NaBH_4$ as $AgNO_3$. The AgMPs were generated by gradually adding drop-by-drop the $AgNO_3$ solution into the

$NaBH_4$ solution. After the addition was complete, the mixture was stirred for an hour. Metallic Ag particles agglomerated because of prolonged churning and were of such size that they could be easily separated by allowing them to settle down. Before being used in the ECR process, the separated AgMPs were repeatedly rinsed with DI water. Morphological and crystallography of AgMPs was carried out by SEM and XRD analyses.

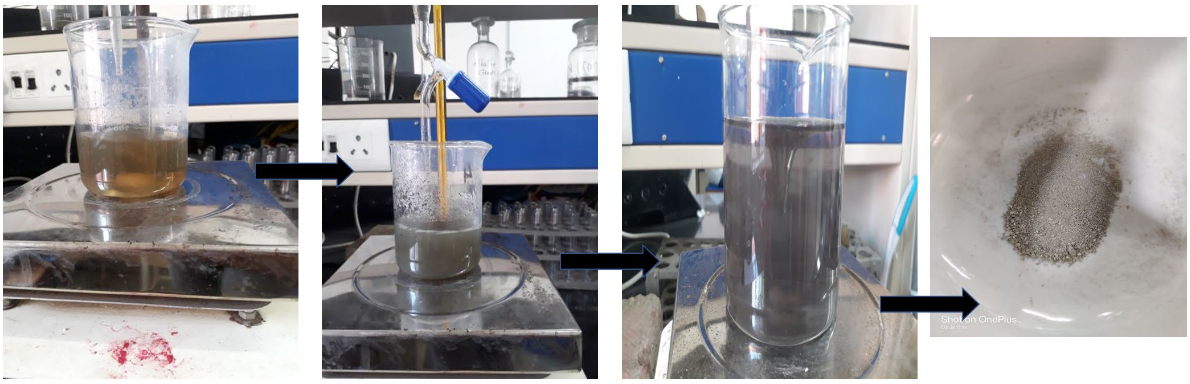

Figure 3: Preparation of AgMPs

3.3.1.3 Preparation of mixed metal oxide (Ti/RuO_2) electrode

Figure 6 shows preparation of Ti/RuO_2. The mixed metal oxide electrode was made using a Grade 1 titanium plate that measured 59 * 48 mm. The Ti plate was first sandblasted, and after a chemical treatment in which it was submerged in 10% oxalic acid for two hours at 80°C to remove impurities from its surface, it was washed twice or three times with DI water. The sol-gel process described by Terezo & Pereira, (2002) was used with few modifications to prepare a Ti/RuO_2 plate. To prepare a precursor solution, ruthenium chloride ($RuCl_3$) was dissolved in a mixture of IPA (isopropyl alcohol) and 1N HCl. A brush was used to apply the precursor solution to the Ti plate, and it was left to dry for 5 minutes at room temperature. After that, the plate was kept for 5 minutes in an oven at 80°C, followed by 5 minutes at 550°C in a muffle furnace to create oxides. This process was repeated until the RuO_2 loading on the plate reached 0.9 mg/cm^2. The electrode was then calcined for an hour at 550°C in a muffle furnace. Before being used for studies, the electrode was cleaned with DI water.

3.3.1.4 Preparation of Ti/Co_3O_4 plate

Figure 6 shows preparation of Ti/Co_3O_4. A 59 * 48 mm of Grade 1 titanium plate was used to prepare the electrode. First, the Ti plate was sandblasted to remove surface oxides. It was then heated in 20% sulfuric acid for two hours to etch the surface into a uniformly roughened one. The Ti plate was then repeatedly washed with acetone, ethanol, and twice-distilled water. A method described by Su et al. (2017) was used with little modifications. Brushing of 1 mol/L of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) solution was carried out for uniform coating over the Ti plate. The Ti plate was coated, and then dried for 10 minutes at 105°C in an oven followed by 10 minutes at 500°C in a muffle furnace to create oxides. This process was repeated until the Co_3O_4 loading on the plate reach 1 mg/cm^2. The Ti plate was next calcined at 500°C for 2hrs and washed several times using deionised water before being used for experiments.

Figure 4: Preparation of Ti/RuO_2 and Ti/Co_3O_4

3.3.2 Experimental setup for ECR of nitrate

3.3.2.1 Nitrate Reduction in an undivided cell

In both divided and undivided cells, nitrate-N reduction tests were performed. The material of the reactor is polyacrylic having dimensions of 6cm*8cm*8cm. During the investigations, an undivided cell (Figure 7) containing 250mL of NO_3-N solution was employed. Na_2SO_4, at a concentration of 2g/L, was added as an electrolyte to induce electrical conductivity. Each electrode's effective area was 59 mm * 48 mm, and there was a 7.0 cm distance between the two electrodes. Application of the required current based on current density was achieved by the DC power supply.

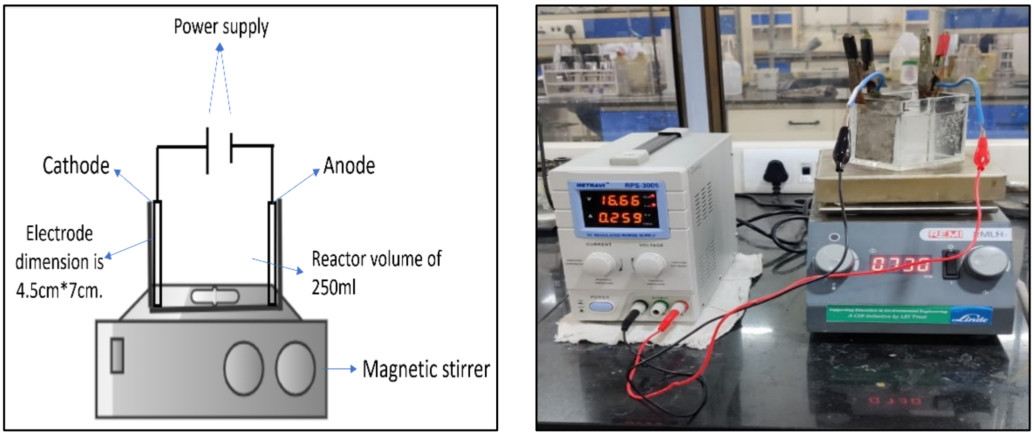

Figure 5: Experimental setup in an undivided cell

3.3.2.2 Nitrate Reduction in a divided cell

A polyacrylic cell (Figure 8) was used wherein the cathode and anode compartments was separated by a cation-exchange membrane (CMI-7000S, Membrane International Inc., USA). 120 mL of a synthetic solution containing stipulated concentration of NO_3-N and 2 g/L Na_2SO_4 were poured into the cathode compartment. The anolyte was a 2 g/L Na_2SO_4 solution prepared in deionized (DI) water. Synthetic solutions of nitrate were made in DI water. The inter-electrode spacings were 3, 5.5, and 7.7 cm unless and until mentioned, and the effective size of each electrode was 59 * 48 mm. DC power supply was used for supplying current based on current density.

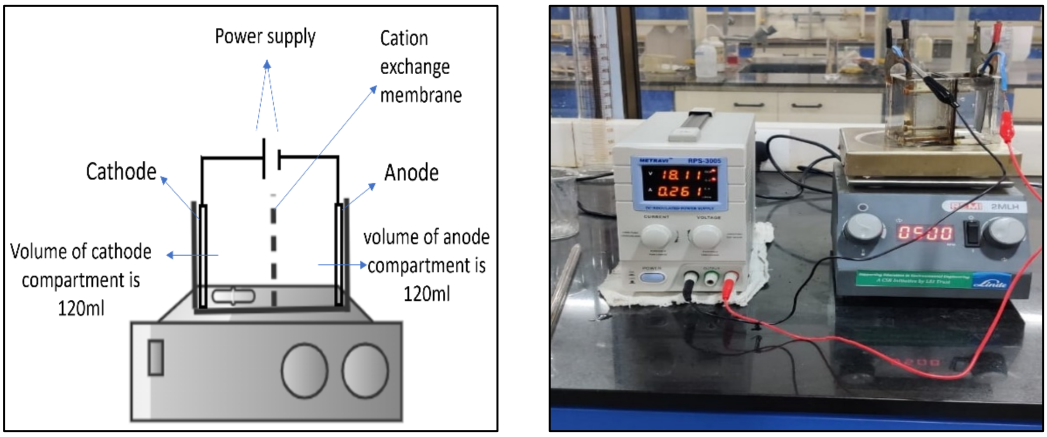

Figure 6: Experimental setup in a divided cell

3.3.2.3 Oxidation of ammonia at the anode in a divided cell

Experiments were conducted for two simultaneous reactions at a time:(1) nitrate reduction in the cathode compartment and (2) anodic oxidation of ammonia produced in cathode compartment. In these experiments, firstly, fresh nitrate reduction was performed in the cathode compartment in the divided cell in the presence of 8mM AgMPs and Ti cathode with anolyte DI water containing 2 g/L sodium sulphate. After 120 min reaction time, the catholyte was separated and transferred to the anode compartment for the next experiment in which a new fresh NO_3-N solution was used as a catholyte. Again, after 120min the catholyte was separated and used as an anolyte for the next experiment with fresh nitrate solution as catholyte. Samples were collected from both compartments for analysis of nitrate-N, nitrite-N, and ammonia-N. Above experiments were conducted considering that during ECR of nitrate, the electricity in the anode compartment is consumed without any fruitful outcome. Thus, it was envisaged that the ammonia formed in catholyte during ECR of nitrate can be oxidized in anode compartment.

3.3.3 ECR of nitrate using a spatially suspended Ag-PVA beads

This section describes the experimental set up for ECR of nitrate in the absence and presence of spatially suspended Ag-PVA beads in an undivided cell as well as a divided cell. The influence of various experimental parameters on ECR of nitrate in a divided cell, such as the effect of the catalyst, the effect of the concentration of Ag-PVA beads, the effect of various cathode materials, the effect of current density, and the reusability of the Ag-PVA beads. Also, the study was carried out using Ag-PVA beads in real water (groundwater) for the ECR of nitrate.

3.3.3.1 Effect of the absence and presence of Ag-PVA beads in an undivided cell

6.67mM Ag-PVA beads were spatially suspended in an undivided cell consisting of 250ml of 25mg/L NO_3-N to evaluate the effect of the catalyst's absence and presence. Graphite (Gr) was used as an anode and iron (Fe) as a cathode. The electrolyte used was 2g/L Na_2SO_4. The current density was 15mA/cm^2 for 90 minutes of electrolysis time.

3.3.3.2 Effect of the absence and presence of Ag-PVA beads in a divided cell

To compare the effect of the catalyst's absence and presence, 6.67mM Ag-PVA beads were spatially suspended in a divided cell consisting of 120ml of 25mg/L NO_3-N in the cathode compartment and 120ml Na_2SO_4 solution in the anode compartment. Fe served as the cathode while Gr served as the anode. 2g/L of Na_2SO_4 was utilized as the electrolyte. The electrolysis process lasted for 90 minutes at a current density of 15mA/cm^2.

3.3.3.3 Effect of concentration of Ag-PVA beads

Experiments were conducted with various Ag-PVA beads concentrations: 6mM, 8mM, and 10 mM (5, 6.67 and 8.33 milimole Ag^0) in the cathode chamber. The anode and cathode materials used were Gr and Fe, respectively. The catholyte used during ECR in the presence of Ag-PVA beads was 120 mL of 2g/L Na_2SO_4 solution containing 25mg/L NO_3-N. 2g/L Na_2SO_4 solution was used as anolyte. The current density was set at15 mA/cm^2. The mass activity (mg of NO_3-N removed/min/g of Ag) of different catalyst concentrations was calculated by the following equation (1-3).

$$\text{Mass of Ag} = \frac{(molecular\ weight\ of\ Ag) * \ (gm\ of\ AgNO_3\ desired\ for\ particular\ concentration)}{molecular\ weight\ of\ AgNO_3} \qquad \text{Equation 1}$$

$$NO_3\text{-N removed} = initial\ NO_3\text{-}N\ (mg/L) * NO_3\text{-}N\ removed\ (mg/L) * Volume\ of\ NO_3\text{-}N\ solution(L) \qquad \text{Equation 2}$$

$$\text{Mass Activity (mg/min/gm of Ag)} = \frac{NO_3{-}N\ removed}{Reaction\ time\ (min) * Mass\ of\ Ag} \qquad \text{Equation 3}$$

3.3.3.4 Effect of various cathode materials in the absence and presence of Ag-PVA beads

Experiments were carried out in divided cell to examine the impact of different cathode materials on the ECR of nitrate in the absence and presence of Ag-PVA beads. Stainless steel (SS), Ti, Cu, Fe and Fe/Sn (Tin coated on Fe) cathodes were examined over 90 minutes of electrolysis at a current density of 15 mA/cm^2.

3.3.3.5 Effect of various current densities in the presence of Ag-PVA beads

Fe as cathode and Gr as anode were used in a divided cell in the experiments. The catholyte was a 120 mL solution of 2g/L Na_2SO_4 containing 25mg/L NO_3-N and 6.67mM Ag-PVA beads. 120 mL of 2g/L Na_2SO_4 solution was used as the anolyte. 5mA/cm^2, 10mA/cm^2 15mA/cm^2, and 20mA/cm^2 were the different current densities studied. Also, mg of NO_3-N removed/ Ah at different current densities was calculated by the following equation 4.

Mg of NO_3-N removed / Ah = $\frac{NO_3-N\ (initial)-NO_3-N\ (final) * Vol.\ of\ solution\ (L)}{Current\ density\ (A) * electrode\ area * reaction\ time\ (h)}$ Equation 4

3.3.3.6 Effect of initial nitrate concentration in the presence of Ag-PVA beads

In the experiments, a divided cell with Fe as the cathode and Gr as the anode was employed. The catholyte was a solution of 2g/L Na_2SO_4 with 6.67mM Ag-PVA beads in a 120 mL volume. The anolyte was a solution of 2g/L Na_2SO_4. The initial nitrate-N concentrations were 25mg/L, 50mg/L and 100mg/L.

3.3.3.7 Reusability of Ag-PVA beads

Gr was used as an anode and Fe as a cathode in these experiments. The catholyte was 120 mL of 2g/L Na_2SO_4 solution containing 25mg/L NO_3-N during ECR in the presence of 6.67mM Ag-PVA beads. The anolyte was 120 mL of 2g/L Na_2SO_4. The current density was tuned to 15 mA/cm^2. Freshly made Ag-PVA beads were utilised in a series of experiments under identical reaction conditions for the study of reusability.

3.3.3.8 ECR of nitrate in real groundwater

Experiments were conducted in a divided cell in the absence and presence of 6.67mM Ag-PVA beads consisting of 120ml of real groundwater in the cathode compartment. In experiments, Gr acted as the anode and Fe as the cathode and the reaction time was 90 minutes along with 15 mA/cm^2 current density. The characteristics of real groundwater were: 15 mg/L NO_3-N, 150 mg/L Cl^-, 8 mg/L SO_4^{2-}, 75 mg/L CO_2^{3-}, 125 mg/L HCO_3^- and 6.5-7.6 pH.

3.3.4 ECR of nitrate using spatially suspended catalyst AgMPs

This section discusses the ECR of nitrate in the absence and presence of AgMPs in an undivided and divided cell. Various influencing factors were studied in divided cell, such as the effect of the catalyst, the effect of concentration of AgMPs, the effect of inter-electrode distance, the effect of various cathode materials, the effect of initial nitrate-N concentration, the effect of current density, and the reusability of the AgMPs catalyst.

3.3.4.1 Effect of the absence and presence of AgMPs in an undivided cell

The effect of the absence and presence of 8mM AgMPs was studied in an undivided cell using a 250ml of 25mg/L NO_3-N and 2g/L Na_2SO_4 as an electrolyte. . Ti served as the cathode and Ti/RuO_2 as the anode. The current density was 10mA/cm^2 for a 120min reaction time.

3.3.4.2 Effect of the absence and presence of AgMPs in a divided cell

The effect of the absence and presence of 8mM AgMPs was studied in a divided cell using a 120 mL of 25mg/L NO_3-N and 2g/L Na_2SO_4 as a catholyte and a 2g/L Na_2SO_4 solution in DI water as an anolyte.

Ti served as the cathode while Ti/RuO_2 served as the anode. The electrolysis process lasted 120 minutes at a current density of 10mA/cm^2.

3.3.4.3 Effect of concentration of AgMPs

In these experiments, 120 mL of a 2g/L Na_2SO_4 solution containing 25mg/L NO_3-N solution was the catholyte comprising different doses of AgMPs such as 4, 6, 8, 10, 14, and 20.8 mM. on ECR of nitrate was studied. Ti/RuO_2 and Ti were used as the anode and cathode materials, respectively. 120 mL of 2g/L Na_2SO_4 solution served as the anolyte. The current density used for the experiments was 10 mA/cm^2 for a 120min reaction time. The mass activity (mg of NO_3-N removed/min/g of Ag) of different catalyst concentrations was calculated by the equations (1-3) as described in section 3.3.3.3.

3.3.4.4 Effect of inter-electrode distance in the presence of AgMPs

In these experiments, a divided cell with Ti as a cathode and Ti/RuO_2 as an anode electrode was employed. A 120 mL solution of 2g/L Na_2SO_4 with 25mg/L NO_3-N and 8mM AgMPs served as the catholyte. The anolyte was a 120 mL solution of 2g/L Na_2SO_4. The inter-electrode distances were varied as 3cm, 5.5cm and 7.7cm.

3.3.4.5 Effect of various cathode materials in the absence and presence of AgMPs

Experiments were conducted with various cathode materials in the absence and presence of AgMPs. Over 120 minutes of electrolysis at a current density of 10 mA/cm^2, various cathodes which are stainless steel (SS), Fe, Fe/Sn (Tin coated on Fe), Cu, and Ti were studied.

3.3.4.6 Effect of various current densities in the presence of AgMPs

In the experiments, a divided cell with Ti as the cathode and Ti/RuO_2 as the anode was employed. A 120 mL solution of 2g/L Na_2SO_4 with 25mg/L NO_3-N and 8mM AgMPs served as the catholyte. The anolyte was a 120 mL solution of 2g/L Na_2SO_4. The varied current densities employed were 5mA/cm^2, 10mA/cm^2, and 15mA/cm^2. The mg of NO_3-N removed/ Ah and current efficiency at different current densities was calculated by equation 4 as described in Section 3.3.3.5.

3.3.4.7 Effect of initial nitrate concentration in the presence of AgMPs

Experiments were conducted in a divided cell with Ti/RuO_2 as the anode and Ti as the cathode. The catholyte was 120 mL volume of a 2g/L Na_2SO_4 solution containing 8mM AgMPs. 2g/L Na_2SO_4 solution in 120 mL served as the anolyte. The effect of 25 mg/L, 50 mg/L, and 100 mg/L initial nitrate-N concentrations were studied.

3.3.4.8 Oxidation of ammonia on the anode in the anodic compartment

Optimized conditions were used for the oxidation of ammonia on the anode. Experiments include Ti cathode with 8mM AgMPs in catholyte at 10mA/cm^2 current density for 120 min reaction time. 120mL NO_3-N solution as catholyte and 2g/L Na_2SO_4 solution as anolyte was used for the 1st experiment, and 2nd experiment fresh 120mL NO_3-N solution was used as catholyte and the catholyte of the 1st experiment (after ECR) was used as anolyte for 2nd experiment.

3.3.4.9 Reusability of AgMPs

For reusability experiments, Ti was employed as the cathode and Ti/RuO_2 as the anode. ECR of nitrate-N was conducted using 120 mL of 2g/L Na_2SO_4 solution with 25mg/L NO_3-N and 8mM spatially- suspended AgMPs in the catholyte. The current density was set to 10mA/cm^2. Fresh AgMPs were prepared and were used in a series of experiments under optimised conditions. At the end of each experiment, used AgMPs were washed with DI water and used for the next experiment.

3.3.4.10 ECR of nitrate in real water (groundwater)

ECR of nitrate in 120mL of real water (groundwater) was performed in the presence (8Mm AgMPs) and absence of AgMPs. Ti/RuO_2 served as the anode and Ti served as the cathode. The reaction duration was 120 minutes, and the current density was 10 mA/cm^2. The characteristics of real water (groundwater) are described in section 3.3.3.8.

3.3.5 Treatment of metal finishing wastewater containing high-concentration nitrate using ECR

This section describes protocol of experiments conducted for the ECR of a high initial concentration of nitrate in simulated metal finishing wastewater. The effect of various influencing factors including the initial nitrate-N concentration and current density, was examined in addition to the reusability of the Ti/Co_3O_4 electrode. Further, experiments were conducted to remove ammonia formed by ECR of nitrate-N using struvite formation. The effect of the molar ratio of Mg:NH_4:PO_4 on struvite formation was examined. Simulated metal-finishing wastewater was prepared in tap water by adding various metals (Zinc = 15mg/L, Copper = 15mg/L, Nickel = 10mg/L, Manganese = 10mg/L and Cadmium = 10mg/L) and the characteristics of tap water were: 150mg/L Cl^-, 8mg/L SO_4^{2-},75mg/L CO_3^{2-}, 125mg/L HCO_3^- and 6.5-7.6 pH.

3.3.5.1 Effect of initial nitrate concentration

Experiments were carried out using Ti/RuO_2 as the anode and Ti/Co_3O_4 as the cathode in a divided cell. 120mL of simulated metal finishing wastewater was used as catholyte and 2g/L Na_2SO_4 solution as anolyte. Three different initial nitrate-N concentrations were studied – 500mg/L, 750mg/L and 1000mg/L at 20mA/cm^2 current density for 180min of reaction time.

3.3.5.2 Effect of current density

The study of the effect of current density on ECR of high concentration of nitrate-N was carried out in a divided cell with Ti/RuO_2 anode and Ti/Co_3O_4 cathode. The influence of different current densities: 10mA/cm^2, 20mA/cm^2 and 30mA/cm^2, was studied.

3.3.5.3 Reusability of Ti/Co_3O_4 electrode

In experiments, Ti/Co_3O_4 served as the cathode while Ti/RuO_2 served as the anode. 120 mL of each catholyte and anolyte prepared of simulated wastewater and 2g/L of Na_2SO_4 respectively was used in a divided cell. The initial nitrate-N concentration was 750mg/L. The current density used for experiments was 20 mA/cm^2. A fresh Ti/Co_3O_4 plate was prepared and used in the series of experiments till the difference was observed in nitrate removal or the selectivity of end-products.

3.3.5.4 Effect of molar ratio of Mg:NH_4:PO_4 on struvite formation

Experiments were conducted for ECR of nitrate in divided cell using Ti/RuO_2 anode and Ti/Co_3O_4 at 20mA/cm^2 current density for 180min. After 180min of reaction, catholyte was separately collected in a beaker. Different molar ratios of Mg:NH_4:PO_4 (0.8:1:0.8, 1:1:1, 1.5:1:1, 1:1:1.5, and 1.5:1:1.5) were studied for struvite formation and ammonia removal. The pH was adjusted to 9 and the reaction time was 1hr.

Table 1: Summary of experimental work using spatially suspended catalyst (Ag-PVA and AgMPs) and modified cathode (Co_3O_4 immobilized on Ti, Ti/Co_3O_4)

Section No.	ECR experiments using Ag-PVA beads		Sections under which results are discussed
3.3.3.1	ECR of nitrate in absence and presence of spatially suspended Ag-PVA beads in undivided cell		4.1.2
	Anode : Gr	Reaction conditions: 250mL of NO_3-N: 25mg/L, current density: 15mA/cm^2, Na_2SO_4 as electrolyte: 2g/L, reaction time: 90min, in absence and presence of Ag-PVA beads: 6.67 mM	
	Cathode Fe		
3.3.3.2	ECR of nitrate in absence and presence of spatially suspended Ag-PVA beads in divided cell		4.1.3
	Anode : Gr	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 15mA/cm^2, reaction time: 90min, in absence and presence of Ag-PVA beads: 6.67 mM	
	Cathode Fe		
3.3.3.3	Effect of concentration of Ag-PVA beads [6mM, 8mM, and 10 mM (5, 6.67 and 8.33 Ag^0)] in divided cell		4.1.3.1
	Anode : Gr	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 15mA/cm^2, reaction time: 90min	
	Cathode Fe		

3.3.3.4	Effect of various cathode materials in divided cell				4.1.3.2
	Anode : Gr	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 15mA/cm^2, reaction time: 90min, in absence and presence of Ag-PVA beads: 6.67 mM			
	Cathode: Stainless steel (SS), Ti, Cu, Fe and Fe/Sn (Tin coated on Fe)				
3.3.3.5	Effect of various current densities [5mA/cm^2, 10mA/cm^2 15mA/cm^2, and 20mA/cm^2]in divided cell				4.1.3.3
	Anode : Gr	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, reaction time: 90min, Ag-PVA beads: 6.67 mM			
	Cathode Fe				
3.3.3.6	Effect of initial nitrate concentration [25, 50, and 100 mg/L] in divided cell				4.1.3.4
	Anode : Gr	Reaction conditions: 120mL of NO_3-N solution as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, reaction time: 90min, Ag-PVA beads: 6.67 mM			
	Cathode Fe				
3.3.3.7	Reusability of Ag-PVA beads				4.1.3.5
	Anode : Gr	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 15mA/cm^2, reaction time: 90min, Ag-PVA beads: 6.67 mM			
	Cathode Fe				

3.3.3.7	ECR of nitrate in real water (groundwater)		4.4
	Anode : Gr	Reaction conditions: 120mL of real water as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 15mA/cm^2, reaction time: 90min, in absence and presence of Ag-PVA beads: 6.67 mM	
	Cathode Fe		

Section No.	**ECR experiments using Ag -MPs**		**Sections under which results are discussed**
3.3.4.1	ECR of nitrate in absence and presence of spatially suspended AgMPs in undivided cell		4.2.3
	Anode : Ti/RuO_2	Reaction conditions: 250mL of NO_3-N: 25mg/L, current density: 10mA/cm^2, Na_2SO_4 as electrolyte: 2g/L, reaction time: 120min, in absence and presence of AgMPs: 8 mM	
	Cathode : Ti		
3.3.4.2	ECR of nitrate in absence and presence of spatially suspended AgMPs in divided cell		4.2.4
	Anode : Ti/RuO_2	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120Ml of 2g/L Na_2SO_4 as anolyte, current density: 10mA/cm^2, reaction time: 120min, in absence and presence of AgMPs: 8mM	
	Cathode : Ti		

3.3.4.3	Effect of concentration of AgMPs [4, 6, 8, 10, 14, and 20.8 Mm] in divided cell				4..2.4.1
	Anode : Ti/RuO_2	Reaction conditions: 120mLof NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 10mA/cm^2, reaction time: 120min			
	Cathode : Ti				
3.3.4.4	Effect of inter electrode distance [3cm, 5.5cm and 7.7cm] in divided cell				4.2.4.2
	Anode : Ti/RuO_2	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 10mA/cm^2, reaction time: 120min, AgMPs: 8mM			
	Cathode : Ti				
3.3.4.5	Effect of various cathode materials in divided cell				4.2.4.3
	Anode : Ti/RuO_2	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 10mA/cm^2, reaction time: 120min, in absence and presence of AgMPs: 8mM			
	Cathode: Stainless steel (SS), Ti, Cu, Fe and Fe/Sn (Tin coated on Fe)				
3.3.4.6	Effect of various current densities [5mA/cm^2, 10mA/cm^2 and 15mA/cm^2] in divided cell				4.2.4.4
	Anode : Ti/RuO_2	Reaction conditions: 120mL of NO_3-N: 25mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, reaction time: 120min, AgMPs: 8mM			
	Cathode : Ti				

3.3.4.7	Effect of initial nitrate-N concentration [25, 50, and 100 mg/L] in divided cell		4.2.4.5
	Anode : Ti/RuO$_2$	Reaction conditions: 120mL of NO$_3$-N solution as catholyte, 120mL of 2g/L Na$_2$SO$_4$ as anolyte, reaction time: 120min, current density: 10mA/cm^2, AgMPs: 8mM	
	Cathode : Ti		
3.3.4.8	Oxidation of ammonia on the anode in the anodic compartment		4.2.4.6
	Anode : Ti/RuO$_2$	Reaction conditions: 120mL of NO$_3$-N: 25mg/L as catholyte, 120mL of final solution of ECR of nitrate-N as anolyte, current density: 10mA/cm^2, reaction time: 120min, AgMPs in cathode compartment : 8mM	
	Cathode : Ti		
3.3.4.9	Reusability of AgMPs		4.2.4.7
	Anode : Ti/RuO$_2$	Reaction conditions: 120mL of NO$_3$-N: 25mg/L as catholyte, 120mL of 2g/L Na$_2$SO$_4$ as anolyte, current density: 10mA/cm^2, reaction time: 120min, AgMPs: 8mM	
	Cathode : Ti		
3.3.4.10	ECR of nitrate in real water (groundwater)		4.4
	Anode : Ti/RuO$_2$	Reaction conditions: 120mL of real water as catholyte, 120mL of 2g/L Na$_2$SO$_4$ as anolyte, current density: 10mA/cm^2, reaction time: 120min, in absence and presence of AgMPs: 8mM	
	Cathode : Ti		

Section No.	Treatment of metal finishing wastewater containing high initial nitrate concentrations using ECR in a divided cell				Sections under which results are discussed
3.3.5.1	Effect of initial nitrate concentration [500mg/L, 750mg/L, and 1000mg/L]				4.5.2
	Anode : Ti/RuO_2	Reaction conditions: 120mL of simulated metal-finishing wastewater as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 20mA/cm^2, reaction time: 180min			
	Cathode : Ti/Co_3O_4				
3.3.5.2	Effect of various current densities [10mA/cm^2, 20mA/cm^2, and 30mA/cm^2]				4.5.3
	Anode : Ti/RuO_2	Reaction conditions: 120mL of simulated metal-finishing wastewater NO_3-N: 750mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, reaction time: 180min			
	Cathode : Ti/Co_3O_4				
3.3.5.3	Reusability of Ti/Co_3O_4				4.5.4
	Anode : Ti/RuO_2	Reaction conditions: 120mL of simulated metal-finishing wastewater NO_3-N: 750mg/L as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, current density: 20mA/cm^2, reaction time: 180min			
	Cathode : Ti/Co_3O_4				
3.3.5.4	Effect of molar ratio of Mg:NH_4:PO_4 on struvite formation				4.5.5.1
	pH 9				

		Various struvite molar ratio of Mg:NH_4:PO_4 (0.8:1:0.8, 1:1:1, 1.5:1:1, 1:1:1.5 and 1.5:1:1.5) on struvite formation to remove remaining ammonia from ECR of nitrate.	

3.3.6 ANALYTICAL METHODS

3.3.6.1 Characterisation of Ag-PVA beads

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDAX) analysis of Ag-PVA beads

Using the process outlined in section 3.3.1.1, Ag-PVA beads were prepared. Both fresh and used beads were cut into thin slices and allowed to air dry. To study the morphology of beads coated by Ag, ,SEM images of dried fresh and used Ag-PVA beads were taken by FEI Ltd., Nova Nano SEM 450 consisting of ultra-high brightness Schottky emitter at 1.4nm and 1kV resolution with magnification of X500. The elemental composition of both fresh and used Ag-PVA beads was investigated using EDAX by Thermo Fisher Scientific, consisting of 0.10-0.25nm resolution and Bruker X Flash 6 with 30 EDS detector.

3.3.6.2 Characterisation of AgMPs

Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) analysis of AgMPs

AgMPs were prepared using the method described in section 3.3.1.2. Fresh and used AgMPs were collected, and vacuum dried for SEM and XRD analysis. The morphological study of dried fresh and used AgMPs was conducted using SEM by Hitachi, Japan SEM (SU1510) at accelerating voltage of 10000Volt and emission current of 84000nA with magnification of X500. Dried fresh and used AgMPs were crushed into fine particles for XRD analysis. The characterization and crystallography of AgMPs before and after ECR treatment was studied by XRD analysis (Rigaku SmartLab SE model, Japan). XRD patterns of vacuum dried fresh and used AgMPs were recorded with a Rigaku SmartLab SE diffractometer with Ni-filtered $Cu_{K\alpha}$ radiation of wavelength 1.5406Å, and structural analysis was performed with Smart Studio II software. The XRD scans were recorded in the 2θ range of 0-80° with the scan speed of 5° min^{-1} in steps of 0.02°.

3.3.6.3 Characterisation of Ti/Co_3O_4

X-ray Diffraction (XRD) analysis of fresh and used Ti/Co_3O_4

The procedure detailed in section 3.3.1.4 was used to prepare Ti/Co_3O_4 electrode. XRD examination of both fresh and used Ti/Co_3O_4 electrodes was done. By using an XRD analysis (Rigaku SmartLab SE model, Japan) (described in Section 3.3.6.2), it was possible to compare the characterisation and crystallography of Ti/Co_3O_4 electrode before and after ECR treatment. The characterisation of effluent-containing white precipitates formed during the ECR process was also carried out. The concentrations of metals before and after treatment of ECR of nitrate were studied using inductively coupled plasma (ICP).

3.3.6.5 Characterisation of struvite

X-ray Diffraction (XRD) analysis of struvite

The removal of remaining ammonia in the ECR of nitrate was done by struvite formation. Struvite was collected separately and allowed to dry at room temperature and then used for further analysis. X-ray diffraction (XRD) analysis (Rigaku SmartLab SE model, Japan) (described in Section 3.3.6.2) was used to investigate the characterisation and crystallography of struvite.