REMOVAL OF AQUEOUS NITRATE USING CATALYTIC ELECTROCHEMICAL PROCESS

A Synopsis

Submitted by

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Janhavi Sanjay Ingle

DECLARATION

I hereby declare that the Thesis entitled **“REMOVAL OF AQUEOUS NITRATE USING CATALYTIC ELECTROCHEMICAL PROCESS”** is submitted by me to Faculty of Technology and Engineering, The M S University of Baroda, Vadodara, India under the guidance of Prof. (Dr) Upendra D. Patel for the degree of Doctor of Philosophy. I also declare that no degree, certificate, or title has been awarded based on this work by any other Institution or University.

Date:

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Abbreviations

ECR	Electrochemical Reduction
NO_3-N	Nitrate-Nitrogen
NO_2-N	Nitrite-Nitrogen
NH_3-N	Ammonia-Nitrogen
TN	Total Nitrogen
Ti	Titanium
Gr	Graphite
Fe	Iron
SS	Stainless Steel
Cu	Copper
Fe/Sn	Tin coated iron
SEM	Scanning Electron Microscopy
EDAX	Energy-dispersive X-ray
XRD	X-ray Diffraction
Mg	Magnesium
PO_4	Phosphate
WWAP	World Water Assessment Programme
WHO	World Health Organization
CPCB	Central Pollution Control Board
AgMPs	Silver metal particles
Ag-PVA	Silver coated on polyvinyl alcohol
USEPA	United States Environmental Agency

ABSTRACT

It is becoming more and more problematic as nitrate levels in water sources are increasing which necessitates the development of its removal techniques. Nitrate may be transported in groundwater through soil or by rain and irrigation water. Additionally, fertilizers and pesticides used in the agricultural sector are the major sources of nitrate in groundwater.

The current work describes electrocatalytic removal of aqueous nitrate using different catalysts – Part 1: spatially suspended catalyst - (A) silver coated polyvinyl alcohol beads (Ag-PVA) catalyst; (B) silver metal particles (AgMPs) catalyst; and Part 2: cathode coated with cobalt oxide on titanium (Ti) plate (Ti/Co_3O_4) catalyst.

Firstly, silver-coated polyvinyl alcohol beads (Ag-PVA) as a catalyst were used for electrocatalytic nitrate removal. In this study, we concluded that nitrate removal was minimal in an undivided cell using graphite (Gr) as anode and iron (Fe) as cathode, restricted to 13% and 28% in the absence and presence of 6.67mM Ag-PVA beads, respectively. In both instances, TN (Total Nitrogen) removal was negligible. Nitrate and TN elimination in a divided cell was 70% and 12% in the absence of Ag-PVA beads, respectively, and increased to 85% and 52% in the presence of 6.67 mM Ag-PVA beads. In the divided cell with 6.67mM Ag-PVA beads, the elimination of nitrate proceeded in the following order: Fe > Ti > Cu > SS > Tin-coated Fe (Fe/Sn). Fe cathode produced little nitrite and maximum conversion to gaseous nitrogen (N_2-N). The effect of different operational parameters on the removal of nitrate in the divided cell was investigated, including the concentration of Ag-PVA beads (5mM, 6.67mM, and 8.33mM), the cathode material (SS, Cu, Ti, Fe, Tin-coated Fe (Fe/Sn)), the current density (5mA/cm^2, 10mA/cm^2, 15mA/cm^2 and 20mA/cm^2), the initial nitrate-N concentration (25mg/L, 50mg/L and 100mg/L), and the reusability of catalyst. The maximum removal of nitrate-N and N_2-N selectivity was attained at a catalyst concentration of 6.67 mM among various concentrations of Ag-PVA beads. The reduction of nitrate increased and selectivity for N_2-N improved when the current density was raised to 15 mA/cm^2. It seems that nascent hydrogen intercalation on Ag^0 results in the creation of reductive species that facilitate nitrate reduction. Ag-PVA beads could be reused for at least 8 times. . Scanning electron microscope (SEM) and Energy-dispersive X-ray (EDAX) analysis of Ag-PVA beads revealed that most of the silver was immobilized on the outer surface of PVA beads. Nitrate removal in real groundwater was also studied. 85% nitrate removal in real water

(groundwater) was achieved in the presence of 6.67mM Ag-PVA beads as compared to 53% in the absence of a catalyst.

Secondly, silver metal particles were used as catalyst for electrocatalytic removal of nitrate. In this investigation, nitrate removal was conducted in undivided and divided cells in the absence and presence of silver metallic particles (AgMPs). The removal of nitrate-N achieved in the absence of a catalyst and presence of 8mM AgMPs was 18% and 63% in 120min reaction time at a current density 10mA/cm^2 in an undivided cell utilising a mixed metal oxide (Ti/RuO$_2$) anode and titanium (Ti) cathode. Additionally, the removal of total nitrogen (TN) was nil in the absence of a catalyst and 15% in the presence of AgMPs in an undivided cell. Under identical experimental conditions, there was a considerable improvement in the removal of nitrate and TN in a divided cell, which went from 77% and 23%, respectively, in the absence of a catalyst to 99% and 60%, in the presence of 8mM AgMPs. The effect of various factors on the removal of nitrate in the divided cell was investigated, including the concentration of AgMPs (4mM, 6mM, 8mM, 10mM, 14mM, and 20.8mM), the inter-electrode distance (3cm, 5.5cm, and 7.7cm), the cathode material (SS, Cu, Ti, Fe, Tin-coated Fe (Fe/Sn)), the current density (5mA/cm^2, 10mA/cm^2 and 15mA/cm^2), the initial nitrate-N concentration (25mg/L, 50mg/L and 100mg/L), and the reusability of catalyst. Ti > Fe > Cu > SS > Fe/Sn was the order in which nitrate was eliminated in a divided cell in the presence of 8mM AgMPs using various cathode materials. With the least amount of nitrite-N and ammonia-N formation, the Ti cathode in the presence of 8mM AgMPs resulted in the highest conversion to nitrogen gas. As the current density rose to 10 mA/cm^2, the selectivity toward nitrogen gas improved and overall nitrate reduction improved. Nascent hydrogen intercalation on metallic silver seems to facilitate the catalytic nitrate reduction by generating reductive species (AgH$_x$). AgMPs were reusable up to 10 times.

Thirdly, a Ti plate coated with cobalt oxide (Ti/Co$_3$O$_4$) was employed as a cathode in a divided cell for the removal of high concentration of nitrate removal in a simulated metal-finishing wastewater. Various factors influencing nitrate removal were studied, including initial nitrate-N concentration (500mg/L, 750mg/L, and 1000mg/L), current density (10mA/cm^2, 20mA/cm^2 and 30mA/cm^2) and reusability of Ti/Co$_3$O$_4$. 95% nitrate-N removal was achieved with 20.8% ammonia-N generation and 72.75% N$_2$-N generation at 750mg/L of initial nitrate-N concentration at 20mA/cm^2 current density in 180min of electrolysis time. The reusability of coated catalyst Ti/Co_3O_4 was about 12 times. Further, struvite formation was studied with an aim to remove the residual ammonia-N. The effect of various 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) on struvite formation for ammonia removal were studied at pH 9. The ammonia concentration remaining after the struvite formation was within the industrial wastewater discharge limits. X-ray Diffraction (XRD) analysis revealed that struvite formed in the current study matched with the pure struvite. It was also noted that various metals in the simulated metal-finishing wastewater were almost completely removed by precipitation during electrocatalytic nitrate removal.

CHAPTER 1: INTRODUCTION

1.1 Background

Groundwater is an essential natural resource with significant social and economic importance. According to World Water Assessment Programme (WWAP, 2009), groundwater provides about half of the world's total freshwater consumption. Siebert et al. (2010) state that groundwater accounts for more than 40% of the world's total consumptive usage in agricultural irrigation. Today, groundwater serves as the primary supply of water for most of the people in India, who rely on it for both household and agricultural purposes.

Globally, the major diffuse pollution hazard to groundwater quality comes from agricultural land use. Falling groundwater levels already pose a danger to 63 percent of India's districts and this water is often being polluted. Significant increases in nutrient concentrations have been seen in both private and public well systems due to extensive usage of fertiliser and animal manure. There are some other sources also which lead to an increase in nitrate levels in groundwater.

1.2 Sources and the effects of nitrate

Human activities which cause nitrate contamination in groundwater are as follows:

- Agricultural fertilisers and sometimes crop overfertilization result in increased agricultural production.
- Industrial wastewater (for example metal industries, fertiliser, and pesticide industries, explosive industries etc)
- municipal septic tanks
- leaking sewage system

Numerous studies have pointed to the usage of large amounts of fertilisers in intensive farming techniques as a major cause of groundwater nitrate contamination (Huno et al., 2018; Sacchi et al., 2013). Manure ponds, industrial discharges, leaking septic and sewage systems, urban forests and grasslands, and river and aquifer interactions are a few other prominent causes of nitrate contamination in groundwater (Archna et al., 2012; Bhatnagar & Sillanpää, 2011; Eltigani et al., 2013). Ant hills, biological soil crusts, and termite mounds have been documented as important contributory sources of nitrate pollution in groundwater in arid and semi-arid regions where there is little or no agricultural activity (Stone & Edmunds, 2014).

The World Health Organization (WHO) prescribes maximum permissible limits of nitrate and nitrite as 50 and 3 mg/L (WHO, 2011) in drinking water. The Indian Standard for Drinking Water permits 45 mg/L for nitrate and 0.5 mg/L for ammonia-N as the maximum levels (IS:10500, 2012). The presence of high quantities of nitrate exceeding the given limits in drinking water may have detrimental effects on human health and the environment. Water with a high concentration of nitrate may cause methemoglobinemia, or "blue baby syndrome," in infants (Choudhary et al., 2022; N. Patel et al., 2022; Picetti et al., 2022). In reality, humans often take nitrate through fruits and vegetables (Brkić et al., 2017; Colla et al., 2018; El-Nahhal, 2018; Hord et al., 2009; Ma et al., 2018). However, chronic consumption of high nitrate levels can lead to gastrointestinal issues as nitrate converts to N-nitrosamines when mixes with stomach acid. Sometimes these N-nitrosamine chemicals may result in cancer (Bondonno et al., 2018; Kapil et al., 2014; Panneerselvam et al., 2022; Parvizishad et al., 2017). Numerous cancers, including gastric, colorectal, bladder, urothelial, and brain tumours, have been linked to prolonged exposure to high nitrate levels in drinking water (CDPH 2014). Eutrophication is a result of increased nitrate levels in rivers (Le Moal et al., 2019). Also, surface water bodies may undergo eutrophication due to nutrient excess (chronic) or agricultural runoff and transport it to the capture zone of a surface water or groundwater intake (acute) (Sousa et al., 2014).

1.3 Need of the study

Many authors have reported more than 100mg/L nitrate concentration in groundwater (Adimalla et al., 2021; Jayarajan & Kuriachan, 2021; Rahman et al., 2021; Ward et al., 2018). So, it is important to remove nitrate contamination from groundwater. There are several methods to treat nitrate like biological treatment (Hurtado-Martinez et al., 2021; Mohseni-Bandpi et al., 2013; Pang & Wang, 2021; Qi et al., 2022; Soares, 2000), reverse osmosis (Epsztein et al., 2015; Lejarazu-larrañaga et al., 2022), ion exchange (Chen & Liu, 2020; Labarca & Bórquez, 2020), electrocoagulation (Apshankar & Goel, 2020; Lacasa et al., 2011; Yazici Karabulut et al., 2021), catalytic hydrogenation (Huo et al., 2017; Jaworski et al., 2020; Santos et al., 2020), photocatalytic reduction (Bahadori et al., 2018; Sychev et al., 2008), nano zero-valent iron (Guo et al., 2015; Hu et al., 2018; H. Sun et al., 2021) and electrochemical treatment (Beltrame et al., 2020; Dash & Chaudhari, 2005; Rao et al., 2019).

Biological denitrification transforms nitrate ions into nitrogen gas utilizing denitrifying bacteria and microorganisms (Chang et al., 2021). But the significant drawback of biological systems is that they require a long time for treatment. Although biological denitrification may easily decrease nitrate, it is not recommended for drinking purposes because of the inherent presence of organic materials and bacteria in treated water. The drawback of the ion exchange method is the absence of destruction of nitrate and the release of nitrate-containing salt water into the environment. The possibility of chemical membrane fouling, and high cost of treatment are main disadvantages of membrane-based systems. The membrane processes generate waste concentrates (brines) with significant nitrate and other ion concentrations. So, the complete destruction of nitrate is difficult. A significant amount of hydrogen is needed in the hydrogenation method which is not only risky but difficult to operate. The requirement of a constant light source photo reduction of nitrate makes these methods tough to use.

A simple and effective method is to be used for the complete removal of nitrate. Electrochemical reduction (ECR) is one of the best processes to remove nitrate from water as it removes the pollutant using a clean reagent that is electrons (S. Popli & Patel, 2017). In the ECR process, the reduction takes place at the cathode. Figure 1 describes the pathways and mechanisms of ECR of nitrate. The labelling of pathways in Figure 1 shows various products that reflects whether they produce ammonia/ammonium (red), nitrogen (blue), or nitrogen oxides (orange). The paths that lead to diverse products are shown by white arrows, while the steps that are often connected to the rate-determining step are denoted by black arrows. Species consumed on the cathode surface while reduction process are denoted by an asterisk (*). As shown in Figure 1, the nitrate ion reduces on cathode surface for direct nitrate reduction. The first step of nitrate to nitrite occurs by all NO_3^- routes and they frequently manage the overall reaction rate. The selectivity of the reaction will be determined by the rates of the steps that diverge at NO*. There are two main techniques to produce ammonia from adsorbed NO*. They are: (1) NO* to hydroxylamine and then reduction of hydroxylamine to ammonia; (2) NO* interacting with hydrogen atoms in a strong reducing environment to produce NH_3. For gaseous N_2 formation, NH^*_2 is generated first by protonation of NO*. Further, reaction between the NH^*_2 and NO* will result in $N_2OH^*_2$, which will then break down into N_2 and H_2O. Thus, nitrate is converted to nitrite, and then further it leads to the formation of ammonia and gaseous nitrogen.

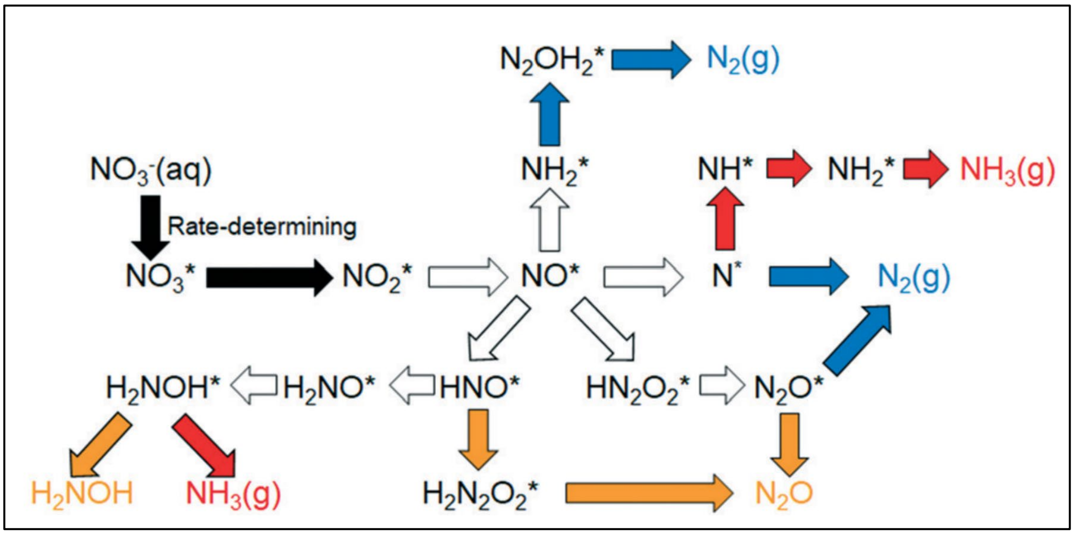

Figure 1: General mechanism of nitrate reduction (Z. Wang et al., 2021)

The ECR of nitrate has been discussed in several research studies (Choi et al., 2020; Mirzaei et al., 2018; Zeng et al., 2020; X. Zhao et al., 2021). ECR of nitrate is studied in an undivided cell and a divided cell which is separated by a cation exchange membrane. Plane cathodes made of iron (Fe), titanium (Ti), graphite (Gr), and aluminium (Al) are reported to be used in the undivided cell (Chauhan & Srivastava, 2022; Govindan et al., 2015; Wu et al., 2019). Graphite felt bismuth (Bi), carbon paper, boron-doped diamond, copper (Cu), titanium (Ti), and aluminium (Al) are some of the plane cathodes that are studied in divided cells (Beltrame et al., 2020; Bosko et al., 2014; Dima et al., 2003; Georgeaud et al., 2011; Rao et al., 2019). Catalysts are being used in the ECR of nitrate to enhance the reduction reaction. This catalyst may be divided in two ways: (1) catalyst immobilised on the cathode (Duan et al., 2019; Gao et al., 2018; Shih et al., 2020; C. Sun et al., 2018) and; (2) spatially suspended catalyst in the reaction mixture (Beltrame et al., 2020; Popli et al., 2021; Zhang et al., 2016).

In comparison to a single-chamber cell (undivided cell), a dual-chamber cell (divided cell) eliminates more nitrate. This is most likely because electrocatalytic nitrate reduction in dual chamber cells is considerably altered by the addition of a cation exchange membrane (Ding et al., 2015). Divided cells separate the anode and cathode compartments and by maintaining the electrodes apart, undesired reactions or side reactions and cross-contamination are avoided. As the membrane separates the catholyte from the anode and obstructs the regeneration of nitrate owing to nitrite oxidation at the anode, nitrate is efficiently eliminated in a divided cell (Garcia-Segura et al., 2018; Genders et al., 1996).

Additionally, the effect of catalyst i.e., the absence and presence of catalyst have effects on the ECR of nitrate. In the absence of a catalyst, the reduction of nitrate ions occurs through direct electron transfer at the electrode surface. The applied potential provides the driving force for the reduction reaction. In the presence of a catalyst, the reaction kinetics of nitrate reduction significantly enhances. Catalyst provides active sites that facilitate electron transfer and promote the specific reduction pathways for nitrate ions, leading to fast and more efficient reduction. The positive side of the presence of a catalyst is that it can influence the selectivity of nitrate reduction directing the reaction towards specific products such as nitrogen gas (N_2), or nitrite (NO_2^-) or ammonia (NH_3). Thus, the choice of catalyst material and reaction conditions can regulate the selectivity of the end-products of nitrate reduction. Regeneration and reusability of the catalyst may be required to restore the catalyst's activity and prolong its lifespan. Thus, catalyst selection, stability, and regeneration are crucial factors to consider for long-term operation and cost-effectiveness. For instance, Jonoush et al. (2020) reported that in comparison to a simple Ni foam (28.16%) and Ni-Fe^0 (45.95%), Ni-Fe^0@Fe_3O_4 nanocomposite electrode achieved 90.19% nitrate removal in the electrocatalytic system utilising 5 mA/cm^2 current density, a pH of 6.2, and 10 mM NaCl in 240 minutes.

Apart from groundwater, various industrial activities and wastewater contain nitrate in high concentration. As indicated in Table 1, many industrial operations and wastewater also contaminate the environment with NO_3^-. As a result of progress in worldwide urbanisation and industrialisation, increasing amounts of NO_3-N is being discharged in environment through industrial wastewater. When nitrate concentrations of up to 3000 mg/L are released from industrial sites along with other chemical waste, they endanger both aquatic and terrestrial life (Bosman, 2009).

Table 1: Nitrate concentration in various industrial wastewater

Source	NO_3^- concentration	Reference
Fertilizer Industry	850 N-mg/L	Zala et al. 2004)
Photovoltaic cell Industry	1000 mg/L	Belkada et al. (2018)

Explosive Industry	3600 mg/L	Shen et al. (2009)
Explosive Industry	3000 mg/L	Cyplik et al. (2012)
Acidic and Saline Industry	750-5750mg/L	Mendrinou et al. (2021)
Metal pickling Industry	200 N-mg/L	Watanabe et al. (2001)
Stainless steel Industry	700 mg/L	Fernández-Nava et al. (2008)
Textile Industry	104 mg/L	Su et al. (2017)
Fertilizer and Nuclear Industry	1694-9032 N-mg/L	Dhamole et al. (2007)
Fertilizer and Nuclear Industry	2000 mg/L	Liao et al. (2013)
Metal Recovery Industry	2200 g/m^3	Hirata et al. (2001)
Metal Finishing Industry	700-1000g/m^3	Gabaldón et al. (2007)

High nitrate effluent from metal industries is discharged directly into water bodies which can contaminate the water and harm the environment (Chanakya & Jeevan Rao, 2010). To remove the remaining undiscovered minerals from the raw mined minerals and tailings, chemicals like nitric and sulfuric acids are utilised, which adds to the contamination of both surface and groundwater systems near mining operations (Moloantoa et al., 2022). Metal finishing operations and wastewater from metal industries are one of the sources of nitrate contamination in water. So, treating such highly concentrated nitrate wastewater is a must. Various methods are being used to remove nitrate from metal-finishing wastewater including biological method, coagulation method, electrochemical process, ion exchange etc. Generally, the biological method is more commonly used for the removal of nitrate but it is limited due to the inhibition by heavy metals present in metal-finishing wastewater (Mpongwana et al., 2022). ECR is one of the efficient methods to remove such highly concentrated nitrate from metal-finishing wastewater (Sim et al., 2012). According to the

Central Pollution Control Board (CPCB) of India, the discharge limit of nitrate-N and ammonia-N for industrial effluent is 20mg/L and 50mg/L, respectively.

Considering the foregoing discussion, the main aim of this research work is to investigate the potential of ECR as a viable method for nitrate removal from water and wastewater using spatially suspended and immobilized catalyst, and to study the factors that affect the efficiency of the process and selectivity of end-products. While dealing with high concentrations of nitrate, especially in industrial wastewater, the concentration of ammonia as an end-product may be greater than the discharge limits. Thus, we also explored ammonia removal by struvite precipitation. Our study consists of two parts: Part 1 – ECR in the presence of spatially suspended catalyst and, Part 2 – cathode coated with catalyst (Ti/Co_3O_4).

Based on the above discussion, the detailed objectives of the study are as under.

1.4 Objectives of the Study

Part 1: ECR of nitrate using spatially suspended catalyst

Part A: silver coated polyvinyl alcohol beads (Ag-PVA beads)

1) To study the synthesis of Ag-coated PVA beads and study its morphology using Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray (EDAX) analysis.
2) To explore the ECR of nitrate in undivided as well as divided cells in the absence and presence of Ag-PVA beads.
3) To study the ECR of nitrate and its selectivity towards the final products.
4) To study the effect of concentrations of Ag-PVA beads (5mM, 6.67mM and 8.33mM).
5) To study the effect of cathode materials (SS, Fe, Fe/Sn, Ti, and Cu).
6) To study the effect of current density (5 mA/cm^2, 10 mA/cm^2, 15 mA/cm^2 and 20 mA/cm^2).
7) To study the effect of initial nitrate-N concentration (25mg/L, 50mg/L, and 100mg/L).
8) To study the reusability of Ag-PVA beads.
9) To investigate the ECR of nitrate in real water (groundwater) using Ag-PVA beads.

Part B: silver metallic particles (AgMPs)

1) To synthesize Ag metallic particles and study its morphology and crystallography using SEM and X-ray Diffraction (XRD) analysis.

2) To explore the ECR of nitrate in undivided as well as divided cells in the absence and presence of AgMPs.
3) To study the effect of various experimental conditions on the selectivity of the final products.
4) To study the effect of concentrations of AgMPs (4mM, 6mM, 8mM, 10mM, 14mM, and 20.8mM).
5) To study the effect of inter-electrode distance (3cm, 5.5cm and 7.7cm).
6) To study the effect of cathode materials (SS, Fe, Fe/Sn, Ti, and Cu).
7) To study the effect of current density (5 mA/cm^2, 10 mA/cm^2, and 15 mA/cm^2).
8) To study the effect of initial nitrate-N concentration (25mg/L, 50mg/L, and 100mg/L).
9) To study the oxidation of ammonia on the anode in an anodic compartment in a divided cell.
10) To study the reusability of AgMPs.
11) To investigate the ECR of nitrate in real water (groundwater) using AgMPs.

Part 2: Treatment of metal finishing wastewater containing a high concentration of nitrate using ECR

1) To synthesize cobalt oxide-coated Ti plate (Ti/Co_3O_4) and characterize it using XRD.
2) To study the effect of initial nitrate-N concentrations (500mg/L, 750mg/L, and 1000mg/L).
3) To study the effect of current density (10mA/cm^2, 20mA/cm^2 and 30mA/cm^2).
4) To study the reusability of Ti/Co_3O_4
5) To study the effect of the molar ratio of Mg:NH_4:PO_4 on struvite formation to remove ammonia formed in ECR of nitrate-N (0.8:1:0.8, 1:1:1, 1.5:1:1, 1:1:1.5 and 1.5:1:1.5).

1.5 Organization of the Thesis

The report includes:

Chapter 1: Introduction, provides a brief overview of nitrate, including its origins, impacts on people and the environment, and treatment options for nitrate-containing water and wastewater. It also includes the need for the study and the overall objectives of the investigation.

Chapter 2: Literature Review, provides a survey and review of treatment methods for nitrate removal from water.

Chapter 3: Materials and Methodology, provides information about the tools, equipment, and experimental techniques needed to complete the study. The experimental work is broken down into different phases, with each segment focusing on a different aspect of catalyst preparation (Ag-PVA beads, AgMPs and Ti/Co_3O_4 electrode), and experimental setup.

Chapter 4: Results and Discussion, contains the experimental findings and comments relating to them and after each phase, the key accomplishments from the study are reviewed.

Chapter 5: Conclusion, highlights significant findings from the research and provides suggestions for further research study.

At the end of each chapter, a list of references cited in the chapter is provided.

At the end of the report, there is a list of publications resulting from the current research.

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CHAPTER 2: LITERATURE REVIEW

2.1 General methods for removal of aqueous nitrate from water and wastewater

Nitrate (NO_3^-) is a common contaminant found in wastewater and water sources. It is a naturally occurring compound that can also be introduced through agricultural runoff, septic tanks, industrial discharges, and improper disposal of sewage and wastewater. While nitrate itself is not toxic, its presence in high concentrations can have adverse effects on human health and the environment. Therefore, nitrate removal from wastewater and water is essential to ensure safe drinking water and protect ecosystems.

This chapter focuses on the overview of various treatment methods - biological (Liu et al., 2021; Rahimi et al., 2020) and physicochemical techniques (Archna et al., 2012; Huno et al., 2018; Matei & Racoviteanu, 2021) for the nitrate removal from wastewater and water.

2.1.1 Biological method

Biological denitrification is a microbial-driven process that occurs under aerobic (Deng et al., 2020; X. Wang et al., 2023; Ye et al., 2020) or anaerobic conditions (Huang et al., 2022; Wan et al., 2018), where bacteria use nitrate as an electron acceptor in the presence or absence of oxygen, respectively. Denitrification relies on a diverse group of bacteria known as denitrifiers, which possess enzymes capable of catalysing the different stages of nitrate reduction. These bacteria obtain energy by utilizing organic carbon sources present in the wastewater or by utilizing endogenous carbon reserves. The denitrification pathway involves the sequential reduction of nitrate to nitrite (NO_2^-), nitric oxide (NO), nitrous oxide (N_2O), and finally, nitrogen gas (N_2). The nitrogen gas is then released into the atmosphere, completing the removal of nitrate from the system.

Hurtado-Martinez et al. (2021) studied a novel modification of aerobic granular sludge technology to treat nitrate-polluted groundwater by introducing very small concentrations of carbon- and oligo-elements-based solution to the groundwater to encourage the growth of denitrifying microorganisms. At 0.15g sodium acetate ($C_2H_3NaO_2$) per L, the denitrification process was effectively completed i.e., 98% of nitrate removal with no nitrite and ammonia in 220 days with 0.15g sodium acetate per litre carbon source was achieved. With average values of mean size and settling velocity of 4.0 mm and 40 m/h, respectively, the granular biomass was compact and dense. Massive parallel sequencing techniques were used to study the prokaryotic and eukaryotic populations. According to influent composition, Comamonadaceae, Rhizobiales, Acinetobacter, and Pseudomonas were the dominating bacterial phylotypes. Haematococcus microalgae was associated with the main eukaryotic phylotype.

Chang et al. (2021) investigated a biotechnological technique for simultaneously removing nitrate, Mn(II), and tetracycline (TC). Through the screening experiment, the anaerobic denitrifying bacterium Zoogloea sp. MFQ7 was discovered. The nitrogen balancing experiment was conducted to learn more about the strain MFQ7's route for converting nitrogen during the denitrification process and they observed that using a nitrogen balance experiment, 83.49% of nitrogen was removed. At a C/N ratio of 2.0, pH of 7.0, Mn (II) of 20 mg/L, temperature of 30°C, and TC of 0.2 mg /L, strain MFQ7 was able to remove the greatest amounts of nitrate (100%), Mn(II) (74.56%), and TC (63.59%) within 96 hours.

Cheng et al. (2020) reported a new strain of fungal known as Fusarium solani (RADF-77) isolated from a denitrification reactor supported by cellulose material (tea residue) which is capable of extracting nitrogen in an aerobic environment. Its average NO_3-N removal rates were measured to be 4.43 mg/(L·h) and 4.5 mg/(L·d) with glucose and tea residue as the only carbon sources, respectively. The ideal parameters were a C/N ratio of 5–15, 150–200 rpm rotating speed, pH of 4.9–6.7, and temperatures of 15–25 °C. The nitrogen balance showed that 53.66% of the nitrogen was removed as gaseous byproducts. When nitrate or ammonia were employed as nitrogen sources, as well as during aerobic incubation, little N_2O generation was observed.

Ali et al. (2021) studied various carbon-to-nitrogen (C/N) ratios in wastewater using Acinetobacter sp. H12 on the bio-removal efficiency of aquatic pollutants like calcium (Ca^{2+}), fluoride (F), and nitrate (NO_3). Acinetobacter sp. H12 was used in a continuous determination experiment to examine the removal of Ca^{2+}, F, and NO_3 at various hydraulic retention times (HRT: 1, 3, and 5 h), C/N ratios (5:1, 3:1, and 2:1), and F concentrations (1.5, 2, and 3 mg L 1) while maintaining a constant pH (6.5) and Ca^{2+} (0.5 mg/L $CaCl_2$). The rates of Ca^{2+}, F, and NO_3 simultaneous bio-removal were 56.31%, 96.33%, and 96.95%, respectively. Without any indication of N_2O emission, nitrogen gas (N_2) was created.

2.1.2 Catalytic Hydrogenation

The process of catalytic hydrogenation is frequently used to remove nitrate from water. In this procedure, hydrogen gas and a catalyst are used to speed up the conversion of nitrate ions (NO_3) into nitrogen gas (N_2). Temperature, pressure, pH, hydrogen flow rate, and contact duration are some of the variables that affect nitrate removal by catalytic hydrogenation. To ensure high conversion rates and reduce the generation of undesirable byproducts, these reaction conditions must be optimised.

Huo et al. (2017) investigated ruthenium's (Ru) strong activity for hydrogenation of nitrate at ambient temperature and pressure on catalyst carbon- and alumina-supported Ru and Pd (palladium). It has been shown that under typical testing conditions, Ru has a strong intrinsic activity in nitrate removal that is five times more than that of Pd. The study showed that nitrite was reduced to $N_{2,}$ and ammonium The authors observed that for nitrate reduction at larger nitrite:hydrogen ratios, selectivity switched towards N_2 from ammonium. The proposed mechanism of the reaction states that parallel pathways involving the adsorbed NO, including (1) sequential hydrogenation to ammonium and (2) sequential hydrogenation of nitrate to nitrite and NO resulting N_2 as major product.

Jaworski et al. (2020) studied the catalytic removal of NO_3^- in groundwater using catalysts ZrO_2, Al_2O_3 and ZrO_2-Al_2O_3 (Zr-Al 10) supported by an active surface Anderson heteropolyanion ($RhMo_6$). Among all catalysts, the $RhMo_6$ phase on the ZrAl-10 support was the most effective for nitrate removal. The $RhMo_6$/ZrAl-10 catalyst appears to have the highest selectivity to N_2 (99.3%) because of its high Rh dispersion (0.755) and the presence of Lewis acid sites (oxygen vacancies) in the tetragonal ZrO_2 modification, which facilitate NO_3 adsorption through electrostatic interactions.

Santos et al. (2020) reported the use of palladium-copper bimetallic (BM) catalysts supporting titanium dioxide and carbon nanotubes for efficient NO_3 removal. Various catalyst loading rates were studied: (1) 1% Pd-1% Cu/CNT gave 98% nitrate removal after 5 hours of reaction with 42% ammonia and 57% N_2; (2) 2.5%Pd-2.5%Cu/CNT (BM 2h) resulting complete nitrate reduction with maximum N_2 selectivity (62%) ; (3) 5% Pd-2.5% Cu/CNT (BM 2h) gave complete nitrate reduction resulting 44% ammonia and N_2 as 56% in 60min. When utilising 5% Pd-2.5% Cu/CNT (BM 2h), the reaction rate for NO_3 conversion is roughly 40 times higher than when using 1% Pd-1% Cu/CNT. The increase in reaction rate was less for 2.5% Pd-2.5%

Cu/CNT (BM 2h) (approximately four times the value obtained for 1% Pd-1% Cu/CNT). 5% Pd-2.5% Cu supported on TiO_2 gave complete nitrate removal in 120min resulting 69% ammonia as a major product.

2.1.3 Ion Exchange

Nitrate removal from water sources is commonly accomplished using ion exchange. On a resin substance, it entails the exchange of nitrate ions (NO_3^-) with other ions, often chloride ions (Cl^-) or sulphate ions (SO_4^{2-}). The foundation of ion exchange is the notion of selective ion adsorption and exchange between the water being treated and a solid resin substance.

M. Ali et al. (2022) investigated a novel type of homogenous ion exchange membrane by fusing polyvinylidene fluoride (PVDF) with a cationic polymer (Al_2O_3 nanoparticles) for the removal of phosphate, molybdate, and nitrate from groundwater. The removal rates of various anions, such as MoO_4^{2-}, PO_4^{3-}, and NO_3^- ions, from PVDF, Al_2O_3, PVDF/Cs, and Al_2O_3-PVDF/Cs-MWCNTs membranes and observed maximum removal of anions using Al_2O_3-PVDF/Cs-MWCNTs. The authors obtained 94.3% molybdate removal, 65.6% phosphate removal, and 85.78% nitrate removal efficiencies. Regeneration and reuse of PVDF/Al_2O_3/Cs-MWCNTs membrane was only one time for molybdate and phosphate removal and hardly 2 times for nitrate removal.

Labarca & Bórquez (2020) studied Purolite A520E resin for the ion exchange treatment, lowering the nitrate concentration to 0.1 mg/L. The authors reported that the residence time needed for the exchange column's ideal flow must be at least 2.1 minutes. The maximum resin capacity, 47.1 mg NO_3/g resin, was not altered by the greater nitrate content in the water, although the resin breakthrough capacity was reduced when the initial concentration rose. With an up-flow mode and a 3% w/v NaCl solution, optimal regeneration was achieved. The authors also studied four distinct commercial membranes for nanofiltration removal of nitrate: NF97, NF99, NF99H, and NF90. Only NF97 and NF90 were able to remove nitrate under Chilean drinking water standards, with rejection rates of 97% and 87%, respectively, in an optimal pressure range of 12–20 bar, whereas the NF90 produced 3.5 times more permeated water than NF97.

Nur et al. (2014) studied four ion exchange resins – Purolite A520E, Purolite A500PS, Purolite FerrIX A33E and Dowex 21K for the effectiveness of removing nitrate in batch and fixed-bed systems with effects of filtration velocity on nitrate removal. Nitrate removal obtained with various resins was 82%, 75%, 40% and 78% for Purolite A520E, Purolite A500PS, Purolite FerrIX A33E and Dowex 21K, respectively. Thus, the nitrate removal was maximum in a fixed bed column in the presence of 1.5g/L Purolite A520E resin.

2.1.4 Photo Reduction

The process of photo reduction depends on light energy's capacity to excite electrons in a photosensitizer or photocatalyst, which then facilitates the reduction of nitrate ions. Nitrate is transformed into nitrogen gas or other reduced nitrogen compounds when excited electrons interact with nitrate. The light source, wavelength, intensity, type of photocatalyst, reaction time, temperature, and pH are parameters that affect nitrate removal by photoreduction.

Hou et al. (2021) studied photocatalytic denitrification on an Ag/SiO_2 core encased in a crystalline TiO_2 shell (Ag/SiO_2@cTiO_2). In addition to increasing the density of photogenerated electrons, Ag's surface plasmon resonance and electron sink effect also helped separate charge carriers in the Ag/SiO_2@cTiO_2 system, which improved nitrate removal. Within 4 hours, using 5wt% Ag/SiO_2@cTiO_2 catalyst with 60 mL quartz tube and 500 W high-pressure mercury lamp placed at 8 cm distance from the tube and emitting light with a 0.377 W/cm^2 intensity, 95.8% nitrate was removed with 93.6% N_2 selectivity.

Shaban et al. (2016) reported photocatalytic treatment using carbon-modified titanium oxide (C/TiO_2) nanoparticles catalyst for nitrate removal from a contaminated seawater. The authors studied various parameters influencing the photocatalytic removal rate of nitrate : (1) catalyst loading: increasing loading from 0.1g/L to 0.5g/L, nitrate reduction increased due to increase in number of e^- evolve in reaction; (2) pH: increasing pH from 3 to 9, nitrate removal decreased which means an acidic medium promotes nitrate ion adsorption to the active regions of the photocatalyst; (3) hole scavenger: nitrate removal reduced when the hole scavenger concentration was greater than 0.04M. (4) initial nitrate concentration: the time needed for full reduction increased as the initial nitrate concentration rises from 50 ppm to 200 ppm. Complete nitrate removal was achieved with the catalyst loading of 0.5 g /L, pH 3, and 0.04 M of formic acid (as hole scavenger) for an initial nitrate concentration of 100ppm.

Bahadori et al. (2018) reported palladium-doped TiO_2 synthesis in nanoscale form using a novel flame pyrolysis (FP) process (Pd-TiO_2-FP),and compared its performance with mesoporous Pd-TiO_2 (Pd-TiO_2-meso). Nitrate reduction achieved with Pd-TiO_2-FP and Pd-TiO_2-meso was 13% and 8.73% respectively with 27% and 45% ammonia generation. On adding a hole scavenger, nitrate reduction decreased resulting in ammonia as a major product.

2.1.5 Nano Zero Valent Iron

The reactive iron nanoparticles easily react with the nitrate ions present in the water due to their large surface area and reactivity. The nitrate ions accept electrons from zero-valent iron nanoparticles, which aids in their reduction to nitrogen gas or other reduced nitrogen molecules. Two basic methods are generally used when applying nano zero-valent iron to remove nitrates: Batch Experiments and Permeable Reactive Barriers (PRB).

Wei et al. (2018) investigated nitrate removal from groundwater using nano zero–valent (nZVI), biochar (BC) and nano zero-valent iron/biochar composites (nZVI/BC). No nitrate removal was achieved with BC whereas 40% and 96.8% were achieved with nZVI and nZVI/BC respectively at pH 6.8 and dosage 4g/L. Various parameters were studied with nZVI/BC : (1) dosage – increasing dosage from 0.5g/L to 4g/L, nitrate reduction increased and remained constant at 5g/L; (2) pH – change in pH from 2 to 12 didn't show any significant change in nitrate reduction; (3) nitrate initial concentration – increasing nitrate concentration, from 10mg/L to 60mg/L increased nitrate concentration. The authors concluded that nZVI/BC maintained extremely effective nitrate removal (75.0%–97.0%) from groundwater resulting in 60.2% N_2 selectivity.

Cho et al. (2015) studied batch experiments to determine the impact of nano-sized magnetite (NMT) on the reduction of nitrate by Fe(0) in groundwater. The amount of nitrate removed during a 36-hour reaction was 67.3% with 10 g/L NMT dosage to 10 g/L Fe(0) to improve nitrate reduction in GW. Cations like Ca^{2+} and Mg^{2+} significantly enhanced the efficiency of nitrate reduction by Fe(0)/NMT, most likely as a result of surface complex formation that aided nitrate transport to the reaction site. In a deactivated Fe(0)/NMT reactor, 10 mM $CaCl_2$ was added to reactivate the reduction process and further decrease the residual nitrate. Fe(0)/NMT also showed exceptional endurance by completing four nitrate reduction cycles in 90 hours.

Song et al. (2020) studied nZVI (nano zero-valent iron), ZVI powder, ZVI powder on activated carbon (AC) and nZVI/AC for nitrate removal from groundwater. Nitrate removal and TN elimination at pH 7.0 was 41.7% and 38.9% for nZVI at a dose of 4.0 g/L, 90% and 17% for ZVI powder at a dosage of 3.0 g/L, 45% and 22% for ZVI/AC at a dose of 3:1. Complete nitrate reduction was achieved using nZVI/AC resulting 66.9% ammonia, 33.1% N_2 and 39% TN removal. The authors obtained that the TN removal rose from 16.8% to 38.9% with an increase in the nZVI/AC mass ratio from 1:2 to 2:1, but it subsequently started to drop when the ratio was raised even higher.

2.1.6 Electro-coagulation

The concept behind electrocoagulation is the destabilization and coagulation of pollutants by producing metal hydroxide or metal oxide species. It entails applying an electric current to produce coagulating agents on the spot that aid in the aggregation and removal of nitrate ions (NO_3^-). Sacrificial anodes, which are commonly constructed of iron or aluminium, disintegrate when an electric current is applied, releasing metal cations into the water. Metal hydroxide or metal oxide flocs are generated when these metal cations interact with water and hydroxide ions produced at the cathode. These flocs capture and adsorb pollutants, such as nitrate ions, making it easier to remove them from the water.

Acharya et al. (2022) investigated the electrocoagulation method for removing nitrates from artificial and natural groundwater. Using a batch procedure and aluminium-aluminium (Al-Al) electrodes, authors studied various pH (6.0-12), initial nitrate concentrations (100-500 mg/L), stirring speeds (100-500 rpm), inter-electrode distances (0.5-2 cm), NaCl dose and electrolysis times (30-180 min). The ideal conditions found were an initial nitrate concentration of 100 mg/L, a maximum 98% nitrate removal efficiency achieved at an inter-electrode spacing of 1 cm, agitation speed of 300 rpm, electrolyte concentration of 1.1688g/L NaCl, current of 1.5 A, and time of 180 min. The removal of nitrate from actual groundwater was 92.5% at optimum parameters.

Amarine et al. (2020) reported electrocoagulation in a batch reactor with two aluminium electrodes. The applied voltage between the electrodes (5–30 V), at pH 7, and the initial nitrate concentration of 100 mg/L were the operational conditions. The outcomes demonstrated that the electrodes' submerged surface and applied voltage had an impact on the removal efficiency. Under the following conditions: pH 7, an electrical voltage of 30 volts, submerged surface of 33.75 cm^2, this removal of nitrate was 94.41% after 150 minutes. However, the addition of Cl enabled a reduction in the generation of nitrite and ammonium and transfers selectivity towards N_2.

Karabulut et al. (2021) investigated the removal of nitrate in groundwater by electrocoagulation (EC) utilising aluminium (Al) and iron (Fe) electrodes. The authors studied the effects of initial pH, different electrode materials, inter-electrode distance, initial conductivity, initial nitrate concentration, and energy consumption at room temperature. According to the study, using Al electrodes showed 80.1% of nitrate removal (initial concentration = 250 mg/L) at initial pH 6, run time = 210 min, current density = 2.31 A/m^2, interelectrode distance = 10 mm, and conductivity = 1000 s/cm. Fe electrodes were shown to have no appreciable impact on nitrate removal (12.4%). The highest nitrate content in groundwater had a removal effectiveness of 62.0% for an Al electrode and 39.0% for a Fe electrode. Compared to the Fe-Fe electrode combination, the Al-Al electrode combination employed in the tests generated greater efficiency.

2.1.7 Summary of general treatment methods of nitrate

Several methods achieve efficient nitrate removal. Here's a summary of some of the most efficient nitrate removal methods whose literature survey was carried out:

Biological Denitrification: Biological denitrification uses specific microorganisms to remove nitrate. This method is highly efficient and environmentally friendly. It can be implemented in wastewater treatment plants, constructed wetlands, or denitrifying bioreactors. However, it requires a carbon source and careful process control.

Catalytic hydrogenation: The possibility of the creation of additional nitrogen-containing compounds is greatly reduced by the very selective nature of catalytic hydrogenation towards nitrate reduction. For the catalytic hydrogenation of nitrate, a variety of catalysts can be used, including non-precious metals like copper (Cu), nickel (Ni), and iron (Fe), as well as valuable metals like palladium (Pd), platinum (Pt), and rhodium (Rh).

Ion Exchange: Ion exchange resins have high selectivity for nitrate ions and can effectively remove them from water. This method offers high removal efficiency and can be easily implemented in both small-scale and large-scale systems. However, it requires periodic resin regeneration and disposal of regeneration chemicals.

Photoreduction: Since photo reduction uses no extra chemicals or reagents, it is an ecologically benign method. It uses light energy, which is cheap, plentiful, and easily accessible, minimising the need for chemical additions and lowering waste production. Photoreduction methods depend heavily on photosensitizers or photocatalysts. They generally consist of semiconducting substances that can absorb light energy and produce electron-hole pairs. Materials including titanium dioxide (TiO_2), zinc oxide (ZnO), and certain chemical dyes are frequently employed which act as electron donors or catalysts to speed up nitrate reduction.

Nano Zero Valent Iron (nZVI): Nano zero-valent iron particles have high reactivity and can effectively reduce nitrate to nitrogen gas. This method offers efficient nitrate removal and has the potential for complete reduction. However, the cost of nZVI production and potential mobility and retention issues of nanoparticles need to be considered.

Electrocoagulation: Nitrate ions may be effectively removed from water using electrocoagulation. The nitrate ions and other pollutants in the water are destabilised by the coagulant species produced during electrolysis, which causes them to coagulate and form bigger flocs. These flocs help to separate the pollutants from the water by trapping them, including nitrate ions.

2.1.8 Findings from Literature Survey

These treatment methods are efficient for nitrate removal, but their usage is limited due to the following drawbacks.

1) For biological nitrate removal, an adequate carbon supply must be available for denitrification. Sometimes there may not be enough organic carbon in the wastewater or water supply to support effective denitrification. The denitrification process might suffer from temperature, pH, and amounts of dissolved oxygen as these are ideal conditions for biological treatment. It is time-consuming as well as the treated water may contain micro-organisms which limits its usage as a treatment process for drinking water.
2) The nitrate removal system's operating complexity and cost are increased by the requirement for a steady supply of high-pressure hydrogen.
3) Nitrate removal by ion exchange resins is restricted and eventually reaches saturation. To remove the nitrate, recharge of the resin bed is required for which a regenerant solution

is necessary and its uses of chemicals, such as acids or brine, can increase operating costs and produce waste streams that require adequate treatment or disposal. The formation of contaminants, organic debris, or particles on the surface of the ion exchange resin is referred to as fouling. The capacity of the resin bed to remove nitrates can be decreased due to fouling.

4) A dependable and enough light source such as sunlight or artificial light sources like ultraviolet (UV) lamps is necessary for photoreduction techniques for reduction reactions. Depending on the energy source, the energy requirements might have an impact on the environment and contribute to operating expenses.
5) Nano zero-valent iron might be introduced into the treated water during the nitrate removal procedure. They may induce permanent iron in the ground in the permeable barrier method which can be difficult to remove separately.
6) Sludge or precipitates are generated as a result of electrocoagulation during the coagulation process. These solids must be removed from the cleaned water and disposed of properly or subjected to further treatment. Sludge or precipitates can be difficult to handle since they require additional infrastructure for handling, storing, and disposing of them.

So, to overcome all these drawbacks an efficient and effective method with the least disadvantages should be used for nitrate reduction. Electrochemical reduction (ECR) is one of the efficient methods for the removal of nitrate a clean reagent electron. The ECR holds significant promise as a method for nitrate removal from water sources. Its selectivity, efficiency, versatility, environmental compatibility, and potential for resource recovery make it an attractive option for addressing nitrate contamination.

2.2 Electrochemical Reduction (ECR) of aqueous nitrate from water and wastewater

2.2.1 Literature survey on ECR of nitrate

ECR is an efficient technology for removing aqueous nitrate from water and wastewater. It includes using an electric current and electrodes to help nitrate ions (NO_3^-) get reduced to nitrite, ammonia, nitrogen gas (N_2) or other reduced nitrogen molecules.

As described in research work of Chauhan & Srivastava (2019), the nitrogen oxidation states for NH_3, N_2H_4, NH_2OH, N_2, N_2O, NO, NO_2^- (nitrite), N_2O_4 (dinitrogen tetroxide), and NO_3^- are, respectively, - III, - II, - I, 0, + I, + II, + III, + IV, and + V. N_2 is the most stable zero oxidation state out of these oxidation states, whereas ammonia has the most reduced state (-III) and nitrate has the highest oxidation state (+V). It is quite challenging to reduce nitrate ions to their most stable zero oxidation state. The study of NO_3 reduction using the electrochemical method has drawn more interest. Some published studies on ECR of nitrate are reviewed as under.

Li et al. (2016) studied iron (Fe) cathode compared to copper (Cu), aluminium (Al) and nickel (Ni) with Ti/TiO_2 nanotube array anode for electrochemical reduction of nitrate in an undivided as well as divided cells. The Fe electrode produced a greater nitrate conversion efficiency of 91% than the Al (78%), Cu (60%) and Ni (36%) electrodes in 4hr electrolysis time at 15mA/cm^2 in the undivided cell. Ammonia was generated at a rate of 28% with the Fe cathode, compared to 33, 36, and 25% with Al, Cu, and Ni cathodes, respectively. Fe cathode in a divided cell, gave greater nitrate conversion efficiency of 99.78% than nitrate removal in an undivided cell (84.3%) in 2.5hr at 15mA/cm^2. Nitrate reduction improved with an increase in current density from 5 to 20 mA/cm^2 the generation of ammonia was enhanced at higher current density because of predominance of N-H bond generation rather than N≡N.

X. Li et al. (2021) investigated charcoal block as cathode and IrO_2RuO_2/Ti as anode for electro-reduction of nitrate to achieve selectivity towards ammonia in an undivided cell. Nitrate conversion rate and ammonia selectivity achieved was 91.2% and 96.0%, respectively, at the ideal potential of 3.6 V. Higher initial nitrate concentration (500mg/L) didn't give promising nitrate removal (55.2%) and selectivity towards ammonia (64.4%) whereas 20 and 110 mg/L initial nitrate concentrations gave similar nitrate removal (>90%) and ammonia selectivity (94-96%) in 2hr of reaction time.

Yin et al. (2019) investigated four composite cathodes: graphite plate (GP), reduced graphene oxide/graphite plate (rGO/GP), copper nanoparticles/ graphite plate (Cu/GP) and Cu/rGO/GP, and graphite as anode for nitrate reduction in a divided cell. Nitrate reduction using GP, GO/GP, and Cu/GP Cu/rGO/GP was 23.27%, 41.12%, 82.79% and 96.86% respectively. As compared to GP, GO/GP, and Cu/GP electrodes, respectively, the response rate constant of the Cu/rGO/GP electrode was 14.08, 8.00, and 1.94 times greater, giving N_2 as the main product. The Cu/rGO/GP electrode's voltammogram profile was comparable to that of the first cycle after 50 scanning cycles, and the percentage of nitrate removal remained at 92.4% after the eighth application, proving the composite electrode's greater stability.

Yao et al. (2021) investigated a copper phosphide self-supported copper foam (Cu_3P/CF) as cathode and Ir-Ru/Ti as anode for ECR of NO_3 in an undivided cell. Investigations were conducted to determine the effect of cathodic voltage, initial NO_3 concentration, initial solution pH, and initial Cl concentration on NO_3 reduction. Lower pH and lower NO_3 concentration were favourable for the efficient removal of NO_3 by Cu_3P/CF. With rising initial Cl concentration, the N_2 selectivity rose. After 5 hours of electrolysis with 1500 mg/L Cl at the bias potential -1.2 V (vs. Ag/AgCl), 84.3% of initial 50 mg NO_{3-}N/L was removed with 98.01% selectivity for N_2.

Chauhan & Srivastava (2019) studied the electrochemical treatment of an actual wastewater containing nitrate (NO_3), ammonium ion (NH_4^+), and chloride ions using Fe cathode and Ti/RuO_2 anode in an undivided cell. The major operating parameters investigated were: current density (J=142.86-428.57 A/m^2), wastewater pH (4–12), and duration (t=15–180 min). The effectiveness of removing TN rises as the applied current density rises. After 180 minutes, NO_3 and TN removal efficiency was 27% and 24% at J=428.57 A/m^2 whereas NO_3 and TN reduction efficiency was 46% and 50% at J=214.29 A/m^2. The elimination of TN and the decrease of nitrate were both shown to be affected by pH. At pH 10 the final nitrate reduction efficiency was 37%, and the TN removal efficiency was 50%.

Gayen et al. (2018) studied Pd-Cu and Pd-In deposited on reactive electrochemical membranes (REMs) as cathodes and REM as anode for electrochemical NO_3^- removal in flow-through mode. Pd loaded with Cu or In was in a 2:1 ratio. Flow-through mode – anode-cathode (43%) flow mode gave more nitrate reduction than cathode-anode (20%) flow mode as H_2 evolution inhibited nitrate reduction in cathode-anode flow mode and in comparison, to the Pd-In/REM, which consistently showed stronger selectivity towards NO_2^- and NH_3, the Pd-Cu/REM exhibited a more favourable product selectivity for both flow modes in 120min reaction time. Nitrate reduced was completely converted to N_2.

Yang et al. (2017) reported nitrate reduction using different Cu-Zn oxides composite cathodes (Ti/CuO, Ti/Cu_5ZnO_x and Ti/$CuZn_5O_x$) and Ti/RuO_2-IrO_2 anode in divided cell separated by Ultrex CMI 7000 membrane. The Ti/Cu_5ZnO_x surpasses the other two materials as after 6hrs of electrolysis at 20 mA/cm^2, the nitrate removal efficiency was 92.3% with maximum N_2 selectivity (33.7%) whereas Ti/CuO and Ti/Cu_5ZnO_x gave 90% and 92% nitrate reduction with almost entire conversion into ammonia. The N_2 selectivity of Ti/$CuZn_5O_x$ is independent of the current density, as minor change was observed from 5 to 20 mA/cm^2, ranging from 14.1% to 17.8%. On the other hand, at current densities of 10 to 20 mA/cm^2, selectivity increases from 17.8% and 12.6% to 36.5% and 28.0%, indicating that the N_2 generation on the Ti/Cu_5ZnO_x and Ti/CuO strongly depends on the current density.

Beltrame et al. (2020) studied electrocatalytic nitrate reduction in a divided cell using palladium-loaded alumina pellets placed in a bag next to a copper plate cathode, and Ti/$70TiO_2 \cdot 30RuO_2$ as an anode. Alumina pellets loaded with varied amounts of Pd (1%, 2.5%, and 5%) were assessed. Nitrate removal was 59% using 1% wt. Pd=alumina pallets with ammonia as a major product. The selectivity to gaseous nitrogen products was independent of palladium loading. In light of this finding, Pd alumina pellets containing 2.5 % wt. Pd was a promising option to get strong selectivity to gaseous chemicals. At 1.1mA/cm^2 and 1.5mA/cm^2 current densities with 2.5% wt. Pd-alumina pellets and pH 6.0–6.5, nitrate reduction was 28% and 49%, resulting in 40% and 35% ammonia and 58% and 64% N_2 production, respectively.

Ye et al. (2020) reported the use of a composite particle in which cobalt (Co) as a catalyst, active carbon (AC) served as the carrier and acetylene black (AB) served as a composite particle (Co/$AC_{0.9}$-$AB_{0.1}$) in an undivided cell containing Ti mesh as cathode and Ti/RuO_2 mesh as an anode. The electro-reduction of nitrate was best suited at neutral pH, while very acidic and alkaline environments significantly reduced the reduction efficiency. The concentration of TN in the effluent reduced from 16.5 to 1.8 mg/L and energy consumption rose from 1.5 to 3.1 kWh/(gN) when the current increased from 0.1 to 0.4A. As the applied current increased, the nitrate gained additional electrons from the particle electrodes on the cathode side, allowing for direct reduction. However, no additional TN removal beyond that obtained at 0.4 A was observed when current was increased to 0.5 A. They concluded that at 0.4 A current, a pH of 7, and a hydraulic retention time (HRT) of 60 min, 95% of the TN was removed.

Zhang et al. (2016) reported the removal of nitrate in the absence and presence of catalyst Pd–Cu/γAl_2O_3 by electrochemical (EC) and electrochemical catalytic (ECC) reactions. The ECC system enhanced nitrate reduction by 2.5 times as compared to EC system. When the current density increased from 2 mA/cm^2 to 15 mA/cm^2, the nitrate conversion rates of the EC system remained at relatively modest levels of 0.20-0.51 mg/L min. Ammonia (65%) was the principal byproduct in the EC system. On the other hand, the ECC system with a suitable current density of 10 mA/cm^2 and 1g/L catalyst dose had a higher nitrate removal rate of 1.08 mg/L min and the nitrogen selectivity was about 80.37%. This was because there was a coupled catalytic reduction of nitrate with the proper amount of in situ hydrogen produced by electrolysis as a reductant.

2.2.2 Findings from the Literature

The salient findings from literature review of electrochemical reduction (ECR) of nitrate are as under. :

(1) Numerous investigations have shown that ECR can remove nitrate effectively, frequently at levels above 90%. Direct conversion of nitrate ions into nitrogen gas or other reduced nitrogen species is made possible by the electrochemical method.

(2) The effectiveness of nitrate removal is significantly influenced by several variables, such as current density, initial nitrate concentration, inter-electrode distance, electrolyte, the presence/absence of a catalyst, and electrode material.

(3) For the elimination of nitrate, studies have evaluated the effectiveness of immobilized and plane cathodes. Due to the improved catalytic activity and selectivity, immobilized cathodes have demonstrated greater nitrate reduction efficiencies than the plane/unmodified cathodes.

(4) The effectiveness and selectivity of electrochemical reduction for the elimination of nitrate are greatly improved by catalysts. In comparison to non-catalytic systems, the inclusion of a catalytic material greatly increases the nitrate reduction efficiency.

(5) The effectiveness of nitrate reduction is influenced by the catalyst loading quantity on the electrode surface. The long-term performance of the catalyst depends on its stability and toughness. Supported catalysts and nanostructured materials have demonstrated remarkable results in the catalytic ECR of nitrate. These catalysts have good stability and resilience to deactivation.

(6) ECR requires an external power supply, making it an energy-intensive operation. However, by choosing appropriate electrode materials, optimization of variables, and considering the entire system design, energy consumption may be optimised. Higher current densities and less energy use in catalytic ECR systems have led to better nitrate removal rates.

(7) The positive side effect of ECR is that it may transform nitrate into inert nitrogen gas or other reduced nitrogen species, reducing waste production or the requirement for chemical regenerants.

According to our knowledge, there are no reports illustrating the impact of noble metal spatially suspended catalysts in the cathode compartment, such as silver, on nitrate removal. Also, no reports have been reported describing the use of a modified cathode (Ti/Co_3O_4) for high nitrate removal in metal-finishing wastewater by the ECR process. The purpose of the current work was to explore the removal of aqueous nitrate using electrochemical reduction (ECR), in the presence of the spatially suspended noble metal catalyst and unmodified or modified cathodes.

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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 colourimetric 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 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.

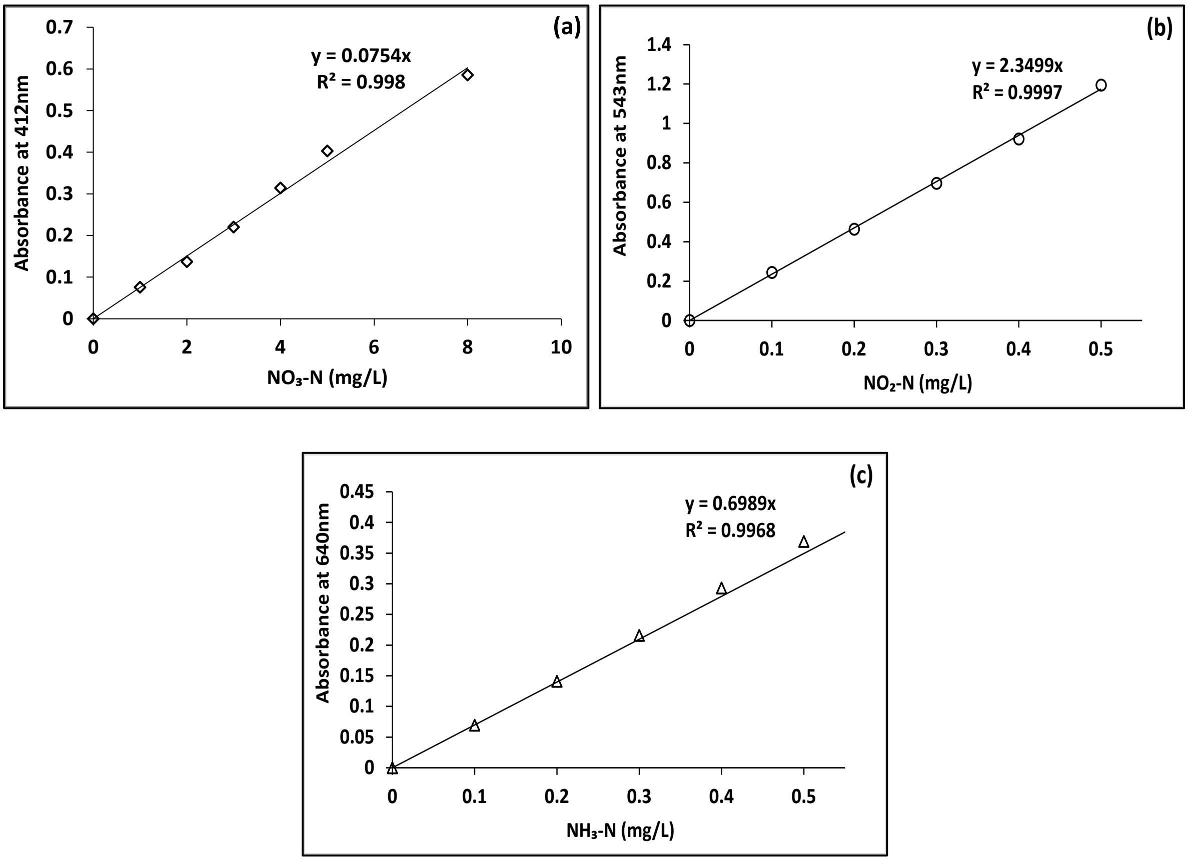

Figure 2 : Calibration plot of NO_3-N (a), NO_2-N (b) and NH_3-N (c)

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 3a 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, as shown in Figure 3b 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 carried out by SEM and EDAX analyses.

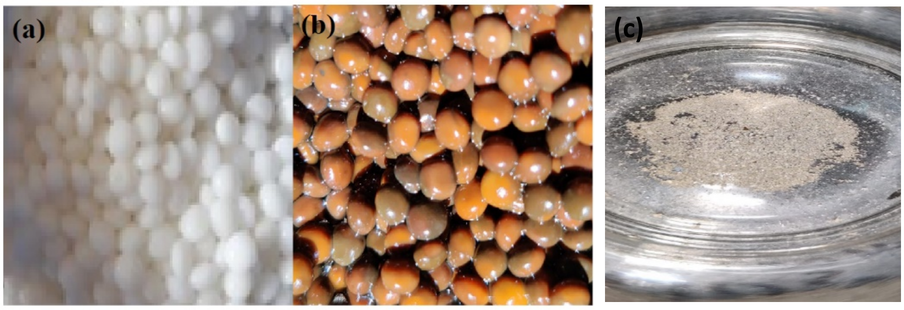

Figure 3: Fresh PVA beads (a), Ag coated on PVA beads (b), and AgMPs (c)

3.3.1.2 Preparation of Ag-MPs

Figure 3c shows as-prepared 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.

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

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

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.

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 4) 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.

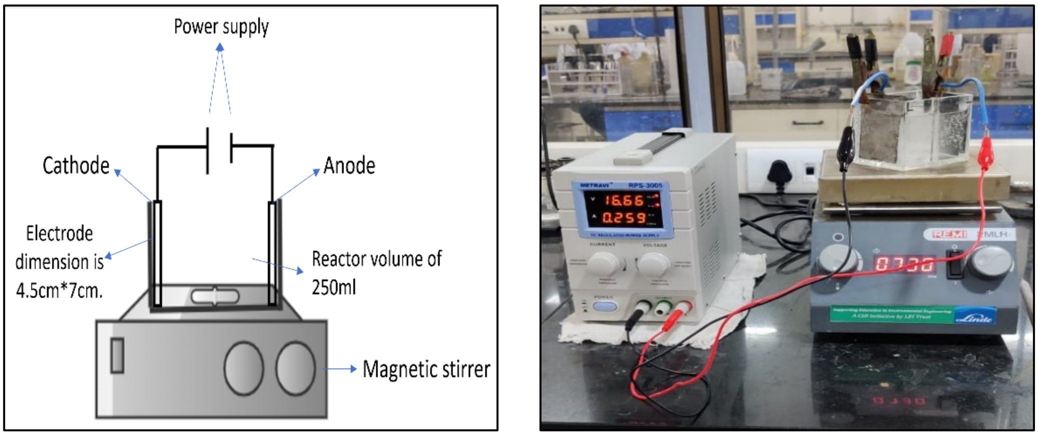

Figure 4: Experimental setup in an undivided cell

3.3.2.2 Nitrate Reduction in a divided cell

A polyacrylic cell (Figure 5) 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.

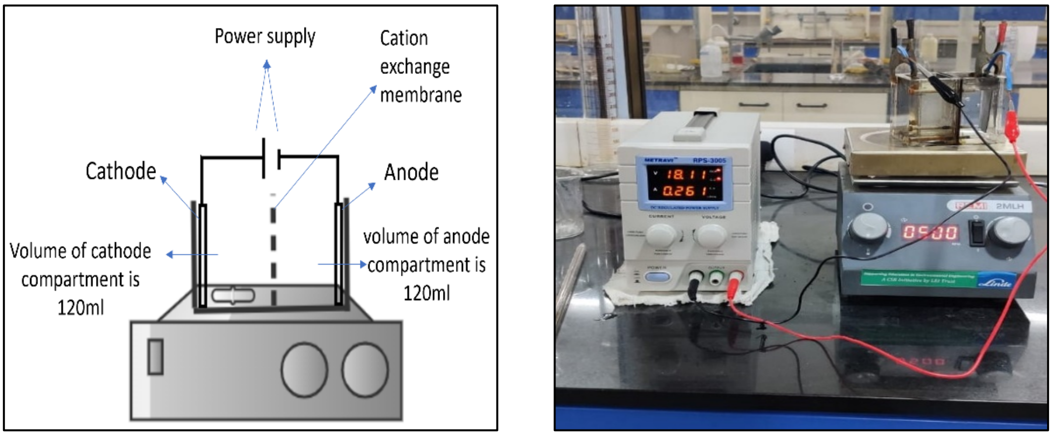

Figure 5: Experimental setup in a divided cell

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 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 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 utilised 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).

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

NO_3-N removed = *initial NO_3-N (mg/L) * NO_3-N removed (mg/L) * Volume of NO_3-N solution(L)* *Equation 2*

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

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.

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

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 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 Na2SO4 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_2^{3-}, 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 2: 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				

	Cathode : Ti	Reaction conditions: 120mL of NO_3-N solution as catholyte, 120mL of 2g/L Na_2SO_4 as anolyte, reaction time: 120min, current density: 10mA/cm^2, AgMPs: 8mM			
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_2SO_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_2SO_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.

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CHAPTER 4: RESULTS AND DISCUSSIONS

In this chapter, results and discussions of numerous experiments carried out throughout the investigation are included. The outcomes of ECR of nitrate using spatially suspended Ag-PVA beads in an undivided cell, as well as divided cell, and the effects of various operational parameters including catalyst concentration, cathode material, current density, initial nitrate concentration, and reusability of Ag-PVA beads studied in the divided cell, are discussed in Section 4.1. The results of ECR of nitrate using spatially suspended AgMPs in undivided and divided cells and the effects of various operational parameters including catalyst concentration, inter-electrode distance, cathode material, initial nitrate concentration, oxidation of ammonia at anode in divided cell and reusability of AgMPs in divided cell are shown in Section 4.2. The involvement of catalysts (Ag-PVA beads and AgMPs) in the production of intermediates and the mechanism of ECR of nitrate are covered in Section 4.3. The outcomes of ECR of nitrate in real water (groundwater) are described in Section 4.4. The removal of high nitrate concentration from simulated metal finishing wastewater using Ti/Co_3O_4 electrode by ECR process and the effects of different parameters including initial nitrate concentration, current density, and reusability of Ti/Co_3O_4 are described in section 4.5. Additionally, section 4.5 includes results of struvite formation and the effect of the molar ratio of Mg:NH_4:PO_4 on struvite formation. Lastly, 4.6 includes references used in this chapter.

4.1 ECR of Nitrate using Ag-PVA beads as a spatially suspended catalyst

The morphological study of Ag-PVA beads was carried out using SEM and EDAX. Experiments were conducted in undivided as well as divided cells. This section represents the results of nitrate reduction in undivided cell and divided cell and the effects of various parameters in divided cell.

4.1.1 Morphological study of Ag-PVA beads

The SEM analysis of a cross-section of an Ag-PVA bead is shown in Figure 6. It may be seen from Figure 6 that most of the silver metal particles were deposited on the bead's surface, which is discernible as a dazzling outer layer. Additionally, the silver layer's thickness is constant across the whole surface indicating uniform deposition. The related EDAX analyses of a whole bead and a close-up of its periphery are shown in Figures 7(a) and 7(b), respectively. The silver content of the bead is extremely low throughout (Figure 7a), and it virtually doubles in the close-up view of the peripheral portion. This shows that the majority of the silver metal particles are immobilised on the sphere's surface and are therefore easily accessible for the catalytic process.

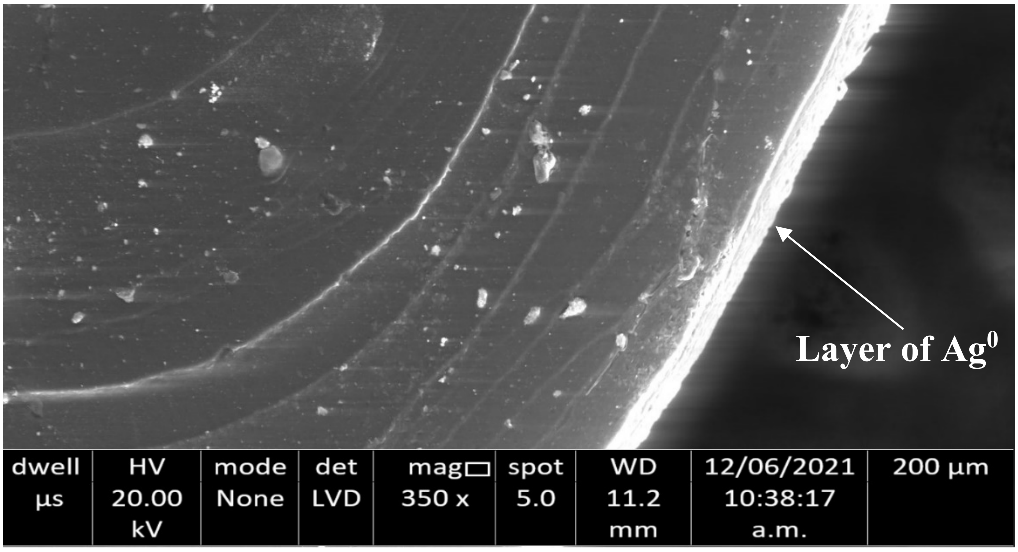
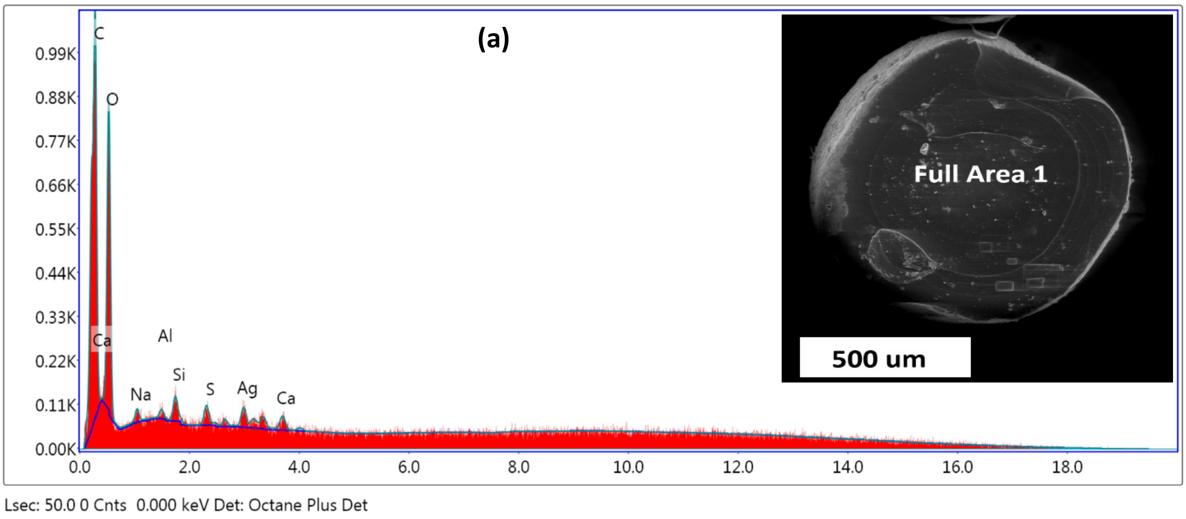


Figure 6 : SEM analysis of Ag-coated PVA bead



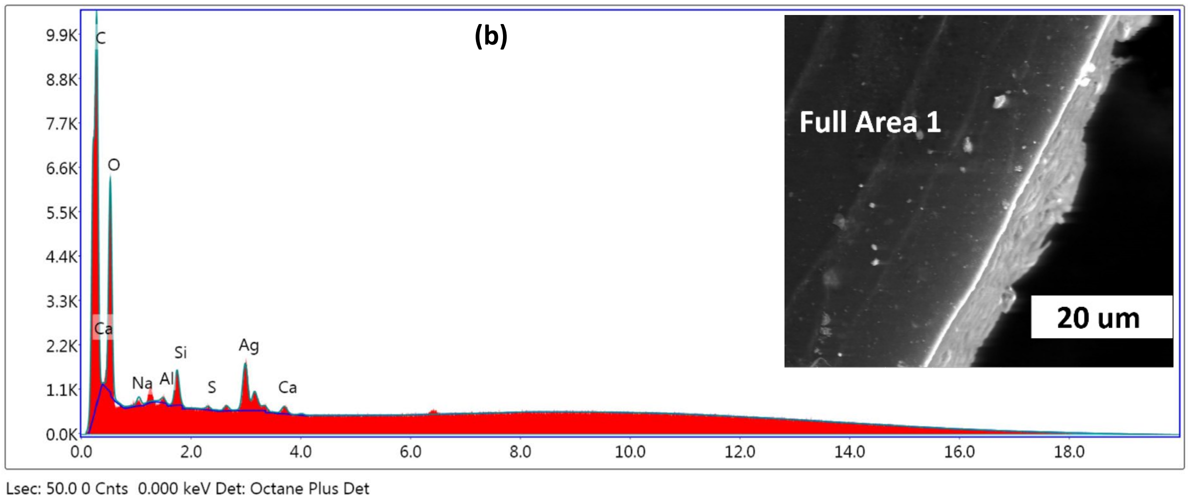


Figure 7 : EDAX spectra of Ag-PVA bead (a), and Ag coated on the surface of PVA bead (b). The inset pictures show the respective SEM images.

4.1.2 Nitrate removal in an undivided cell

Figure 8 shows NO_3-N reduction in an undivided cell with Fe as the cathode and Gr as the anode at a current density of 15 mA/cm^2 in both the absence and presence of 6.67mM Ag-PVA beads. There was no evidence of TN elimination in the undivided cell since the nitrate reduction was just 13%, with the end-products being 8% NH_3-N and 5% NO_2-N. Yet, in the presence of Ag-PVA beads, 28% of the original nitrate was eliminated, producing NH_3-N as the final by-product. It was significant to notice that the brown colour of the Ag-PVA beads diminished when introduced to an undivided cell, most likely as a result of the oxidation of the Ag metallic particles on the beads. Thus, the removal of nitrate in an undivided cell was low irrespective of the presence or the absence of Ag-PVA beads.

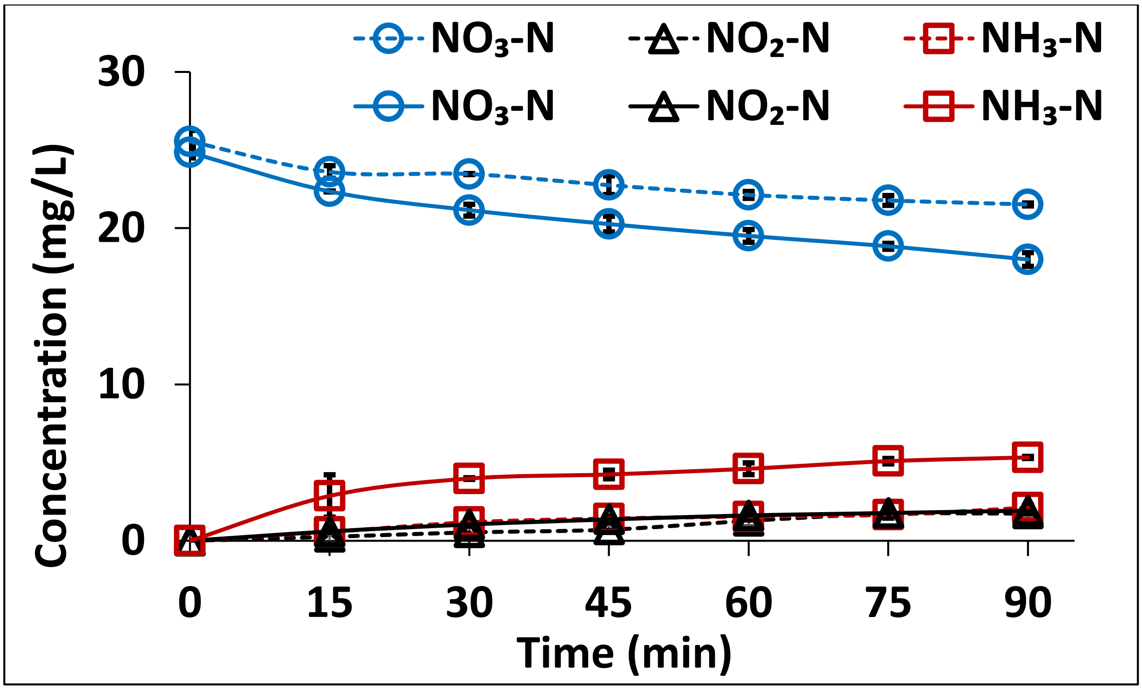


Figure 8 : Undivided cell - Time course profile of NO_3-N removal in the absence (dotted line) and presence (solid line) of Ag-PVA beads

(Reaction conditions: cathode: Fe, anode: Gr, NO_3-N: 25mg/L, Na_2SO_4 as electrolyte: 2g/L, Ag-PVA beads: 6.67 mM, current density: 15mA/cm^2, reaction time: 90min)

The published research reports that nitrate removal in undivided cells is much lower than that in divided cells. For instance, Dash & Chaudhari (2005) reported that after a 9-hour reaction at 140 mA/cm^2 current density, the reduction of nitrate in an undivided cell utilising Gr electrode was restricted to 8%. According to Ding et al. (2015), the removal of nitrate from an undivided cell was about 7 times lower than that of a divided cell. Further research was carried out utilising a divided cell due to the ineffectiveness of nitrate reduction in an undivided cell.

4.1.3 Nitrate removal in a divided cell

The results of nitrate reduction utilising Fe cathode and Gr anode in a divided cell in the absence and presence of Ag-PVA beads are shown in Figure 9. Both in the absence and presence of Ag-PVA beads, the nitrate elimination followed the 1st-order reaction kinetics. It should be emphasised that the nitrate reduction rose to 85% in the presence of 6.67mM Ag-PVA beads as opposed to 70% in the absence of beads. Although this improvement in removal was rather little, it is crucial to remember that the TN removal climbed to 52% as opposed to

16% in the absence of beads. Hence, the addition of beads boosted the selectivity towards nitrogen synthesis as well as enhanced the nitrate reduction.

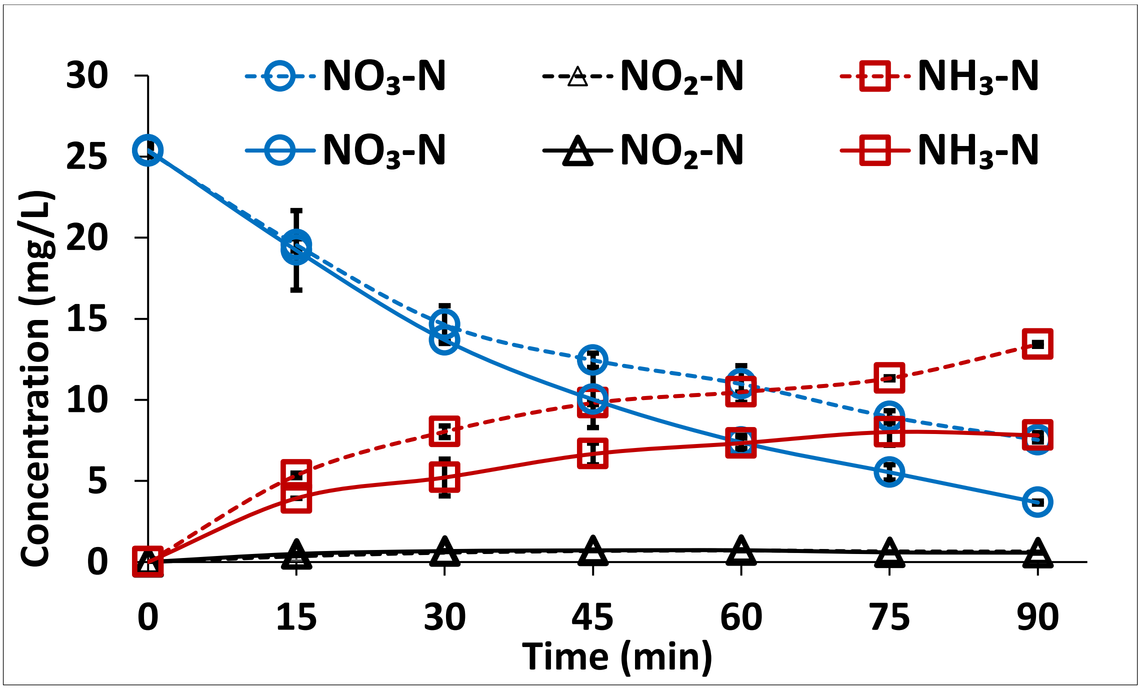


Figure 9 : Divided cell - Time course profile of NO_3-N removal in the absence (dotted line) and presence (solid line) of Ag-PVA beads

(Reaction conditions: cathode: Fe, anode: Gr, NO_3-N: 25mg/L, Na_2SO_4 as electrolyte: 2g/L, Ag-PVA beads: 6.67 mM, current density: 15mA/cm^2, reaction time: 90min)

According to Zhang et al. (2016) , in a divided cell ammonia was the main product of nitrate reduction in the absence of a catalyst but the inclusion of a Pd-Cu/-alumina catalyst changed the selectivity towards N_2. Due to greater nitrate removal and greater selectivity toward the formation of nitrogen, further studies were conducted in the divided cell in the presence of Ag-PVA beads.

Lei et al. (2022) investigated electro reduction of nitrate using silver surface. Authors coated Ag on a ZnO (zinc oxide) nano wall, and they achieved 66% of nitrate reduction at -0.6V applied potential. The distinct surface-enhanced Raman signals (SERS) of N=O, HNH, and NH_3 showed that nitrite, ammonia, and nitrogen were produced at the end.

4.1.3.1 Effect of concentration of Ag-PVA beads

Table 3 displays the impact of different catalyst concentrations on the nitrate reduction, the mass activity of the catalyst (mg NO_3-N removed per g Ag per min), and selectivity towards NO_2-N ($S_{NO_2\text{-}N}$), NH_3-N ($S_{NH_3\text{-}N}$), and N_2-N ($S_{N_2\text{-}N}$) in a divided cell. The catalyst concentrations are 5, 6.67, and 8.33 mM (≈ 730 Ag-PVA beads). Figure 10 describes nitrate removal and end-products generated at 15mA/cm^2 current density for 90min reaction time. It may be noted that that using 5 and 8.33mM Ag-PVA beads, the nitrate reduction was 77 and 70%, respectively, while using 6.67mM Ag-PVA beads, the maximum reduction of 85% was attained. It's noteworthy to observe that the selectivity of the final products was also impacted by the catalyst concentration. The selectivity for N_2-N production was lowest (19.4%) and greatest (78%) in the presence of 5 and 6.67 mM Ag-PVA, respectively. While the mass activity was somewhat lower at 6.67 mM Ag-PVA than at 5 mM, the selectivity for the production of N_2-N was highest and that for NH_3-N was lowest (62.1 and 37.7%, respectively). As a result, 6.67mM Ag-PVA beads were chosen as the ideal dosage for further research.

Beltrame et al. (2020) investigated electrochemical nitrate removal using Pd-coated alumina pellets as a catalyst with various Pd contents (1%wt. Pd, 2.5%wt. Pd, and 5%wt. Pd loaded pellets). According to the authors, nitrate removal dropped from 59% at 1% wt Pd loading to 50% at 5% wt Pd content.

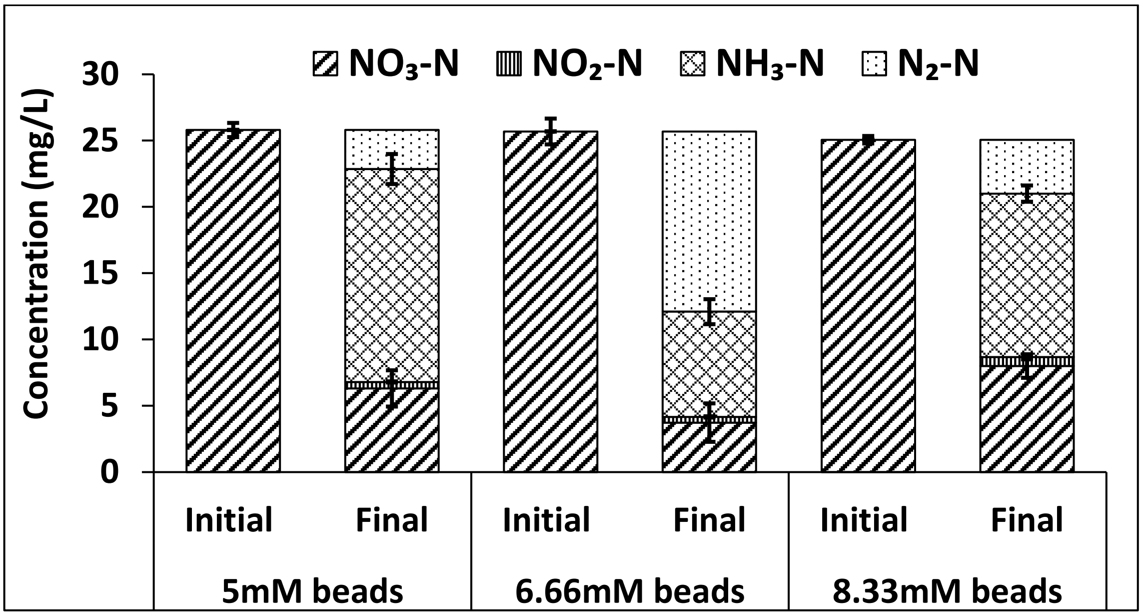


Figure 10 : Removal of NO_3-N with various catalyst concentrations

(Reaction conditions: cathode: Fe, anode: Gr, NO_3-N: 25mg/L, Na_2SO_4 as an electrolyte: 2g/L, current density: 15mA/cm^2, reaction time: 90min)

Table 3: Effect of Ag-PVA catalyst dose on nitrate reduction and selectivity for end-products

Catalyst Dose	Nitrate conversion (%)	Mass Activity (mg of NO_3-N removed/min /gm of Ag)	Concentration (mg/L)		$S_{NO_2\text{-}N}$ (%)	$S_{NH_3\text{-}N}$ (%)	$S_{N_2\text{-}N}$ (%)
			NO_2-N	NH_3-N			
5mM	77±0.9	0.40	0.48	16.05	2.6±0.7	78.0±1.6	19.4±0.7
6.67mM	85±0.5	0.36	0.43	7.93	1.2±0.9	37.7±1.0	62.1±0.8
8.33mM	70±1.2	0.22	0.69	2.9	2.9±1.6	64.3±0.4	32.9±0.6

Reaction conditions: NO_3-N: 25mg/L, cathode: Fe, anode: Gr, Na_2SO_4: 2g/L as electrolyte, current density: 15mA/cm^2, reaction time: 90 min

* Note: To calculate the selectivity for end-products, nitrate removal (%) is considered to be 100%.

4.1.3.2 Effect of cathode material

For nitrate removal, a variety of materials including SS, Fe, Fe/Sn, Cu, and Ti were employed as cathodes. To examine the simultaneous impact of Ag-PVA beads and the cathode material, experiments were conducted both in the absence and presence of a catalyst. Table 4 shows the details of nitrate conversion with different cathode materials in the absence and presence of 6.67mM Ag-PVA beads, as well as the selectivity for ammonia ($S_{NH_3\text{-}N}$), nitrite ($S_{NO_2\text{-}N}$), and nitrogen ($S_{N_2\text{-}N}$). The cathode material and the presence of Ag-PVA beads have an impact on nitrate removal and selectivity of end-products, as shown in Table 4. Overall, it should be highlighted that the addition of Ag-PVA beads enhanced nitrate removal and nitrogen selectivity.

Table 4: Nitrate conversion with various cathodes and their selectivity after 90min electrolysis

Cathode electrode	Absence of Catalyst				Presence of catalyst			
	NO_3-N conver	$S_{NO_2\text{-}N}$ (%)	$S_{NH_3\text{-}N}$ (%)	$S_{N_2\text{-}N}$ (%)	NO_3-N conver	$S_{NO_2\text{-}N}$ (%)	$S_{NH_3\text{-}N}$ (%)	$S_{N_2\text{-}N}$ (%)

	sion (%)				sion (%)			
SS	47±0.6	10.6±1.9	49.0±0.3	40.4±0.2	65±1.6	9.2±0.5	26.2±0.6	64.6±0.5
Fe	70±0.2	ND	75.7±0.4	24.3±0.4	85±0.8	1.2±0.4	37.7±0.6	62.1±0.2
Fe/Sn	21±0.4	19.1±1.1	80.9±0.9	ND	59±1.7	5.0±0.7	35.6±0.7	59.4±0.5
Cu	70±1.2	5.7±0.5	52.9±0.7	41.4±0.5	75±1.3	9.3±1.4	37.3±0.3	53.4±0.4
Ti	70±0.5	8.6±0.7	54.3±0.6	37.1±1.4	72±1.1	4.1±0.4	51.5±0.4	44.4±0.8

Conditions: NO$_3$-N: 25 mg/L, anode: Gr, Na$_2$SO$_4$: 2g/L as electrolyte, current density: 15 mA/cm^2, Ag-PVA: 6.67mM, reaction time: 90min

Note: To calculate the selectivity for end-products, nitrate removal (%) is considered to be 100%. ND means not detected.

Figure 11 shows the nitrate reduction and generation of nitrite-N, ammonia-N, and nitrogen-N after 90min reaction time in the absence and presence of 6.67mM Ag-PVA beads catalyst at 15mA/cm^2 current density. The extent of nitrate elimination in the absence of Ag-PVA catalyst went as follows: Fe > Ti > Cu > SS > Fe/Sn. In comparison to Fe and Cu cathodes, Cu and Ti cathodes showed stronger selectivity towards nitrite production. When using Fe cathode, nitrite production was minimal.

The Fe cathode produced excellent results for nitrate reduction when Ag-PVA beads were present as well, whereas Fe/Sn produced the least. The nitrate removal in the presence of Ag-PVA beads followed the order: Fe > Ti > Cu > SS > Fe/Sn. The presence of the catalyst with Fe cathode resulted in the lowest conversion to nitrite along with the maximum nitrate removal, and the largest nitrogen gas conversion. Due to the serious health concerns connected with nitrite, the USEPA has set a strict limit of 1 mg/L NO$_2$-N. (ATSDR - Agency for Toxic Substances and Disease Registry, 2013). Thus, Fe was selected as a cathode for further research because it delivered the lowest nitrite formation and the maximum nitrogen gas selectivity in the presence of Ag-PVA beads.

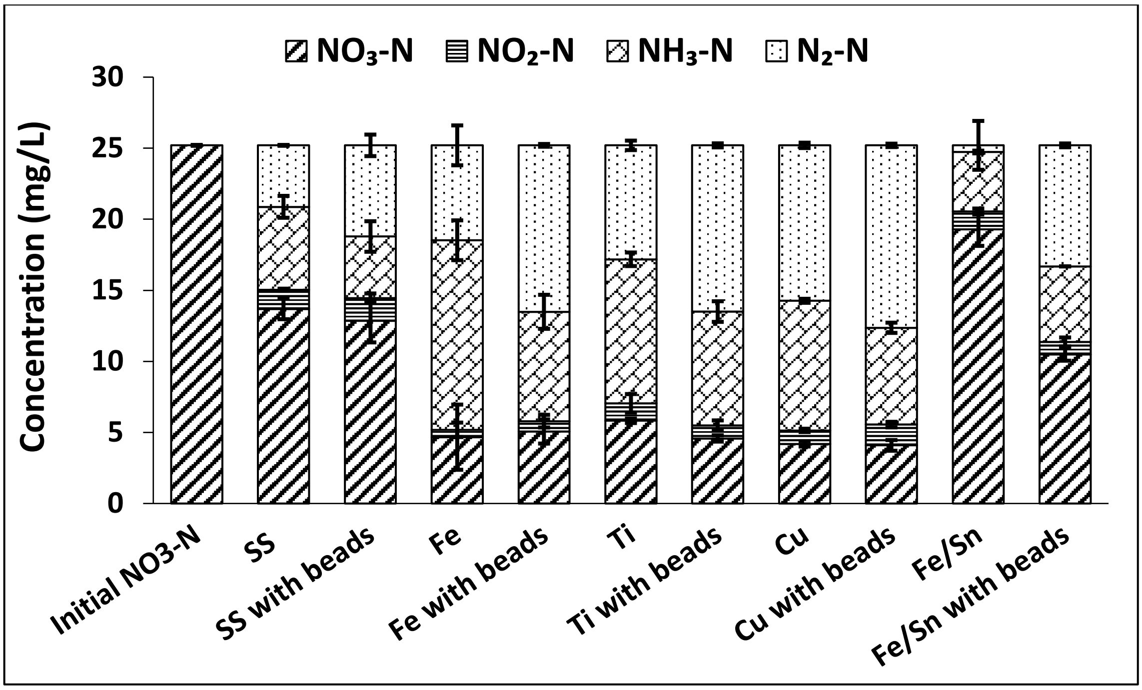


Figure 11 : Nitrate reduction using various cathode materials in absence and presence of Ag-PVA beads

(Reaction conditions: NO_3-N: 25mg/L, 6.67mM Ag-PVA beads, anode: Gr, Na_2SO_4 as electrolyte: 2g/L, current density: 15mA/cm^2, reaction time: 90min)

The published literature has findings on the impact of cathode material that are comparable to our results. For instance, employing a Ni-Cu sponge as the cathode, Beltrame et al. (2020) reported a 44% removal of nitrate with nitrite as the primary result. Moreover, Pérez-Gallent et al., (2017) showed that the Cu cathode increased the generation of nitrite in an alkaline media during the electrocatalytic reduction of nitrate. Li et al. (2016) studied a divided cell with Al, Fe, Ni, and Cu cathodes and a Ti/TiO_2 nanotube array anode, it was discovered that Fe was the most effective cathode among them, reducing nitrate by 91% and being most selective for N_2.

4.1.3.3 Effect of current density

One of the most crucial variables in the ECR process is the current density. As seen in Figure 12, the impact of various current densities, including 5, 10, 15, and 20mA/cm^2, on nitrate removal and the end-product selectivity was investigated. At current densities of 5, 10, 15, and 20 mA/cm^2, respectively, the NO_3-N removal was 74%, 80%, 86%, and 80%, while TN removal was 19, 43, 53, and 42%. Thus, %nitrate removal increased from 74 to 86% with an increase in current density from 5 to 15 mA/cm^2, and slightly decreased to 80% with further increase to 20 mA/cm^2. Moreover, the ammonia accumulation at the end of 90 min was highest at 20 mA/cm^2 current density. The nitrite generation was consistently lower than 1 mg/L, irrespective of the current density variation. According to Lan et al. (2016), when current density increases, hydrogen production at the cathode rises, inhibiting the formation of N≡N bonds and promoting the formation of N-H bonds. Consequently, a 15 mA/cm^2 current density was deemed ideal.

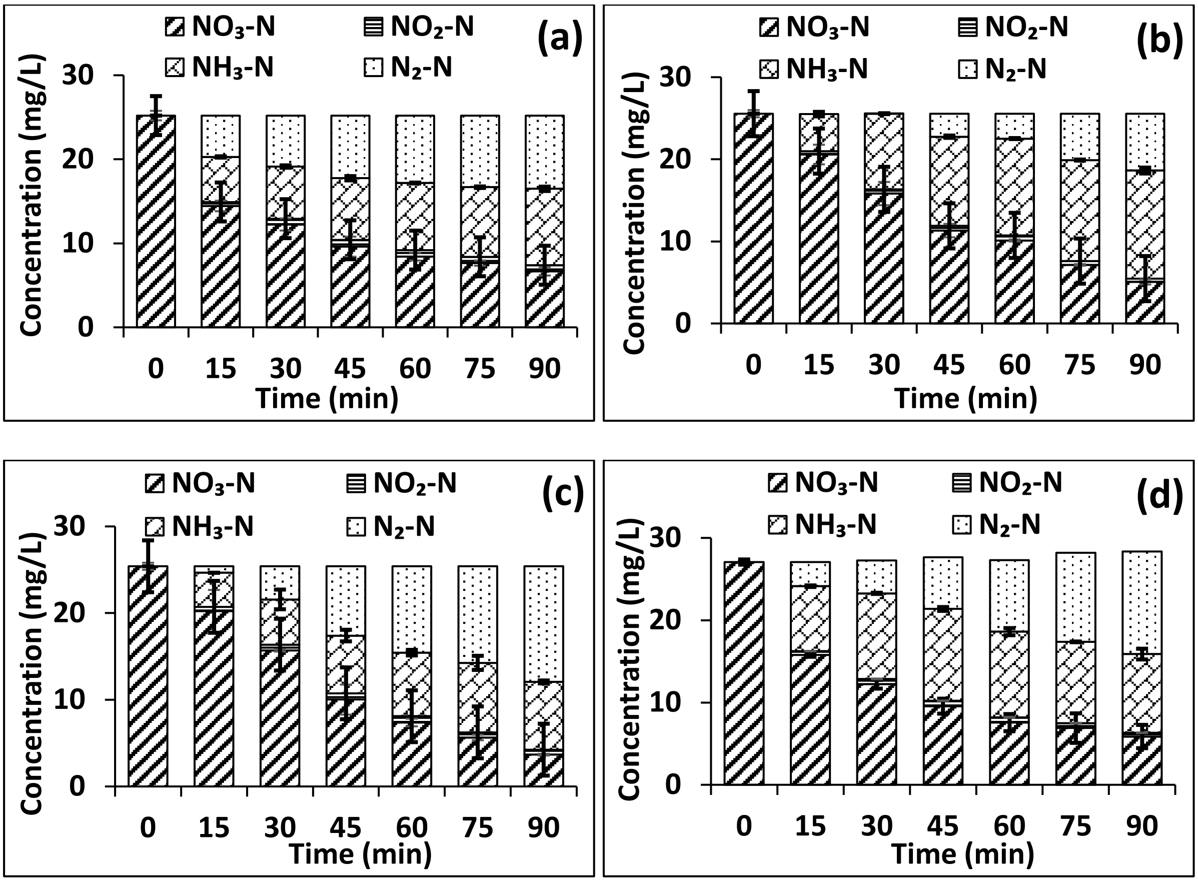


Figure 12 : Effect of current density on nitrate removal (a)5mA/cm^2, (b)10mA/cm^2, (c)15mA/cm^2, and (d)20mA/cm^2

(Reaction conditions: NO_3-N Concentration: 25 mg/L, anode: Gr, cathode: Fe, Ag-PVA: 6.67mM, reaction time: 90 min)

A comparison of the accumulation of end-products at the end of 90 min reaction time at varying current densities is shown in Figure 13. The specific removal of NO_3-N is (mg NO_3-N removed/Ah) is also shown in Figure 13 as an inset. It may be seen that with increasing current density, the specific NO_3-N removal declined almost linearly, most likely due to loss of electrical energy in unfavourable reactions.

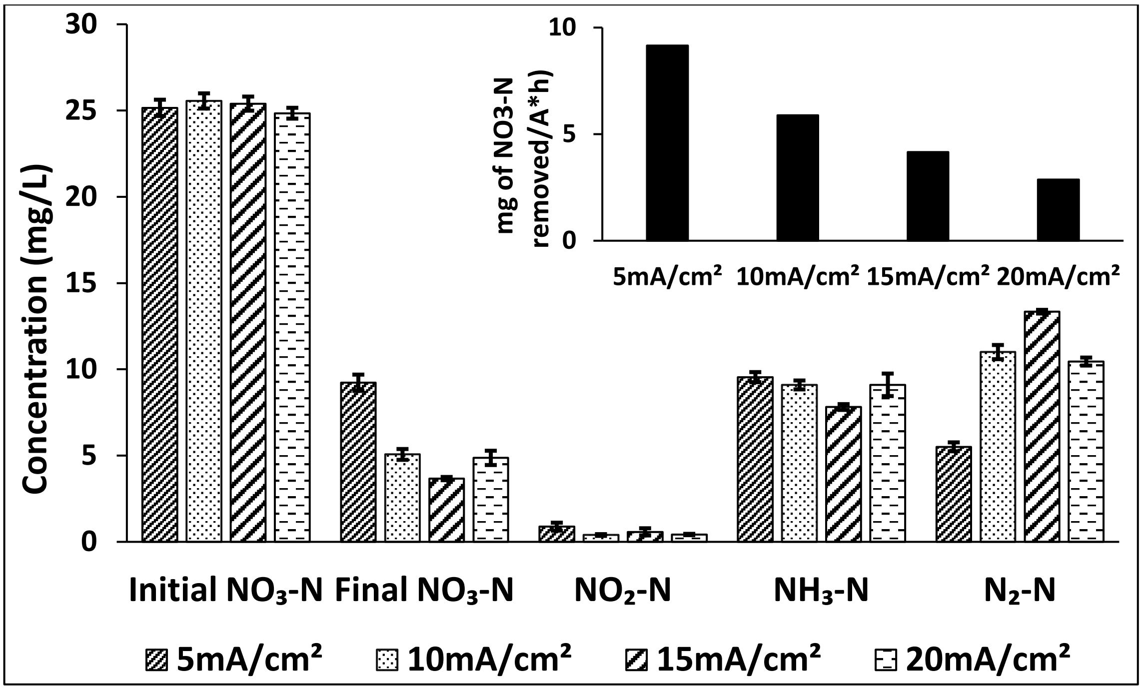


Figure 13 : Effect of current density in the presence of Ag-PVA beads. Inset figure shows specific energy consumption for nitrate removal.

(Reaction conditions: NO_3-N Concentration: 25 mg/L, anode: Gr, cathode: Fe, Ag-PVA beads: 6.67mM, reaction time: 90 min)

4.1.3.4 Effect of the initial nitrate concentration

Figure 14 shows the effects of various initial nitrate concentrations (25, 50, and 100 mg/L) assessed on the reduction of nitrate at a current density of 15 mA/cm^2 in the presence of 6.67mM Ag-PVA beads for 90 minutes of electrolysis time. The nitrate removal was more than 90% for all three initial nitrate concentrations which means it is an independent parameter. However, when the initial nitrate concentration increased, NO_2-N and NH_3-N generation also increased. Thus, the initial nitrate concentration had an impact on product selectivity. According to Su et al. (2017), the end-product selectivity may change when the starting concentration of NO_3-N increases because more electrical energy may be required to decrease NO_3-N to manufacture NH_3-N rather than H_2O to produce H_2.

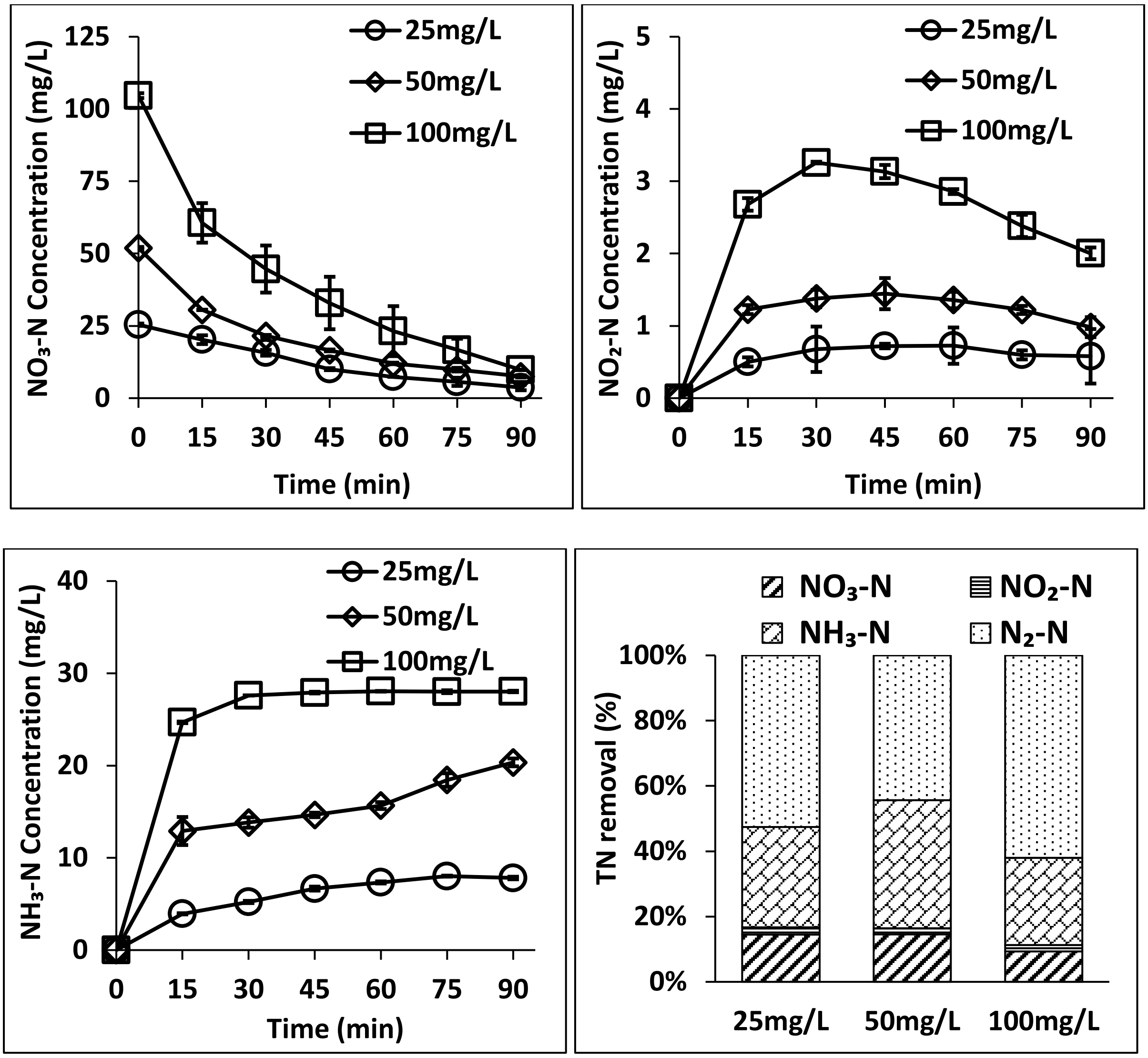


Figure 14 : Effect of initial nitrate concentration

(Reaction conditions: anode: Gr, cathode: Fe, current density: 15mA/cm^2, Ag-PVA beads: 6.67mM, reaction time: 90 min)

4.1.3.5 Reusability of Ag-PVA beads

Catalysts must be reusable to be used on a wider scale. Ag-PVA beads' capacity to be reused for NO_3-N reduction is shown in Figure 15. As can be observed, there was no discernible decline in catalytic activity after 8 consecutive reaction cycles using the Ag-PVA beads. But after 8th cycle, nitrate reduction decreased from 86% to 78% for 9th cycle and 72% for 10th cycle. Also, it was observed that after 10 consecutive reuse, there was negligible change in NO_2-N accumulation (Figure 15b). It's interesting to note that after the eighth cycle, ammonia formation (Figure 15c) became more selective which results in decrease of TN removal (Figure 15d). Ag layer sloughing was not noticed. However, it was found that the dark brown colour of the Ag-PVA beads lightened to light brown as the number of reuses increased. This may be related to the oxidative degradation of Ag. Zhao et al. (2021) tested a Cu nanoparticle cathode modified with nitrogen-doped porous carbon for electrochemical removal of nitrate, and they found that the stability of cathode was for 5 cycles of the process.

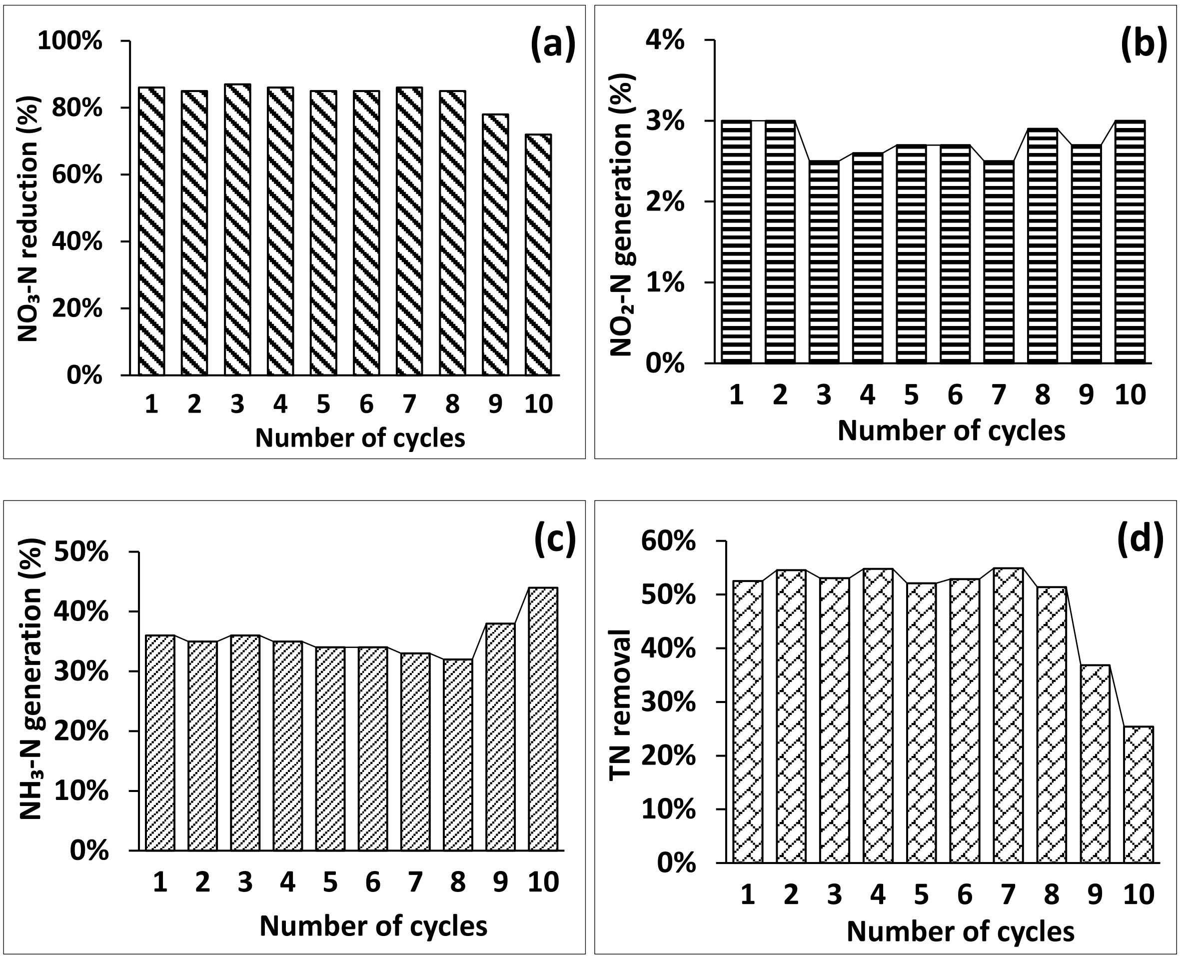


Figure 15 :Reusability of Ag-PVA beads

(Reaction condition: cathode: Fe, anode: Gr, NO_3-N: 25 mg/L, reaction time: 90 min, current density: 15 mA/cm^2, Ag-PVA: 6.67mM)

Following are the salient observations from section 4.1:

1. SEM and EDAX confirmed the proper coating of silver (Ag) on polyvinyl alcohol beads (PVA).
2. Presence of Ag-PVA beads in an undivided as well as divided cell enhanced nitrate reduction. Not only nitrate reduction but selectivity was also changed in the presence of a catalyst.
3. The concentration of Ag-PVA beads also played an important role in nitrate reduction.

4. Fe cathode gave prominent results among other cathode materials in the presence of a catalyst resulting in nitrogen gas as the maximum by-product.
5. Increasing current density was favourable for an increase in nitrate reduction up-to some point as further increasing changed the selectivity.
6. Increasing initial nitrate concentration gave almost similar nitrate reduction but had an impact on selectivity.
7. The reusability of Ag-PVA beads was good enough.

4.2 ECR of Nitrate using AgMPs

The morphological and crystallography study of AgMPs was carried out using SEM and XRD. In both undivided and divided cells, experiments were carried out. The findings of nitrate reduction in undivided and divided cells, as well as the impacts of different parameters in divided cell, are discussed in this section.

4.2.1 Morphological study of AgMPs

The morphological analysis was done by SEM. Two distinct magnifications of the SEM images of fresh and used AgMPs are shown in Figure 16. It was discovered that AgMPs of different sizes were polydisperse. . It may be seen that the AgMPs are highly aggregated particles with sizes ranging from as low as 0.05 mm (Figure 16a and 16c) to as large as 0.4 mm (Figure 16b and 16d).It should be observed that the morphology of fresh and used AgMPs has not significantly changed. Initially, the particles formed were in nanometre size. However, deliberately promoting the agglomeration of these nanoparticles to form larger Ag metal agglomerates that can be easily separated from the reaction medium by gravity settling. The SEM images of AgMPs used in our study (Figure 16) shows that the particle size ranges from 50 to 400 micron. We also confirmed the size of AgMPs by settling velocity calculations using Stoke’s law and found that the particles were ≥30 micron in size.

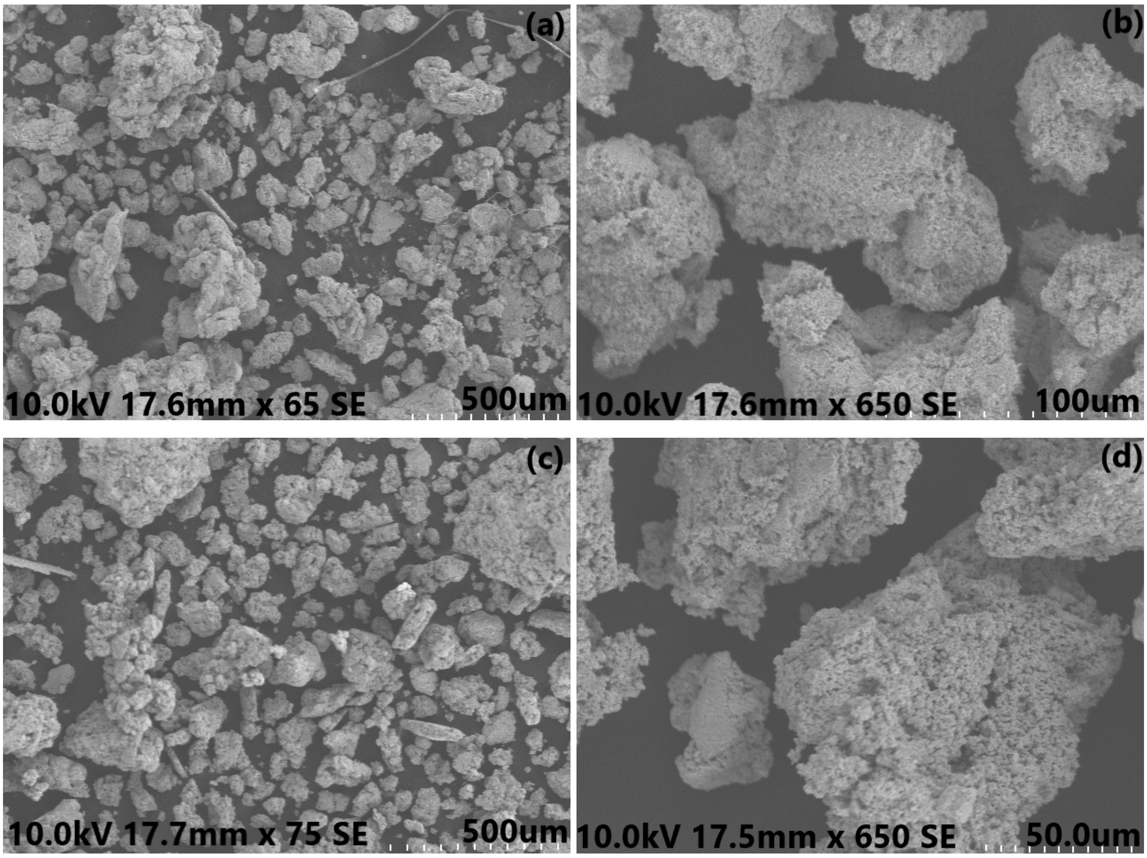


Figure 16 : SEM analysis of fresh AgMPs (a) and (b); used AgMPs (c) and (d)

4.2.2 Crystallographic study of AgMPs

The XRD analysis of both fresh and used AgMPs is shown in Figure 17. A chemical reduction procedure efficiently synthesised pure silver metal particles, according to an XRD examination. Peaks were found for both samples at 38, 44, 64, and 78 degrees, which match the facets of the crystal planes' Braggs reflections (111), (200), (220), and (311) at 2θ (degree). According to JCPDS file No. 04-0783, these peaks match the face-centred cubic (fcc) structure of silver. Additionally, tiny peaks were discovered in the examination of used AgMPs and are indicated in Figure 17 with "*". These peaks supported the creation of a minor quantity of Ag_2O in the used AgMPs, according to JCPDS file No. 12-793 and Ng et al. (2016).

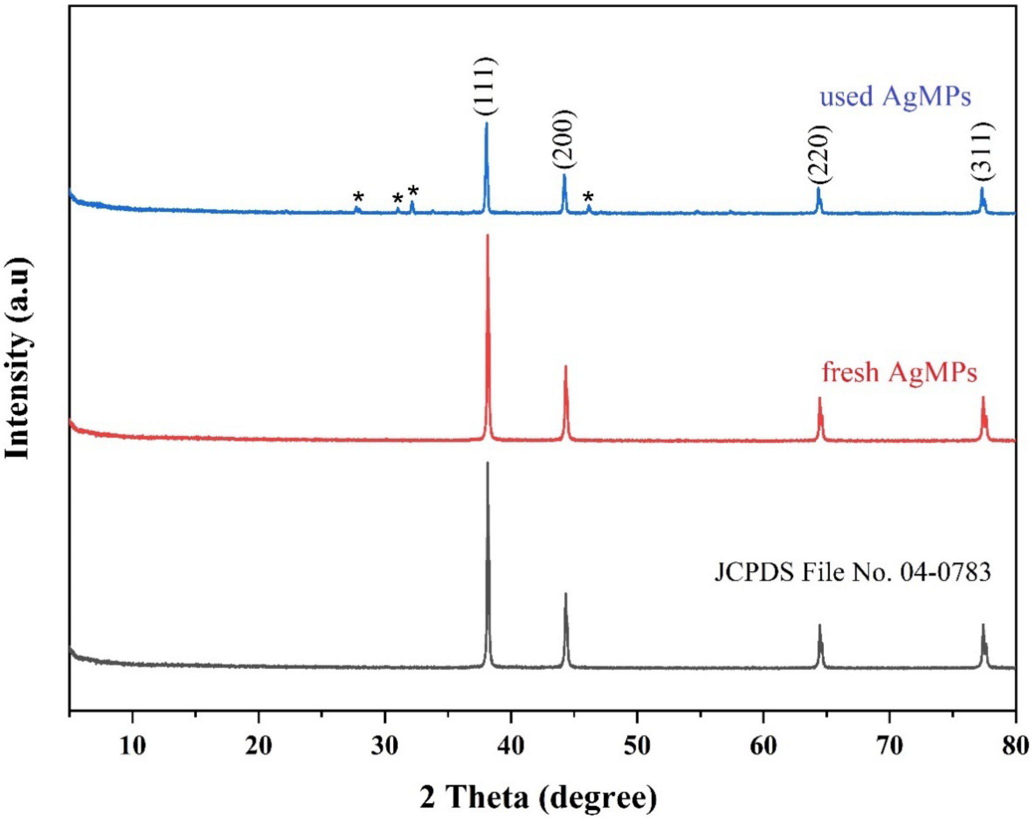


Figure 17 : XRD analysis of fresh and used AgMPs

Table 5 and 6 shows the size of silver crystallites using Scherrer's equation. Since the AgMPs were required to be finely ground for XRD analysis, the size of particles depicted in Table 1A and 1B is smaller than that determined by SEM analysis. Nevertheless, it proves that AgMPs are agglomerated particles.

X-ray diffraction (XRD) was used to detect the purity, crystalline nature, and particle size of synthesized silver particles. The particle size of the fresh and used AgMPs were calculated by using Scherrer's equation (1) as follows:

$$D = \frac{K\lambda}{\beta\ (\frac{1}{2})\ cos\ \theta} \qquad \textit{Equation (1)}$$

where D is average crystallite size and β is line broadening in radians (full width at half maximum of the peak in radians). λ is wavelength of X-ray and θ is Braggs angle. K is constant (geometric factor = 0.94)

Table 5 and 6 described the Full width at half maximum (FWHM) and crystal size of fresh and used AgMPs at different angles.

Table 5 : Full width at half maximum (FWHM) and size calculation of fresh AgMPs

Sr. No.	2θ (degree)	d-spacing (Å)	FWHM (°)	Size (nm)
1.	38.14	2.35	0.09	91.72
2.	44.32	2.04	0.12	71.06
3.	64.45	1.44	0.11	83.81
4.	77.40	1.23	0.14	75.77

Table 6 : Full width at half maximum (FWHM) and size calculation of used AgMPs

Sr. No.	2θ (degree)	d-spacing (Å)	FWHM (°)	Size (nm)
1.	33.80	2.64	0.10	82.04
2.	38.04	2.36	0.12	71.19
3.	44.22	2.04	0.13	65.95
4.	46.16	1.96	0.11	79.25
5.	64.35	1.44	0.12	78.50
6.	67.31	1.38	0.14	70.99
7.	76.65	1.24	0.17	60.93
8.	77.30	1.23	0.14	73.02

4.2.3 Nitrate removal in an undivided cell

Figure 18 displays the outcomes of nitrate reduction in the undivided cell utilising a Ti cathode and a Ti/RuO_2 anode during a 120-minute electrolysis duration. In an undivided cell, the maximum amount of nitrate reduction was limited to 18% and almost entire amount of nitrate removed was transformed to NH_3-N. In the presence of 8 mM AgMPs, the nitrate reduction rose to 63%, yielding 13% NO_2-N, 35% NH_3-N, and 15% N_2-N in the undivided cell.

In the literature, similar findings have been described. Ye et al. (2020) explored nitrate reduction utilising Ti/RuO_2 and Ti mesh plates as the anode and cathode, respectively, in the presence of cobalt-coated activated carbon particles. According to the authors, ammonia was produced as a byproduct of nitrate reduction that was oxidised on the anode. According to the published study results, undivided cell remove nitrate far less effectively than divided cell.

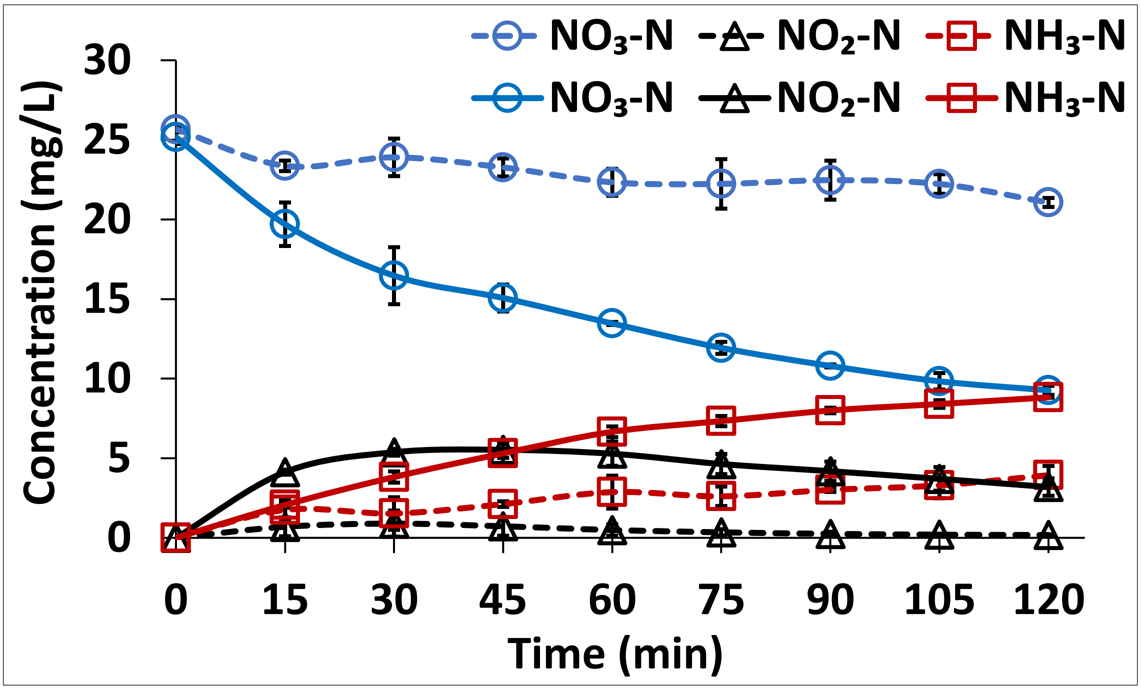


Figure 18 : NO_3-N removal in the absence (dotted line) and presence (solid line) of AgMPs in an undivided cell

(Reaction conditions: NO_3-N: 25 mg/L, cathode: Ti, anode: Ti/RuO_2, current density: 10 mA/cm^2, Na_2SO_4 as electrolyte: 2 g/L, AgMPs: 8mM, reaction time: 120 min, inter-electrode gap: 7.7 cm)

For instance, Szpyrkowicz et al. (2006) examined several reactor configurations for the electrochemical reduction of nitrate and proposed that the membrane reactor (i.e., divided cell) yields more nitrate removal than the undivided cell. Further research was carried out utilising a divided cell since the nitrate reduction process and selectivity towards N_2 in an undivided cell did not seem to be promising.

4.2.4 Nitrate removal in a divided cell

The outcomes of nitrate reduction in a divided cell using a Ti cathode and a Ti/RuO_2 anode during a 120-minute reaction period are shown in Figure 19. In the divided cell, nitrate was reduced by 77% while NH_3-N (57.7%), NO_2-N (12.8%), and N_2-N (29.5%) were produced in the absence of AgMPs. However, in the presence of 8mM AgMPs, nitrate reduction rose to 99% and N_2-N production increased to 60%. As a result, AgMPs improved nitrate reduction as well as the selectivity for N_2-N production. The most favoured by-product of nitrate reduction, N_2-N, must be emphasised here.

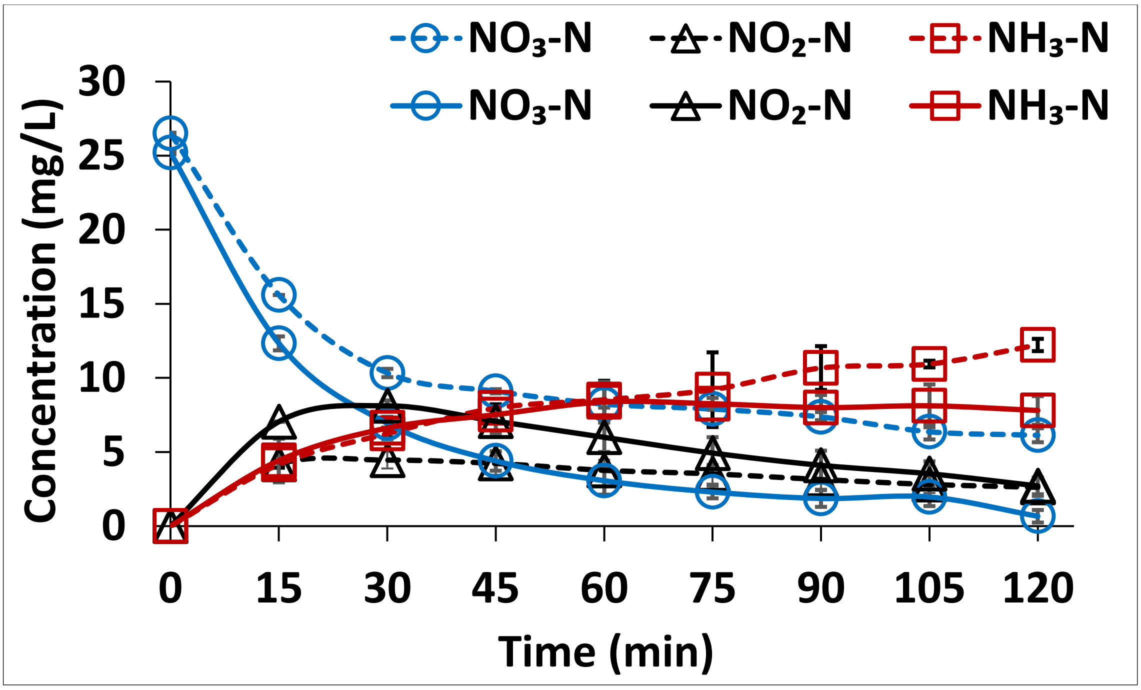


Figure 19 : NO_3-N removal in the absence (dotted line) and presence (solid line) of AgMPs in a divided cell

(Reaction conditions: NO_3-N: 25 mg/L, cathode: Ti, anode: Ti/RuO_2, current density: 10 mA/cm^2, Na_2SO_4 as electrolyte: 2 g/L, AgMPs: 8mM, reaction time: 120 min, inter-electrode gap: 7.7 cm)

As a result, experimental circumstances that encourage N_2-N formation coupled with more nitrate removal are recommended. Jonoush et al., 2020 investigated Ni foam and catalyst Ni-Fe^0@Fe_3O_4 for ECR of nitrate and reported 28.16% (Ni foam) and 90.19% (Ni-Fe^0@Fe_3O_4) nitrate removal, respectively at 5mA/cm^2 after 240min of electrolysis.

The reductive electrochemical conversion of nitrate all the way to nitrogen in the presence of silver metal catalyst is already reported. Recently, Hamam & Maiza, (2022) demonstrated electrochemical catalytic reduction of nitrate on a silver nanoparticles-polypyrrole composite film leading to the formation of nitrogen gas as the final product. The authors further stated that Ag's strong electrical conductivity and inherent catalytic activity for nitrate reduction resulted in N_2 formation. Similarly, Couto et al. (2016) also reported the formation of N_2

during electroreduction of nitrate using a carbon fiber cathode electrodeposited with silver nanoparticles.

4.2.4.1 Effect of concentration of AgMPs

Figure 20 displays the effect of the concentration of AgMPs on nitrate removal. In a divided cell, the selectivity towards NO_2-N ($S_{NO_2\text{-}N}$), NH_3-N ($S_{NH_3\text{-}N}$), and N_2-N ($S_{N_2\text{-}N}$) is shown in Table 5 along with the effect of different catalyst concentrations on nitrate removal. The mass activity of the catalyst (mg NO_3-N removed per gm Ag per min) is also shown in Table 7 . It can be observed that when AgMPs concentration grew from 4 mM to 8 mM, nitrate removal increased from 83 to 99%; however, there was a little decline in nitrate removal (from 99 to 95%) as AgMPs concentration climbed further. As a result, the order of nitrate reduction for different concentrations of AgMPs was: 8mM > 10mM > 14mM > 20.8mM > 6mM > 4mM. It is notable that the catalyst concentration also affected the selectivity of the final products. With 4mM AgMPs present, $S_{N_2\text{-}N}$ and $S_{NH_3\text{-}N}$ were 32 and 44%, respectively. However, despite the mass activity being somewhat lower than that at 4 mM, the selectivity towards N_2-N (60%) was highest, while that for the NH_3-N (31%) formation was lowest, in the presence of 8mM AgMPs. This observation is similar to the one noted in the case of Ag-PVA beads. It was observed that with increasing concentration of Ag-PVA beads, the selectivity towards ammonia was increased and N_2-N decreased. As a result, 8mM AgMPs were determined to be the optimal dose for additional research. Figure 20 shows the effect of the concentration of AgMPs on the nitrate removal and the end-product formation after 120min reaction time.

Table 7: Effect of AgMPs dose on end-product selectivity and nitrate reduction

Catalyst Dose	Nitrate conversion (%)	Mass Activity (mg of NO_3-N removed/min/g Ag)	Concentration (mg/L)		$S_{NO_2\text{-}N}$ (%)	$S_{NH_3\text{-}N}$ (%)	$S_{N_2\text{-}N}$ (%)
			NO_2-N	NH_3-N			
Absence	76 ± 0.9	-	2.61	11.72	12.8±0.6	58.0±0.4	29.1±1.1
4mM	83 ± 0.5	0.411	4.78	7.24	16.0± 1.3	44.0±1.4	32.0±1.2
6mM	92±0.9	0.362	3.81	12.92	14.0± 0.2	48.0 ±0.3	38.0±0.5
8mM	99 ±1.0	0.289	2.47	7.81	10.0± 1.9	31.0±0.9	60.0±0.5
10mM	97 ± 0.7	0.227	3.87	9.04	14.4± 0.4	34.0±0.4	46.0±0.8

14mM	95 ± 1.8	0.156	4.06	8.28	17.0±0.4	35.1±1.9	47.9±1.3
20.8mM	95 ± 1.9	0.088	3.87	8.38	15.8±0.4	34.8±0.6	49.4±0.1

Reaction conditions: NO_3-N: 25 mg/L, cathode: Ti, anode: Ti/RuO_2, current density: 10 mA/cm^2, Na_2SO_4: 2g/L as an electrolyte, reaction time: 120 min, inter-electrode gap: 7.7 cm

∗ Note: To calculate the selectivity for end-products, nitrate removal (%) is considered to be 100%.

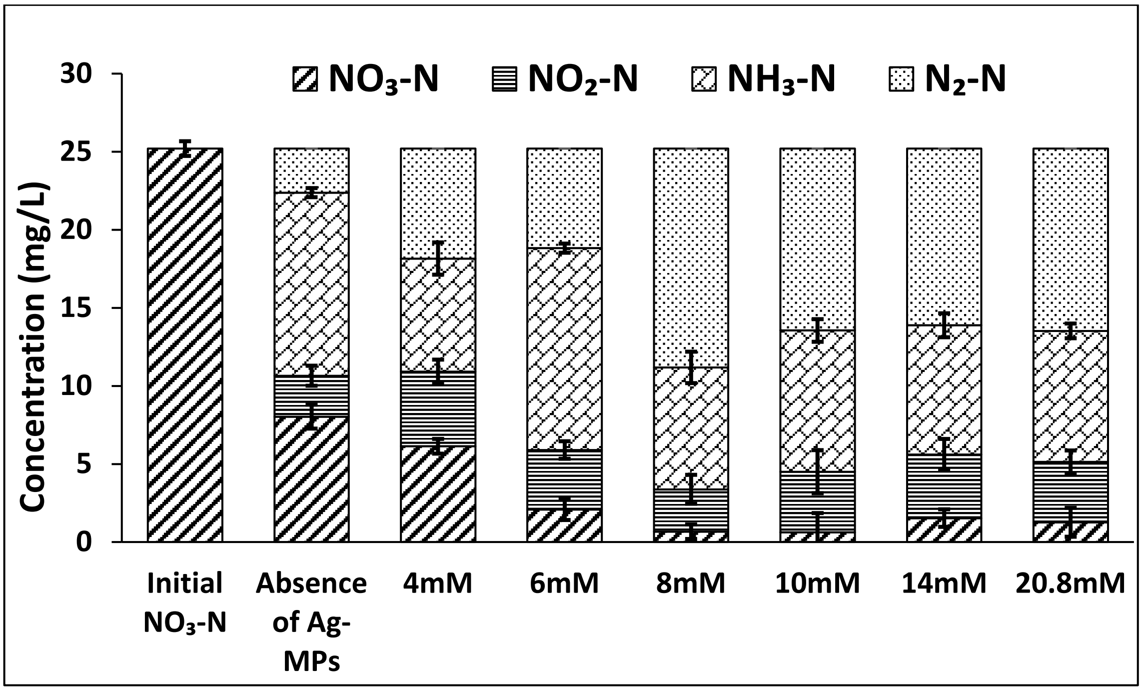


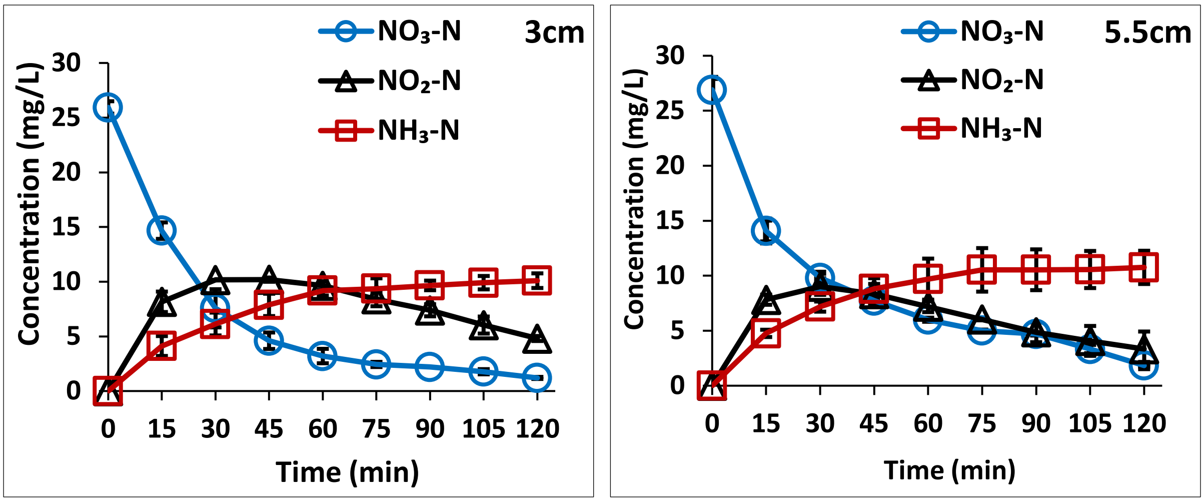
Figure 20 : Effect of various concentrations of AgMPs catalyst

(Reaction conditions: NO_3-N: 25 mg/L, cathode: Ti, anode: Ti/RuO_2, current density: 10 mA/cm^2, Na_2SO_4: 2g/L as electrolyte, reaction time: 120 min, inter-electrode gap: 7.7 cm)

To study catalytic nitrate removal, Zhang et al. (2016) employed Pd and Cu coated alumina pellets with various Pd:Cu (1:0.29, 3:0.88, 5: 1.46, and 7:2.08 mg/cm^2) concentrations. According to authors, when Pd:Cu loading rose from 1:0.29 to 3:0.88 mg/cm^2, nitrate removal increased from 55.8% to 95% in 60min reaction time. However, lower N_2 selectivity was observed as the metal concentration in catalyst increased, with ammonia as major by-product.

4.2.4.2 Effect of inter-electrode distance

Figure 21 displays nitrate removal in a divided cell using different inter-electrode spacing (3, 5.5, and 7.7 cm) in the presence of 8 mM AgMPs at the end of 120min reaction time. It may be noted that nitrate removal was ranging from 93-99%, almost irrespective of the varying inter-electrode spacing. However, the inter-electrode spacing has a considerable impact on the end-products' selectivity. Figure 21 shows that the nitrite buildup after the reaction was inversely linked to inter-electrode spacing. The greatest TN elimination and the least accumulation of nitrite occurred at an inter-electrode gap of 7.7 cm. Therefore, 7.7 cm was found to be the ideal inter-electrode spacing for further research. The proportion of AgMPs that could be brought within the electric field between the electrodes appears to have been directly impacted by the inter-electrode distance. In other words, at an inter-electrode spacing <7.7 cm, at any time during the reaction, a part of AgMPs would be at the flip side of the cathode, i.e., on the other side of the electrical field. Thus, the contribution of AgMPs to catalytic reduction of nitrate will be lesser at inter-electrode spacing <7.7 cm, affecting the end-product selectivity. The maximum possible electrode gap at which all the AgMPs could be brought under an electrical field and made accessible for nitrate reduction was 7.7 cm.



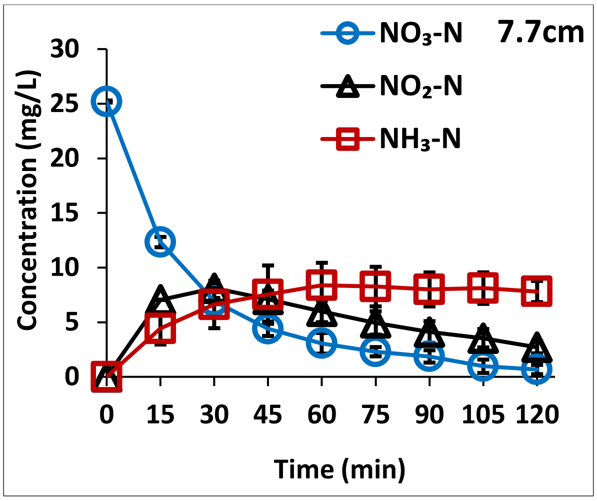


Figure 21 : Effect of inter-electrode spacing on NO$_3$-N elimination in a divided cell in the presence of AgMPs

(Reaction conditions: NO$_3$-N: 25 mg/L, anode: Ti/RuO$_2$, cathode: Ti, AgMPs: 8mM, Na$_2$SO$_4$ as electrolyte: 2 g/L, current density: 10 mA/cm^2, reaction time: 120 min)

4.2.4.3 Effect of the cathode material

Numerous cathode materials, including SS, Cu, Ti, Fe, and Fe/Sn, were investigated for nitrate removal. To evaluate the influence of the catalyst and the cathode material, experiments were conducted both with and without the AgMPs catalyst. Table 8 displays the conversion rate of nitrate in the absence and presence of an 8 mM AgMPs catalyst as well as their selectivity towards NO$_2$-N ($S_{NO_2\text{-}N}$), NH$_3$-N ($S_{NH_3\text{-}N}$), and N$_2$-N ($S_{N_2\text{-}N}$) at the end of 120 minutes of electrolysis. It is important to note that, as indicated in Table 6, both the cathode material and AgMPs affect the level of nitrate removal and the selectivity of end-products.

Table 8: The selectivity of nitrate conversion using various cathodes and their end-products

Cathode Electrode	Absence of Catalyst				Presence of catalyst			
	NO$_3$-N conversion (%)	$S_{NO_2\text{-}N}$ (%)	$S_{NH_3\text{-}N}$ (%)	$S_{N_2\text{-}N}$ (%)	NO$_3$-N conversion (%)	$S_{NO_2\text{-}N}$ (%)	$S_{NH_3\text{-}N}$ (%)	$S_{N_2\text{-}N}$ (%)
SS	50±0.2	6.0±0.9	57.7±1.1	36.3±0.8	88±0.3	14.6±1.2	54.2±1.1	31.2±1.7
Ti	77±1.3	12.8±0.4	57.7±0.6	29.5±0.6	99±0.1	10.0±2	31.0±1.7	60.0±0.3
Cu	74±1.6	55.0±0.4	27.9±1.0	17.0±0.6	95±0.7	8.0±0.1	50.9±0.9	41.1±1.2

Fe	73±0.9	2.3±1.2	75.8±1.6	21.9±1.8	98±0.1	1.4±0.1	51.0±0.2	47.6±0.3
Fe/Sn	25±1.1	10.7±0.8	83.0±1.4	6.3±1.4	59±0.7	6.9±0.8	54.9±1.6	38.2±0.5

Conditions: NO_3-N: 25 mg/L, anode: Ti/RuO_2, current density: 10 mA/cm^2, Na_2SO_4: 2g/L as electrolyte, 8mM AgMPs, reaction time: 120 min, inter-electrode gap: 7.7 cm

Note: To determine the selectivity for end-products, nitrate conversion (%) is assumed to be 100%.

As it can be observed, in the absence of AgMPs, nitrate was eliminated by different cathode materials in the following order: Ti > Cu > Fe > SS > Fe/Sn. Nitrate removal from Ti, Cu, and Fe cathodes was essentially comparable; however, the main conversion was into N_2-N, NO_2-N, and NH_3-N, respectively. On the other hand, nitrate removal occurred in the presence of AgMPs in the order Ti > Fe > Cu > SS > Fe/Sn. In this case, as well, nitrate was eliminated by >95% using Ti, Cu, and Fe cathodes, however, the main transformation was into N_2-N, NH_3-N, and NH_3-N, respectively. AgMPs changed the selectivity of final products as a result. This observation is similar to the one noted in the case of Ag-PVA beads i.e., the presence of Ag-PVA beads changed the final selectivity from ammonia to N_2-N. Figure 22 displays the effect of cathode material in the absence and presence of AgMPs.

Cu cathode, interestingly, produced the highest conversion to nitrite and ammonia, respectively, in the presence and absence of AgMPs. In the published literature, higher nitrate-to-nitrite conversion employing Cu cathode in the absence of any catalyst is observed (Reyter et al., 2011; Roy et al., 2016). Cu and Polypyrrole coated Cu (PPy/Cu) electrodes were tested by Çirmi et al. (2015) for the removal of nitrate, and they observed the highest conversion to nitrite using Cu cathode and to ammonia using PPy/Cu cathode. According to reports, nitrate ions may readily bind to the Cu cathode and then undergo a direct electron transfer to form nitrite. Also, using Cu cathode in the absence and presence of Ag-PVA beads, gave maximum conversion to nitrite and ammonia. However, when a catalyst is present, ammonia synthesis is facilitated by two processes: (1) the adsorption of an available proton in the solution on the catalyst, and (2) the reduction of the proton via electron transfer to yield atomic hydrogen (H_{ads}) which combines with reduced nitrogen to form ammonia. Figure 22 shows nitrate reduction in the absence and presence of 8mM AgMPs catalyst with the use of various cathode materials at 10mA/cm^2 current density for 120min reaction time.

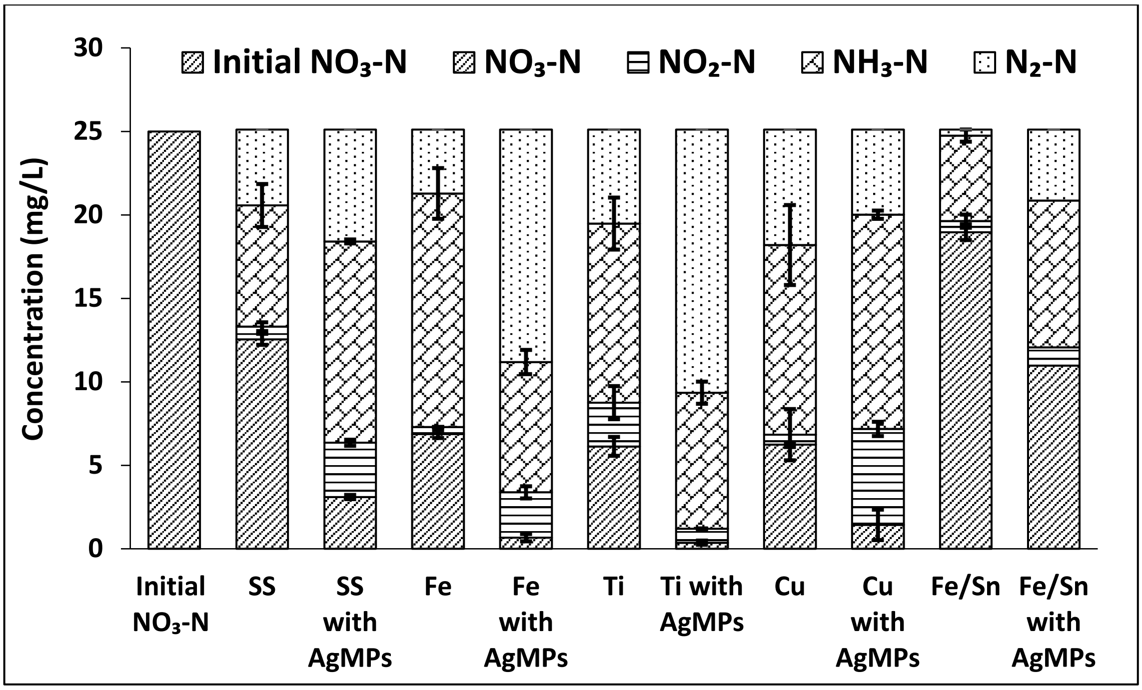


Figure 22 : Nitrate reduction using various cathode materials in the absence and presence of AgMPs

(Reaction conditions: NO_3-N: 25 mg/L, anode: Ti/RuO_2, AgMPs: 8mM, Na_2SO_4 as electrolyte: 2 g/L, current density: 10 mA/cm^2, reaction time: 120 min)

Fe and Ti cathodes are relatively similar in their ability to reduce nitrate in the presence of AgMPs, however, Ti has a stronger selectivity towards N_2-N (60%) than Fe (47.6%). Fe is also more quickly corroded in both alkaline and acidic pH settings, which reduces the stability of Fe electrodes (Garcia-Segura et al., 2018). Ti cathode was therefore employed for further research. It is well-known that Ti's intrinsic hydrogen evolution reaction (HER) activity is low (T. Zhang et al., 2021). In other words, the hydrogen evolution on Ti as a cathode is less. This lower hydrogen evaluation is beneficial for the electroreduction of nitrate as it reduces the competition between the evolution of hydrogen and the reduction of nitrate ions on the cathode. As a result, more electrons can be channelled for the nitrate reduction pathway, leading to the highest formation of N_2 as the final product.

4.2.4.4 Effect of current density

Current density is one of the elements that have the most impact on the electrochemical reduction process of nitrate. Studies on current densities of 5, 10, and 15 mA/cm^2 were carried out to assess the impact on the selectivity for the end-products and nitrate removal.

As seen in figure 23, NO_3-N removal was 90, 99, and 93% at current densities of 5, 10, and 15mA/cm^2, respectively, whereas TN removal was 30%, 60%, and 41%. As a result, when the current density was increased from 5 to 10 mA/cm^2, the nitrate reduction rose along with an increase in N_2-N generation. Nitrite generation peaked at a current density of 5 mA/cm^2 (21%) and subsequently decreased to negligible levels as the current density increased to 10 mA/cm^2. Additionally, Figure 23 displays mg NO_3-N eliminated every amp-hour. Due to side reactions, the energy needed to remove NO_3-N rises practically linearly with the current density.

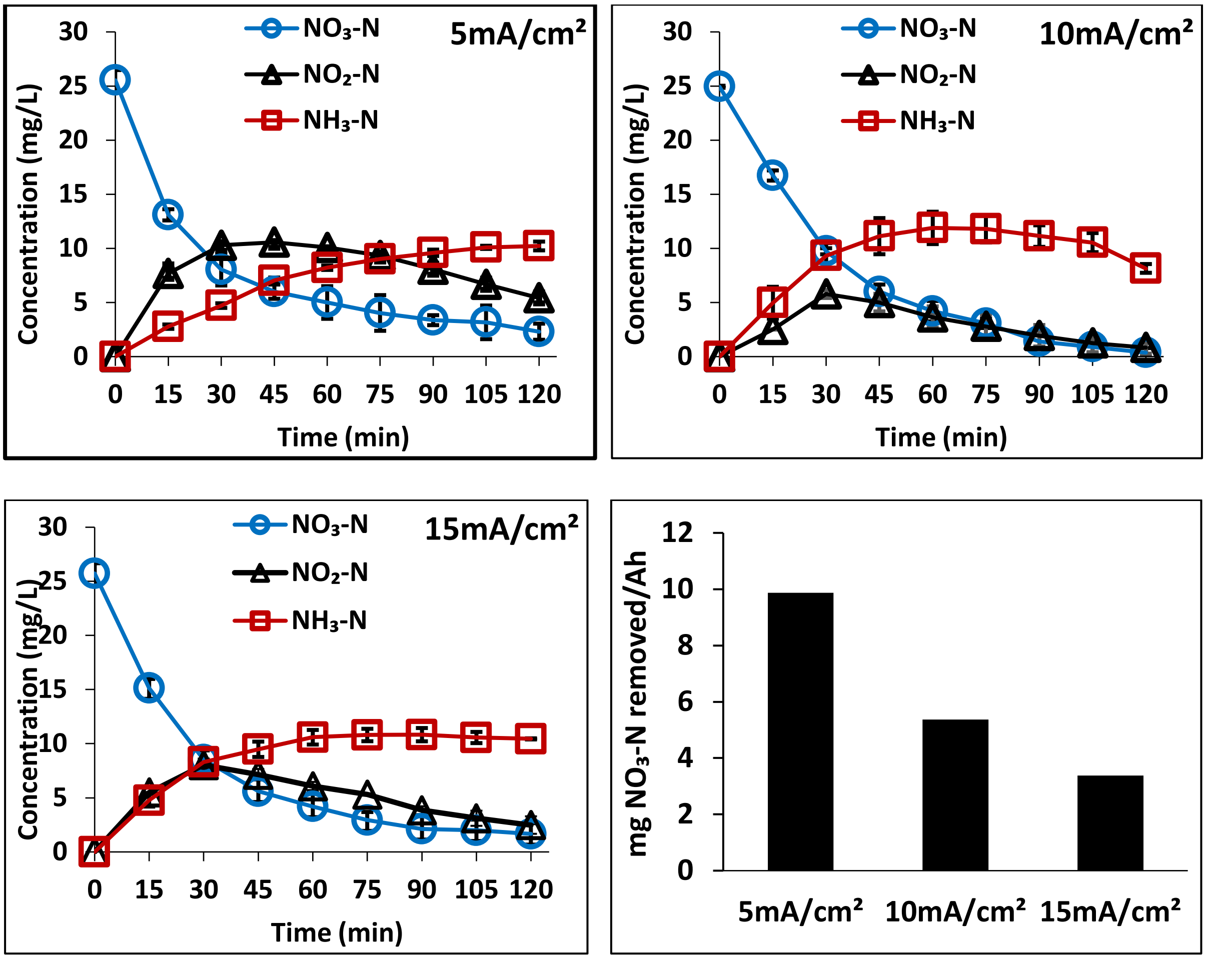


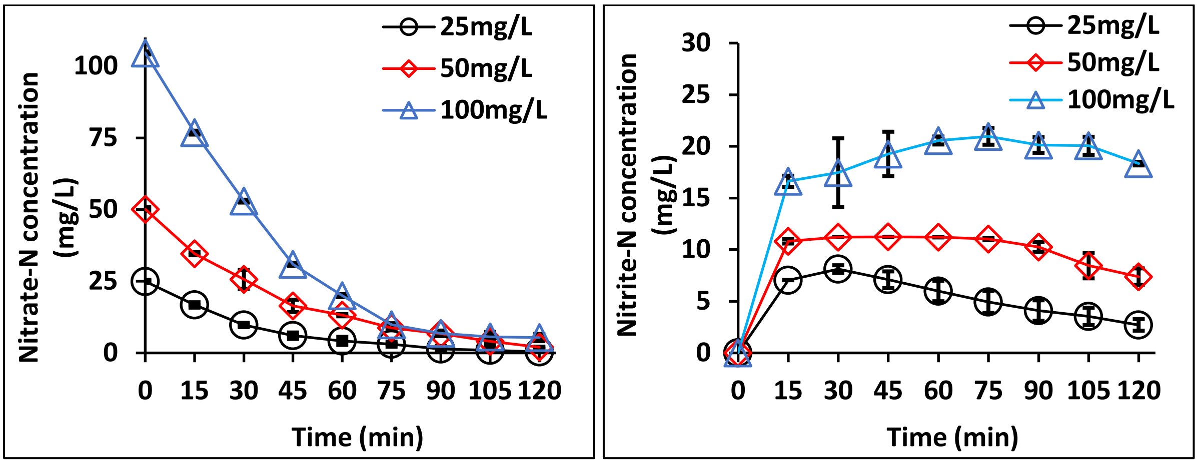
Figure 23 : Effects of current density on nitrate removal and selectivity of end-products

(Reaction Conditions: NO_3-N Concentration: 25 mg/L, cathode: Ti, anode: Ti/RuO_2, catalyst concentration: 8mM AgMPs, reaction time: 120 min; inter-electrode distance: 7.7cm)

It was found that the reduction of nitrate marginally fell to 93% with increasing selectivity in favour of ammonia generation as the current density was raised to 15 mA/cm^2. This observation is similar to the one noted in the case of Ag-PVA under similar experimental conditions. Li et al. (2016) hypothesised that when current density increased, more hydrogen was produced, promoting the combination of N-H and discouraging the formation of N≡N, which boosts the creation of ammonia. On the other hand, Sahu et al. (2014) suggested that when the current density was too low, it was challenging to completely convert nitrate to nitrogen. Additionally, even if nitrate removal is boosted by increasing current density, an excessive amount of current density causes the electrocatalytic system to use more energy. So, it was decided that 10 mA/cm^2 current density was optimal.

4.2.4.5 Effect of initial nitrate concentration

According to the nitrate reduction mechanism stated by Chauhan & Srivastava (2022) and Zou et al. (2021), the process is highly dependent on the initial nitrate concentration. On the reduction of nitrate at a current density of 10mA/cm^2 in the presence of 8mM AgMPs for 120min of electrolysis time, the effects of different initial concentrations (25, 50, and 100 mg/L NO_3-N) were evaluated as depicted in Figure 24. It may be observed that with an increase in the initial nitrate concentration, the formation and accumulation of NO_2-N and NH_3-N increased, with corresponding decrease in the formation of N_2-N. Thus, nitrate removal and product selectivity were influenced by the initial nitrate concentration. A similar observation was obtained with Ag-PVA beads that is as initial nitrate-N concentration increases, change in selectivity occurs.



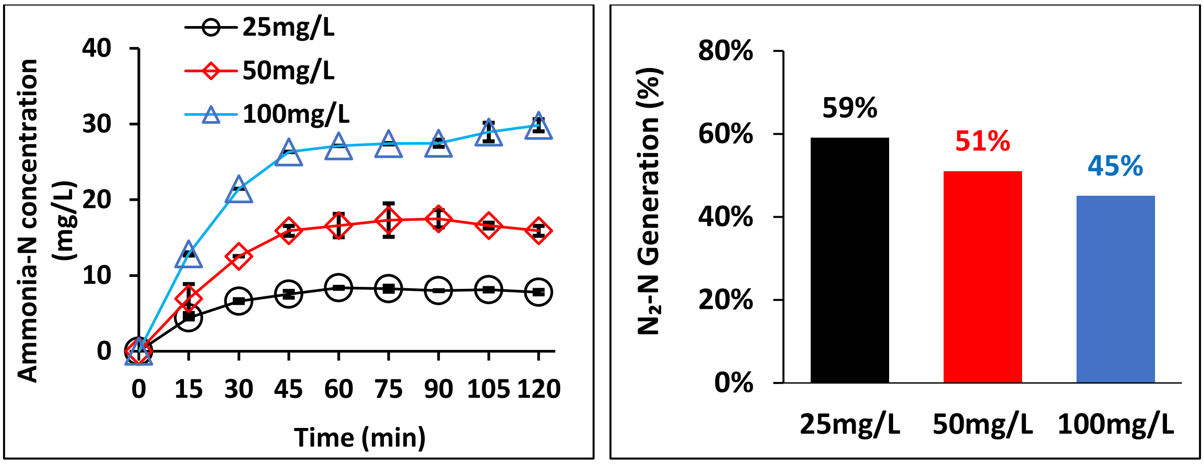


Figure 24 : Effect of initial NO_3-N concentration on nitrate reduction and its selectivity

(Reaction Conditions: cathode: Ti, anode: Ti/RuO_2, catalyst concentration: 8mM AgMPs, current density: 10mA/cm^2; reaction time: 120 min)

Table 9 shows the first-order nitrate removal rate constant values at varying initial nitrate concentrations. The first-order nitrate removal rate constant values decreased with increase in the initial nitrate concentration. According to Li et al. (2016), the cathode's restricted ability to adsorb nitrate ions as well as competition from other ions and byproducts such as nitrite and ammonia may cause the nitrate removal rate to decrease as the nitrate concentration increases. Additionally, when the initial nitrate concentration increases, the cation exchange membrane in the divided cell is more prone to corrosion and clogging, which results in a slower rate of nitrate removal. According to Su et al. (2017), when the starting concentration of NO_3-N increases, more electrical energy may be required to decrease NO_3-N to manufacture NH_3-N instead of H_2O to produce H_2, changing the end-product selectivity.

Table 9: Effect of the initial nitrate concentration on 1st-order removal rate constant and nitrate removal efficiency

Initial NO_3-N concentration (mg/L)	1st-order Rate constant (min^{-1})	R^2	NO_3-N reduction efficiency (%)
25	0.0322	0.9945	99
50	0.0247	0.9918	96

100	0.0220	0.9908	94

(Reaction Conditions: cathode: Ti, anode: Ti/RuO_2, catalyst concentration: 8mM AgMPs, current density: 10mA/cm^2; reaction time: 120 min)

4.2.4.6 Simultaneous nitrate reduction-ammonia oxidation for TN removal

In a divided cell, while the electrical energy is fruitfully used for reduction of a target pollutant in the cathode compartment, the energy in the anode compartment is lost without any useful outcome. Therefore, the experiments were conducted by filling the catholyte of an ECR experiment (containing residual concentrations of mainly ammonia, and small concentrations of nitrate and nitrite) in the anode compartment rather than a plane sodium sulfate solution as an anolyte. Such an arrangement will provide an advantage of simultaneous reduction of nitrate in the cathode compartment and the oxidation of ammonia in the anode compartment. Figure 25 demonstrates the scheme and results of simultaneous nitrate reduction-ammonia oxidation experiments. In the 1st experiment, the fresh catholyte contained 25mg/L NO_3-N and 2g/L Na_2SO_4, and the anolyte was a 2g/L Na_2SO_4 in DI water. Ti acted as a cathode and Ti/RuO_2 acted as an anode in the presence of 8mM AgMPs in cathode compartment at 10mA/cm^2 current density in all the experiments. The results obtained in the catholyte were: NO_3-N reduction was ≈99% with 32.9% NH_3-N and 64% N_2-N generation. In 2nd experiment, the catholyte was a fresh 25mg/L NO_3-N solution and 2g/L Na_2SO_4, and the catholyte of the first experiment containing residual ammonia was taken as anolyte. The results obtained were that NO_3-N reduction was similar to the 1st experiment i.e., ≈99% but the concentration of NH_3-N in the catholyte was increased to 60% and N_2-N concentration was decreased to 25%. On the other hand, ammonia was almost eliminated from the anolyte. This experiment cycle was continued to determine the fate of ammonia. For the 3rd experiment, again a fresh 25mg/L NO_3-N solution was as catholyte and the catholyte of 2nd experiment was taken as anolyte. The results obtained in the 3rd experiment were that NH_3-N concentration was again increased (75%) and N_2-N concentration decreased (5%) in the catholyte, with almost complete removal of ammonia in the anolyte. We performed the mass balance of ammonia for each experiment and found that the mass of ammonia eliminated from the anode compartment was almost similar to the mass of ammonia increased in the catholyte. In other words, there was no oxidation of ammonia in the anode compartment. It may be easily understood that under acidic conditions in the anode compartment (due to evolution of oxygen gas and accumulation of hydrogen ions), the ammonia will exist as NH_4^+

ions which facilely pass through the cationic exchange membrane to the negatively charged cathode, leading to a constant buildup of ammonia in the catholyte.

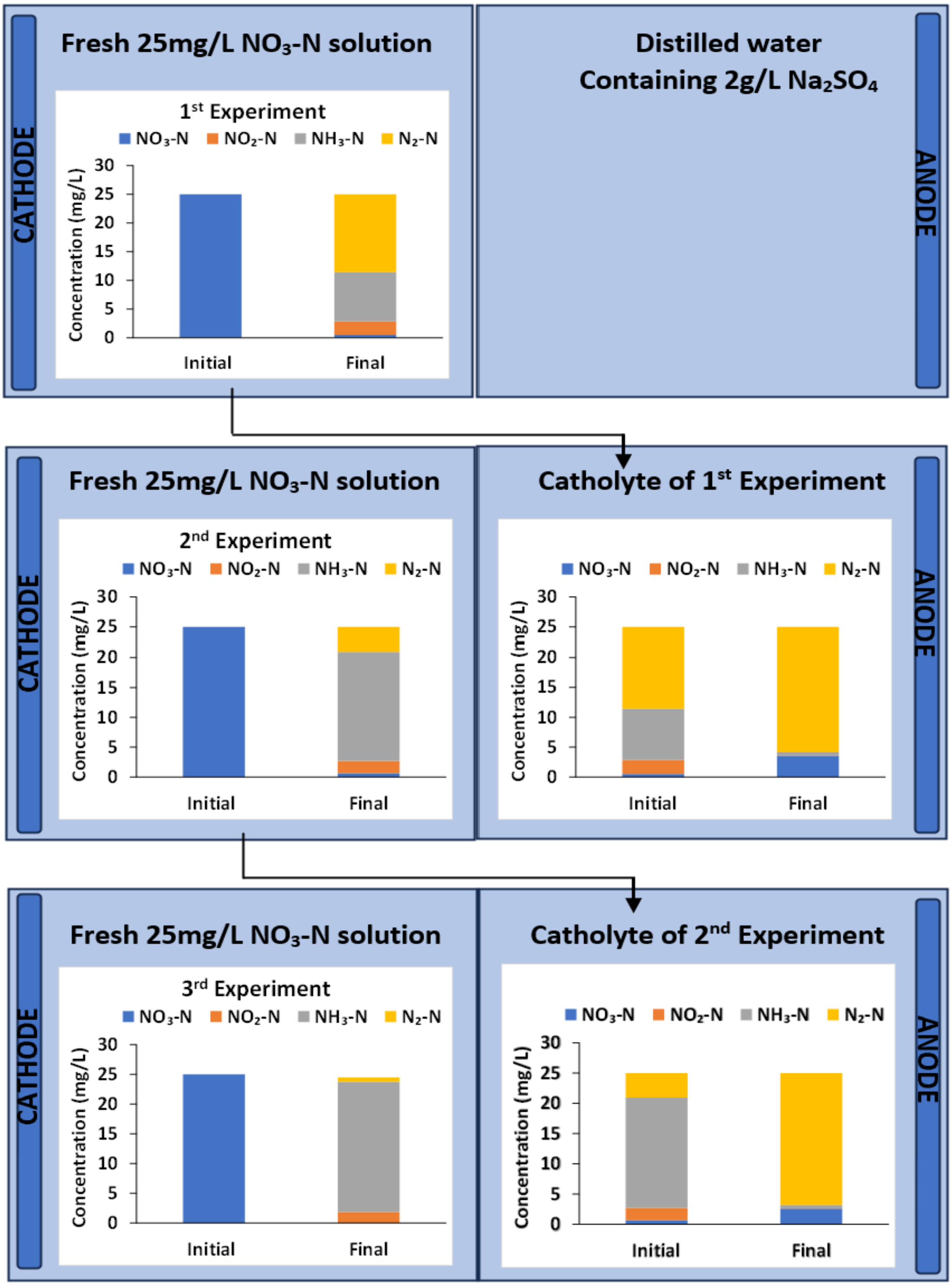
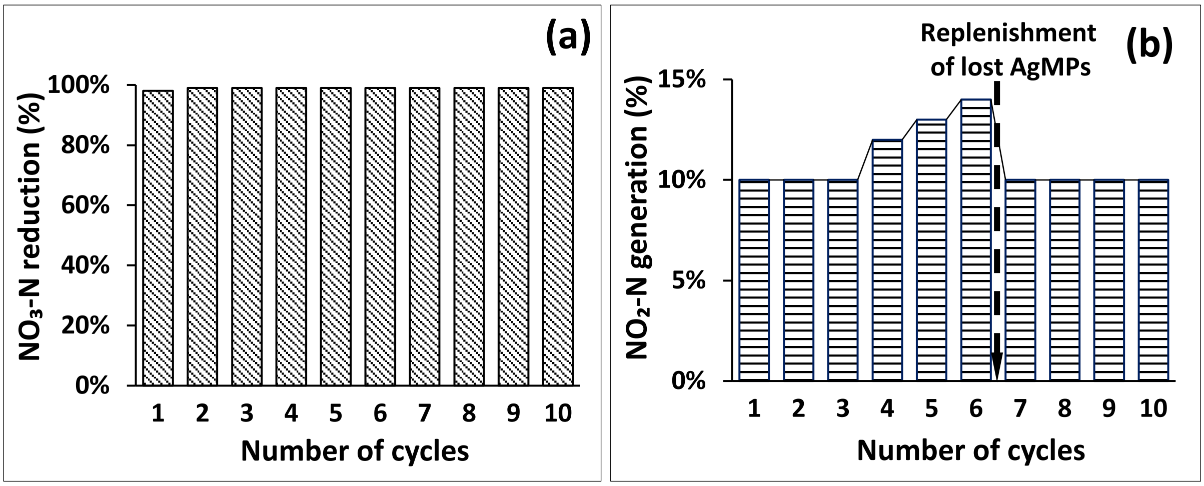


Figure 25 : Experiments and results of simultaneous nitrate removal and ammonia oxidation

4.2.4.7 Reusability of AgMPs

Only reusable catalysts may be employed on a wider scale. Figure 26 depicts the ability of AgMPs to be recycled for NO_3-N reduction. Even after 10 consecutive cycles of use, the AgMPs' catalytic activity for nitrate removal was almost unchanged. It was interesting to see that after the third reuse, TN elimination somewhat decreased and NO_2-N build-up slightly increased. It may be noted that at the end of each reusability experiment, the AgMPs were separated by settling, washed, and reused for the next experiment. During these repeated cycles of separation and washing, some particles are inadvertently lost. When we noticed change in selectivity of end-products, after the 6th use, we measured the dry mass of AgMPs and noted ≈10% reduction in mass as compared to the original mass employed in the 1st use. Thus, we added fresh AgMPs (~0.013 g) to restore the original mass. It may be seen that the initial selectivity towards N_2 and nitrite generation and TN elimination was restored after the addition of lost AgMPs mass after the sixth cycle. Thus, the AgMPs could be reused at least ten times. It may be possible that silver metal may dissolved in the catholyte. We measured the concentration of aqueous silver ions in the catholyte solution following several re-uses. The concentration of aqueous silver ions was around 0.08 mg/L, which is significantly below the requirements for drinking water in India (IS 10500). Santos et al. (2020) employed a Pd-Cu-loaded carbon nanotube as a catalyst for the reduction of nitrate and reported that the catalyst could be reused 5 times; however, selectivity towards ammonia generation increased with repeated usage. As demonstrated by Popli & Patel (2017), RB5 dye was electrochemically reduced using silver nanoparticles three times.



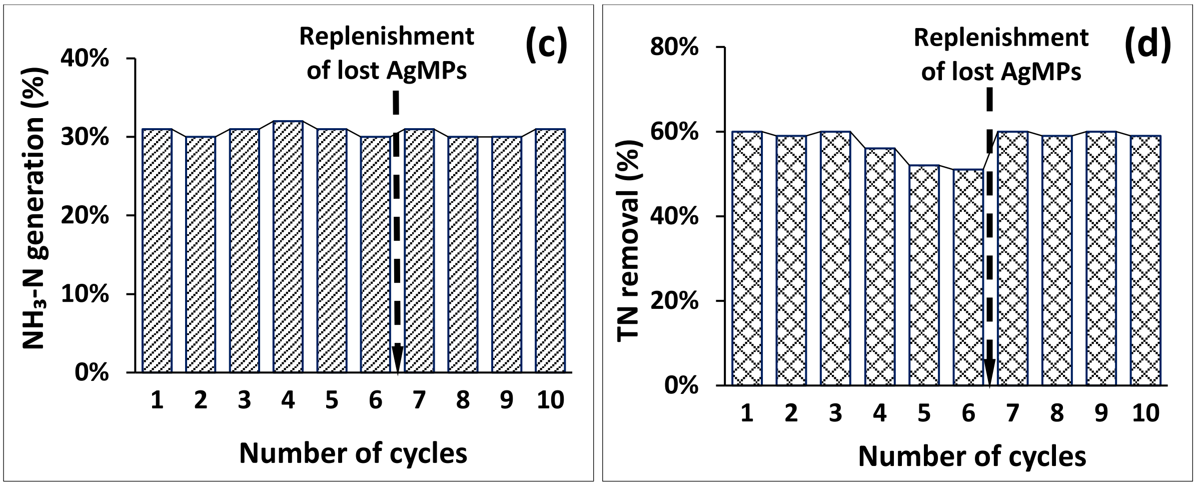


Figure 26: Reusability of AgMPs (a) nitrate reduction, (b) nitrite generation, (c) ammonia generation, and (d) TN removal

(Reaction condition: NO_3-N: 25 mg/L, cathode: Ti, anode: Ti/RuO_2, current density: 10 mA/cm^2, reaction time: 120 min, Na_2SO_4: 2g/L, catalyst concentration: 8mM AgMPs, inter-electrode distance:7.7cm)

Following are the salient observations from section 4.2:

1. SEM and XRD confirmed the proper synthesis of silver metal particles (AgMPs).
2. Nitrate reduction was boosted by the presence of an AgMPs catalyst in both undivided and divided cells. In the presence of the catalyst, the selectivity for N_2 generation is significantly improved.
3. The highest selectivity for N_2-N formation and nitrate removal was observed when Ti was used as the cathode.
4. As the current density increased (5 to 10mA/cm^2), nitrate reduction also increased. Further increasing current density (10 to 15mA/cm^2), affected the selectivity.
5. Increasing the initial concentration of nitrate resulted in a similar nitrate removal, although the selectivity of end-products was significantly impacted.
6. Reusability of AgMPs was very good with negligible solubility of Ag in treated water.

4.3 Mechanism of catalytic electrochemical nitrate removal in the presence of a spatially suspended silver catalyst

Equations 1-4 state that the principal quasi-stable intermediate generated by electrochemical reduction, before being completely reduced to ammonia or nitrogen gas, is nitrite (Garcia-

Segura et al., 2018; Koparal & Öütveren, 2002). Both ammonia (NH_3) and nitrogen (N_2) are thermodynamically the most stable forms of nitrogen (Zeng et al., 2020). The conversion of nitrate (NO_3^-) to nitrite (NO_2^-) (Eqs. 1 and 2) and the conversion of nitrite (NO_2^-) to ammonia (NH_3)/nitrogen (N_2) (Eqs. 3 and 4) are the two steps that separate the reduction of nitrate (NO_3^-).

$NO_3^- + H_2O + e^- \rightarrow NO_2\cdot + 2OH^-$ (1)

$NO_2\cdot + e^- \rightarrow NO_2^- + 2H_2O$ (2)

$3NO_2^- + 12H^+ + 10e^- \rightarrow 1.5N_2 + 6H_2O$ (3)

$NO_2^- + 7H^+ + 8e^- \rightarrow NH_3 + 2H_2O$ (4)

There may be two reaction pathways that contribute simultaneously to the reduction of nitrate in the cathode compartment in an electrocatalytic process using a divided cell: (1) nitrate reduction by catalytic hydrogenation, and (2) direct nitrate reduction on the cathode (Hôrold et al., 1993; Z. Zhang et al., 2016).

In the absence of a spatially suspended catalyst, the process of nitrate ion adsorption on the cathode, which is necessary for nitrite production, is sluggish and severely impacted by interference from other anions (Tong et al., 2017). On the other hand, the spatially dispersed catalyst (such as Ag-PVA and AgMPs) in the cathode chamber serve as micro-cathodes which offers a much greater surface area for nitrate adsorption leading to enhanced nitrate removal. Moreover, proton reduction on these Ag micro-cathodes results in the formation of nascent hydrogen, which is intercalated in Ag^0 to create highly reductive AgH_x species, as suggested in Equations 4-6, that may reduce nitrate.

$NO_3^- + AgH_x \rightarrow NO_2^- + H_2O + Ag^0$ (4)

$NO_2^- + AgH_x \rightarrow 0.5N_2 + OH^- + H_2O + Ag^0$ (5)

$NO_2^- + AgH_x \rightarrow NH_3 + OH^- + H_2O + Ag^0$ (6)

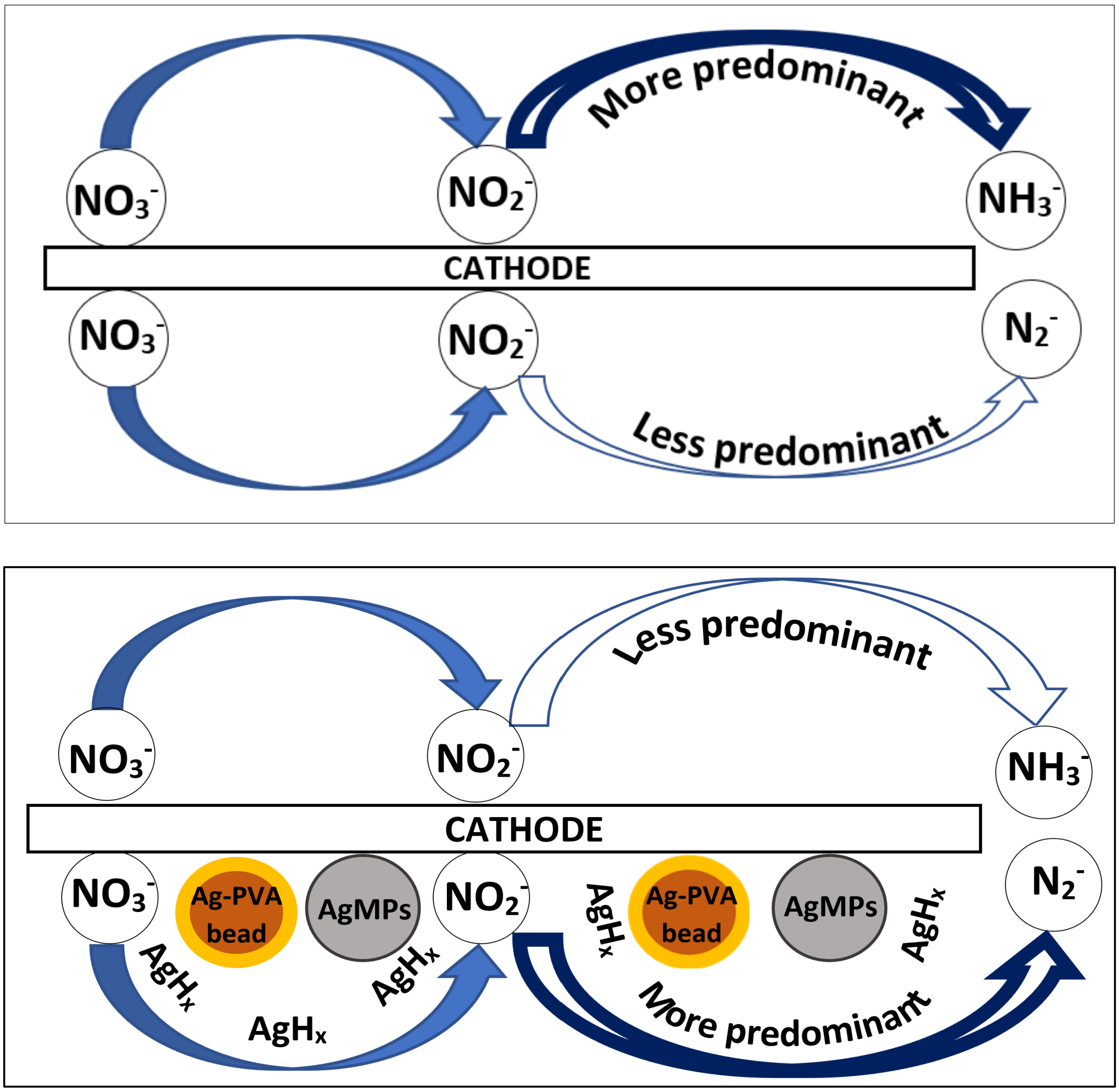


Figure 27 : Mechanism of nitrate reduction on the cathode in the absence and presence of Ag-PVA beads and AgMPs

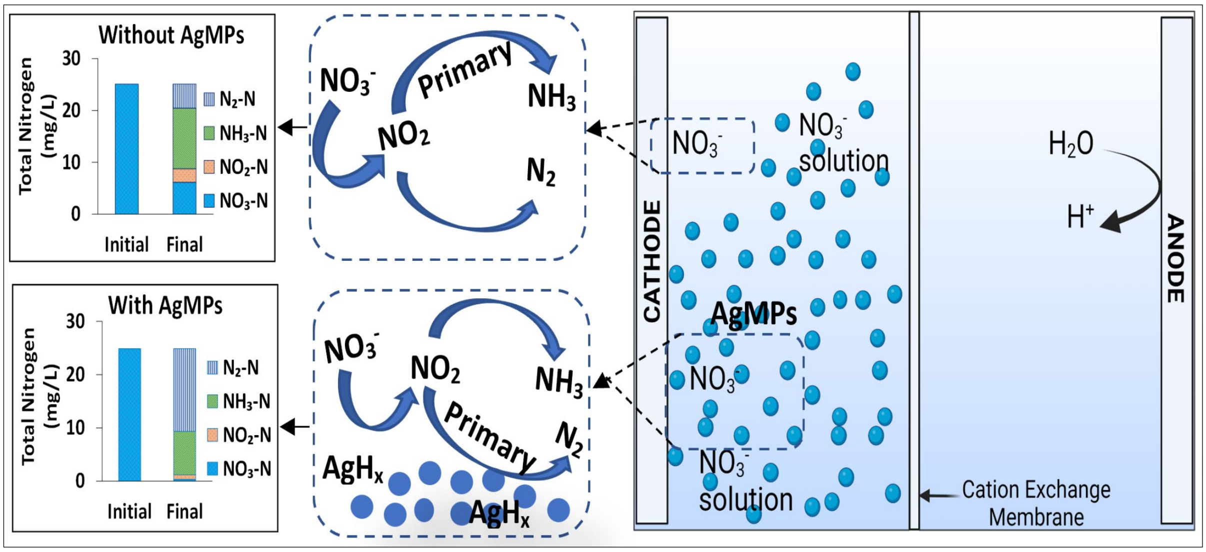


Figure 28 : Mechanism of nitrate reduction on the cathode in the absence and presence of AgMPs

Based on the description above, Figure 26 and Figure 27 visually illustrate a nitrate removal method in both the presence and absence of Ag-PVA beads and AgMPs. The formation of AgHx is already reported (Baba et al., 2001). It has already been shown that AgH_x may be used to reductively degrade aquatic contaminants (Ingle & Patel, 2022; U. D. Patel & Suresh, 2008; U. Patel & Suresh, 2006; S. Popli & Patel, 2017). As a result, AgHx species also contribute to nitrate reduction in addition to the direct reduction on the cathode, resulting in improved removal. Additionally, the AgHx species modify the selectivity of finished products. The outcomes showed that the addition of a spatially suspended catalyst increased the selectivity towards N_2.

4.4 ECR of nitrate in groundwater using spatially suspended catalyst

The ECR of nitrate in groundwater was investigated using a spatially suspended catalyst at optimised conditions. Table 10 provides descriptions of the characteristics of groundwater.

Table 10 : Characteristics of real water (Groundwater)

Parameters	*Values*
Nitrate-N	*15 mg/L*
Sulphates	*8 mg/L*
Chlorides	*150 mg/L*
Carbonates	*75 mg/L*
Bicarbonates	*125 mg/L*
pH	*6.5-7.6*

Figure 29 displays the nitrate-N reduction in a divided cell in the absence and presence of 6.67mM Ag-PVA beads after 90 minutes of electrolysis at a current density of $15 mA/cm^2$. It was discovered that the presence of a catalyst improved nitrate removal in groundwater and altered selectivity as well. In the presence of Ag-PVA beads, the reduction of nitrate increased from 53% to 85%. In the presence of the catalyst, NO_2-N (3%), NH_3-N (57%) and N_2-N (24%)

were, as opposed to 53% of NO_2-N, 52% of NH_3-N, and nil N_2-N generation in the absence of the catalyst.

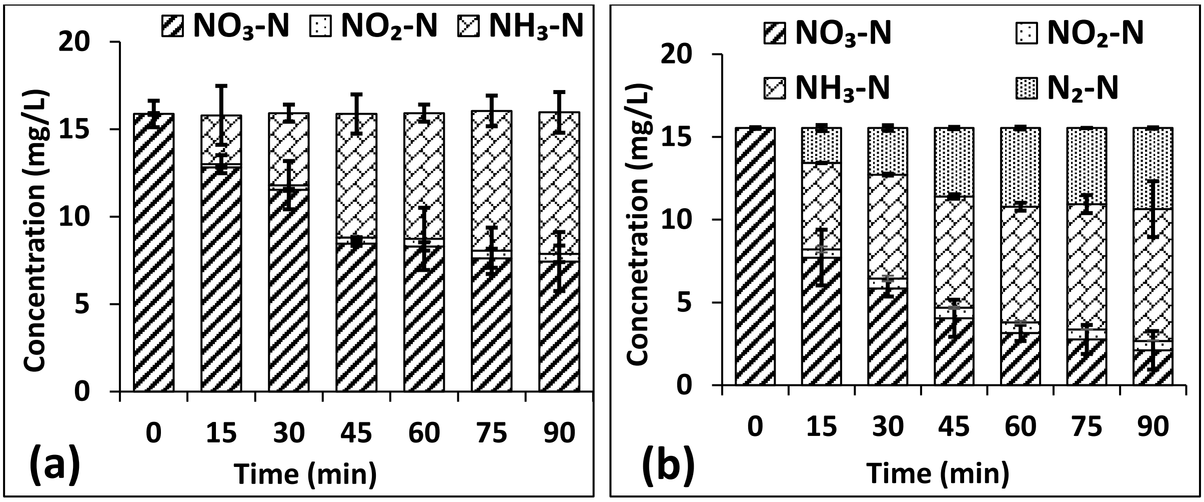


Figure 29 : Nitrate removal in the absence (a) and presence of Ag-PVA (b) beads in groundwater

(Reaction condition: Groundwater, cathode: Fe, anode: Gr, current density: 15 mA/cm^2, reaction time: 90 min, Ag-PVA: 6.67mM)

The nitrate reduction in a divided cell with the absence and presence of 8mM Ag-MPs is shown in Figure 30 after 120 minutes of electrolysis at a current density of 10mA/cm^2. It was found that catalyst presence enhanced the removal of nitrate from groundwater and changed the selectivity also. 24% of nitrate-N was reduced in the absence of a catalyst which rose to 59% in the presence of a catalyst. In the absence of a catalyst, the selectivity for NO_2-N and NH_3-N was 9.5 and 13.7%, respectively while no N_2-N generation was noted. In the presence of AgMPs, NO_2-N generation was negligible, and NH_3-N and N_2-N generation was 24 and 34%, respectively. Comparison of results depicted in Figures 29 and 30 with the nitrate removal results obtained in the synthetic solution shows that the performance of both Ag-PVA and AgMPs is adversely affected in the real groundwater. Additionally, the selectivity of end-products was also severely affected as indicated by a significant decrease in N_2-N production. One of the reasons for the poor performance of ECR in the presence of suspended catalysts in groundwater could be the competition for the adsorption of nitrate with other anions. Moreover, silver metal is known to corrode in the presence of chloride ions forming AgCl (Ha & Payer, 2011; Park et al., 2023) which will abate the access of reactants to Ag metal. It is also important to note that under the optimum conditions the performance of Ag-PVA is better than AgMPs for nitrate removal from groundwater. This is exactly opposite to what observed in the synthetic nitrate solution wherein, the performance of AgMPs was better than Ag-PVA. It seems that polyvinyl alcohol (PVA) support may resist the deactivation of Ag due to chloride ions. It has been shown that the catalyst support can play important role in preventing deactivation of catalyst during catalytic reactions (Agryle and Bartholomew, 2015; Yuan and Keane, 2003). The catalytic activity rapidly decreases as a result of loss of surface area, pore constriction, and ultimately pore blockage on the active sites (Jung et al., 2021).

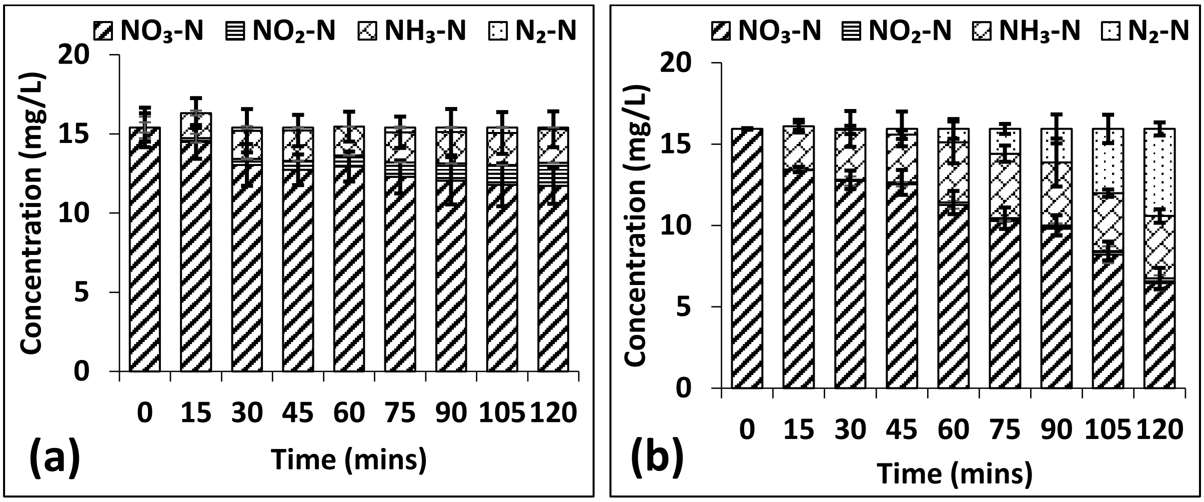


Figure 30 : Nitrate removal in the absence (a) and presence (b) of AgMPs in groundwater

(Reaction conditions: Groundwater, anode: Ti/RuO_2, cathode: Ti, 8mM Ag-PVA beads, Na_2SO_4: 2g/L as electrolyte, reaction time: 120 min)

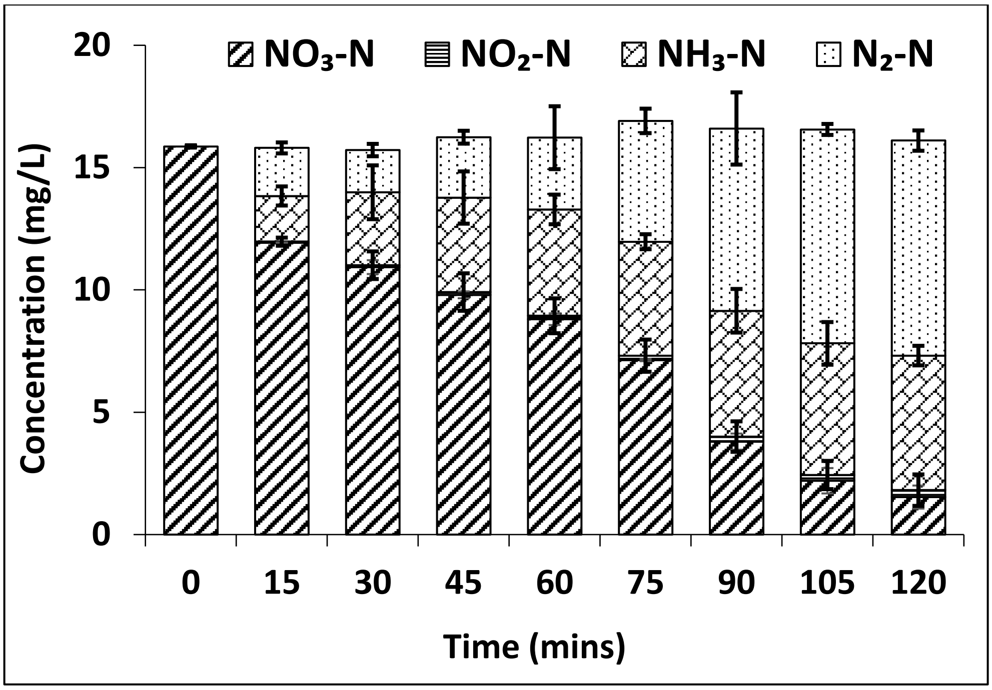


Figure 31 : Nitrate removal using Ti/Co_3O_4 in groundwater

(Reaction conditions: Groundwater, anode: Ti/RuO_2, cathode: Ti/Co_3O_4, Na_2SO_4: 2g/L as electrolyte, reaction time: 120 min)

Due to the reduced performance of suspended catalysts, it was pertinent to evaluate a catalyst which gives efficient removal of nitrate in real water as well as in the wastewater containing high nitrate concentration. Thus, we conducted ECR experiments using a Ti cathode with Co3O4 immobilized on it (Ti/Co_3O_4). Figure 31 shows the ECR of nitrate in groundwater using Ti/Co_3O_4 cathode and Ti/RuO_2 anode at 10mA/cm^2 current density for 120min electrolysis time. It is observed that using Ti/Co_3O_4 cathode, nitrate reduction increased with increasing selectivity towards nitrogen. 95% nitrate reduction was achieved resulting in 39 and 55% selectivity for NH_3-N and N_2-N, respectively.

Comparison of Figures 29, 30 and 31 shows that that the performance of Ti/Co_3O_4 for nitrate removal and selectivity for N_2-N was superior to the suspended silver catalysts. In the presence of Ag-PVA beads and AgMPs, nitrate reduction achieved was 85 and 59%, respectively whereas Ti/Co_3O_4 gave 95% nitrate reduction in real water (groundwater). Additionally, N_2-N selectivity in presence of Ag-PVA beads and AgMPs was 24 and 34%, respectively. N_2-N achieved in presence of Ti/Co_3O_4 was 55%. Less N_2-N selectivity was achieved using spatially suspended catalyst compared to Ti/Co_3O_4 and this may be due to rapid deactivation of suspended catalyst (Ag-PVA beads and AgMPs) in the presence of chloride ions. The detrimental impact of Cl ions on inactivation of Ag catalyst was maximum compared to other anions (Sontakke et al., 2011). Experiments were conducted under ideal conditions using spatially suspended catalyst (AgMPs) with immobilised catalyst (Ti/Co_3O_4). But no significant change was observed on ECR of nitrate using both catalyst. Figure 32 shows the ECR of nitrate using AgMPs with Ti/Co_3O_4 cathode. The results were similar to that obtained with individual use of Ti/Co_3O_4 cathode.

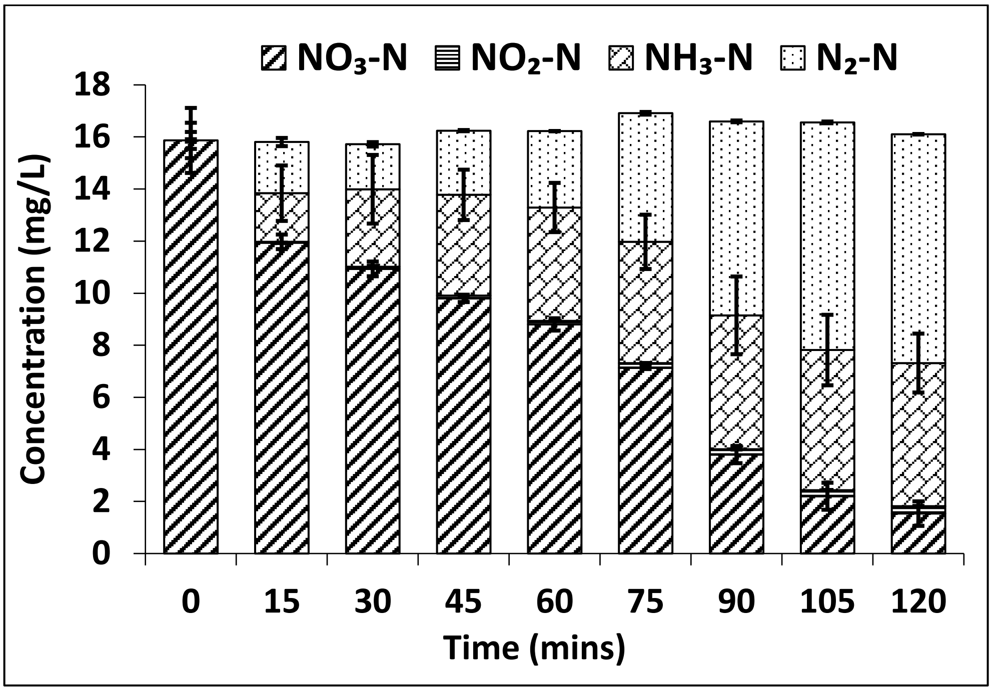


Figure 32 : Nitrate removal using AgMPs with $Ti/Co_{ss}O_4$ in groundwater

(Reaction conditions: Groundwater, anode: Ti/RuO_2, cathode: Ti/Co_3O_4, 8mM AgMPs, Na_2SO_4: 2g/L as electrolyte, reaction time: 120 min)

For this reason, we explored the use of an immobilised catalyst (Ti/CO_3O_4) intending to increase the removal of nitrate and improve conversion to N_2-N while treating real water. So further, experiments for the ECR process were conducted using cathode-coated catalyst Ti/Co_3O_4 for high nitrate concentration in simulated metal finishing wastewater.

4.5 ECR of high nitrate concentration in metal finishing wastewater using catalyst-coated cathode (Ti/Co_3O_4)

This research study includes various parameters for ECR of high nitrate concentration from simulated metal finishing wastewater including initial nitrate-N concentration, current density, and reusability of Ti/Co_3O_4. Table 11 describes the characteristics of simulated metal finishing wastewater referred from Gabaldón et al. (2007).

Table 11: Characteristics of Simulated metal finishing wastewater

Parameters	*Values*
Nitrate-N	*500-1000 mg/L*
Sulphates	*2000 mg/L*
Chlorides	*150 mg/L*
Carbonates	*75 mg/L*
Bicarbonates	*125 mg/L*
pH	*6.5-7.6*
Zinc	*15mg/L*
Copper	*15mg/L*
Cadmium	*10mg/L*
Manganese	*10mg/L*
Nickel	*10mg/L*

4.5.1 XRD analysis of Ti/Co_3O_4

Figure 32 describes the XRD analysis of fresh and used Ti/Co_3O_4 electrodes. XRD is used to analyse the phase structures of Co_3O_4 films produced at the Ti plate. According to Figure 32, peaks suggest the cubic phase of the Co_3O_4 standard (JCPDS File No. #42-1467). Over time, pollutants including oxidation products, organic residues, or species present in wastewater may build up on the surface of a used plate. By interfering with the scattering of X-rays, these pollutants can alter the diffraction pattern and lessen the intensity of XRD peaks (Al-Nuaim et al., 2023; L. Yang et al., 2017). Thus, it can be depicted that a negligible difference is observed in the XRD analysis of fresh and used Ti/Co_3O_4.

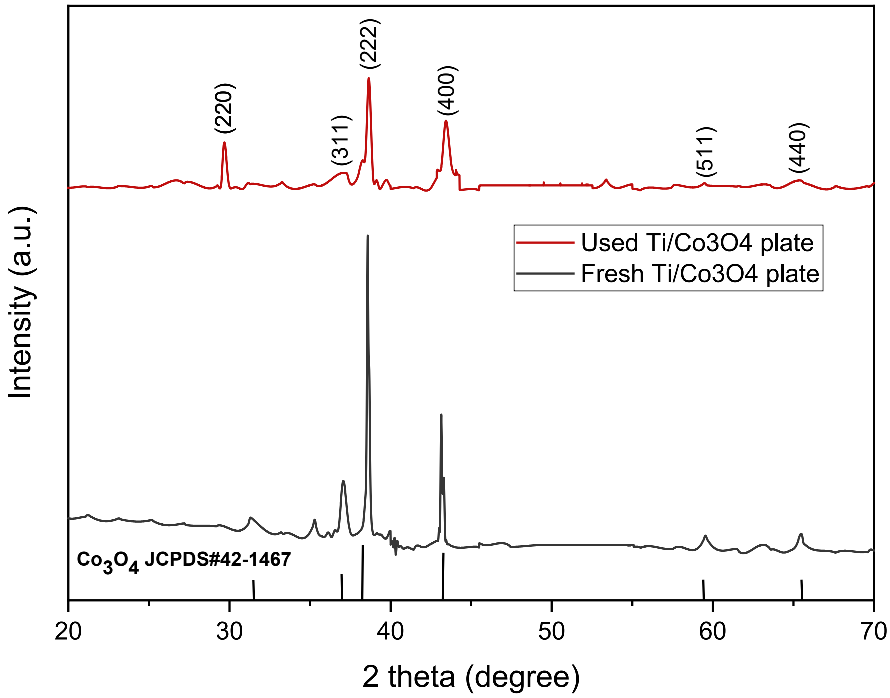
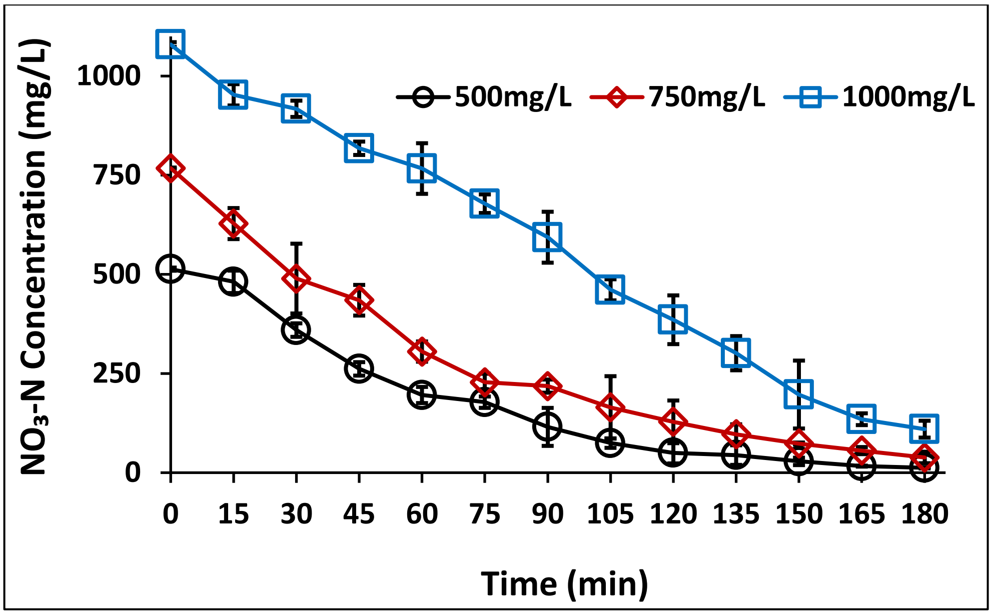
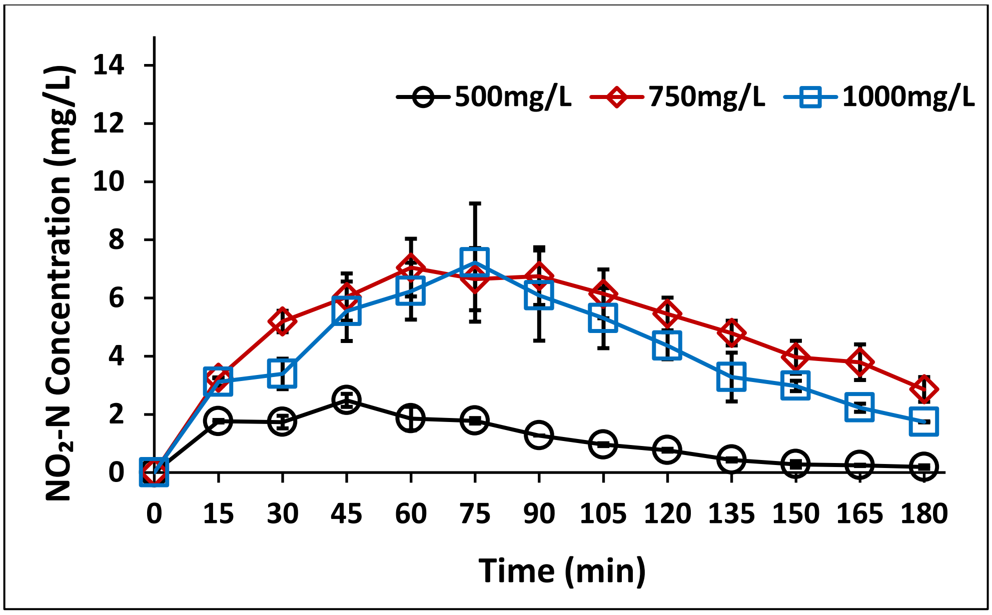


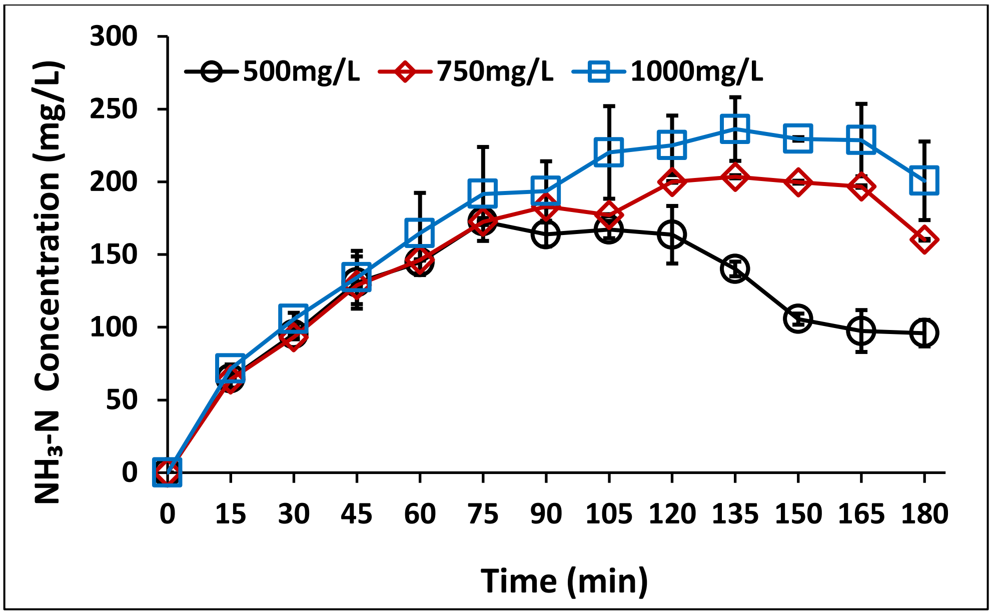
Figure 33 : XRD analysis of fresh and used Ti/Co_3O_4

4.5.2 Effect of initial nitrate concentration

Figure 33 shows the effect of various initial nitrate-N concentrations (500, 750 and 1000 mg/L NO_3-N) on the reduction of nitrate at a current density of 20 mA/cm^2 using Ti/Co_3O_4 cathode and Ti/RuO_2 anode for 180 minutes of electrolysis time. Figure 33 demonstrates that nitrate removal was 97%, 95% and 90% for 500, 750, and 1000mg/L initial nitrate concentration, respectively. NO_2-N accumulation was <4 mg/L at the end of 180 min, irrespective of the initial nitrate-N concentration. However, accumulation of NH_3-N was ~95 mg/L at initial nitrate-N concentration of 500 mg/L and increased to ~190 mg/L at initial nitrate-N concentration of 1000 mg/L. Also, N_2-N generation marginally decreased as the initial nitrate concentration increased. Thus, the initial nitrate-N concentration didn't have much impact on nitrate removal and product selectivity as products were formed according to the increasing rate of initial concentration.


NO₃-N Concentration (mg/L)
1000
750
500
250
0
0
15
30
45
60
75
90
105
120
135
150
165
180
Time (min)
500mg/L
750mg/L
1000mg/L


NO₂-N Concentration (mg/L)
14
12
10
8
6
4
2
0
0
15
30
45
60
75
90
105
120
135
150
165
180
Time (min)
500mg/L
750mg/L
1000mg/L



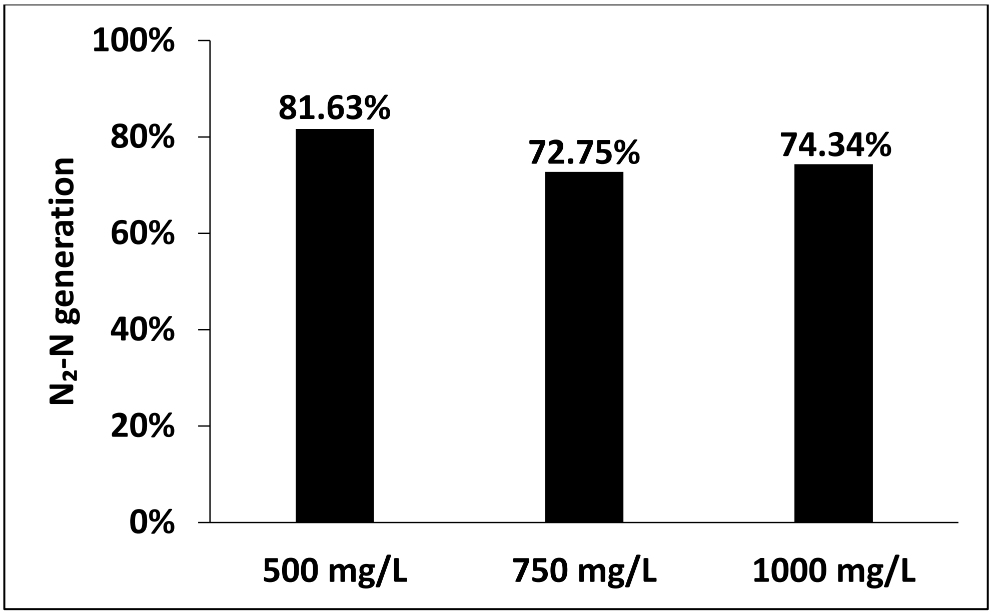


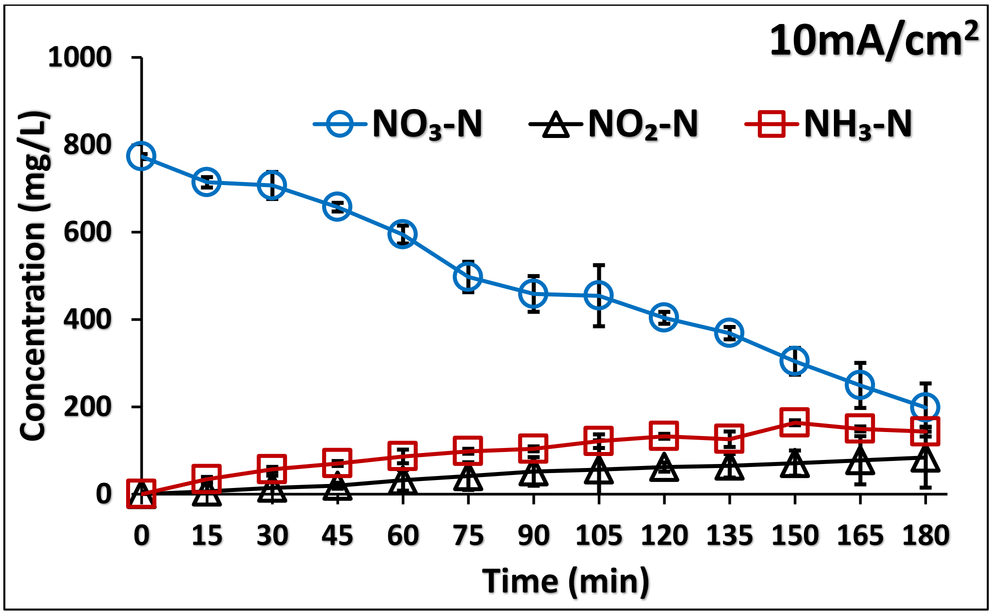
Figure 34 : Effect of initial nitrate concentration

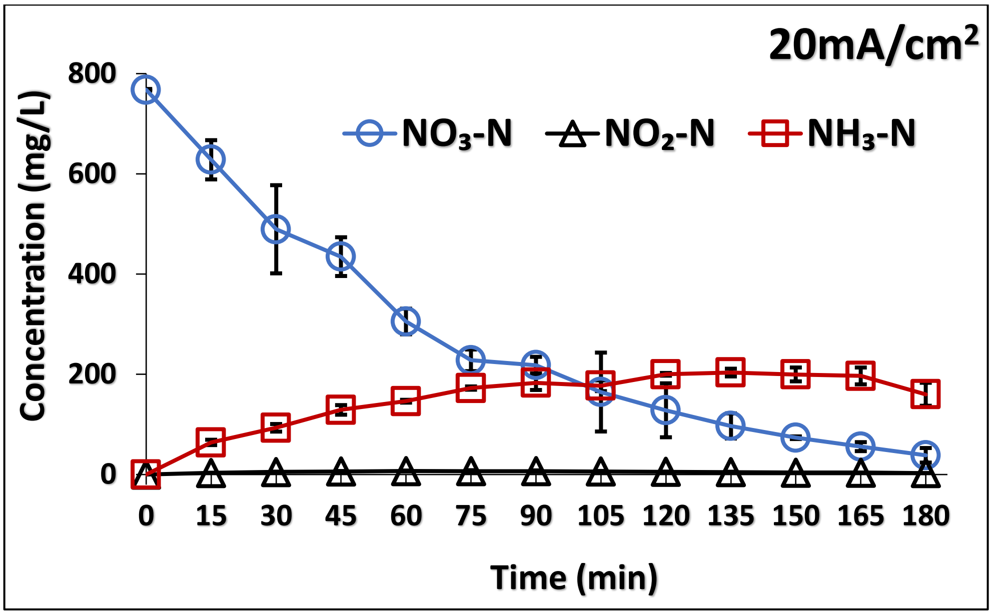
(Reaction conditions: Cathode: Ti/Co_3O_4, Anode: Ti/RuO_2, current density: 20mA/cm^2, Na2SO4 electrolyte: 2g/L, reaction time: 180min)

Su et al. (2017) studied nitrate removal by ECR process in actual textile wastewater and they observed that after 3 hours of treatment at 25 mA/cm^2 current density, the NO_3-N removal efficiency for raw wastewater was 59%. A little amount of NH_4-N (1%) was found, and 58% of the TN was successfully removed. Also, authors studied NO_3-N removal efficiency of Fenton pretreated wastewater using Ti/Co_3O_4 cathode. They achieved 93% nitrate removal with 32% NH_4-N generation. NO_2-N was negligible and TN removal was 61% after 3hrs of treatment.

4.5.3 Effect of current density

Current density is one of the factors that has the most impact on the electrochemical reduction process. . Studies were conducted using Ti/Co_3O_4 cathode and Ti/RuO_2 anode for 180min electrolysis time to determine the effect on the selectivity for the end-products and nitrate removal at current densities of 10, 20 and 30 mA/cm^2. Figure 34 shows that at current densities of 10, 20 and 30 mA/cm^2, respectively, NO_3-N removal was 74, 95, and 100%, whereas TN removal was 45%, 74%, and 79%. N_2-N selectivity increased as the current density increased. It was observed that N_2-N selectivity was almost similar with 20 mA/cm^2 and 30 mA/cm^2 current density.





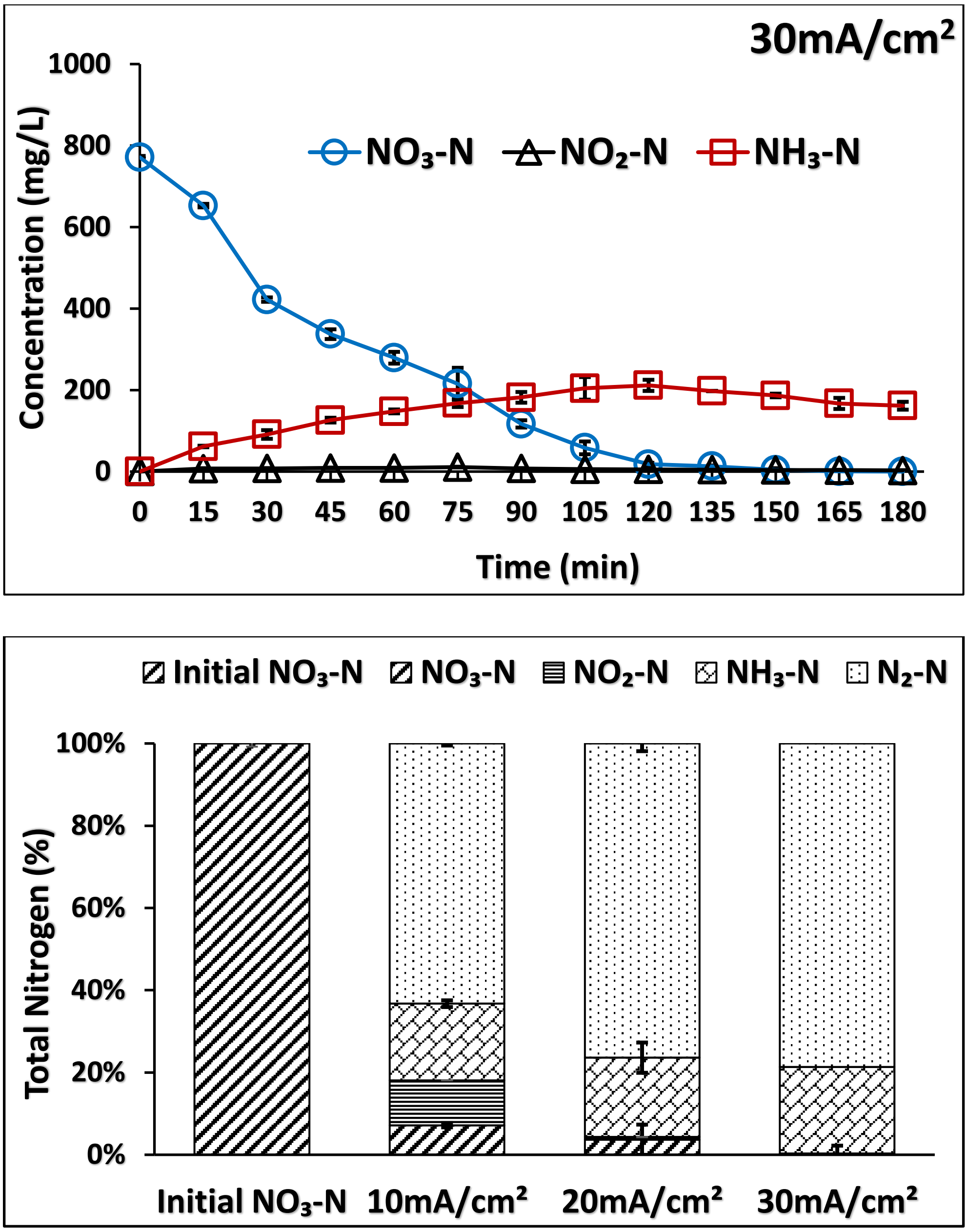


Figure 35 : Effect of current density on nitrate removal

(Reaction Conditions: Simulated metal finishing wastewater NO_3-N Concentration: 750 mg/L, cathode: Ti/Co_3O_4, anode: Ti/RuO_2, reaction time: 180 min; inter-electrode distance: 7.7cm)

W. Li et al. (2016) examined the nitrate removal in a divided cell at various current densities. The nitrate removal efficiency rose steadily as the current density rose from 5 to 20 mA/cm^2. However, from 15 mA/cm^2 to 20 mA/cm^2, the nitrate removal rate increased slowly. So, the optimum nitrogen selection rate was found at a current density of 15 mA/cm^2. Sahu et al. (2014) stated that increasing current density boosts nitrate removal performance but excessive current density also promotes electrode corrosion and dissolution. Also, it increases the energy consumption of the electrocatalytic system.

Thus, N_2-N was the major product obtained at the end of the treatment. Further, we conducted experiments to study the lifespan of Ti/Co_3O_4 electrodes.

4.5.4 Reusability of Ti/Co_3O_4

Catalysts must have a longer life span in order to be used on a wider scale. . Figure 35 illustrates the ability of Ti/Co_3O_4 electrodes to be recycled for NO_3-N reduction. Experiments were conducted at 20mA/cm^2 using Ti/Co_3O_4 cathode and Ti/RuO_2 anode for 750mg/L NO_3-N concentration in simulated metal finishing wastewater for 60min of reaction time. As can be seen, the Ti/Co_3O_4 electrode can be used for 12 continuous reaction cycles before showing any detectable loss in catalytic activity. It's noteworthy to observe that ammonia formation changed after the 12th cycle to become more selective. Sloughing of the cobalt oxide layer was noticed after 15 number of cycles. ICP (Inductively Coupled Plasma) was used to determine the concentration of dissolved cobalt in the treated solution, and it was found that only 0.06mg/L was present after 180min of reaction time. ICP was also used to detect the concentration of metals in treated wastewater is shown in Figure 36. All metals present in simulated metal finishing wastewater were efficiently removed during the ECR process. It is possible that some of the metal ions may be reduced in the cathode compartment and deposited on Ti/Co_3O_4 cathode altering the selectivity of end-products after repeated uses.

Y. Zhang et al. (2018) investigated reusability of Cu/Ni (copper on nickel foam) electrode for nitrate reduction in real textile wastewater and reported that Cu/Ni electrode can be used for 8cycles without leaching Cu during the treatment.

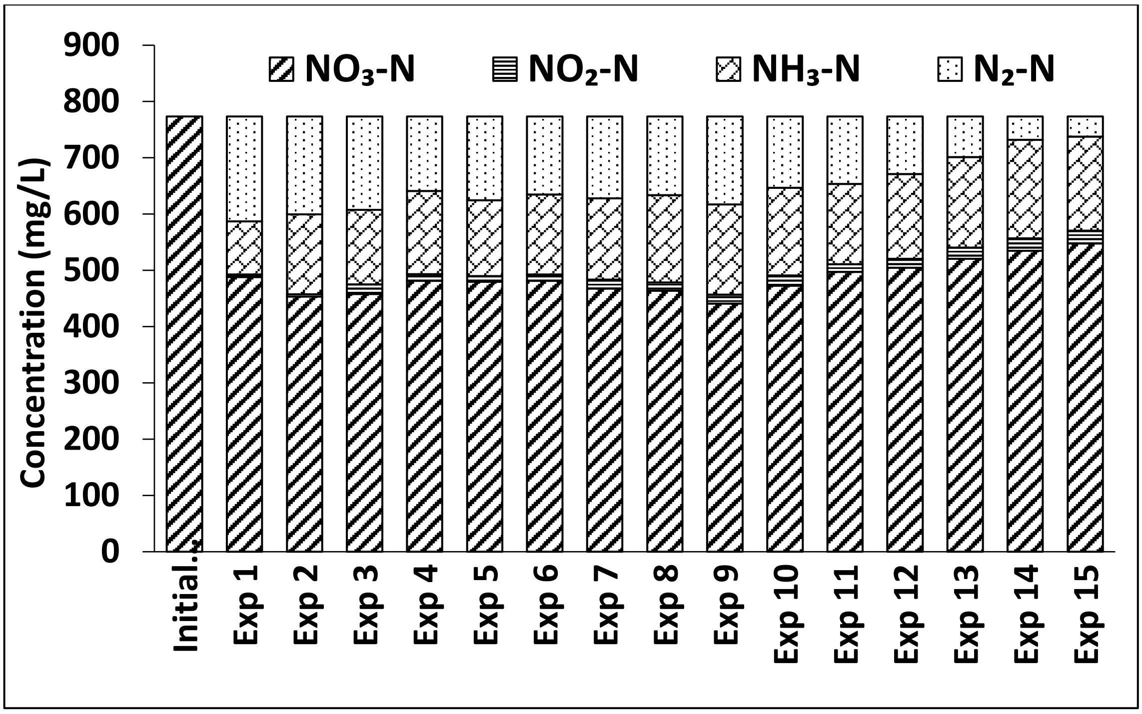


Figure 36 : Reusability of Ti/Co_3O_4 cathode

(Reaction Conditions: Anode: Ti/RuO_2; cathode: Ti/Co3O4; current density: 20mA/cm^2; simulated metal finishing wastewater containing nitrate-N: 750mg/L; reaction time 60min)

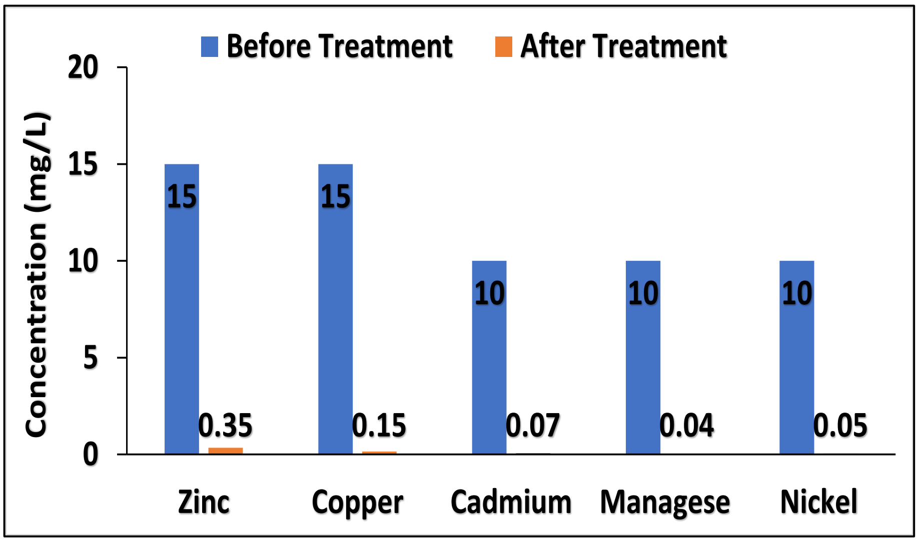


Figure 37 : Concentration of metals before and after treatment

(Reaction Conditions: Anode: Ti/RuO_2; cathode: Ti/Co_3O_4; current density: 20mA/cm^2; simulated metal finishing wastewater containing nitrate-N: 750mg/L; reaction time 180min)

During the ECR process for nitrate-N removal in simulated metal finishing wastewater, white precipitated were formed. Besides the reduction of metal ions to corresponding metal form, the metal ions may also get precipitated as metal hydroxide due to high pH in the cathode compartment. These precipitates were collected as they were easily settleable and dried at room temperature for XRD analysis. Figure 37 shows the XRD analysis of precipitates formed during the ECR of nitrate. It can be seen that the precipitates contain all the metals initially present in the metal finishing wastewater.

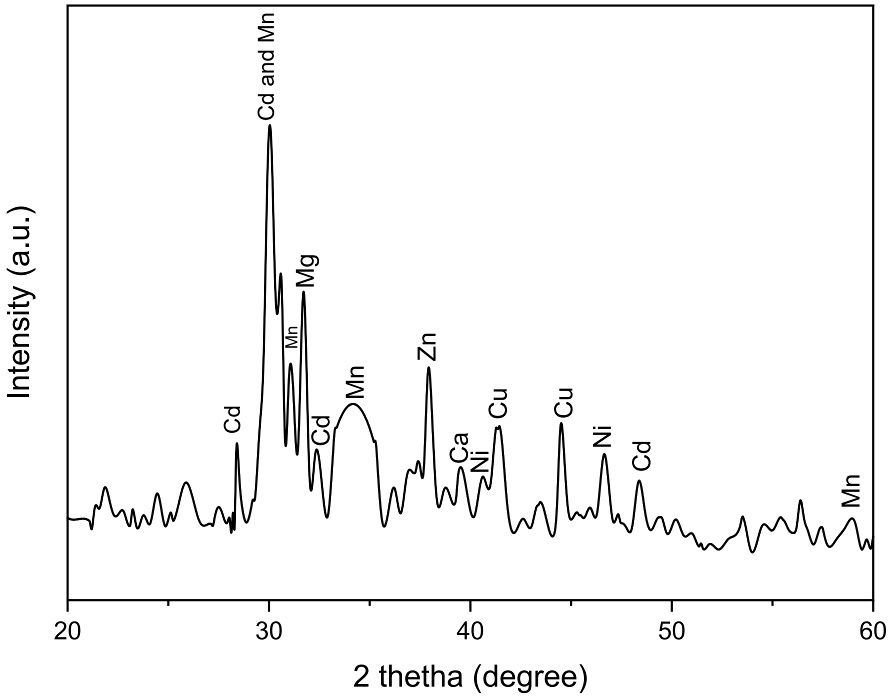


Figure 38 : XRD analysis of precipitates formed in treated water

4.5.5 Struvite formation for ammonia removal

As noted in section 4.5.2, during the ECR of metal finishing wastewater, the accumulation of NH_3-N was as high as ~190 mg/L at the initial nitrate concentration of 1000 mg/L. The discharge limit for NH_3-N in the treated wastewater is 50 mg/L in India. Thus, it was necessary to remove ammonia. Precipitation of ammonia as struvite is an efficient method to recover ammonia for use as a fertilizer. Struvite (magnesium ammonium phosphate) is a substance that is frequently used in wastewater treatment operations to remove ammonia. Struvite crystals develop when there is enough amount of magnesium, ammonium, and phosphate ions, and they either adsorb or integrate the ammonium ions (Perera et al., 2019). As a result, the ammonia in the effluent is eliminated. It provides a considerate method for reducing ammonia levels and recovering valuable substances from wastewater.

Struvite offers several benefits: (1) Struvite precipitation can efficiently remove ammonia from wastewater and lower the content to tolerable limits (Kumar & Pal, 2015). (2) Resource recovery: because struvite includes phosphate and nitrogen, which can be extracted and used to make fertilisers or other useful products (Puchongkawarin et al., 2015; Ryu et al., 2012; Talboys et al., 2016). (3) Ammonia may corrode and foul pipelines, pumps, and other equipment. Struvite removal increases the lifespan of the wastewater treatment system and protects the infrastructure. In general, a pH of around 9 (González-Morales et al., 2021; Hao et al., 2008) is considered optimal for struvite formation, as it provides the necessary conditions for the precipitation of magnesium, ammonium, and phosphate ions to form struvite crystals.

Our study includes the removal of remaining ammonia generated from the ECR of nitrate by struvite formation. XRD analysis was carried out to study the crystallography of struvite. Additionally, the effect of various 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) on struvite formation were studied by adjusting pH at 9. For phosphate analysis, a colourimetric method (stannous chloride method, APHA Methods 4-163) was used.

XRD analysis of struvite (Mg:NH_4:PO_4 = 1.5:1:1.5) is shown in Figure 38. For struvite analysis, the sample was dried at room temperature for 24hrs, and the dried sample was used for XRD analysis. Peaks were discovered at various angles which correspond to the Braggs reflections of the facets of the crystal planes at 2θ which was confirmed by JCPDS File No. 77-2302 for struvite. The XRD peaks observed in the struvite formed in the present study also closely matched with those reported by Lee et al. (2015) and Jabr et al. (2019).

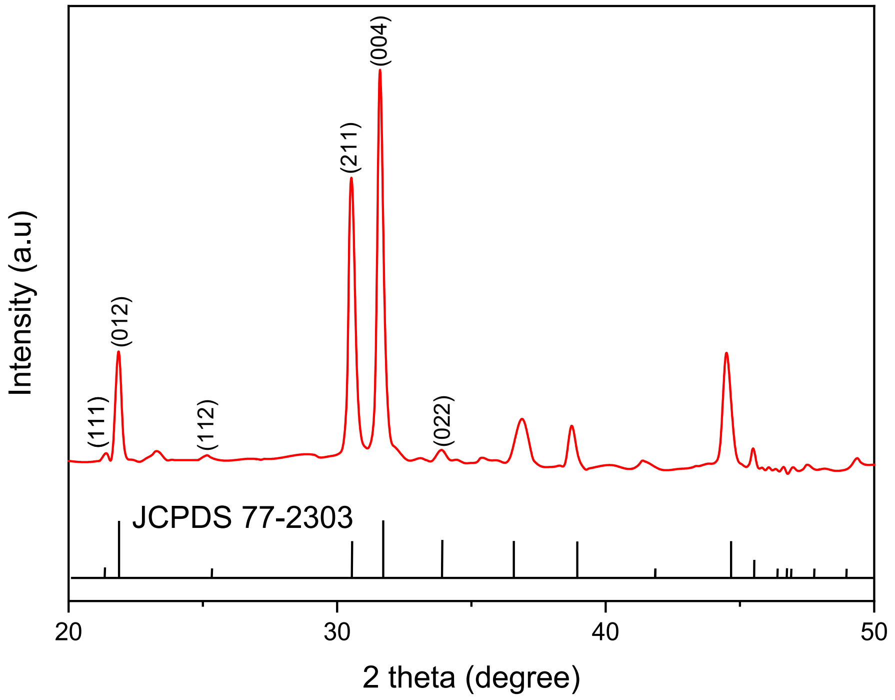


Figure 39 : XRD analysis of struvite

4.5.5.1 Effect of molar ratios of Mg:NH_4:PO_4 on struvite formation for removal of ammonia

Various struvite 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) at pH 9 on struvite formation were studied to remove remaining ammonia from treated metal finishing wastewater. A 1.5:1:1.5 molar ratio was found to be the most effective for removing the most ammonia, which allowed concentrations of wastewater from simulated metal finishing processes with high nitrate content to be finally processed while removing ammonia below discharging levels. 80% ammonia was removed by struvite formation with minimum residual of PO_4 (3.5-3.8mM).

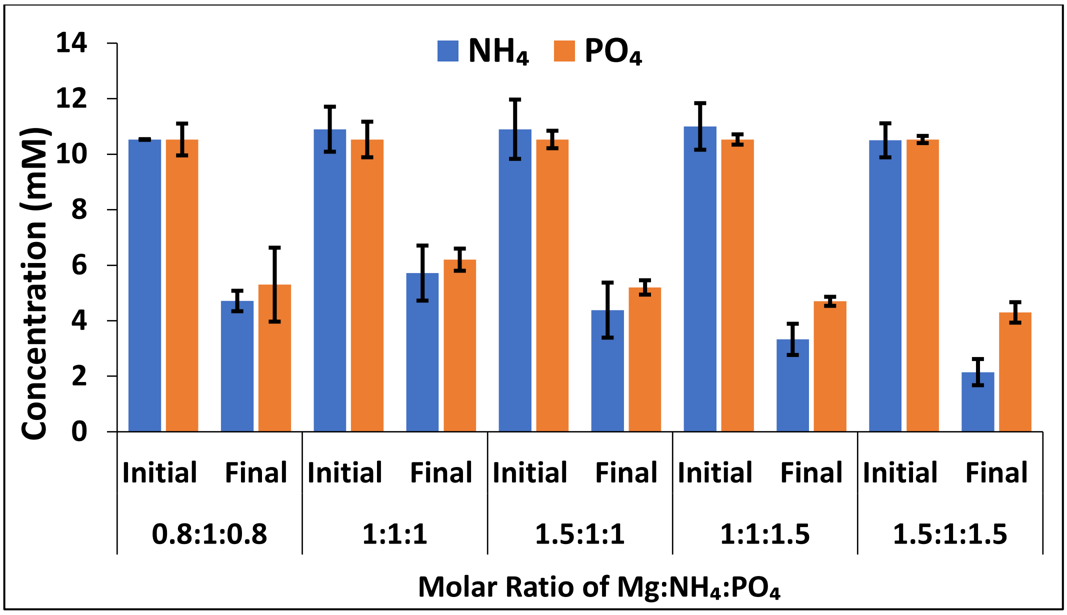


Figure 40 : Ammonia removal by struvite formation

Zhou & Wu, (2012) showed that 98% ammonia-N was removed with 2.32mg/L PO_4^{3}-P residue at 1.10:1:1.31 molar ratio of Mg/N/P. One factor that contributed to the molar ratio exceeding the predicted value of Mg/N/P 1:1:1 was the synthesis of $Mg_3(PO_4)_2$, which slowed the pace of struvite precipitation and resulted in the usage of Mg_2^+ in unpredictably high levels (Ohlinger et al., 1998). This meant that driving out all available phosphate that was accessible could need a surplus of magnesium. In fact, the majority of the reported molar ratios in the literature were frequently at odds with the ones predicted by theory. According to the literature, the observed Mg/N and P/N values ranged from 1.1 to 1.67 are suitable (Parsons & Doyle, 2002).

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CHAPTER 5: CONCLUSION

PART 1: Spatially suspended catalyst

Part 1 (A) Ag-PVA beads

1) The addition of Ag-PVA beads considerably increased the degree of nitrate elimination and the selectivity towards nitrogen gas generation in both the undivided and divided cells.
2) The concentration of Ag-PVA beads, the cathode material, and the current density all had a significant impact on the end-product selectivity and nitrate elimination.
3) Fe provided the maximum removal of nitrate ions with the best selectivity for nitrogen gas and the least selectivity for nitrite formation among the several cathode materials evaluated.
4) At a dosage of 5 mM Ag-PVA, the catalyst's mass activity (mg NO_3-N removed per g Ag per min) was at its maximum, whereas at a dose of 6.67 mM Ag-PVA, the selectivity for the creation of N_2-N (62.1%) was at its best and that for the formation of NH_3-N (37.7%) was at its lowest.
5) The effect of initial nitrate concentration didn't affect on ECR of nitrate but had little effect on selectivity.
6) The selectivity for nitrogen gas and nitrate removal increased with a rise in current density from 5 to 15 mA/cm^2, whereas the selectivity for NH_3-N production rose with a rise to 20 mA/cm^2.
7) Beads made of Ag-PVA may be recycled eight times without suffering much catalytic activity loss.
8) The ECR of nitrate in a genuine groundwater sample produced a removal rate of 85%, demonstrating the relevance of the current investigation in the field.
9) This work provides the first demonstration of the effectiveness and great reusability of Ag-PVA beads as a catalyst for the removal of nitrate and TN from water.

Part 1 (B) AgMPs catalyst

1) In both the undivided and divided cells, the addition of AgMPs significantly enhanced the degree of elimination of nitrates and the selectivity for nitrogen gas production.

2) The elimination of nitrate and the selectivity of the end-products were significantly influenced by the concentration of AgMPs, electrode distance, current density, and other experimental factors including the cathode material.
3) Ti had the maximum nitrate removal, the best nitrogen gas selectivity, and the least amount of nitrite formation of all the cathode materials studied.
4) The most mass activity of the catalyst (mg NO_3-N removed per g Ag per min) was achieved at the maximum AgMPs dosage of 4 mM, while the selectivity of the 8 mM AgMPs was maximum for the synthesis of N_2-N (60%) and lowest for the production of NH_3-N (31%).
5) The rate of NO_3-N elimination reduces as the initial nitrate concentration rises. The selectivity for nitrogen gas as a final product and the removal of nitrate both increased with a boost in current density from 5 to 10 mA/cm^2, but the selectivity for ammonia generation was improved with an additional increase to 15 mA/cm^2.
6) The catalytic activity of AgMPs may be renewed repeatedly without suffering considerably 10 times. In this study, it is demonstrated for the first time how effectively and repeatedly nitrate and TN may be removed using AgMPs as a catalyst.
7) The ECR of nitrate in a real groundwater sample produced a nitrate removal rate of 59%, demonstrating the relevance of the current investigation in the field.

PART 2: Treatment of metal finishing wastewater containing high nitrate concentration using the ECR process

(1) Ti/Co_3O_4 considerably increased the rate of nitrate removal and the selectivity for nitrogen gas generation in divided cell.

(2) 95% nitrate removal was obtained with 750mg/L initial nitrate concentration with 95% selectivity towards N_2-N (72.75%) at 20mA/cm^2 in 180min.

(3) Complete nitrate removal was achieved at 30mA/cm^2 but due to more energy consumption, 20mA/cm^2 current was good enough to remove nitrate with good selectivity towards nitrogen gas.

(4) The reusability of coated catalyst Ti/CO_3O_4 was about 12 times.

(5) The molar ratio of Mg:NH_4:PO_4 affected the struvite formation for ammonia removal. Among all ratios, 1.5:1:1.5 molar ratio gave maximum ammonia removal giving its concentration in dischargeable limit.

(6) The other metals in metal finishing wastewater were successfully removed to be negligible in treated water.

Recommendation

The method proposed in this study might be simply scaled up and utilised to remove nitrate and TN from real wastewater on a large scale. Future tests on the removal of nitrate from diverse groundwater samples and improvements to the reusability of Ag-PVA beads and AgMPs as spatially suspended catalysts. Future studies can be conducted on the ECR of nitrate using Ti/Co_3O_4 in various wastewater and water samples.

Publications

1. **Janhavi Ingle**, U D Patel, “Electrochemical reduction of aqueous nitrate using metallic silver particles as a spatially suspended catalyst”. Journal of Environmental Chemical Engineering (Impact Factor: 7.968). (Revised manuscript under review).
2. **Janhavi Ingle**, U D Patel, “Electrochemical reduction of nitrate in the presence of silver-coated polyvinyl alcohol beads as a spatially suspended catalyst”. Journal of Water Process Engineering (Impact Factor: 7.34). Volume 49, October 2022, 103082. https://doi.org/10.1016/j.jwpe.2022.103082.
3. **Janhavi Ingle,** U D Patel, “ Electrochemical reduction of nitrate using Ti/Co_3O_{SS} in metal-finishing wastewater”. **Manuscript under preparation.**

Conferences

1. Janhavi Ingle, U D Patel, entitled “**Electrochemical nitrate reduction of nitrate using different metal oxide cathodes and Ti/RuO_2 anode”** International Conference on Recent Advances In Applied Sciences and Engineering (RAISE 2023), held on 12th – 13th April 2023 at The Maharaja Sayajirao University of Baroda, India. (Oral presentation)
2. Janhavi Ingle, U D Patel, entitled **"Electrochemical reduction of nitrate with different metal oxide cathodes"** International Symposium on Sustainable Urban Environment (ISSUE-2022), held on 11th-14th October 2022 at Sustainable Cluster, UPES, Dehradun, India. (Poster presentation)
3. Janhavi Ingle, U D Patel, entitled **"Catalytic Electrochemical reduction of nitrate in the presence of Ag-PVA beads"** 1st International Conference on Advances in Water Treatment and Management (ICAWTM-22), held on 25th-26th March 2022 at Pandit Deendayal Energy University, Gandhinagar, Gujarat, India. (Oral presentation)

Annexure

S1. Calibration plots of nitrite and nitrate and sample calculation

Nitrate-nitrogen (NO_3-N)

The concentration of NO_3-N was determined by APHA Method 4-115. Also, separately NO_2-N was determined by APHA Method 4-115. Absorbance at 220nm and 275nm for nitrate, as well as nitrite, was measured, and a standard calibration plot was prepared for nitrate (Plot 1a) and nitrite (Plot 1b). A spectrum of nitrate is shown in Figure S1a and nitrite in Figure S1b.

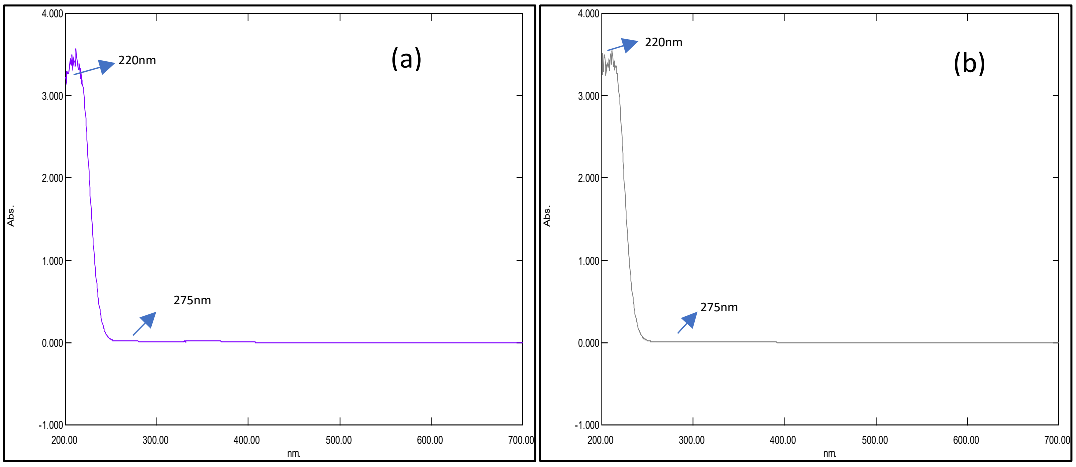
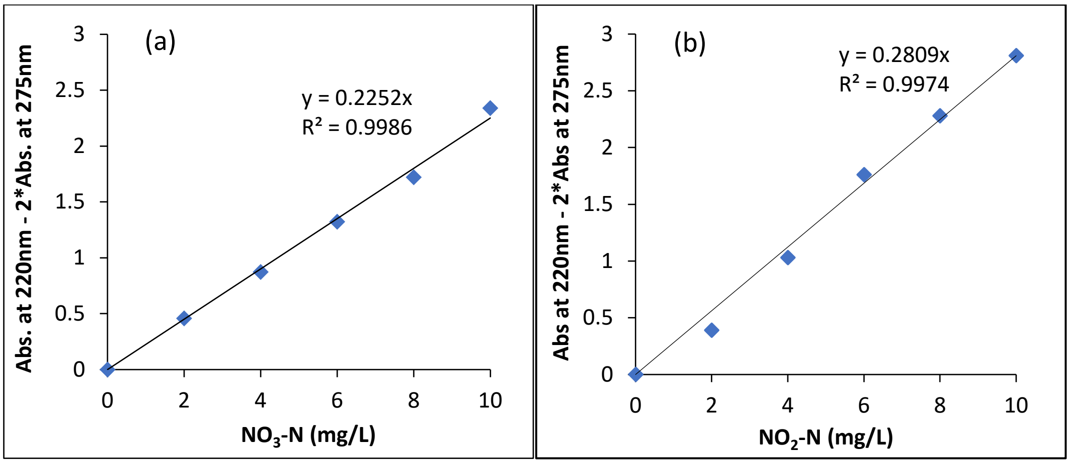


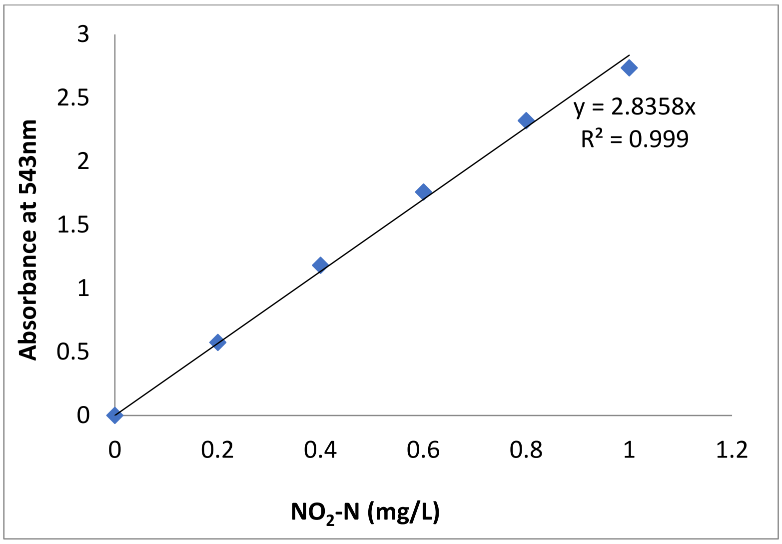
Figure 1. Spectrum of NO_3-N (a) and NO_2-N (b) absorbance at 220nm and 275nm



Plot 1. Standard calibration plot of NO_3-N (a) and NO_2-N (b) determined by APHA Method 4-115

Nitrite- Nitrogen (NO_2-N)

The concentration of nitrite was determined by APHA Method 4-112, N(1-naphthyl) Ethylenediamine Dihydrochloride (NEDA) method. Absorbance at 543nm was measured and a standard calibration plot was prepared (Plot 2).



Plot 2. Standard calibration plot of NO_2-N determined by APHA Method 4-112

Calculation of residual nitrate concentration after 15min of reaction time.

Step 1: Total absorbance of nitrate + nitrite = $Abs_{at220} - 2*Abs_{at275}$

= 0.497 – 2*0.018

= 0.461

Step 2: Absorbance of nitrite (by APHA Method 4-112) = 0.222

∴The concentration of nitrite in the sample = 0.222 / 2.835 (from Plot 2)

= 0.0783

Step 4: Absorbance at (220nm-2*275nm) of nitrite = 0.0783 * 0.289 (from Plot 1b)

= 0.022

Step 5: Net Absorbance of nitrate = Total absorbance of (nitrate + nitrite) – Absorbance of nitrite at (220nm - 2*275nm)

= 0.461 – 0.022

= 0.439

Net Nitrate concentration = 0.439 / 0.2252   (from Plot 1a)

= 1.949 mg/L

As the sample was diluted 10times, ∴ 1.949 * 10 = 19.49 mg/L

So, after 15min, nitrate concentration = 19.49 mg/L

Similarly, residual nitrate concentration was achieved after every reaction time.