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 shown in Figure 1.

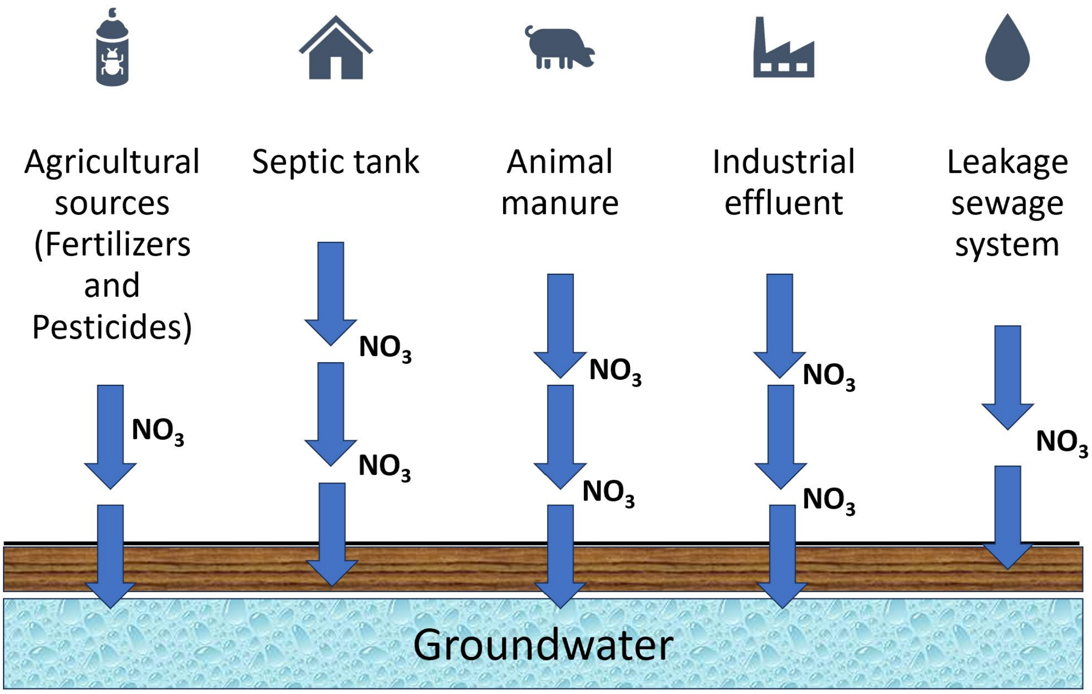

Figure 1: Sources of nitrate contamination in groundwater

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). Wastewater from several industrial operations often contains nitrates and other nitrogenous chemicals. As a result of their operations, manufacturing companies, chemical plants, and food processing units may release industrial effluents that contain nitrate-rich wastewater. An unexpected leak or improper disposal of these effluents might cause nitrate pollution of groundwater. Ammonium nitrate is a vital component of explosive compositions used by industries involved in the production or use of explosives. Wastewater containing ammonium nitrate may leak nitrate into the nearby soil and groundwater if it is handled or disposed of improperly.

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). Overall, nitrate contamination in groundwater is often a result of multiple interacting factors, including agricultural practices, urbanization, industrial activities, and natural processes. Effective management strategies and regulatory measures are needed to mitigate nitrate pollution and protect groundwater quality for human consumption and ecosystem health (Adimalla et al., 2021; Panneerselvam et al., 2022; Tanwer et al., 2023).

The World Health Organization (WHO) prescribes maximum permissible limits of nitrate and nitrite as 50 and 3 mg/L (Herschy, 2012 ; 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 (BIS, 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. In India, many places have been reported to have more nitrate contaminant levels in groundwater than the prescribed limit. The nitrate contamination range reported is 59mg/L to 215mg/L (Devaraj et al., 2020; Pant et al., 2020; A. Roy et al., 2020). Nitrate concentrations as high as 300mg/L in groundwater is also reported (Kshetrimayum & Thokchom, 2017). 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). However, 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 risky however 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 advanced 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 2 describes the pathways and mechanisms of ECR of nitrate. The labelling of pathways in Figure 2 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 2, 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.

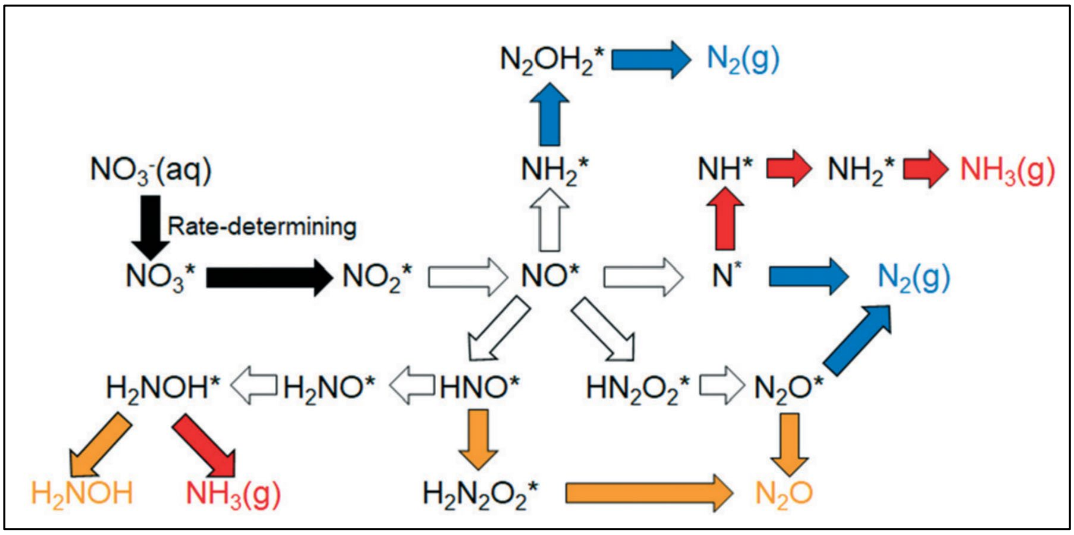

Figure 2: General mechanism of nitrate reduction (Z. Wang et al., 2021)

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)
Source	**NO_3^- concentration**	**Reference**
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, however, 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 high concentrations of 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

The overall objective of this research work was to study electrocatalytic reduction of nitrate in water and metal-finishing wastewater using relatively low-cost catalysts such as silver metal and cobalt oxide with an aim to maximize the conversion of nitrate into innocuous nitrogen gas. The following paragraphs show detailed objectives.

Part 1: ECR of nitrate using spatially suspended catalyst (Ag-PVA beads and AgMPs)

Experiments were conducted to study synthesis process of catalysts. Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) was used to study the morphological and crystallography of catalysts. Experiments were carried out in undivided as well as divided cell in absence and presence of catalysts to explore the ECR of nitrate. The effect of various operating parameters (concentration of catalyst, cathode material, current density, inter-electrode distance, initial nitrate concentration and reusability) were studied using catalysts. Experiments were carried out to study the effect of catalyst in groundwater.

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.