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 (J. 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 various 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 exceedingly 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, manganese (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 carbon/nitrogen (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 has 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, however, 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 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 function 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; however, 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 variations in temperature, pH, and concentration of dissolved oxygen. 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 by catalytic hydrogenation is quite challenging as 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 a permanent source of iron in the ground in the permeable barrier method which can be difficult to remove.
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 manage 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 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.

J. F. Su et al. (2024) investigated the bimetallic palladium (Pd) and tin (Sn) catalysts, which are electrochemically deposited on stainless steel mesh support (Pd–Sn/SS) for the selective conversion of harmful nitrate (NO_3^-) into nitrogen (N_2) gas. The findings show that the bimetallic makeup of the Pd–Sn/SS electrodes significantly affected the nitrogen selectivity, nitrate transformation efficiency, and reaction pathway for nitrate reduction. An excellent nitrate conversion of 95%, nitrogen selectivity of 88%, and nitrogen production of 82% are discovered in the electrode constructed from Pd:Sn = 1:1 (mole ratio).

Xue et al. (2023) studied a high-performance electrode boronization of nickel foam that produces a consistent ammonia production rate of 19.2 mg h^{-1} cm^{-2} with a high Faradaic efficiency of 94% for the conversion of NO_3^- to NH_3. The electrode is generated by direct boronization of nickel foam and has electron-abundant surfaces. By transforming acid-stable surface nickel oxides into dyadic nanosheets made of metallic nickel and amorphous nickel borates, the micro-processing lowers the work function and starts a local electric field for the nickel foam, which encourages the adsorption and transformation of nitrate anions.

Z. Liu et al. (2023) investigated the electrocatalytic reduction for elimination of nitrate. The nitrate was reduced in a flowthrough electrochemical reactor using a Pd-Cu modified carbon nanotube membrane that was prepared using the electrodeposition technique. The membrane that was produced with a 1:1 Pd:Cu ratio showed a comparatively high N_2 selectivity and nitrate removal efficiency. At potentials lower than −1.2 V, the membrane eliminated nitrate almost entirely (~99%). When the Pd:Cu=1:1 membrane was operating at −0.8 V, the nitrate removal efficiency was 56.2% and the N_2 selectivity was 23.8%. In acidic circumstances, nitrate removal was improved, but N_2 selectivity was reduced.

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 improved by catalysts. In comparison to non-catalytic systems, the inclusion of a catalytic material 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.

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 and relatively low-cost catalyst and unmodified or modified cathodes. According to our knowledge, there are no reports illustrating the impact of spatially suspended noble metal 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.