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Catalytic degradation of ammonia and nitrate from wastewater - A critical review

Manali Date^{1*}, Dipika Jaspal^{2*}

^{1*}Department of Civil Engineering, Symbiosis Institute of Technology (SIT), Symbiosis International (Deemed University) (SIU), Lavale, Pune, Maharashtra, India

^{2*}Department of Applied Science, Symbiosis Institute of Technology (SIT), Symbiosis, International (Deemed University) (SIU), Lavale, Pune, Maharashtra, India

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ABSTRACT

The foibles in extant wastewater treatment technologies release untreated nitrate and ammonia containing compounds into different potable water sources. The toxicity and fatal effects of entrained nitrate and ammonia produce lethal health consequences upon being consumed. Novel methods obtained by combining light, electrical, and chemical energy have opened new frontiers of pronounced efficiency and reduced demerits. These methods lead to the destruction of nitrate instead of just removing it by adsorption on the surface of another material. Photochemical (PC) and electrochemical (EC) reactions offer a vast scope for degrading harmful ammonia and nitrates from wastewater. The catalyzed form of these processes has been found to be meritorious over non-catalyzed techniques due to several advantages like improved efficiency, lower energy input, lower reaction time, and product selectivity towards N₂ gas over nitrate and nitrite. This paper presents a review of significant research that has been performed using PC, EC, and photoelectrochemical (PEC) to remove ammonia and nitrate from wastewater. Not much research is available on the combined and simultaneous use of PC and EC oxidation and reduction processes which have immense potential as future methodologies for treating municipal and industrial wastewater to remove these toxic inorganic nitrogenous compounds. High ammonia and nitrate removal efficiencies at the laboratory scale have been reported using specific combinations of catalysts, pH, cell composition, electrodes, electrical input, and reaction time by electrochemical denitrification. However, they lack practical viability. Catalyzed photochemical processes are successful in removing ammonia and nitrate to a large extent and are practically viable if carried out using natural sunlight. Combined PC and EC, i.e., PEC oxidation and reduction processes, eliminate the occurrence of toxic intermediates and give about 90 % to 98 % conversion of ammonia and nitrate in the form of nitrogen gas.

*Corresponding author: Tel: 020-39116454

E-mail: dipikaj@sitpune.edu.in

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1. Introduction

Industries often dispose of their untreated nitrogen-bearing toxic wastes, mainly as ammonia (NH_3) and nitrate (NO_3^-) compounds, into water bodies or the ground and finally directly or indirectly join the water table [1]. As observed by Chauhan et al., nitrate was primarily released from the wastewater of pharmaceuticals, fertilizers, explosives, and other process industries. The usage of ammonia or nitrate containing fertilizers to improve the crop yield was in excess quantities, and the unabsorbed portion of the compounds eventually flowed down the soil profile, becoming a part of the groundwater [2]. Ammonia (released mainly from agricultural and related industries wastewater) and nitrate are readily soluble in water and migrate into groundwater [3]. Their rate of leaching is dependent on their respective soil properties [4]. Excess nitrogen and phosphorus compounds in water can lead to eutrophication and increased biomass production, resulting in the depletion of oxygen in the water, making it septic, and disrupting the balance of aquatic life [5]. Not all forms of nitrogen are toxic to life, but the compounds of utmost significance are ammonia and nitrates. The total inorganic nitrogen constitutes ammoniacal nitrogen, nitrite (NO_2^-), and nitrate, as these oxides have high stability. The maximum allowable concentration of ammonia nitrogen ($\text{NH}_3\text{-N}$) in drinking water is 0.5 mg/L as per the Bureau of Indian Standards (BIS), and that of nitrate nitrogen ($\text{NO}_3\text{-N}$) is 10 mg/L as per the BIS and World Health Organization (WHO) guidelines [6]. The intake of nitrogenous compounds like nitrate, nitrite, and ammonia may lead to a plethora of problems. Ammonia is toxic and causes several damaging effects on the human body. Nitrate is not directly harmful, but its subsequent transformation into nitrite when it enters the human body is harmful due to the formation of carcinogenic and mutagenic N-nitrosamines compounds, e.g., gastric cancer [2]. Elevated nitrate contamination in water can cause congenital disabilities, such as infant methemoglobinemia [7] of blood, also known as the blue baby syndrome in children. Therefore, the removal of toxic nitrogenous compounds from water becomes necessary. Several methods have been explored for the removal of nitrogenous

toxicants from wastewater. These denitrification methods include physical [8], chemical [9], physiochemical [10], and biological [11,12] processes. Chemical and biological methods have been extensively tried and tested in the past for treating a diverse range of pollutants in wastewater like electro dialysis [13], precipitation [14], adsorption [15], ion exchange [16], membrane-filtration [17], air-stripping [18], etc. Biochar is a recently developed green material for the removal of ammonia and nitrate from wastewater by adsorption [19,20]. However, this also seems to have demerits like difficulty in quantification [19] and interference of other competing ions [20] making it less viable practically. The limitations of all the above methods are due to expensive technology, environmental pollution issues, generation of sludge, and long-term waste disposal problems. The major drawback of biological methods is that they require a suitable carbon source, [12] inferring that these methods are applicable only for wastewater treatment and not for water treatment. But there has been considerable upgradation in the biological methods overcoming many of these drawbacks. The two most recent methods include Anaerobic ammonium oxidation (ANAMMOX) [21] and microalgae-bacteria consortia [22]. The denitrification process involves the conversion of aqueous ammonia (NH_4^+) into nitrates, nitrites, and/or nitrogen gas (N_2) by oxidation. These nitrates and nitrites are converted into nitrogen gas by reduction [23]. Hence, both oxidation and reduction reactions are essential for removing these inorganic forms of nitrogen in wastewater. Advancements in the conventional methods of oxidation and reduction have opened an arena of newer, more improved, and more environmentally efficient set of oxidation and reduction processes in the form of advanced oxidation processes (AOP's) [24] and advanced reduction processes (ARP's) [25]. The treatment techniques are routed through various electrochemical (EC) [26] and photochemical (PC) [27] approaches in the presence or absence of catalysts. When these techniques are carried out in the presence of a catalyst under the effect of light and external electric potential, they are known as photocatalysis and electrocatalysis, respectively.

These methods can be combined and performed in the presence or absence of catalysts to improve their efficiency and are known as Photoelectrochemical (PEC) methods [28]. A critical review of the methodology and mechanism of the PC, EC and PEC methods and their applications in oxidation, as well as the reduction of ammonia and nitrate compounds, has been done in this paper. This paper gives an insight into the pros and cons and the research gaps existing in these techniques.

2. Catalyzed and non-catalyzed photochemical (PC) process

A non-catalyzed photochemical process occurs by the irradiation of dissolved oxygen, thereby generating an oxidant species. But the subsequent decrease of dissolved oxygen discontinues the reaction after some time. This creates a need for research and development of novel catalyzed photocatalytic processes. The basic principle applicable in catalyzed PCs is the generation of reactive oxygen species by indenting light on a photocatalyst. A photocatalyst is a substance that does not directly take part in the reaction, but it actuates the reaction by absorbing light and generating the required electron/hole combinations. The light source may be natural sunlight (visible spectrum range) or an artificial UV

lamp. In simple words, the photochemical reaction is actuated by the absorption of light/photons by the catalyst. If the bandgap of the photocatalyst is narrow, it absorbs many light photons, and a lesser amount of energy is required to accelerate the speed of the chemical reaction.

A semiconducting material is the best-suited material for a photocatalyst due to its ability to conduct electricity when subjected to light of sufficient intensity (wavelength) at room temperature. The semiconductor absorbs the incident photon, which has higher energy than that of the bandgap of the material. Figure 1 explains the mechanism occurring in any photochemical process. These generated energy carriers (e^- and h^+) migrate to the surface [29]. The photocatalytic reaction is dependent on the energy potential of the valence band (E_{vb}), energy potential of the conduction band (E_{cb}), and the required reaction potential for the oxidation and reduction reactions. Heterogeneous redox photocatalysis is a widely adopted method of contaminant removal in wastewater applications. The catalyzed PC reaction overcomes the limitation of the noncatalyzed process, and it is a noteworthy approach for indemnification of toxicity imparted by ammonia and nitrate compounds in wastewater.

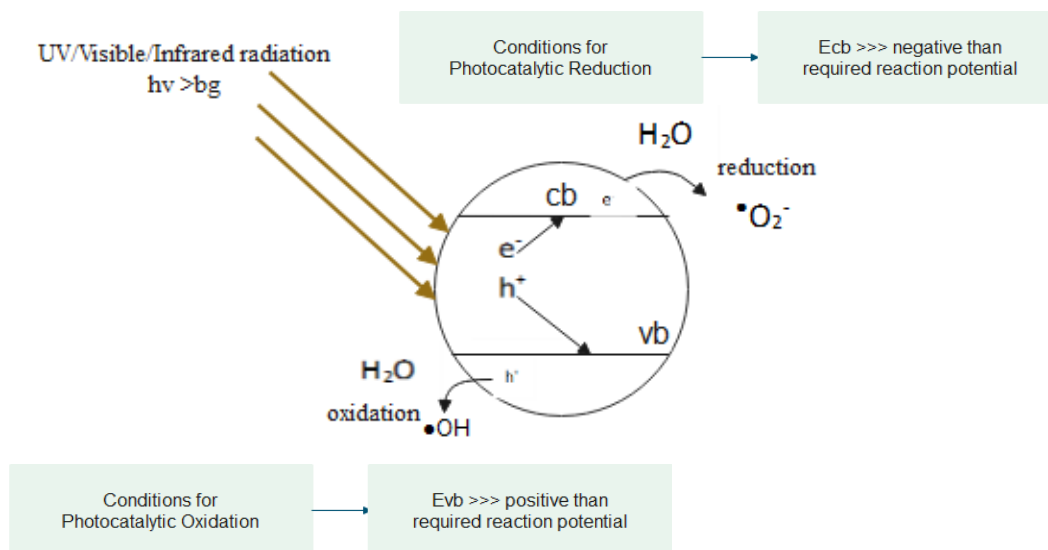


Fig. 1. Process of photochemical reaction on the surface of a catalyst

2.1. Use of photocatalysts

Researchers have demonstrated the use of transitional metal oxides of semiconducting type belonging to group IV or a combination of group III or V of the periodic table as catalysts for increasing the rate of the chemical reaction. These possess an appropriate band gap energy (E_{bg}) value in between the filled valence band and the empty conduction band to photogenerate electron/hole pairs upon irradiation of light [30]. Research analysts have observed that in the case of TiO_2 , at pH 7, E_{vb} is +2.69 v and $E_{cb} = -0.51$ V, while the E_{vb} of $\cdot OH$ is +2.29 V and that of $\cdot O_2^-$ is -0.33 V. E_{vb} and E_{cb} of TiO_2 is larger than an E_{vb} of $\cdot OH$ and an E_{cb} of $\cdot O_2^-$, these conditions are suitable for the oxidation and reduction reaction of aqueous forms of ammonia and nitrate, respectively. PC reactions yield satisfactory results when used for the removal of toxic inorganic nitrogen compounds, i.e., ammonia and nitrates from wastewater. The application analysis of three groups of oxides as photocatalysts, namely Binary oxides (TiO_2 , V_2O_5 , ZnO , Fe_2O_3), ternary oxides ($ZnFe_2O_4$), quaternary oxides ($Bi_4Nb_xTa_{1-x}O_8$), were studied [31]. Cocatalysts, as additional catalysts, were used along with the primary catalyst, influencing the product selectivity [32]. A catalyst may be loaded with a suitable cocatalyst to obtain the specific end products. A noble metal was used as a cocatalyst due to its high conversion efficiency and its inert nature. Studies by Gao et al. are indicative of the efficiency of any cocatalyst; they inferred that the performance of a cocatalyst could be enhanced by decreasing the size of the catalyst, increasing the surface area for increased mass transfer and reaction rate at a reduced cost [33]. Several noble metals such as Pd, Pt, Ru, Rh, Ag, and Au have been investigated and used in the PC processes in prior studies to oxidize ammonia and reduce nitrate. Studies reported that the end product obtained was N_2 using the Pd or Pt catalysts regarding the oxidation of ammonia and for the Ag catalysts in the case of reducing nitrate. However, in presence of the Ru, Rh, and Au cocatalysts or in the absence of any cocatalysts for the oxidation of ammonia, the end products obtained were NO_3^- and NO_2^- . [34]. Hence, further research is required to divert the conversion into harmless N_2 gas to the least extent possible.

2.2. Factors affecting Photocatalysis

Photocatalysis of ammonia and nitrate, being a chemical process, is dependent on several experimental factors, mainly pH, ammonia concentration, and nitrate concentration, reducing agent concentration, photocatalyst concentration, cocatalyst activity, and temperature [35]. During the reaction, the temperature increased and was cooled by maintaining a water bath/water jacket [36]. Moreover, the end product was dependent on all the above-mentioned independent conditions. Another important factor affecting photocatalysis is the state of the photocatalyst, i.e., powder form or its immobilization on the substrate material. More efficiency is achieved when the catalyst is used in powder form, as powder form provides a higher specific surface area. An immobilized catalyst gave consistent results due to its easy recyclability and reusability, as investigated by Abdel et al. [37]. The process of catalyzed PC oxidation of ammonia gave favourable results in slightly alkaline conditions [38], while the catalyzed PC reduction process was efficient in acidic to neutral pH conditions. Moreover, the presence of suspended solids and their implicit turbidity lowered the efficiency of the photochemical process. These could be reduced by pre-treatment before applying it to real municipal and industrial wastewater.

2.3. Photocatalytic degradation of ammonia and nitrate

Photocatalysts possess the potential to generate negative energy carriers in the conduction band (e^-_{cb}) and holes in the valence band (h^+_{vb}) when subjected to photo energy by irradiation [39]. Whenever enough energy photons of suitable wavelength (i.e., energy higher than the bandgap energy) are absorbed, the electron gets excited, causing splitting of the combined charge carriers and the formation of individual charge carriers (e^-_{cb} in the conduction band and h^+_{vb} holes in the valence band). The excited state of the photocatalyst repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such interactions. These charge carriers may recombine or may react further with any electron donor or acceptor on the surface of the photocatalyst to

form O_2^- , HOO , OH free radicals. These are the primary oxidative hydroxyl radicals in the PC oxidation and reduction reaction methodology for ammonia and nitrate elimination. Secondary radicals may also be produced based on the contents of the water and wastewater sample, mainly Cl^\bullet , $SO_4^{\bullet-}$, H_2O_2 , or Fe^{2+} (Fenton's reagent) [40], which further accelerate the ammonia oxidation and nitrate reduction process and create a possibility of simultaneous oxidation and reduction [41]. Chloride ions enhanced the adsorption of ammonia and gave a faster oxidation rate for ammonia degradation.

2.3.1. Photocatalytic oxidation of ammonia

In catalyzed PC-AOPs for ammonia (photochemical-advanced oxidation processes), researchers have tried using different light sources and catalyst-cocatalyst to obtain the best suited combinations for attaining optimum output. Photocatalytic reaction for the oxidation of NH_4^+ / NH_3 using a Xe lamp in the presence of suspended TiO_2 powder as the photocatalyst gave similar results to those performed in the presence of sunlight, with the conversion into NO_3^- and NO_2^- along with N_2 gas; the effects of parameters like pH, photocatalyst concentration, temperature, and flowrate were studied by Bensen et al. [42]. He found that almost half of the ammonia was degraded in less than six hours under alkaline conditions at a pH of 9.9 and 0.01% (w/v) TiO_2 , the majority of which was converted into N_2 gas. The use of doped or coated TiO_2 could improve NH_3 adsorption on the photocatalyst surface, giving a higher removal. There were two mainly different reaction series or pathways concluded for the oxidation of ammonia [43] based on the type of cocatalyst used in the photochemical reaction, as depicted in Table 1. The efficiency of removal of ammonia by using titanium nano particles in a study by Hashemi et al. [44] was found to be 97%. In a recent study by Li et al. [45], g- C_3N_4 /rGO/ TiO_2 Z-scheme photocatalysis was used for the removal of NH_3 -N and $\cdot OH$ radicals and $\cdot O_2^-$ radicals were produced on TiO_2 . These led to oxidation of NH_3 -N to NO_3^- . The reduction of this

NO_3^- into N_2 occurred further on the conduction band of g- C_3N_4 .

Table 1. Series of reactions in case of Ru, Rh, Ag, Au, Pd, Pt catalyst

Reaction mechanism for Pd, Pt catalyst	
Step 1.	$NH_3 + h^+ = \cdot NH_2 + H^+$
Step 2.	$\cdot NH_2 + \cdot NH_2 = N_2H_4$
Step 3.	$\cdot N_2H_4 + \cdot N_2H_4 = N_2H_2 + H_2$
Step 4.	$N_2H_2 = N_2 + H_2$
Reaction mechanism for Ru, Rh, Ag, Au catalyst	
Step 1.	$NH_3 + \cdot OH = \cdot NH_2$
Step 2.	$\cdot NH_2 + \cdot OH = NH_2OH$
Step 3.	$NH_2OH + \cdot O_2^- = O_2NHOH$
Step 4.	$O_2NHOH + \cdot OH^- = NO_2^-$
Step 5.	$NO_2^- + \cdot OH = HON_2$
Step 6.	$HON_2 = NO_3^-$

2.3.2. Photocatalytic reduction of nitrate

In PC-ARPs (photochemical-advanced reduction processes), the photogenerated electrons behave as reductants for the contaminant nitrates, which are highly stable and water-soluble. The selectivity of product N_2 is most crucial and is highly affected by the addition of different cocatalysts. A study in this regard was conducted by Kato et al. [46]. They used tantalates as the photocatalyst and nickel (Ni) loaded on TiO_2 as the cocatalyst as Ni (1 wt.%) / $KTaO_3$ in a synthetic KNO_3 (0.010 mol/L) solution in a reactor of volume 400 mL. Photocatalytic reduction of nitrate with water as the hole scavenger was performed to reduce nitrate to nitrogen. Nitrite and ammonia were formed as toxic by-products after 25 hours of irradiation. Conversion efficiencies obtained were 39% and 44% for NH_3^+ and NO_2^- , respectively; tantalate was found to be a better photocatalyst over TiO_2 [46]. Studies by Suhadolnik et al. [47,48] concluded that TiO_2 was the best semiconductor for photocatalytic oxidation and reduction with high selectivity towards N_2 . Ag was found to be the best cocatalyst for reduction [49]. Formic acid was revealed to be the most efficient hole scavenger over TiO_2 for synthetic water. Photocatalyst (nanoparticles) and cocatalyst combination of Ag/ TiO_2 [39] were used in this research work. PC reduction of nitrate was obtained only under acidic to neutral pH, and there was no removal witnessed in basic/alkaline conditions. The nitrate to formate ratio was 1:1.

Conduction band electrons were responsible for reduction instead of the radicals for such a proton-coupled reaction and adsorption mechanism. Also, it was observed that in the range of pH 3.5 to 4, conversion suddenly shifted into nitrite instead of nitrogen. This emphasized the significance of maintaining appropriate pH in such type of reactions [39]. Anderson et al. perceived that the reaction pathways for the PC reduction of nitrate varied based on using a hole scavenger to carry out the reduction process, and several intermediates and different end products were obtained [50]. He also experimentally detected that the Au cocatalyst did not enable any nitrate removal. Siveria et al. [51] studied nitrate removal in water with salinity and brackish concentration by using ilmenite as the photocatalyst. Oxalic acid was used as a reducing agent, which is eco-friendly. About 73% of the Total Nitrogen (TN) was removed, and other affecting factors were also studied. Simulated sunlight was used in the removal of nitrate over anatase TiO_2 by means of a photoreduction mechanism in this recently conducted work. The rate at which the photodegradation of NO_3^- using anatase TiO_2 occurred was observed to be more than that of

rutile TiO_2 . About 94% conversion of NO_3^- was found to have occurred in a reaction time of four hours and gave 100% nitrogen selectivity [52].

3. Catalyzed and Non-Catalyzed Electrochemical (EC) process

Electrochemical methods constitute the use of a cathode and anode assembly immersed in an electrolyte containing the contaminant solution in an undivided or divided reactor cell. A DC supply was to be provided for the passing of current and an electrolyte for the exchange of ions/electrons [53]. Ewans et al. deciphered those reactions as electrochemical reactions in which the chemical reaction was induced due to charge transfer between the electrodes and across the interface between the electrode and electrolyte [54]. For any electrochemical reaction, the correct combination of cathode and anode affects the product selectivity in oxidation and reduction processes. A noncatalyzed EC process has similar shortcomings to that of a non-catalyzed PC process; the use of catalyzed EC methods can solve the limitations of non-catalyzed ECs. Figure 2 explains the mechanism of an electrochemical reaction occurring on the surface of different forms of catalyst exposed.

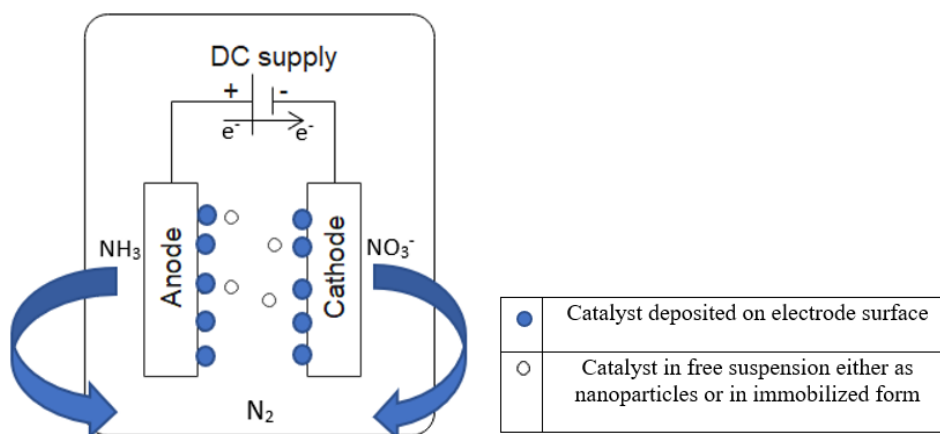


Fig. 2. Process of electrochemical reaction on the surface of a catalyst.

3. Use of electrocatalysts

Electrochemical nitrate (NO_3^-) reduction gives ammonium and nitrite simultaneous oxidation of in-situ generated ammonium and nitrite into nitrogen gas (N_2), removing the toxic inorganic

nitrogen compounds from the wastewater. A study of noble metals like Ag, Au, Pd, Pt, Ir, Sn, and Fe was carried out in the EC oxidation of ammonia and reduction of nitrate [55,56]. Further, noble metals were loaded on the surface of catalysts forming bimetallic catalyst systems or cocatalysts

systems. Catalysts used in the electrocatalysis process for the oxidation and reduction of ammonia and nitrate, respectively, are either in the form of suspension or immobilized on the surface of the electrode, or immobilized on any other inert material, which is freely suspended in the contaminant sample, as observed by Deganello et al. [57]. The rate of denitrification is a function of the number of active sites for denitrification; hence, the combined effects of the catalytic hydrogenation and electrochemical reduction of nitrate are noteworthy in catalyzed EC. This was done by the spatial distribution of the powdered form of nanoparticles of a single or bimetallic catalyst (cocatalyst) and introduced into the cathode chamber of an EC cell to develop a new catalytic EC nitrate reduction system [58]. The nitrate reduction rate and selectivity were significantly enhanced due to the coupling reaction of catalytic hydrogenation with the in situ generated hydrogen as a reducing agent. Zhang et al. [59] used Pd-Cu bimetallic catalyst immobilized alumina, which suitably increased the removal of nitrate and improved the selectivity towards nitrogen gas.

3.2. Electrocatalytic degradation of ammonia and nitrate

3.2.1. Electrocatalytic oxidation of ammonia

Studies by Marincic et al. suggested very little removal was obtained for a 0.5-2.0 mM concentration of ammonia by direct EC oxidation reaction. This process of direct oxidation was carried out on Ti or Ta or a platinized graphite anode and a S.S. cathode at pH 5-8, occurred by a mechanism of direct electron transfer on the anode and dehydrogenation [60]. Direct EC oxidation of ammonia, as per the work of Zollig et al., was difficult on graphite electrodes at pH 9 [61]. If the reaction was catalyzed by the noble metals Pt and Ru (immobilized by pulse deposition technique) on the graphite electrode (Pt Ru/graphite electrode), catalytic EC oxidation showed high activity, as reported by Qing et al. Further, they performed an indirect EC oxidation aided by chloride ions for the synthetic wastewater of the aquaculture industry, which was found to be a pseudo-order reaction dependent on NaCl concentration and current density. Similar results were obtained on synthetic

and real aquaculture wastewater induced by Cl⁻ ions but with a longer duration of time required for the same type and concentration of real aquaculture wastewater [62]. The electrocatalytic oxidation of NH₄⁺-N [63] was performed using a catalytic anode of TiO₂/Co-WO₃/SiC in the presence of the chlorine derived species HOCl, ClO⁻ and the active species Cl[•] (Eq. 1) ClO[•] (Eq. 2), [•]H at a current density of 1 mA/cm², and a reaction time of two hours. This resulted in about a 98.3% removal of ammonia. Such chlorine-mediated reactions were accompanied by the formation of toxic by-products, like perchlorates, chlorinated organics, and Cl₂ gas [12].



With the aim of increasing the efficiency of the EC oxidation process, several hybrid methods have been implemented by the amalgamation of EC with other treatment techniques. EC-oxidation and membrane filtration [43] improved the mass transfer in the form of flow-through mode. As experimented by Liu et al. in EC oxidation and electrocoagulation, Fe²⁺ and Fe³⁺ ions were generated in situ by anodic dissolution from the Fe or Al electrodes. EC oxidation and Electron-Fenton involved the formation of hydroxyl radicals in situ through reaction of Fe²⁺ (obtained from iron anode) with H₂O₂ at the cathode [43]. Another study was conducted by Sun et al. using zero valent iron (ZVI) on the RuO₂-Ir O₂/Ti plate and graphite as the composite anodes. The ZVI nanoparticles worked as a catalyst and helped to increase the efficiency of the oxidation of ammonia, and subsequently obtain N₂ gas [53].

3.2.2. Electrocatalytic reduction of nitrate

The reduction of nitrate occurs in a single or divided electrochemical cell reactor; division is made by means of a dividing compartment, such as a suitable cathode exchange membrane (CEM) [64]. Reduction of nitrate by Chauhan et. al. in a synthetic nitrate solution having an initial NO₃⁻ concentration of 100 mg/L and NaCl concentration of 300 mg/L using an Al cathode and Tr/RuO₂ anode at pH 6. The reduction of nitrate occurred simultaneously with the oxidation of by-products like NH₄⁺ in a reaction time of 120 minutes. The

nitrate removal efficiency of 95% with 100% selectivity of N_2 gas was obtained [1]. A novel 3d Pd-Cu (OH)₂/CF cathode [65] converted nitrate to ammonia, which further oxidized to nitrogen gas by active chlorine species; the conversion to ammonia was 98.8% in 45 minutes. The overall conversion to N_2 gas was 98.7% in a contact time of 60 minutes. Study of different cathodes by Rao et al. and fellow researchers [66] inferred the order of the activity of cathodes by C>Ti>Fe>Ci>Al. A cathode composed of carbon paper (C) gave the maximum removal of about 47.7% in a reaction time of 120 minutes at 40 mA/cm² using a Ti/PbO₂ anode. A novel electrochemical system [67] was developed for simultaneous nitrate and ammonia removal into the end product as N_2 in a single undivided cell with a Ti/IrO₂ anode and Cu cathode in the form of circular transformation to remove multiple contaminants in a single undivided cell. An optimum concentration of NaCl was used to support and fasten the reaction. Here, the Cl⁻ ions oxidized to form hypochlorite and hypochlorous, which mediated the reaction mechanism. Bimetallic systems involving the use of cocatalysts gave a higher efficiency in comparison to a single catalyst system as adsorption played the most important role in the reduction of nitrate; such bimetallic systems enabled a larger rate of adsorption [68]. As per the findings of Barrabes et al. [69], for a bimetallic system of catalyst in the EC reduction of nitrate, the ratio of the primary to the promoter catalyst played a vital role in terms of end product selectivity. Sn was found as the best promoter in this regard, and Pd performed well at higher palladium to lower promoter metal. Monometallic catalysts based on Pd/Pt provided reduced support sites to perform the nitrate-to-nitrite conversion, whereas for the iron catalyst, the reduction mechanism revolved around the redox couples Fe⁰/Fe²⁺ or Fe³⁺ and/or Fe²⁺/Fe³⁺. In a study by Niu et al. [70], CuCo₂O₄ composite supported by porous carbon nanofibers was used as an electrocatalyst. This led to the transfer of charge but inhibited the reaction of hydrogen evolution. This led to preferential catalyzed production from nitrate to nitrites and further conversion to ammonia by internally confined CuCo₂O₄ nanoparticles.

4. Limitations

PC and EC oxidation and reduction processes for converting ammonia and nitrates to nitrogen gas have their own limitations, as they generate several toxic and harmful intermediates. Another limitation is the chance of recombination of the energy carriers (electrons and holes) in PC, thereby hindering the entire process. In addition, the drawback of any conventional EC lies in the limited mass transfer. These limitations, however, can be dealt with by integrating the PC and EC process, i.e., the PEC process, wherein the sufficient electric potential is available to prevent the recombination of photon activated holes and electrons [47].

5. Catalyzed photoelectrochemical (PEC) process

PEC was only applied to wastewater treatment in the 1980s [35]. Since then, research in this technology has grown vehemently, as this technique has many merits to offer over conventional methods in treating wastewater pollutants. The degradation of pollutants by integrating photocatalytic and electrocatalytic methods for successfully removing inorganic nitrogenous compounds of ammonia and nitrates into non-toxic, harmless N_2 is possible since the integration of both methods is easy and efficient. The composition of a photoelectrode was obtained by immobilization of a semiconducting substance onto an electrically conducting substance and high conductivity of solution [47,48]. In photocatalytic and electrocatalytic reactions, Garcia et al. explained that the rate of the reaction was limited by the transfer of mass onto the surface of the electrode/catalyst from the bulk solution [71]. As the photogenerated electrons migrated to the surface of the photocatalyst, they were trapped by the noble metals, which prevented the recombination of photogenerated holes and photogenerated electrons [67]. These separated surface electrons and holes in bulk performed the role of reductant and oxidant, respectively. In this method, a thin photoanode was simultaneously subjected to light and electric potential. The electrical energy in the PEC process could be retrieved by a solar panel; hence, no external energy input is required, and the technique becomes environment friendly [40]. PC and EC methods are found to be successful in fixing

ammonia and nitrate when applied separately; the merger of the two methods was found to significantly increase the efficiency of the reactions [43].

5.1. Photoelectrocatalytic degradation of ammonia and nitrate

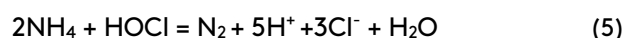
The photoelectrocatalysis process for the oxidation of ammonia and the reduction of nitrate is an evolving technology. The success of research in this methodology is because it can be made environmentally friendly by applying natural and free energy sources like solar energy to power the electrical section of the reactor. Several novice research techniques in the field of PEC have been tried and tested, the observations of which are mentioned in the subsequent sections. Ren et al. studied the mechanism of the degradative oxidation of ammonia [38], where PEC was performed under UV light in the presence of TiO₂/Pt nanoparticles and under anoxic conditions. Amide radical was the first active intermediate species, which converted into hydrazine, followed by diazene which ultimately decomposed into N₂ and H₂ gas. Another mechanism studied was deprotonation [38].

5.1.1. Photoelectrocatalytic oxidation of ammonia

Indirect EC oxidation (mediated by chlorine) and UV light oxidation were performed [72] in drinking water for abatement of ammonia, wherein HOCl mole disassociated into •OH and •Cl and the water was disinfected due to UV light. The synergistic effect of the EC process and UV light irradiation on ammonia in the chlorinated aqueous solution [73] using non-photoactive RuO₂/Ti and IrO₂/Ti anode was more than 1.5 times more efficient than the EC and PC processes, where about 97% of the ammonia was converted to nitrogen. It was found that the current density was the most influential factor, whereas pH and ammonia were the least influential. The UV-C photoelectrochemical process was performed using seawater as the electrolyte [74] for ammonium removal from wastewater containing rejected sludge dewatering waste; it gave an 86% removal of ammonia at an initial pH of 8.4 and made the water acidic during the reaction, as observed from the following set of reactions (Eq. 3 and 4).



The reaction kinetics was found to be of the first order. It was carried out in a continuous flow reactor with Pt as the anode and graphite as the cathode at a 1.8 A current. The COD was reduced simultaneously with ammonium oxidation during the hydraulic retention time (HRT) of 10 min to 110 min, which was optimized by RSM. Eq. 5 shows the end product formation as nitrogen gas.



In another study by Zhang et al., ammonia was oxidized to nitrate, nitrite, and nitrogen gas in 90 minutes with a total nitrogen efficiency of 98.4% using a Pd-Cu-modified Ni foam (Pd-Cu/NF) anode and WO₃/FTO [75]. It was converted to Cl• by photoholes in the wastewater containing nitrate and ammonium in a 1:1 ratio. When the reaction time was increased to 105 minutes, the removal of 98% ammonia as nitrogen was observed. Lu et al. [76] removed ammonia from highly chlorinated wastewater using Cl-based radicals using titania nanotubes in the form of an optimized Ar-TNT-500 °C photoanode. This could oxidize and convert ammonia into N₂ and nitrate. About 86% of nitrogen and 14% of nitrate were obtained.

5.1.2. Photo electrocatalytic reduction of nitrate

A p-GaInP₂ electrode in a nitrate bearing solution was claimed to be the first research study for a photo electrocatalytic reduction using Ga or In metals as the catalyst by Wang et al. [2]. Noble metals were observed to be used more in practice for the research of catalyzed EC, PC, and PEC reduction; the conversion trend showed more quantities of conversion into intermediate nitrite. This generated the need for further reduction techniques into harmless nitrogen gas. Simultaneously combined photoelectrocatalytic oxidation-reduction was carried out to oxidise NH₄⁺ and reduce NO₃⁻ reduction in a single reactor [25]. This was performed with an anode as AgI/TiO₂ nanotubes and a cathode as autotrophic denitrifying biofilms in the pH range of neutral to alkaline. At a pH of 8, nearly 89.6% removal of nitrate was obtained at a voltage of 3V. The following Table 2 gives a fair summary about the general characteristics of photochemical, electrochemical and photoelectrochemical processes.

Table 2. Major takeaways from the reviewed processes

Wastewater constituent	Catalyzed photochemical process	Catalyzed electrochemical process	Catalyzed photoelectrochemical process
Degradation of Ammonia (By oxidation)	Oxidizing agent is required. Not much research is performed hence offers a great scope.	Many research studies are available till now in this field of catalyzed oxidation-reduction of inorganic nitrogen i.e., ammonia and nitrate by electrochemical ways. Its subsequent conversion occurs in the form of toxic and non-toxic end products. No data is available regarding the most efficient electrocatalyst in terms of removal percentage and end product selectivity in different types of wastewaters.	Insufficiently explored for oxidation-reduction of inorganic nitrogen i.e., ammonia and nitrate.
Degradation of Nitrate (By Reduction)	Reducing agent is required. Process is suitable only for wastewater and not for potable/drinking water. Comparatively more research is performed.		Limited data interpretations can be made about the most reliable combination of inert metal catalyst with TiO ₂ from view point of efficiency and product selectivity.

6. Conclusions

PC and EC methods were found to be reliable in the treatment of inorganic toxic nitrogen contaminants: the major advantage being the degradation of contaminant and its conversion into harmless N₂. TiO₂ was found to be the best semiconductor for catalyzed PC oxidation and reduction with high selectivity towards N₂. Pd and Pt were reported as the best cocatalysts for the PC oxidation reactions. Ag was observed to be the best cocatalyst for PC reduction. Formic acid was the most efficient hole scavenger over TiO₂ for PC reduction. Au was found to be ineffective in the PC oxidation process. The catalyzed PC oxidation of ammonia gave favourable results at slightly alkaline pH conditions, while the catalyzed PC reduction process was efficient at acidic to neutral pH conditions. The presence of suspended solids and turbidity were found to have an impact on the efficiency of the photochemical process. Chlorine mediated PC and EC oxidation processes increased the efficiency of the oxidation processes and showed significant influence on the oxidation mechanism. Free chlorine was found to be highly active and reacted with NH₄⁺ to form several intermediate oxidative species. Since the final conversion was into nitrogen gas, free chlorine was liberated at the end, which confirmed the oxidation of ammonia into harmless nitrogen gas. Chloride ions had no significant effect on the PC and EC

reduction reactions. The PC reduction research for nitrate removal is progressing at a faster pace than PC oxidation and has moved from the lab scale to the pilot-scale. However, little information is available on the usage of the photocatalytic reduction of nitrate in potable and drinking water. Overall, PC is less practical and is currently at lab-scale research only and has limitations, such as the generation of toxic intermediates like nitrate, which is less reliable in real wastewater. Catalytic EC oxidation and the reduction of nitrates have been extensively studied. However, little data is available to conclude the best catalyst for the mentioned process. As per the review, the combined PEC is the most recent and advanced technique for treating ammonia and removing nitrogenous wastes. The recombination of the energy carriers (electrons and holes) remains a demerit of the PC process. This is prevented in PEC due to sufficient electric potential to prevent the recombination of holes and electrons. In the same way, the primary drawback of any conventional two-electrode (divided/undivided cell) electrochemical reaction is the limited mass transfer, which can be improved in the PEC approach. The major drawback of separately performing PC and EC processes is that these form several toxic and harmful intermediates before the end products. Not much research is available on the PEC techniques, especially for treating nitrogen contaminants and removing toxic ammonia and nitrate compounds from water and wastewater,

which leaves a vast scope of research in this area. An additional merit is that all the PC, EC, and PEC methods are useful for wastewater. The research gaps to be pondered in these techniques are the life cycle cost analysis, long-term operation, maintenance issues, and the selection of the right catalyst to prevent the formation of harmful by-products.

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