NITRATE REDUCTION FROM SYNTHETIC WASTEWATER EMPLOYING MBBR TECHNOLOGY – A LITERATURE REVIEW

VINAY SHARMA[1], Dr. J.K. SHRIVASTAVA[2]

[1]*M.Tech Scholar, Department of Chemical Engineering, Ujjain Engineering College, Ujjain (456010) – Madhya Pradesh*

[2]*Professor, Department of Chemical Engineering, Ujjain Engineering College, Ujjain (456010) – Madhya Pradesh*

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Abstract - *With reference to present day context Nitrate has became a serious threat for human society. Ever-increasing industrialization, severe level of wastes (effluents) from municipalities and industries are the prominently responsible causes for increased level of nitrate. Through Nitrate, water bodies and water reservoirs are adversely affected and consequently Eutrophication of Lakes takes place on a greater extent. Due to this upper surface of water bodies becomes full of solid wastes and effluents which globally affects entire marine system and imbalances the hydrologic cycle. Nitrate poisoning can occur through enterohepatic metabolism of nitrate due to nitrite being an intermediate. Humans are subject to nitrate toxicity, with infants being especially vulnerable to methemoglobinemia. Methemoglobinemia in infants is known as blue baby syndrome. Methemoglobin occurs in normal people in concentrations of 0.5-3.0%. When concentrations of methemoglobin exceed 10%, clinical symptoms of methemoglobinemia occur. Any concentration above 50% can result in death. Apart from this various other harmful diseases are in context arising due to high concentration of Nitrate in wastewater. In freshwater or estuarine systems close to land, nitrate can reach concentrations that can potentially cause the death of fish. While nitrate is much less toxic than ammonia, levels over 30 ppm of nitrate can inhibit growth, impair the immune system and cause stress in some aquatic species. However, in light of inherent problems with past protocols on acute nitrate toxicity experiments, the extent of nitrate toxicity has been the subject of recent debate. Thus, we have opted to study on a Nitrate removal mechanism through MBBR technology by a cost-effective means. In our study we have used sponge based bio-carriers which have high porosity band low density. Our bio-carrier filling fraction is 1/5 by volume; through this filling fraction we could achieve satisfactory reduction of nitrate from effluent/wastewater. In this we have used a spontaneous Nitrification and Denitrification process (SND). This was done to make experiment study economically feasible. In our study it has been revealed that high concentration of nitrates restricts the bacterial growth in bio-carriers.*

***Key Words*: Nitrate, MBBR, Bio-film, Bio-carriers, PU, SND.**

(A) INTRODUCTION

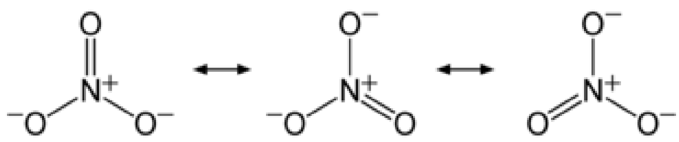
1. NITRATE

1.1 NITRATE

Nitrate is a polyatomic ion with the molecular formula NO^{-3} and a molecular mass of 62.0049 u. Organic compounds that contain the nitrate ester as a functional group ($RONO_2$) are also called nitrates.

1.2 STRUCTURE

The anion is the conjugate base of nitric acid, consisting of one central nitrogen atom surrounded by three identically bonded oxygen atoms in a trigonal planar arrangement. The nitrate ion carries a formal charge of −1. This results from a combination formal charge in which each of the three oxygens carries a $-^{2}/_{3}$ charge, whereas the nitrogen carries a +1 charge, all these adding up to formal charge of the polyatomic nitrate ion. This arrangement is commonly used as an example of resonance. Like the isoelectronic carbonate ion, the nitrate ion can be represented by resonance structures:



1.3 PROPERTIES AND DIET

Almost all inorganic nitrate salts are soluble in water at standard temperature and pressure. A common example of an inorganic nitrate salt is potassium nitrate (saltpeter). A rich source of inorganic nitrate in the human body comes from diets rich in leafy green foods, such as spinach and arugula. NO^{-3}(inorganic nitrate) is the viable active component within beetroot juice and other vegetables.

Dietary nitrate may be found in cured meats, various leafy vegetables, and drinking water; nitrite consumption is primarily determined by the amount of processed meats eaten, and the concentration of nitrates in these meats. Nitrate and water are converted in the body to nitric oxide, which could reduce hypertension. Anti-hypertensive diets, such as the DASH diet, typically contain high levels of nitrates, which are first reduced to nitrite in the saliva, as detected in saliva testing, prior to forming nitric oxide.

1.4 OCCURRENCE

Nitrate salts are found naturally on earth as large deposits, particularly of nitratine, a major source of sodium nitrate.

Nitrates are produced by a number of species of nitrifying bacteria, and the nitrate compounds for gunpowder (see this topic for more) were historically produced, in the absence of mineral nitrate sources, by means of various fermentation processes using urine and dung.

Nitrates are found in fertilizers.

As a byproduct of lightning strikes in earth's nitrogen-oxygen rich atmosphere, nitric acid is produced when nitrogen dioxide reacts with water vapor.

1.5 USES

Nitrates are mainly produced for use as fertilizers in agriculture because of their high solubility and biodegradability. The main nitrate fertilizers are ammonium, sodium, potassium, and calcium salts. Several million kilograms are produced annually for this purpose.

The second major application of nitrates is as oxidizing agents, most notably in explosives where the rapid oxidation of carbon compounds liberates large volumes of gases (see gunpowder for an example). Sodium nitrate is used to remove air bubbles from molten glass and some ceramics. Mixtures of the molten salt are used to harden some metals.

Explosives and table tennis balls are made from celluloid. In the early 20th century, most motion picture film was made of nitrocellulose, but the intense flammability of the film led to it being replaced with "safety film" by the mid-20th-century.

Although nitrites are the nitrogen compound chiefly used in meat curing, nitrates are used in certain specialty curing processes where a long release of nitrite from parent nitrate stores is needed. The use of nitrates in food preservation is controversial. This is due to the potential for the formation of nitrosamines when nitrates are present in high concentrations and the product is cooked at high temperatures. The effect is seen for red or processed meat, but not for white meat or fish. The production of carcinogenic nitrosamines may be inhibited by the use of the antioxidants vitamin C and the alpha-tocopherol form of vitamin E during curing.

Under simulated gastric conditions, nitrosothiols rather than nitrosamines are the main nitroso species being formed. The use of either compound is therefore regulated; for example, in the United States, the concentration of nitrates and nitrites is generally limited to 200 ppm or lower. They are considered irreplaceable in the prevention of botulinum poisoning from consumption of cured dry sausages by preventing spore germination.

Research has shown that dietary nitrate supplementation delivers positive results when testing endurance exercise performance.

1.6 DETECTION

The historical standard method of testing for nitrate is the Cadmium Reduction Method, which is reliable and accurate although it is dependent on a toxic metal cadmium and thus not suitable for all applications. An alternative method for nitrate and nitrite analysis is enzymatic reduction using nitrate reductase, which has recently been proposed by the US Environmental Protection Agency as an alternate test procedure for determining nitrate. An open source photometer has been developed for this method to accurately detect nitrate in water, soils, forage, etc.

Free nitrate ions in solution can be detected by a nitrate ion selective electrode. Such electrodes function analogously to the pH selective electrode. This response is partially described by the Nernst equation.

1.7 TOXICITY

1.7.1 POISONING

Nitrate poisoning can occur through enterohepatic metabolism of nitrate due to nitrite being an intermediate. Nitrites oxidize the iron atoms in hemoglobin from ferrous iron(II)to ferric iron(III), rendering it unable to carry oxygen. This process can lead to generalized lack of oxygen in organ tissue and a dangerous condition called methemoglobinemia. Although nitrite converts to ammonia, if there is more nitrite than can be converted, the animal slowly suffers from a lack of oxygen.

1.7.2 HUMAN HEALTH EFFECTS

Humans are subject to nitrate toxicity, with infants being especially vulnerable to methemoglobinemia. Methemoglobinemia in infants is known as blue baby syndrome. Methemoglobin occurs in normal people in concentrations of 0.5-3.0%. When concentrations of methemoglobin exceed 10%, clinical symptoms of methemoglobinemia occur. Any concentration above 50% can result in death. Through the Safe Drinking Water Act, the United States Environmental Protection Agency has set a maximum contaminant level of 10 mg/L or 10 ppm of nitrates in drinking water. This particular standard was set to prevent methemoglobinemia in infants. Infants exposed to water containing nitrates are at highest risk of developing blue baby syndrome during the first 6 months of life. In the United States, it is estimated that 40,000 infants younger than 6 months live in homes with water contaminated with nitrates. This is due to low concentrations of nitrate metabolizing triglycerides during this developmental period. Private water systems, such as well water in agricultural areas, are more likely to have nitrate levels above the maximum contaminant level (MCL). Well water is not treated and tested as often as municipal water. Rural well-water near agricultural fields can become contaminated with nitrates due to manure, fertilizers, or septic tanks. Exposure commonly occurs when formula is mixed with well-water containing nitrates or infants under 6 months are fed vegetables washed with the contaminated drinking water. It is important to note that infants who are breastfed by mothers who ingest water with concentrations of nitrates (100 ppm) are not at risk of methemoglobinemia. It is recommended that foods like green beans, carrots, spinach, squash, and beets are not fed to infants less than 3 months. These foods have naturally occurring nitrates which can be harmful to the infant. High levels of nitrate in fertilizer may also contribute to elevated levels of nitrate in the harvested plant.

Not only are infants under 6 months a concern for nitrate exposure, but pregnant women with altered physiological states and compromised immune systems can be at risk. Pregnant women show a decrease in methemoglobin levels with increasing gestation. Exposure to nitrate in groundwater during pregnancy at concentrations above the MCL was associated with increased risk for anencephaly. A study done in Texas and Iowa found that mothers of babies with spina bifida were twice as likely to ingest 5 mg or more of nitrate daily from drinking water as mothers of babies without major birth defects. Mothers of babies with limb deficiencies, cleft palate, and cleft lip were, respectively, 1.8, 1.9 and 1.8 times more likely to ingest 5.42 mg or more of nitrate daily than mothers of babies without major birth defects.

While there is evidence that shows nitrates can affect infants and pregnant women, recent evidence shows there are significant scientific doubts as to whether there is a causal link. Blue baby syndrome now is thought to be the product of a number of other factors such as gastric upset, such as diarrheal infection, protein intolerance, heavy metal toxicity etc., with nitrates playing a minor role.

Some adults may be more susceptible to the effects of nitrates than others. In these adults, the methemoglobin reductase enzyme may be under-produced or absent in certain people who have an inherited mutation in the enzyme. Such individuals cannot break down methemoglobin as rapidly as those who do have the enzyme; leading to increased circulating levels of methemoglobin (the implication being that their blood is not as oxygen-rich as that of the others). Diets rich in green, leafy vegetables typically accompany an increased nitrate intake. A wide variety of medical conditions, such as food allergies, asthma, hepatitis, and gallstones, may be linked with low stomach acid; these individuals also may be highly sensitive to the effects of nitrate.

Methemoglobinemia may be treated with methylene blue, which reduces ferric iron(III) back to ferrous iron(II) in affected blood cells.

Another human health effects from the ingestion of nitrate is in the form of processed meat. This form of ingestion may increase the risk pancreatic cancer. Processed meat can be cured with nitrate-based salt to decrease bacterial growth and improve flavor. When ingested, nitrate can become N-nitroso compounds (NOC), a probable human carcinogen. In a study performed by the US Government, there was a positive correlation between nitrate intake of more than 3g/day and pancreatic cancer in men. However, there are few data points which results in only a borderline significance.

1.7.3 AQUATIC TOXICITY

In freshwater or estuarine systems close to land, nitrate can reach concentrations that can potentially cause the death of fish. While nitrate is much less toxic than ammonia, levels over 30 ppm of nitrate can inhibit growth, impair the immune system and cause stress in some aquatic species. However, in light of inherent problems with past protocols on acute nitrate toxicity experiments, the extent of nitrate toxicity has been the subject of recent debate.

In most cases of excess nitrate concentrations in aquatic systems, the primary source is surface runoff from agricultural or landscaped areas that have received excess nitrate fertilizer. This will contribute to Eutrophication and can lead to algae blooms which may result in anoxia and the formation of dead zones, these blooms may cause other changes to ecosystem function, favoring some groups of organisms over others. As a consequence, as nitrate forms a component of total dissolved solids, they are widely used as an indicator of water quality.

2. MBBR TECHNOLOGY/MECHANISM

Moving bed biofilm reactor (MBBR) is a type of wastewater treatment process which employs thousands of polyethylene biofilm carriers operating in mixed motion within an aerated wastewater treatment basin. Each individual biocarrier increases productivity through providing protected surface area to support the growth of heterotrophic and autotrophic bacteria within its cells. It is this high-density population of bacteria that achieves high-rate biodegradation within the system, while also offering process reliability and ease of operation.

This technology provides cost-effective treatment with minimal maintenance since MBBR processes self-maintain an optimum level of productive biofilm. Additionally, the biofilm attached to the mobile biocarriers within the system automatically responds to load fluctuations.

2.1 PROCESS DESCRIPTION/OVERVIEW

The MBBR system consists of an aeration tank (similar to an activated sludge tank) with special plastic carriers that provide a surface where a biofilm can grow. The carriers are made of a material with a density close to the density of water (1 g/cm³). An example is high-density polyethylene (HDPE) which has a density close to 0.95 g/cm³. The carriers will be mixed in the tank by the aeration system and thus will have good contact between the substrate in the influent wastewater and the biomass on the carriers.

To prevent the plastic carriers from escaping the aeration it is necessary to have a sieve on the outlet of the tank.

2.2 ADVANTAGES

The MBBR system is considered a biofilm process. Other conventional biofilm processes for wastewater treatment are called trickling filter, rotating biological contactor (RBC) and biological aerated filter (BAF). Biofilm processes in general require less space than activated sludge systems because the biomass is more concentrated, and the efficiency of the system is less dependent on the final sludge separation. A disadvantage with other biofilm processes is that they experience bioclogging and build-up of head loss.

MBBR systems don't need a recycling of the sludge, which is the case with activated sludge systems.

The MBBR system is often installed as a retrofit of existing activated sludge tanks to increase the capacity of the existing system. The degree of filling of carriers can be adapted to the specific situation and the desired capacity. Thus an existing treatment plant can increase its capacity without increasing the footprint by constructing new tanks.

When constructing the filling degree can be set to, for example, 40% in the beginning, and later be increased to 70% by filling more carriers. Examples of situations can be population increase in a city for a municipal wastewater treatment plant or increased wastewater production from an industrial factory.

Some other advantages compared to activated sludge systems are:

i. Higher effective sludge retention time (SRT) which is favorable for nitrification

ii. Responds to load fluctuations without operator intervention

iii. Lower sludge production

iv. Less area required

v. Resilient to toxic shock

Process performance independent of secondary clarifier (due to the fact that there is no sludge return line)

(B) LITERATURE REVIEW

Libing Chu *et al.,* (2017)

As per this study, it has been observed that the types of Bio-carriers have significant effect on the reduction of many undesirable contents of wastewater. In this study they have compared biodegradable polycaprolactone (PCL) and polyurethane foam – a non biodegradable bio-carrier for the removal of organic as well as nitrogen based impurities i.e. ammonium, Nitrite, Nitrate with low C/N ratio with the help of moving bed biofilm reactor (MBBR).

The reactor with polyurethane (PU) has shown efficient TN removal (59%) at low level of Nitrate i.e. < 5 mg/l in effluent this is because of simultaneous nitrification and denitrification (SND) on the other hand reactor with polycaprolactone (PCL) has shown less TN removal in initial stage because it is a solid carbon source, its degradation rate is very slow due to which the microbial assimilation rate gets lower down, which causes low denitrification rate.

As per their conclusion, it has been figured out that if we want to use biodegradable Bio-carriers then we have to increase its porosity meanwhile we can develop improvised PU Bio-carriers (i.e. PU Bio-carriers impregnated with solid carbon substitutes).

Xinbo Zhang *et al.,* (2016)

This study is based on the effect of packing fraction on the working and efficiency of sponge based moving bed biofilm reactor (MBBR). Their experience has shown us that the simultaneous nitrification and denitrification (SND) increases with increase in the filling percentage i.e. SND were 85.5 ±8.7%, 91.3±9.4%, 93.3±10.2% in 10%, 20%, 30% filling fraction reactor respectively. In their study it has been observed by me that as per their experiment result, if a 12 l reactor fill up to 12% by sponge (15×15×15) mm Bio-carriers then the process would achieve maximum biomass accumulation per gram of sponge.

Nguyen *et al.,* (2016)

This experiment was conducted to study the effect of size and type of sponge Bio-carriers on the removal of micronutrients and other organic components from wastewater under aerobic conditions. Their observation has revealed that there has been no effect on removal efficiency of reactor with respect to variation in filling fractions i.e. we need to worry about the specification of sponge Bio-carriers like in the case of other Bio-carriers

Chu and Wang *et al.,* (2016)

According to this study, use of polyurethane sponge (PU) based Bio-carriers (20% filing fraction in MBBR) in case of low C/N ratio, has shown that TOC and ammonium removal has been 90% and 65% at HRT of 14 hrs respectively.

Luo *et al.,* (2016)

This study has revealed that there has been a variation in sorption capacity of polyurethane (PU) sponge based moving bed biofilm reactor (MBBR) for micro pollutants like removal efficiency of carbamazepine -22.9% & for b-

Wang., Xia., Chen., Zhao *et al.,* (2016)

This experiment showed that Nitrogen-removal from municipal wastewater through SND is successful in the MBBR single-reactor. Chemical dosing onto the MBBR using ferrous sulphate heptahydrate is a highly effective method for the removal of phosphorus from wastewater. The general performance of the MBBR, with respect to COD, BOD, TN removal, is not significantly affected by the chemical addition. To meet the EC phosphorus discharge standards, the optimum dose of iron (II) is 1:1.3 (P:Fe). The combined chemical precipitation and moving bed biofilm system is a very effective process for complete nutrient removal, with average TN and TP removal efficiencies of 89.1% and 90.6% respectively, during optimum and economical conditions.

A.A.L.Zinatizadeh *et al* (2015)

The MBBRs filled with two types of carriers with different geometry, Ring form and Kaldnes-3 ,at packing rate of 50%(v/v) showed good performances in COD removal(>85%). The system with Ring form media could achieve more TN removal efficiency than that of the process with Kaldnes-3, indicating that anoxic condition is favored with Ring form.

Feng Quan, Wang Yuxiao *et al.,* (2015)

As per this study, the MBBRs filled with PUF carriers at packing percentage of 20%, 30%, and 40% (v/v) showed good efficiency in COD removal. The prosequencing analysis, predicted that the proteobacteria, Bacteriodetes and Verrucomicrobia were the three most abundant phyla.

Bo Fu, Xiaoyi Liao, Lili Ding et *al.,* (2015)

As per this study, FISH (fluorescence in situ hybridization) analysis shows that dominance of both Betaproteobacteria ammonia- oxidizing bacteria & Nitrospira – like Nitrite-oxidizing bacteria were negatively correlated to C/N ratios.

Sequence analysis of DGGE bands has predicted the presence of anoxic denitrifying bacteria Agro bacterium tumefactions and Rhizobium sp. There observation predicted that oxygen gradient is a responsible factor for SND process.

Andreottola *et el.,* (2015)

This experimental study was performed to evaluate the application of an MBBR system for the upgrading of an overloaded municipal wastewater treatment plant (MWWTP). The MBBR solution was considered to offer several advantages including good potential in nitrification process, easiness of management and the possibility to use the existing tank with very few modifications. A pilot-scale experiment was undertaken to develop the design parameters for the full-scale upgrade. The final configuration was a two stage MBBR system. The upgraded configuration was able to handle a 60% increase in flow rate with good performance. (Andreottola et al., 2015)

Rodgers & Zhan *et al.,* (2015)

This research presented a review of four types of moving medium biofilm reactors for the treatment of wastewater. Review is based on published case studies and covers:

1. The rotating biological contactor (RBC);

2. The moving bed biofilm reactor (MBBR);

3. The vertically moving biofilm reactor (VMBR); and

4. The fluidized-bed reactor (FBR).

They conclude that the MBBR is a good process for upgrading existing wastewater treatment Systems.

Weiss *et al.,* (2015)

This experiment presented an evaluation of the use of an MBBR system for the enhancement of nitrogen removal in a secondary treatment wastewater plant. It concludes that the MBBR process is capable of achieving desired nitrogen removal requirements in a smaller overall bioreactor volume. However, the advantages of the MBBR system have to be weighted up against the capital cost of purchasing the proprietary MBBR attached growth media and the increased energy costs for the aeration. (Weiss, Alvarez, Tang, Horvath & Stahl, 2015).

Verma *et al.* (2015)

This experimented presented a survey of aerobic bio-filtration processes for wastewater treatment. They assess a range of conventional and advanced bio-filtration systems including MBBR systems. It concludes that the MBBR process is a good one for upgrading existing wastewater treatment systems. However, they also mentioned that for fluidized systems, generally (including MBBR systems), capital costs are comparatively low, operating costs are higher due to pumping/aeration requirements. (Verma, Brar, Blais, Tyagi & Surampalli, 2015)

Kermani M., Bina B., *et al.,* (2009)

As per this experimental study, removal of biological nitrogen and phosphorus from synthetic wastewater was done by a lab scale moving bed biofilm process. Also, kinetic analysis of the process with reference to phosphorus and nitrogen removal is studied with different mathematical models. For nutrient removal, the moving bed biofilm process is applied in series with anaerobic, anoxic and aerobic units in four separate reactors that were operated continuously at different loading rates of phosphorus and nitrogen and different hydraulic retention times.

(C) CONCLUSIONS

MBBR systems are broadly reported in the research literature as having a range of desirable characteristics, including:

i. Provides excellent pollutant removal performance;
ii. Suitable for a wide range of effluent sources and types;
iii. Ease of Management – Good stability and no sequencing;
iv. Can be retrofitted with ease into existing tanks to extend asset life and performance;
v. Required a smaller tank volume compared to AS systems for the same treatment flow rate;
vi. Higher effluent treatment flow rates compared to similar capacity AS plants;
vii. Lower capital cost compared to an AS plant with similar performance characteristics.

Particular capital costs of MBBR systems include the purchase of proprietary attached growth media, which may be offset against the typically reduced overall cost for the smaller plant size required compared to traditional treatment plant technology. MBBR systems generally have an increased energy requirement for aeration on a tank unit volume basis, which may be offset against the typically smaller tank unit volume required for the same flow rate of effluent treatment compared to traditional treatment plant technology. Many Researchers identified MBBR technology as appropriate for upgrading the performance and for treatment capacity of existing plants, particular if plant expansion is constrained by space limitations. Many Researchers have recommended the use of a pilot-scale evaluation to determine suitable design and operating parameters for full-scale plant development. After referring to research literatures pertaining to MBBR, it could be firmly drawn that there is broad range of advantages of MBBR. But bio-carriers being used in MBBR to treat wastewater are quite expensive and have less surface area for bacterial growth or say biofilm generation. Hence, we have decided to perform our nitrogen removal study using a cheap and feasible bio-carrier, for this we have opted a cubical shaped polyurethane (PU) sponge bio-carriers as in place of moving bed.

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