"A Review Of Techno-Economic Comparison Of Chemical-Coagulation And Electro-Coagulation For Nitrate Removal"

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***Abstract*- One of the biggest concerns is the increase of nitrate in the receiving waters. The main source of increase in nitrate concentration in ground water and surface water is excessive use of nitrogen based chemical fertilizers . High nitrate concentrations have contributed to negative effects on human health and on the environment. all countries and organizations restricted nitrate concentration in drinking water within the range 45-50 mg/l as NO_3^- or 10-11.3 mg NO_3^- N/L Common treatment methods for nitrate removal include several physicochemical and biological processes. Many advanced wastewater treatments are used for nitrate removal but these treatments are very expensive to apply at community level for removal of nitrate from ground water as well as from surface water. So chemical coagulation which is a primary treatment and electro-coagulation are reviewed as simple technologies in this paper. Chemical-coagulation is a low cost method and also gives good efficiency, cost depends on the type of coagulant used whereas electro-coagulation is an expensive treatment and gives highest removal efficiency as compared to chemical-coagulation., for electro-coagulation cost depends on the type of electrode used.**

I. INTRODUCTION

One of the biggest concerns is the increase of nitrate in the receiving waters. High nitrate

Concentrations have contributed to negative effects on human health and on the environment. Common treatment methods for nitrate removal include several physicochemical and biological processes, but few of them have been found effective and economically for application to groundwater and surface water treatment systems. However, chemical and electrochemical treatments has potential as a possible treatment methods to remove nitrate in ground water as well as surface water.

Nitrogen compounds are very important pollutants in domestic and industrial wastewaters when these wastewaters discharged into drinking water reservoirs and cause several environmental problems . Among several N species, nitrate is the most stable and it is produced when nitrogen from ammonia or other sources combines with oxygenated water . In water, nitrate has no taste or smell and can be identified by a chemical test. Nitrate is a serious environmental pollutant, as it is generally a problem associated with anthropogenic activities. Ordinary sources of nitrate pollution include discharge of chemical fertilizers, animal wastes, septic tanks, and municipal sewage treatment systems. Fertilizer is the largest supplier to nitrate pollution. Excessive application of agricultural fertilizers has been known to cause penetration of large quantities of nitrates into underground and surface waters.

As per the literature in Gujarat state 22 parts of the districts are having nitrate concentration more than 45 mg/l(International Journal Of Chem. Tech Research). Many technologies are used for removal of nitrate such as reverse osmosis, electrodialysis, ion exchange and biological treatment. There is no treatment is given at community level for removal of nitrate. So in this study chemical coagulation and electro coagulation technologies are reviewed as simple technologies as compared to advanced wastewater treatments. Both technologies are compared for techno economic aspects for removal of nitrate.

II. NITRATE

Nitrate is naturally occurring ions that are part of the nitrogen cycle. The nitrate ion is the stable form of combined nitrogen for oxygenated systems. Although chemically unreactive, it can be reduced by microbial action. Chemical and biological processes can further reduce nitrite to various compounds or oxidize it to nitrate (WHO, 2011)

NO_3^- and nitrite are naturally occurring inorganic ions, which are part of the nitrogen (N_2) cycle. Microbial action in soil or water decomposes wastes containing organic nitrogen first into ammonia, which is then oxidized to NO_2^- and NO_3^- .Because NO_2^- is easily oxidized to NO_3^-, is the compound predominantly found in groundwater and surface waters under oxidizing conditions. Contamination with N containing fertilizers, including anhydrous ammonia, as well as animal or human natural organic wastes, can raise the concentration of NO_3^- in groundwater. NO_3^- containing compounds in the soil are generally soluble and readily migrate into groundwater. (Shomar, et al., 2008)

Nitrate pollution of surface and groundwater's has become a major problem in some agricultural areas (Meyer, et al., 2005)

Table 1: Physicochemical properties of nitrate .

Properties	**Nitrates**
Acid	Conjugate base of strong acid HNO_3; pKa = −1.3
Salts	Very soluble in water
Reactivity	Unreactive

SOURCES OF NITRATE

- Heavy utilization of artificial fertilizers
- The intense exploitation of farms
- The ubiquity of agriculture-related industries
- Discharge of chemical fertilizer and human and animal waste
- Urban runoff
- Land filling

EFFECTS OF NITRATE

Several health problems may be caused by excess nitrate in water sources. Nitrate Ions in groundwater have many adverse effects on human. In humans, water contaminated with nitrate has been related to outbreaks of infectious diseases, childhood diabetes and decrease iodine uptake, but the current studies are incomplete. Other studies indicates that high nitrate uptake can lead to abortion in animals such as cattle .

Nitrate is hazardous to infants and pregnant women due to the risk of methemoglobinaemia , also called the "blue-baby syndrome". Reduction of nitrate to nitrite in the stomach of infants occurs, where nitrite will bind to haemoglobin and form methaemoglobin in the red blood cells.

In drinking water, nitrate may cause different types of cancer in humans who are exposed to high amounts (WHO, 2011).

Another health concern, which has been under study for many years, is nitrate contaminated drinking water's link to non-Hodgkin's lymphoma and stomach cancer. Although this link is very tenuous and controversial, research and surveys are ongoing in an attempt to document the connection. The United States National Research Council found some suggestion of an association between high nitrate intake and gastric and/or gesophageal cancer. However, individual exposure data were lacking, and several other plausible causes of gastric cancer were present. Connections exists between nitrate intake and several disorders and adverse effects, however there is still a lack of compelling evidence (WHO, 2011) .

III. NITRATE STANDARD LIMITS

Despite conflicting research findings, standards have been set for nitrate in drinking water. The U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for nitrate is 10 mg NO_3-N/L (USEPA, 2009), whereas the World Health Organization (WHO) and the European Community have set an MCL of 50 mg NO_3-/L which is equal to 11.3 mg NO_3-N/L (WHO, 2011) . Ontario Ministry of the Environment and Health Canada have set the maximum acceptable concentrations (MAC) of nitrate in drinking water of 45 mg NO_3-/L (10 mg NO_3-N/L) (Ontario Ministry of the Environment, 2006) (Health Canada, 2012) . The MAC of nitrate as regulated by the National Health and Medical Research Council and Engineering Services Division Ministry of Health Malaysia are

also 50 mg NO_3^-/L (11.3 mg NO_3-N/L) (Health Australia, 2004) (Health Malaysia, 2004) .

The organizations concerned with drinking water quality and many governments have paid a great attention for nitrate limitation in the drinking water. Table (2) lists some international standards of nitrate concentration in drinking water according to some international water quality guidelines. It can be noticed that all countries and organizations restricted nitrate concentration in drinking water within the range 45-50 mg/l as NO_3^- or 10-11.3 mg NO_3-N/L , which indicates that nitrate is a matter of concern that should be treated well.

Table 2 International standards for nitrate concentration in drinking water

Country/organization	Nitrate concentration	Reference
WHO	50 mg/L as NO_3^-/l	(WHO,2011)
The USEPA	10 mg/L as NO_3-N/l	(USEPA,2009)
Canada	45 mg/L as NO_3^-/l	(Health Canada.2012)
Ontario Ministry Of The Environment	10 mg/L as NO_3-N/l	(Ontario Ministry Of The Environment,2006)
Australia	50 mg/L as NO_3^-/l	(Health Australia,2004)
India	50 mg/L as NO_3^-/l	IS 10500
Malaysia	50 mg/L as NO_3^-/l	(Health Malaysia,2004)

IV. FINDINGS FROM DIFFERENT RESEARCH PAPERS FOR REMOVAL OF NITRATE BY CHEMICAL-COAGULATION AND ELECTRO-COAGULATION

Review for chemical-coagulation

1. The concentration of nitrites or nitrates of an effluent sample can be reduced by about 25 percent by flocculating the sample, adjusted to pH 6.0, with 250 ppm of alum used as a coagulant (S.K.Malhotra et al.)

2. Lime at 150 mg/l reduced nitrate concentration from 70 to 0 mg/l (100% removal), followed by PAC from 70 to 4.8 mg/l (93.1% removal) and by alum from 70 to 8 mg/lnitrate (88.5% removal) . There was no further significant decrease in nitrate concentration when the dosage of the coagulants was increased above 150 mg/l. Hence, the optimum dosage for the effective removal of nitrate from MSM and the groundwater samples was found to be 150 mg l–1 for lime and PAC. Similarly, in the groundwater samples the level of nitrate was reduced from 50 to 3.1 and 4.9 mg/l, respectively, when lime and PAC were used at the concentration of 150 mg/l. The use of lime as a chemical coagulant gave the highest nitrate removal rate of 93.8%, whereas for alum, the nitrate removal rate was only 74.3%. The removal rate of nitrate was invariable as the concentrations of alum, lime and PAC were increased (Pudukadu Munusamy et al.).

Review for electro-coagulation

1.A minimum of 55 min electrolysis time is required to reduce nitrate concentration from 45 mg/L-N to maximum acceptable level at a current value of 2.5 A. At an operating current of 2.5A, the nitrate removal efficiency can reach up to 90%. Maintaining high pH in the range 9 to 11 was favourable for this process (Mohammad M. Emamjomeh et al.)

2.The energy yield of generated hydrogen was ~54 % of the electrical energy demand of the electrocoagulation process. With the reduction of the net energy demand, electrocoagulation may become a useful technology to treat water associated with

power production. The results also showed that the optimized removal efficiency of 95.9 % was achieved at an optimum current density of 0.25 A/dm^2 and a pH of 7.0 using aluminum as anode and cathode with an energy consumption of 6.26 kWh/m^3 (Engracia Lacasa et al).

3.Electrocoagulation is an effective technology for the removal of nitrates from wastewaters. For the same reagent dose (in molar units), the same amount of nitrate removal was obtained using both iron and aluminium anodes. Small amounts of ammonium ions are produced during electrocoagulation with aluminium electrodes. Coagulation cannot compete with electrocoagulation for this particular application. For the same reagent doses that achieve significant nitrate removal using electrocoagulation, coagulation exhibits no nitrate removal (Jothinathan Lakshmi et al).

4.The results showed that the electrocoagulation process can reach nitrate to less than standard limit. pH, electrical potential difference, total dissolved solids and number of electrodes have direct effect and initial concentration of nitrate has reverse effect on nitrate removal. This study also showed that under optimum condition, nitrate removal from Kerman water distribution system was 89.7 %. According to the results, Electrocoagulation process is suggested as an effective technique in nitrate removal (M. Malakootian et al).

5.In electroreduction, removal of nitrate to an allowable concentration has been accomplished at the pH range of 5–7 with energy consumption value of 1×10^{-3} kWh g^{-1}. In electrocoagulation, an allowable concentration of nitrate has been achieved at the pH range of 9- 11 with energy consumption value of 0.5×10^{-4} kWh g^{-1}. Full removal of nitrate was also possible but with higher energy consumptions for these two methods (ASavas Kopara et al.,2001).

6.The operating costs of the electro-coagulation process depend on concentration of pollutants. The electro-coagulation with iron electrodes at low values of current density is the most economical process for removing the three pollutants studied.According to obtained results, removal of arsenate seems to be technically and economically more interesting. The same applies for phosphate removal in which operation cost seems reasonable. On the opposite, nitrate removal seems to be very expensive by electro-coagulation, because of the low efficiency (Engracia Lacasa et al.).

7.At pH – 2 Nitrate converts into ammonia and nitrogen and at pH – 8 Nitrate converts into only nitrogen. Maximum reduction obtained at pH – 8 without sludge formation at time duration of 8 hours (P K Raghu Prasad et al.,2005).

8.The experimental results show that Cr (VI) and nitrate removal are enhanced by an increase in the current intensity. In addition, a desirable concentration of nitrate and Cr (VI) was achieved in the pH range between 4 and 8 over 120 min. As pH increased, Cr (VI) removal efficiency decreased, and the removal efficiency of nitrate increased. During the EC process, the Cr (VI) ion was reduced at the cathode and precipitated as $Cr(OH)_3$, and nitrate removal was complete and accompanied by the precipitation of $Al(OH)_3$ produced in the solution from the anode release. It is that nitrate can be removed completely from model wastewater by using the EC process. Moreover, the oxidation reduction potential decreased as the current intensity increased. This behavior can reduce the nitrate ions to N2 gas. The results show that, with an increase in time and current intensity, the rate of anode dissolution increased. The results of this study have shown that simultaneous nitrate and Cr (VI) removal can be achieved by coupling the cathodic reduction of the nitrate and Cr (VI) ions with the oxidation of ammonia operated by chlorine and an increase in the pH as a result of the Al (OH)3 produced in the solution by anode release (Abbas Rezaee et al.,2011)

9.Energy consumption of up to 0.87×10^{-3} kWh/g-N with conversion yields of 55–60% were noticed at pHs of 6–7 after 120 min. Lower energy consumption of 0.1 × 10−3 kWh/g-N resulted in nitrate conversion yields of almost 43% after only 40–80 min. No nitrite or ammonia appeared to form at 5.3 V for D = 7.2 mm and neutral pH. Parameters simulation allowed to predict the nitrate conversion yield in correlation with the process selectivity according to the energy constraint, and conversely. This opens promising prospects for low-cost nitrate removal without generating nitrite or ammonia (Bachagha Talhia et al).

V. CONCLUSION

Chemical coagulation

Lime alum and PAC are used as a coagulant for removal of nitrate among which alum gives highest nitrate removal efficiency.

Electro coagulation

Effect of pH : Removal efficiency of nitrate increases with increase in pH .

Effect of nitrate initial concentration : If nitrate concentration more in the sample , efficiency of removal decreases.

Effect of electrodes connection methods : the nitrate removal efficiency with monopolar connection was higher than the bipolar electrodes connection method.

Effect of electrode kind : Iron electrodes have more efficiency in nitrate removal than aluminum electrodes. Using Iron electrodes has limits due to the production of color and corrosion.

Effect of electrode number : With increases in electrode number, the nitrate removal efficiency increases.

Effect of applied potential : As the applied potential increased, the time to achieve steady-state concentration was reduced and percent removal increased.

Effect of electrode distance : As the distance between electrode decreases , nitrate removal efficiency increases.

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