Nitrate reduction using zero-valent iron and effect of corrosion inhibitor on reduction

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Abstract - *The objective of this work is to study reduction of nitrate concentration using zero-valent iron (ZVI) which has its application in permeable reactive barriers (PRBs). Also, to find out effect of concrete penetrating corrosion inhibiting admixture (CPCIA) EPCO-KP 200 on performance of ZVI in nitrate reduction. Experiments were carried out for a period of 60 days to find out optimum percentage of EPCO-KP 200 by measuring parameters like pH, conductivity, sulphate content and iron content of the solutions containing steel bars and different percentages of EPCO-KP 200. Best results were found with 1.6% and this percentage was chosen to carry out further batch experiments for nitrate reduction. Batch experiments were carried out to study nitrate reduction using synthetically prepared nitrate solution of 30mg/l and different dosages of ZVI. Best results were obtained with 0.5gm as it gave higher reduction in same time interval compared to 1gm and 0.25gm. Also, performance of corrosion inhibitor was found to be effective to increase the life span of ZVI as nitrate reduction with EPCO-KP 200 in presence of 0.5gm ZVI was found to be slow compared to reduction without EPCO-KP 200.*

***Key Words*: Nitrate, ZVI, reduction, corrosion inhibitor, EPCO-KP 200.**

1. INTRODUCTION

Nitrate when present in high concentration in drinking water possess many problems to human health. This may occur mainly in groundwater. People may suffer from diseases such as methemoglobinemia, gastric or intestinal cancer due to drinking of water with high nitrate concentration [1]. Therefore it is necessary to treat the water and bring it to safe consuming levels. Steps should be undertaken to prevent leaching of nitrate in the soil which will be more profitable than treating the nitrate contaminated water. This can be done by optimum use of nitrate based fertilizers in agriculture. Leach pits and slurry stores can also be constructed in the areas where manure is stored [2]. Treatment processes for example reverse osmosis, ion exchange, will be effectual in diminishing the nitrate concentrations for drinking water. Such processes are helpful in bringing down the nitrate concentration to recommended level of 45mg/l [3] rather than removing the entire nitrate.

1.1 Reduction of nitrate using zero-valent iron

Reduction with zero-valent iron (ZVI) is well known technology which has found its application in reduction of various oxo-anions [4], Nitro aromatic compounds[5], Halogenated organic compounds [TCE] and heavy metals [6].According to [7] reduction of nitrate with ZVI takes place as follows

$$4Fe^0 + NO_3^- + 7H_2O \longrightarrow 4Fe^{2+} + NH^{4+} + 10OH^- \quad \text{.............(1)}$$

$$Fe^0 + 2H_2O \longrightarrow Fe^{2+} + H_2 + 2OH^- \quad \text{.....................................(2)}$$

As per the above mentioned equations, Fe^0 gets oxidized to Fe^{2+} i.e. it gets corroded hence looses its capacity of reducing nitrate. Therefore in these experiments an attempt has been made to retard the corrosion of ZVI using a concrete penetrating corrosion inhibiting admixture (CPCIA) EPCO-KP 200, designed for protecting the reinforcement bars in concrete against chloride attack. It is a bipolar inhibitor, which retards the corrosion process both at the cathodic and the anodic sites. The process is chemical and not physical. The electron density distribution causes the inhibitor to be attracted to both anodic and cathodic sites. EPCO KP-200 by virtue of its vapour pressure diffuses and gets deposited on the steel in a monomolecular layer. The molecules are water soluble and possess binding energy to metal surfaces higher than the binding energy of water dipoles and chlorides from the metal surface [8].Firstly, experiments were carried out to study the mechanism of oxidation of iron and its inhibition using cement admixture EPCO KP-200 and to determine the optimum dosage of the admixture by directly exposing steel to different concentration of EPCO-KP 200.Secondly, different experiments were conducted by varying dosage of ZVI to check nitrate reduction at regular time intervals. In addition to this, studies were undertaken to check the effect of EPCO-KP 200 on performance of ZVI in nitrate reduction.

2. MATERIALS AND METHODS

2.1 Materials and reagents

Chemicals used are Sulphate buffer solution, Barium chloride ($BaCl_2$, Nice Chemicals LR grade, 99% pure), Hydroxylamine hydrochloride ($HONH_2.HCl$, Finar Reagents, LR Grade, 98% pure), concentrated Hydrochloric acid (HCl, Rankem, 35% pure), 1,10,Phenathroline monohydrate ($C_{12}H_8N_2H_2O$, Loba Chemicals LR grade, 99.5% pure), Ammonium acetate (CH_3COONH_4, Nice Chemicals LR grade,96% pure), Potassium nitrate (KNO_3^-, Nice Chemicals LR grade 99% pure), White phenol (C_6H_5OH, Jyothi Chemicals LR grade, 99% pure), Potassium hydroxide (KOH, Nice Chemicals LR grade, 85% pure),Steel bars of three different diameters 8 mm, 10 mm, 12 mm (Tata Tiscon), Rust cleaner (WD 40), hard sponge, 6 Plastic air tight containers, EPCO-KP 200 (Krishna Coenchem Ltd), Zero valent iron (Varsha iron) Demineralised water, Solutions with different percentages (0.7%,1%,1.3%,1.6%) by volume of EPCO-KP 200 was prepared using demineralised water. Stock nitrate solution of 1000 mg/l was prepared by dissolving 7.21 gm of KNO_3 in 1000 ml of demineralised water.

2.2 Preparation of EPCO-KP 200-Nitrate solution

Initially, 1.6 % of EPCO-KP 200 solution was prepared by mixing 16 ml of EPCO-KP 200 to 984 ml of demineralised water to make it upto 1000ml. Then, 0.216 gm of KNO_3 was added to the same solution to get 30 mg/l concentration of nitrate ion.

2.3 Methods

The experimental study was divided into two sections. Section-I comprised of finding the optimum dosage of EPCO-KP 200 for carrying out batch experiments. Section-II involved carrying out nitrate reduction batch experiments using ZVI and optimised dosage of EPCO-KP 200. In section-I, three steel bars of different diameters (8mm, 10mm and 12mm) with length of 150 mm each were taken and cleaned with a rust cleaning agent (WD 40). A hard sponge was cut and fixed to the container lids of six air tight containers. Further, each hard sponge attached to the container lids were fixed with three different bars each of 8mm, 10mm and 12mm diameters. Each container was filled with different solutions upto1.9 L mark. The different solutions were sea water, demineralised water, and solutions containing different percentages of admixture (0.7%, 1%, 1.3%, and 1.6% of 1.9 litres of demineralised water). Further, the bars fixed to the sponge of container lids were suspended in the solutions. The solutions containing rods were collected and analysed at a regular interval of 7 days for a period of 60 days. The parameters analysed were pH, Conductivity, Sulphate and Iron. The studies were carried out using standard analytical methods for the measurement of above mentioned parameters [9].

In section-II,experiments were carried out using Borosilicate glass vial of capacity 30 ml. Stock nitrate solution of 1000 mg/l was prepared by dissolving 7.21 gm of Potassium Nitrate (KNO_3) in 1000 ml of demineralised water. Standard solution of 30 mg/l prepared from stock solution was used for the experiment. ZVI passing through 600μm seive size was used for the experiment. Triplicate samples for the experiment were prepared .Nitrate solution of 30 mg/l was taken into a Borosilicate glass vial and was completely filled to ensure zero head space. To this, 1 gm of ZVI was added and the vials were placed on a rotor for providing end to end rotation. Speed of the rotor was maintained at 30 rpm. The experiment was carried out for different contact time (1h, 2h, 4h, 6h, 8h, 15h, 24h) and dosages of ZVI (1gm, 0.5gm, 0.25gm). After each contact time, the vials were removed from the rotor and centrifuged (Remi R-4C) at 1000 rpm to separate solid and liquid. The supernatant liquid was filtered using filter paper and tested for nitrate concentration. Duplicate samples for control were prepared in similar manner without addition of ZVI.

Similar method was followed to study the effect of corrosion inhibitor using the prepared EPCO-KP 200-Nitrate solution instead of only nitrate solution. Dosage of ZVI which gave maximum reduction in the same time interval was selected for these experiments.

3. RESULTS AND CONCLUSIONS

3.1 Effect of pH and conductivity on oxidation of iron

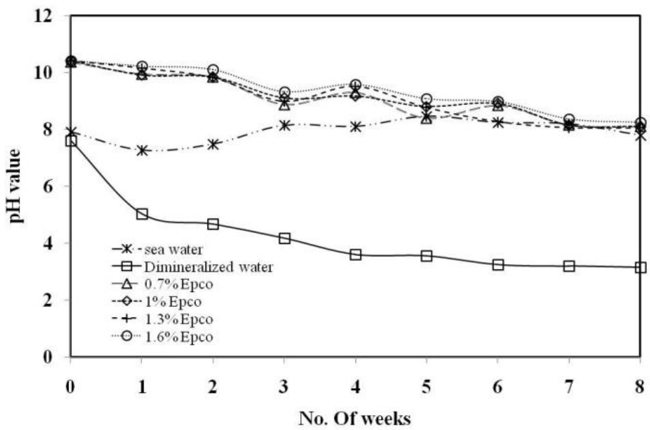

Chart-1: Graph showing variation of pH in sample solution containing iron rods

It can be clearly seen that pH of the sea water remained in the range of 7.9-8.24. All the solutions containing different percentages of EPCO showed the pH variation in alkaline range from 10.3-8.01. However, demineralised water in presence of iron rod showed pH variation from neutral range of 7.6 to acidic range of 3.15.

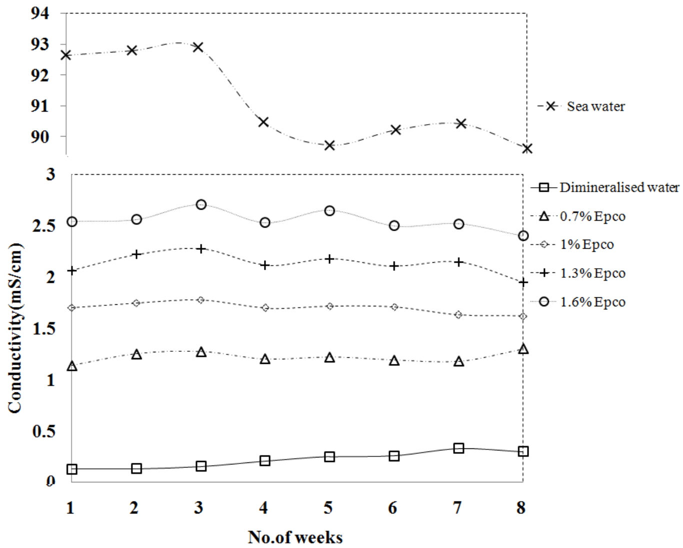

Chart-2: Graph showing variation of Conductivity in sample solution containing iron rods

It can be clearly seen that conductivity of sea water is very high compared to rest of the sample solutions and is in the range of 92.65 mS/cm- 89.62 mS/cm. All the solutions containing different percentages of EPCO-KP 200 did not show much variation in the conductivity. Container with demineralised water showed slight increase in the conductivity. It can be conclude using Eh-pH diagram for Fe-O-H system [10] that the dominant species in corrosion products are in the form of ferrous (Fe^{2+}) in case of sea water and demineralised water and the alkaline pH and the conductivity range of EPCO solutions suggest that the iron will be in the ferric form as a corrosion product.

3.2 Variation of sulphate content in different experimental setups

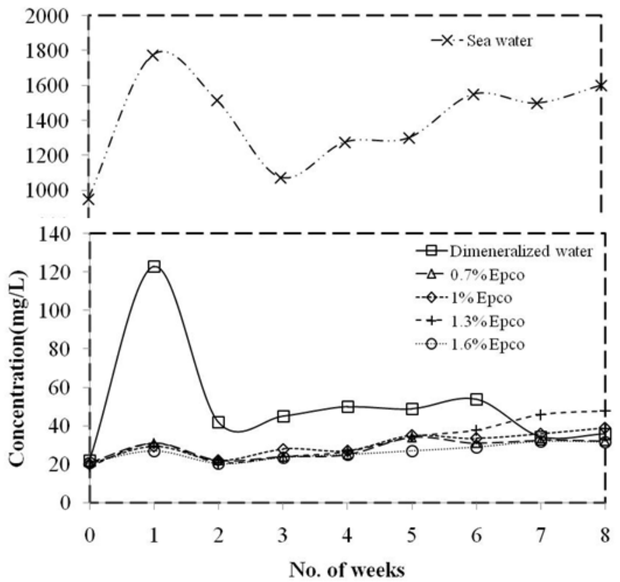

Chart-3: Graph showing variation of sulphate in sample solution containing iron rods

The plot shown by demineralised water shows an initial sudden increase in the sulphate content in the first week and from second week it shows a decrease. For solution of different percentages of EPCO-KP 200, we can see a slight increase in the sulphate content, which could be because of sulphate compounds present in admixture during its manufacturing process.

3.3 Variation of iron content in different experimental setups

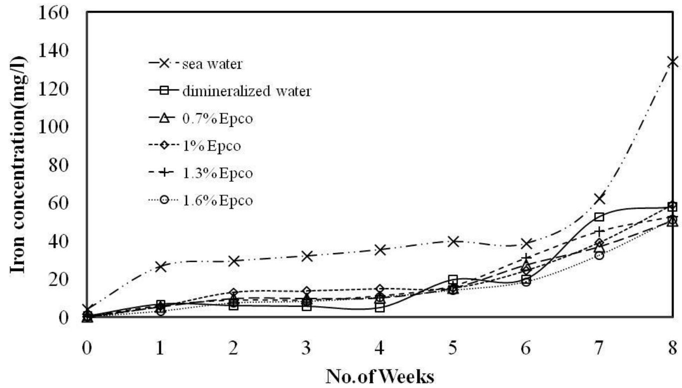

Chart-4: Graph showing variation of iron in sample solution containing iron rods

It was found that every week iron concentration was increasing in case of rods dipped in sea water. Steep increase of iron was seen between 7th and 8th week. The overall iron concentration in the solution increased from 4.15 mg/l-134.11 mg/l. Similar trends were seen for other solutions containing iron rods. However the increase in iron concentrations was very less in demineralised water and EPCO solutions compared to sea water. The solution containing 1.6% of EPCO showed least iron concentration in the solution which varied from 0.35mg/l – 51.31mg/l.

Fig-1: Solutions on the 1st day of experiment

Fig-2: Solutions on the 60th day of experiment

It can be clearly seen that containers with sea water and demineralised water turned to more dark red compared to rest all samples containing EPCO solutions, which proved that iron concentrations were comparatively high in case of sea water and demineralised water. Container with 1.6% of EPCO showed lighter colour among all samples which proves that corrosion of iron was least in this particular combination. Hence 1.6% of EPCO was considered as best percentage and used for further batch experiments.

3.4 Effect on nitrate reduction using different dosages of ZVI

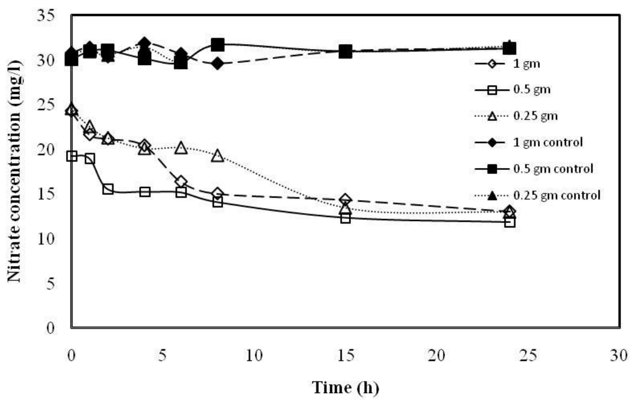

Chart-5: Graph showing comparison between different dosages of ZVI in reducing nitrate concentration

Chart-5 depicts that nitrate reduction was higher with the dosage of 0.5 gm ZVI. From the observation we can state that higher dosage of ZVI need not give higher removal. Similar findings were reported by earlier researchers [11]. They found out that chainlike aggregates were formed due to the electrostatic force between the nZVI particles. This suggests that the particles do not exist in individual forms due to spontaneous aggregation of particles [11].

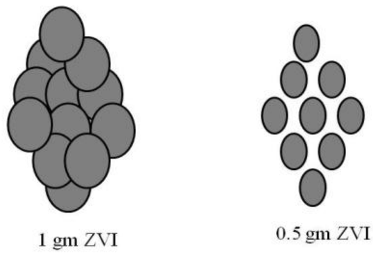

Fig-3: Animation showing the agglomeration of ZVI and free particles of ZVI which play significant role in nitrate reduction

Therefore to check the effect of EPCO-KP 200 on performance of ZVI in nitrate reduction, dosage of 0.5 gm of ZVI was selected.

3.5 Effect of 0.5 gm ZVI on nitrate reduction with 1.6% of EPCO-KP 200

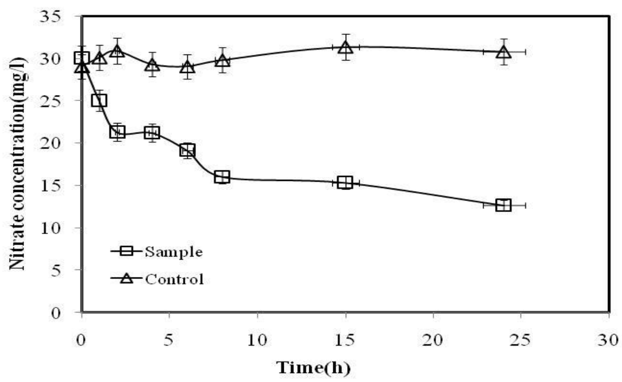

Chart-6: Nitrate reduction in presence of 0.5gm ZVI and 1.6% of EPCO-KP 200

From Chart-6, it is clear that nitrate concentration reduced from 30mg/l at 0 h to 16.03mg/l (46.20% reduction) at 8 h of reaction time. After 24 h, nitrate concentration was found to be 12.66 mg/l (58.91% reduction). Almost complete recovery of nitrate was obtained in control samples without ZVI.

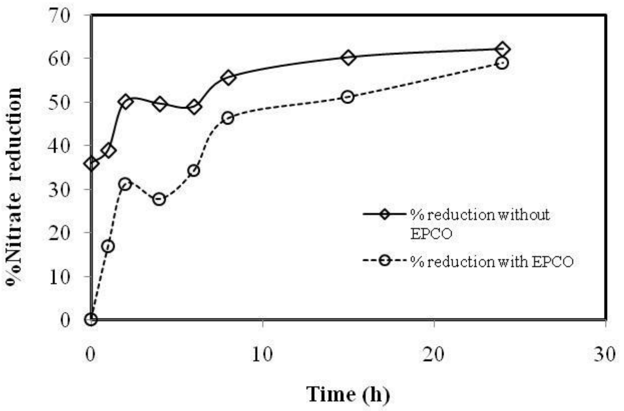

Chart-7: Graph showing percentage reduction of nitrate using 0.5gm of ZVI with and without EPCO-KP 200

Above graph shows that percentage reduction of nitrate using 0.5 gm of ZVI with EPCO-KP 200 is less than compared to percentage reduction without EPCO-KP 200. This proves that EPCO-KP 200 inhibits the corrosion of ZVI. This study could help in increasing the life span of ZVI in PRBs which could reduce the cost of its replacement. The mechanism of nitrate reduction in presence of 1.6% of EPCO-KP 200 is as shown in the figure below.

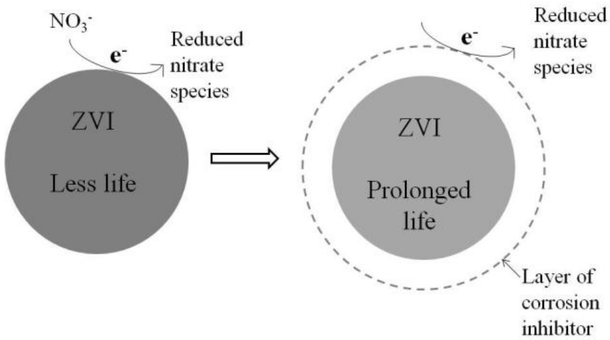

Fig-4: Animation showing proposed mechanism for reduction of nitrate using ZVI in presence of EPCO-KP 200

Fig-4 depicts that oxidation of ZVI in absence of corrosion inhibitor takes place faster which leads to higher corrosion and less life of the ZVI. Though in the other case, the corrosion inhibitor forms a layer on the surface of the ZVI and protects its core structure from oxidation. This layer helps in reducing the rate of corrosion and ultimately leads to prolonged life of ZVI.

From the above study following conclusions are obtained. With the test results put forth in graphical form and comparing with different percentages of admixture, optimum dosage of admixture was concluded to be 1.6%. From the batch experiments carried out for nitrate reduction using ZVI in presence of different dosages of ZVI(1gm, 0.5gm, 0.25gm) dosage of 0.5gm ZVI gave higher reduction in same time compared to 1gm and 0.25 gm. This suggests that higher dosage need not lead to higher removal. Analysis of results of the experiments for nitrate reduction in presence of 0.5 gm ZVI and EPCO-KP 200, proved that percentage reduction of nitrate with EPCO-KP 200 is less than compared to percentage reduction without EPCO-KP 200.Which suggests that corrosion inhibitor works effectively and can be used to increase the life span of ZVI. From the conclusions drawn, it can be understood that concrete penetrating corrosion inhibiting admixture (CPCIA) which is designed for protecting the reinforcement bars in concrete, can also find its application in Environmental sector by using in PRBs with ZVI to decontaminate ground water.

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