

## POTENTIALS OF USING SAND IMMOBILIZED ON ZERO VALENT IRON NANOPARTICLES FOR WATER TREATMENT

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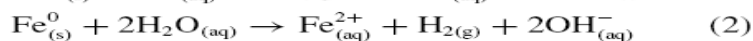
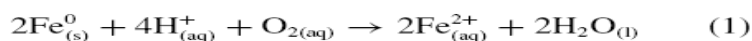
### ABSTRACT

Water treatment in a classical sand filtration versus zero valent iron nanoparticles (nZVI) filtration unit at different filtration time (0.73-35min) was investigated. The data obtained indicated that nZVI unit was very effective for removal of phosphorus, dissolved organic carbon (DOC) and pathogenic bacteria as compared to classical filtration unit. However, such efficiency of zero valent iron nanoparticles unit was strongly dependent on the filtration time. The removal of DOC, phosphorus and pathogenic bacteria was significantly increased from 19.36 to 70.11% from 25 to 87.5% and from 10.23 to 95.15 % respectively at increasing the filtration time from 0.73 to 35 min. respectively. Nevertheless, the removal of nitrogenous compounds in nZVI unit was accompanied with a conversion of nitrate into ammonia, which obviously should be avoided. The ammonia concentration was increased from 0.5 to 1.37 mg/l at increasing the filtration time from 0.73 to 35 min. respectively.

**Keywords:** Water; Classical sand filtration; Zero Valent iron nanoparticles; ammonia; pathogenic bacteria

### 1. INTRODUCTION

Zero Valent iron nanoparticles (NZVI) represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. These particles have large surface area and high surface reactivity. Equally important, they provide enormous flexibility for in situ applications,(Zhang,2003); Metallic or zero-valent iron ( $Fe^0$ ) is a moderate reducing reagent, which can react with dissolved oxygen(DO) and to some extent with water:



The above equations are the classical electrochemical/corrosion reactions by which iron is oxidized from exposure to oxygen and water. The corrosion reactions can be accelerated or inhibited by manipulating the solution chemistry and/or solid (metal) composition. Since early 1990s, the iron corrosion chemistry has been put into productive use in the treatment of hazardous and toxic chemicals (Gillham & O'Hannesin,1994; Orth & Gillham, 1996; O'Hannesin & Gillham,1998). INP have been extensively studied to remediate pollutants such as chlorinated organic compounds and metal ions (Zhang 2003; Lowry and Johnson 2004; Wang and Zhang 1997), nitrate (Choe et al.2000), Cr and Pb (Ponder et al. 2000), carbon tetrachloride and benzoquinone (Nurmi et al.2005), metalloids such as arsenic (Kanel et al.2005, 2006)

and organic compounds (Joo et al.2004). Phosphorus (P) exists in water in both particulate and dissolved forms. The usual forms of P in aqueous solutions are orthophosphates, polyphosphates, and organic phosphates (Mezenner and Bensmaili 2009). Phosphorus is necessary for the growth of organisms and plants and is an indicator of surface water quality. Excessive P presents in natural waters is known to cause eutrophication (Penn and Warren 2009). Run-offs from agriculture, including animal agriculture, are the major non-point sources. The amount of P compounds in these sources should be controlled to prevent eutrophication in lakes and other surface waters. Accelerated eutrophication not only affects the aquatic life but indirectly hinders the economic progress of communities that depend on aquatic food and other resources (Cleary et al. 2009). Dissolved phosphate of 0.02 mg/L is considered to have potential that lead to profuse algal growth in waters (USEPA 1995). Nitrate ( $\text{NO}_3^-$ ) contamination of groundwater is a widespread environmental problem, and has been associated with agricultural runoff, leaching of nitrogen fertilizers, concentrated animal feeding operations, food processing, and industrial waste effluent discharge (Su and Puls 2004). Ingestion of nitrate in drinking water by infants can cause dangerous oxygen deficit in the blood, i.e., the “blue baby” syndrome (Fan and Steinberg 1996; Nolan et al. 1997). In order to limit the health impact of nitrate in drinking water, the U.S. EPA (1995) established a maximum contaminant level (MCL) of 10 mg/L as  $\text{NO}_3^-$ -N.

The main objective of this investigation is to assess the impact of sand immobilization on Zero Valent iron nanoparticles for water treatment.

## 2. MATERIAL AND METHODS

### 2.1. Characterization of raw water

Raw water samples were collected from Sharky water treatment plant intake Alexandria water Company, Alexandria, Egypt. The characteristics of raw water used in the experiments are presented in Table 1.

**Table 1. Mean characteristics of raw water used in the experiments**

Parameter	Nitrate	Nitrite	Ammonia	Phosphorous	pH	DOC	Electric Conductivity ( $\mu\text{s}/\text{cm}$ )	Plate count cfu/ml
Values	10.1±	0.54±	0.46±	0.31±	7.8±	62.8±	587.5±	558±
(mg/l)	0.8	0.2	0.5	0.11	0.2	1.9	39.747	22.01

### 2.2. Experimental set-up

Continuous experiments were carried out in a two identical filtration units (Fig.1). Those reactors were designed and manufactured from Perspex material. The filtration units are cylindrical shape with a total volume of 15 ml for each. The 1<sup>st</sup> reactor was filled with sand (75% v/v) with a diameter of 1.5 cm and the 2<sup>nd</sup> reactor was occupied with iron nanoparticles (75% v/v) with a diameter of 1.5cm. The height and diameter of the reactors were 10, 1.5cm., respectively. The reactors were continuously fed with raw water and operated at different conditions, Table 2.

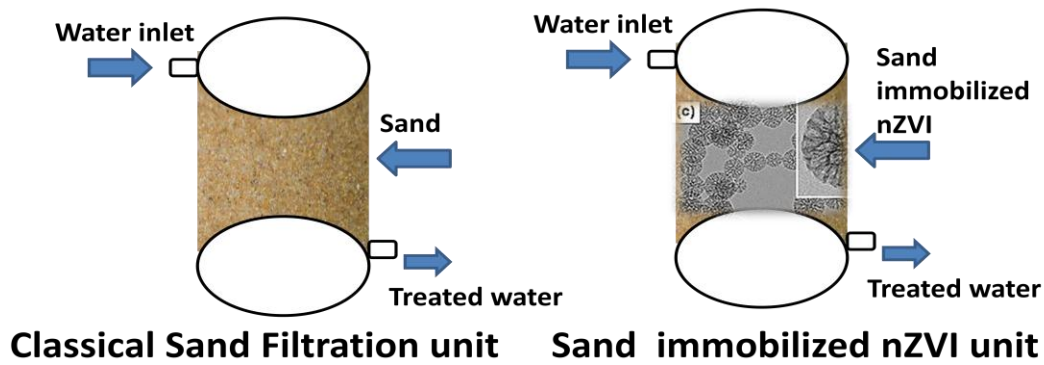


Fig. 1. Filtration units for water treatment

Table 2. Operational conditions

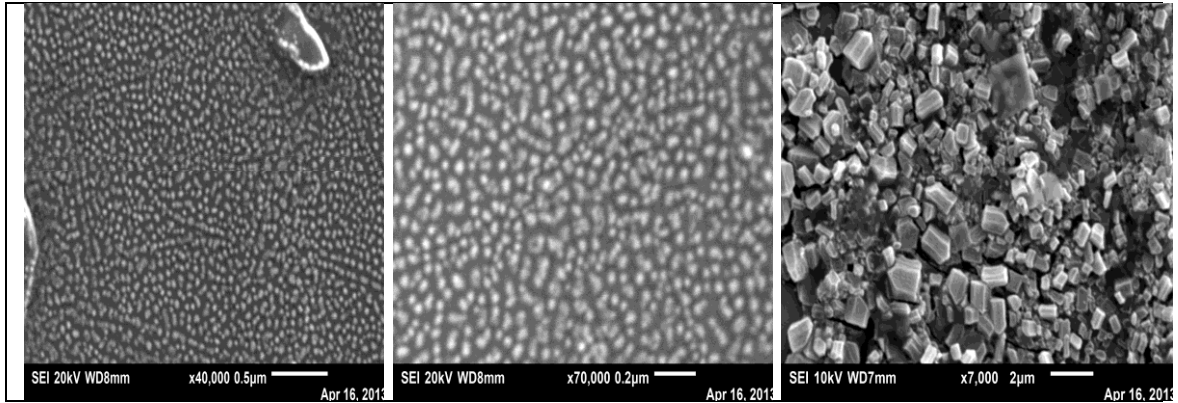
Parameter/Run	Run 1	Run 2	Run 3
Flow rate (Q/l.d)	0.288	4.147	13.8
Filtration time (min)	35	2.4	0.7

### 2.3. Preparation of Iron nanoparticles (nZVI)

Synthesis of nZVI is based on borohydride reduction of Fe (II) (Wang and Zhang 1997, Wang, et al. 2006a). In this study, iron (II) chloride tetra hydrate (FeCl<sub>2</sub>. 4H<sub>2</sub>O) and sodium borohydride (NaBH<sub>4</sub>) were used for iron (II) and borohydride sources respectively (R.Yuvakkumara, 2011)

The reaction is:  $Fe^{2+} + 2BH_4^- + 6H_2O \rightarrow Fe^0 + 2B(OH)_3 + 7H_2 \uparrow$

For the synthesis of 1.5 g of nZVI; 5.34 g FeCl<sub>2</sub>.4H<sub>2</sub>O was dissolved in a 4/1 (v/v) ethanol/water mixture (24 ml ethanol + 6 ml deionized water) and stirred on a magnetic stirrer. On the other hand, 1 M sodium borohydride solution was prepared; 3.05 g NaBH<sub>4</sub> was dissolved in 100 ml of deionized water. The final BH<sub>4</sub><sup>-</sup> / Fe<sup>2+</sup> ratio is adjusted to 3, since excess borohydride is needed for better growth of nanoparticles. The borohydride solution is poured in a burette and added drop by drop (1 drop per 2 seconds) into iron chloride solution with vigorous hand stirring. After the first drop of sodium borohydride solution, black solid particles immediately appeared and then the remaining sodium borohydride is added completely to accelerate the reduction reaction. The mixture was left for another 10 minutes of stirring after adding the whole borohydride solution. The vacuum filtration technique was used to separate the black iron nanoparticles from the liquid phase. Two sheets of whatman filter papers were used in filtration. The solid particles were washed with deoxygenated demineralized water (>100ml/g) then three times with 25 ml portions of absolute ethanol to remove all of the water. This washing process is probably the key step of synthesis since it prevents the rapid oxidation of zero valent iron nanoparticles. The synthesized nanoparticles were finally dried in oven at 323 K overnight. For storage, ethanol was added to preserve the iron nanoparticles from oxidation. The prepared nZVI are presented in photos 1, 2 and 3.



nZVI used for water treatment

## 2.4. Analytical methods

Grab samples of water intake and effluent samples were collected and analyzed for nitrate, nitrite, phosphorous, dissolved organic carbon, heterotrophic plate count and faecal coliform count. All analysis was carried out according to the APHA (2005).

## 3. RESULTS AND DISCUSSION

### 3.1. Dissolved organic carbon (DOC) removal

The results in Fig.1 show the effect of contact time on the removal efficiency of dissolved organic carbon (DOC) in classical filtration and zero-valent iron nanoparticles unit. Increasing the filtration time from 0.73 to 35 min significantly increased the removal efficiency of DOC in zero-Valent iron nanoparticles filtration unit. However the efficiency of DOC removal was remained unaffected by increasing the filtration time in classical filtration unit. This indicates that iron nanoparticles filtration is more effective for removal of DOC than classical filtration. The DOC removal efficiency was increased from 31.41 % to 63.09 % on increasing the filtration time from 0.73 to 35 min, respectively. A promising conclusion is reached when the  $R^2$  values of both techniques are 0.297 and 0.947 for the classical and zero valent iron nanoparticles techniques, respectively.

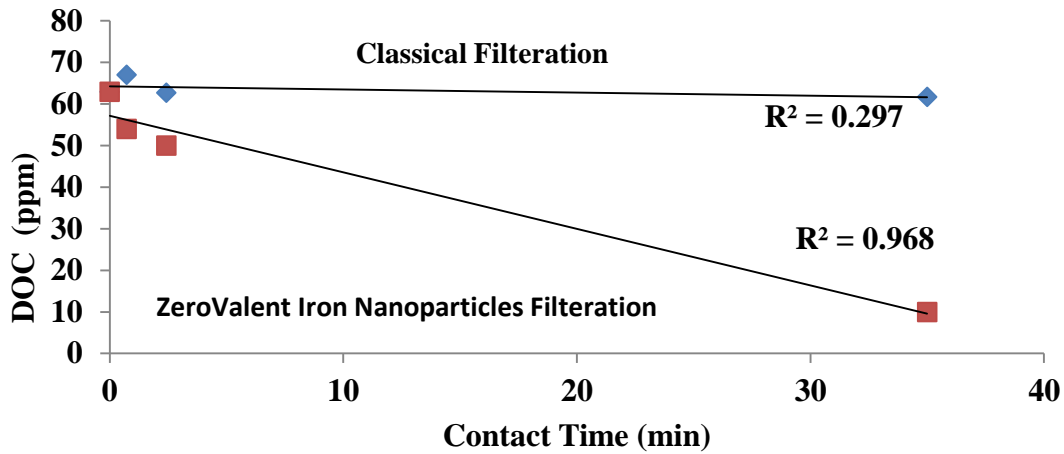


Fig.1 Comparison between the efficiency of classical sand filtration and zero valent iron nanoparticles unit for removal of DOC

### 3.2. Nitrogenous compounds removal

The effect of filtration time on the removal efficiency of nitrogenous compounds in terms of nitrate, nitrite and ammonia in a classical filtration and zero-valent iron nanoparticles are presented in Figs. 2, 3 and 4. The results revealed that increasing the filtration time from 0.73 to 35 min. significantly increases the removal efficiency of nitrate in zero-Valent iron nanoparticles filtration unit. However, reduction of nitrate was accompanied with increasing the ammonia concentration in the treated water as shown in Fig. 4. This indicates that iron nanoparticles would increase ammonia concentration in the treated water which should be avoided. The efficiency of classical sand filter for nitrate and ammonia removal was poor as shown in Figs. 3 and 4.

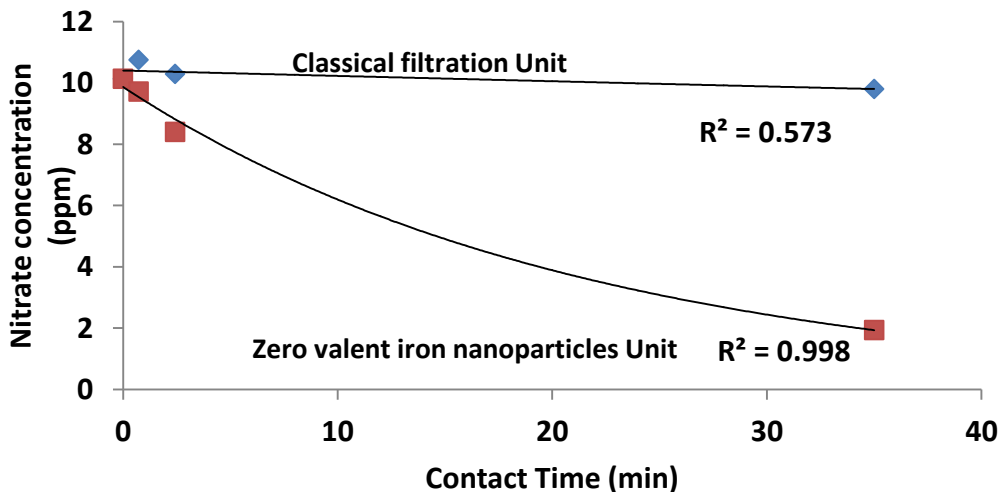


Fig. 2 Comparison between the efficiency of classical filtration and zero valent iron nanoparticles unit for removal of nitrate at different filtration time

Fig. 3 shows the removal efficiency of nitrite in classical sand filtration and zero-Valent iron nanoparticles unit at different filtration time. Similar trend was observed for removal of nitrite in zero-Valent iron nanoparticles unit where increasing the contact

time from 0.73 to 35 min significantly increased the removal efficiency of nitrite from 11 to 89.09 % respectively.

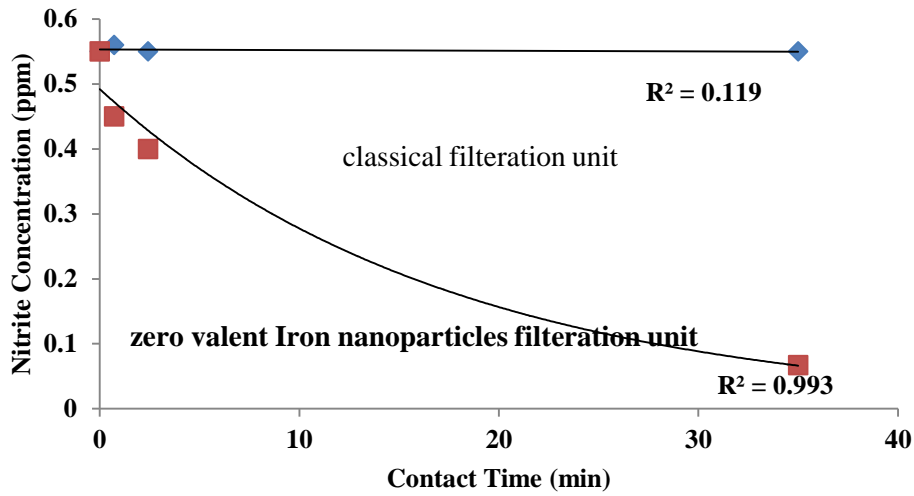


Fig. 3 comparison between the efficiency of classical filtration and Zero Valent iron nanoparticles unit for removal of nitrite at different filtration time

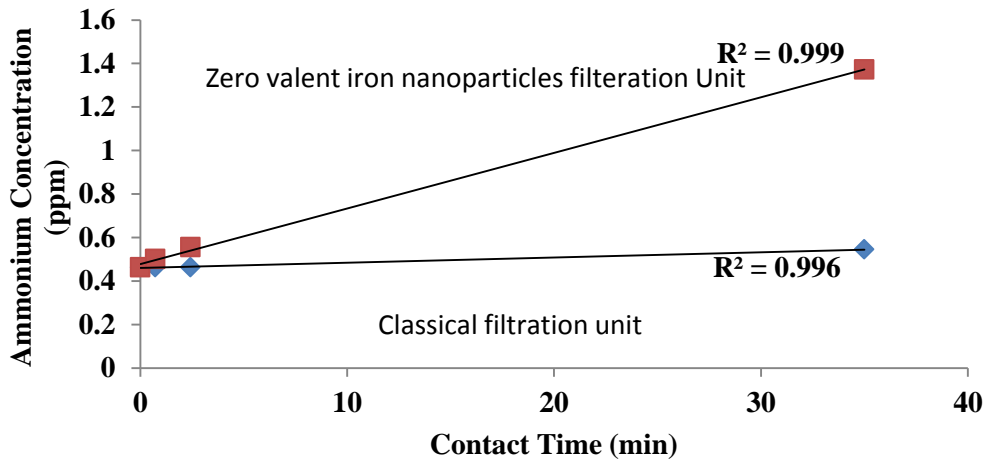


Fig. 4. Comparison between the efficiency of classical filtration and zero valent iron nanoparticles unit for removal of ammonia at different filtration time

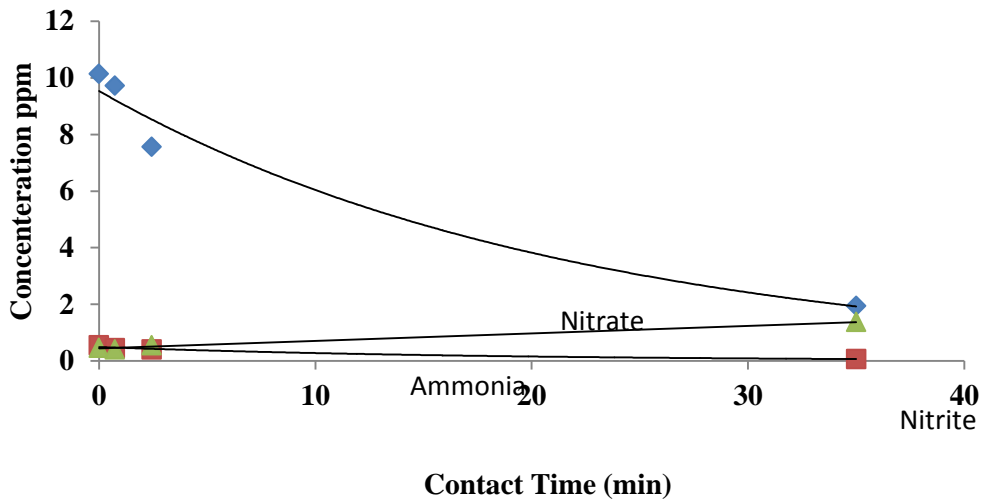


Fig. 5 Nitrogenous compounds removal in classical filtration unit versus nZVI unit

### 3.3. pH values

The results show the effect of contact time on the variation of pH values in a classical filtration and zero valent iron nanoparticles unit as shown in Fig.5a. The pH values were increased from 7.80 to 8.8 in the nZVI due to reduction of nitrate to ammonia.

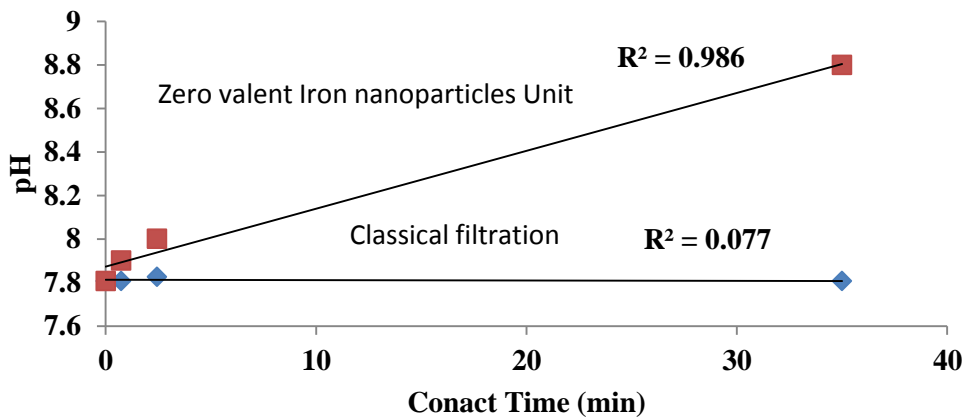


Fig. 5a The relationship between contact time and pH values in a classical sand filtration unit and nZVI unit

### 3.4. Phosphorous removal

The effect of contact time on the removal efficiency of phosphorous in a classical filtration and nZVI nanoparticles unit are illustrated in Fig. 6a. The results showed that zero-valent iron nanoparticles filtration unit is very effective for removal of phosphorous as compared to the classical filtration unit. Increasing the filtration time from 0.73 to 35 min. significantly increased the removal efficiency of phosphorous

from 55.33 to 83.66 % respectively. On a variation of filtration contact time from 0.73 to 35min, the removal efficiency of phosphorous increased from 55.33 to 83.66% respectively in nZVI filtration unit. A promising phosphorous removal technique was concluded when the  $R^2$  value was 0.984 in nZVI filtration unit.

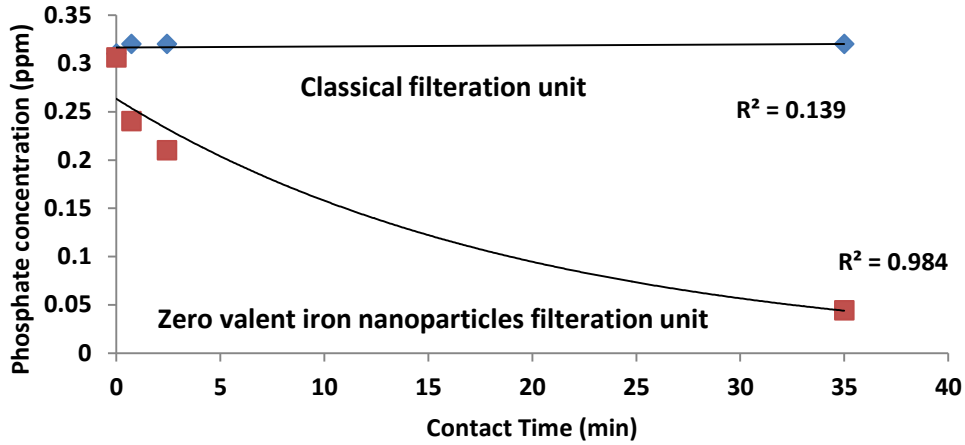


Fig. 6.a Phosphorous removal in a classical sand filtration versus Zero Valent iron nanoparticles unit.

The mechanism of phosphate removal by NZVI in the present study can be explained based on point of zero charge (PZC) and ligand exchange (Eq. 2, Karageorgiou et al. 2007, and Fig. 3). PZC for NZVI is around 7.7 (Giasuddin et al. 2007), and when pH is less than PZC the surface of NZVI is positively charged which makes the surface suitable for  $PO_4^{3-}$  sorption.

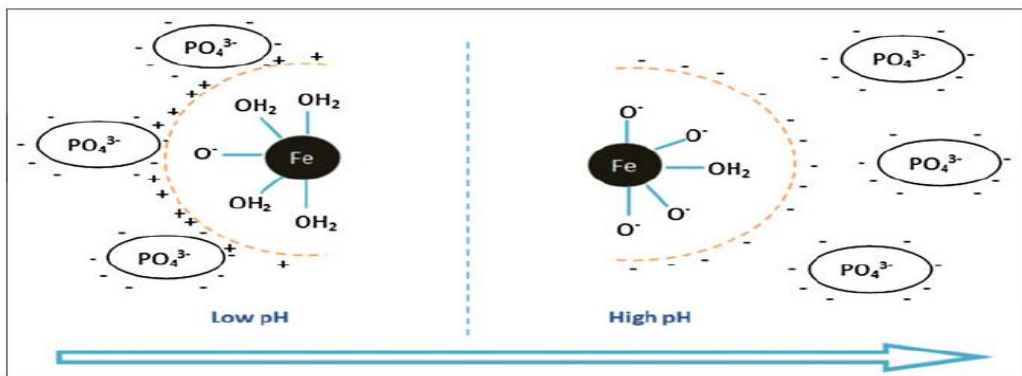
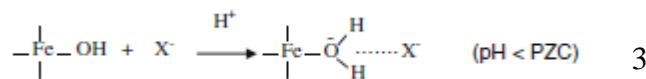


Fig. 6b Phosphate sorption by NZVI under various pH conditions (after Cordray 2008). Lower pH is more conducive for phosphate adsorption while desorption is the dominant phenomenon at higher pH





### 3.5. Pathogenic bacteria removal

Fig. 7 shows the efficiency of pathogenic bacteria removal in classical filtration versus nZVI unit. Pathogenic bacterial removal in nZVI unit was significantly higher than those obtained in a classical filtration unit. This mainly can be attributed to Several recent studies have reported on the antimicrobial activity of nanoparticulate zero-valent iron (ZVIN)( Lee, C.,2008, Auffan, M.,2008). However the ZVIN exhibited a stronger antimicrobial activity than other iron-based nanoparticles, and that the inactivation of E. coli, Staphylococcus aureus by ZVIN was greater under deaerated than air-saturated conditions (Boxall, A.B, 2007).The main mechanism by which antibacterial drugs and antibiotics work is via oxidative stress generated by ROS. (Sies H., 1997)ROS, including superoxide radicals(O<sub>2</sub>-), hydroxyl radicals (-OH), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), and singlet oxygen (1O<sub>2</sub>), can cause damage to proteins and DNA in bacteria(Kim JS, Kuk E,2007) In this case, FeO could be the source that created ROS leading to the inhibition of St. aureus. A similar process was described by Keenan et al in which Fe<sup>2+</sup> reacted with oxygen to create hydrogen peroxide, consequently reacted with ferrous irons via the Fenton reaction and produced hydroxyl radicals which are known to damage biological macromolecules. (Touati D., 2007).However, the small size of nanoparticles can also contribute to bactericidal effects. Lee et al reported that the inactivation of Escherichia coli by zero-valent iron nanoparticles (Lee C, Kim JY,2008) attributed to the penetration of the small particles (sizes ranging from 10–80 nm) into E. coli membranes. Nano-Fe0 could then react with intracellular oxygen, leading to oxidative stress and eventually causing disruption of the cell membrane.

On variation of filtration contact time in nZVI filtration unit, the removal efficiency of pathogenic bacteria was significantly increased from 10.39 to 95.16 % at increasing the filtration time from 0.73 to 35 min. respectively. A promising solution of bacteria removal was reached when R2 values are 0.319 and 0.999 for the classical and nZVI filtration units, respectively.

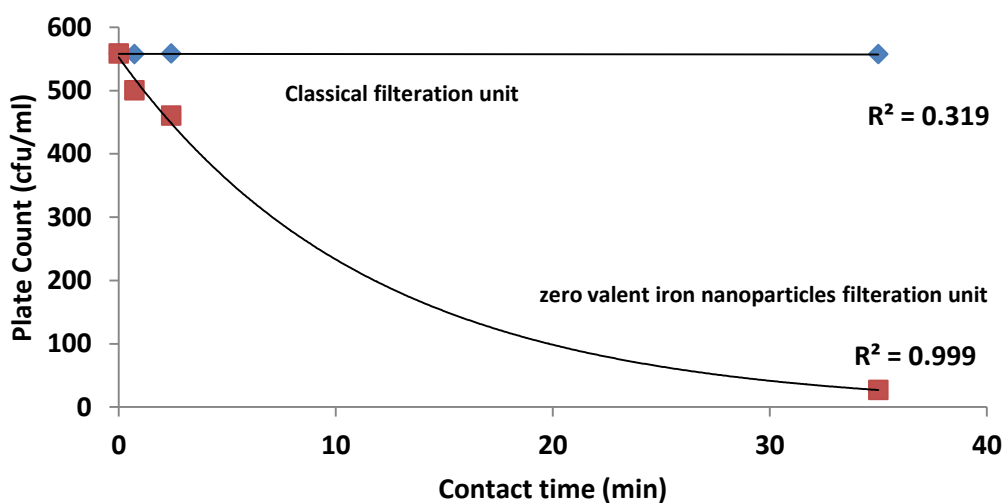


Fig. 7. Pathogenic bacteria removal in a classical sand filtration versus Zero Valent iron nanoparticles

#### 4. CONCLUSIONS

- Zero Valent Iron nanoparticles (nZVI) filtration unit is very effective for water treatment as compared to classical filtration unit
- The efficiency of nZVI is strongly dependant on the filtration time
- The removal efficiencies of DOC, phosphorus and pathogenic bacteria were significantly increased from 31.41 to 66.09%, from 55.33 to 83.66% and from 10.93 to 95.15% respectively at increasing the filtration time from 0.73 to 35 min. respectively.
- The removal of nitrogenous compounds in nZVI unit was accompanied with a conversion of nitrate into ammonia, which obviously should be avoided.
- The ammonia concentration was increased from 0.46 to 1.37 mg/l at increasing the filtration time from 0.73 to 35 min. respectively.

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