Degradation of Chlorinated Organic Pollutants Via Synthesis of Zero Iron Nanoparticles in Aqueous Systems

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ABSTRACT

Nanotechnology is a branch with a great potential and boost today. Nano materials are being widely used for the remediation of toxic pollutants. This study evaluates effectively of using commercial zerovalent iron (ZVI) powder and laboratory-synthesized nanoscale zerovalent iron (NZVI) particles unde different conditions (temperatures, time and pH) to eliminate chlorinated organic pollutants as pentaclorophenol (PCP) and trichloroethylene (TCE) from aqueous systems. The effect of pH, temperature, and contact time on chlorinated organic pollutant removal was investigated. The description of produced NZVI particles was done via XRD investigation. The dechlorination of PCP or TCE was measured as an indication of increasing chloride ion. The results showed that the maximum removal of PCP (100%) and TCE (95%) by NZVI could be achieved at lower pH as well as increasing temperature, and increasing time of reaction. Also, the results showed that NZVI was more effective to remove pollutants compared to ZVI powder. The removal effluence by NZVI was increased 21% and 34% for PCP and TCE respectively compared with ZVI powder. Nanoscale zero-valent iron (NZVI) is considered as an excellent reduction catalyst due to fast degradation of chlorinated pollutants. Thus, in future applications where NZVI is used to remediate sites contaminated with chlorinated organic pollutants.
Keywords: Nano zerovalent iron, trichloroethylene, pentachlorophenol, chlorinated compound

INTRODUCTION

Nanotechnology has widespread application potential today. Nano materials are being widely used for the remediation of toxic pollutants (Saleh and Gupta 2011). Nano zerovalent iron has become a precious material for its remediation abilities of environmental (Cloete, *et al.* 2010 and O'Carroll, *et al.* 2013). Surface area of nZVI is 30 times greater than granular iron per unit volume (up to 33.5 m^2/g). Very large surface area of nZVI equals large number of reactive sites for degradation. As for,its more reactive (10 to 1,000 times) than granular iron. Iron in oxidation state 0 is very unsteady, thus reactive and represents one of the strongest reducers (Lv *et al.* 2013). High reactivity and relatively large surface area facilitate to combine processes reduction, sorption and coagulation into one technological step. Final reaction is ferrous and ferric oxides and hydroxides that are commonly found in nature. Those qualities become the technology environmentally friendly. nZVI has been shown as an efficient tool for the treatment of various contaminants in aqueous systems (Zhang, 2003 and Zi, *et al.* 2006,Nunez, *et al.* 2011,). The removal mechanism by nZVI concerns the direct transfer of electrons to the contaminants transforms into non-toxic, less toxic species or more biodegradable species (Tosco *et al.* 2014; Raychoudhury and Scheytt, 2013). Polluted water has always been a serious problem to the environment. A wide variety of pollutants, including halogenated organics, nitro aromatic compounds, heavy metals, and anions, has been tried to remediate by utilizing the reduction reaction mechanism (Crane and Scott, 2012). Particular, Organic contaminants, such as Pentachlorophenol, Trichloroethylene, Trichloroethane, Dinitrotoulene, and Trinitrotoluene, are present at several sites, and these contaminants are listed as priority pollutants by the United States Environmental Protection Agency (USEPA) due to their toxicity and carcinogenicity. The pollution is persistent in the environment and they are transformed or degraded extremely slowly by natural processes (Vogel *et al.*,

1987). The United States Environmental Protection Agency specified 0.001mg/l as the maximum limit of PCP in drinking water, while the European Union limited the maximum PCP discharge concentration in industrial effluents to 1–2 mg/l (Estevinho *et al.* 2006). The maximum permissible limit of TCE in drinking water is 0.005 mg L^{-1} as per US Environmental Protection Agency guidelines (Water Quality Treatment, 1990). This study evaluates effectively of using commercial zerovalent iron (ZVI) powder and laboratory synthesized nanoscale zerovalent iron (NZVI) particles under different conditions (temperatures, Time and pH) to remove pentaclorophenol (PCP) or trichloroethylene (TCE) from synthetic aqueous solution.

MATERIALS AND METHODS

Synthesis of zero iron nanoparticles

Nanoscale zerovalent iron (nano ZVI) was formed by adding 1:1 volume ratio of NaBH$_4$ (0.8 M) into FeCl$_3$.6H$_2$O (0.2 M) and mixing the solution vigorously under room temperature for 5 min. Ferric iron was reduced by borohydrate thus nano ZVI was formed as the following equation (Sun *et al.*2006):

$$4Fe^{3+} + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + 6H_2$$

Nano ZVI was filtrated through 0.45 micron filter paper thus washed several times with DI water to get remove excessive borohydrate. Nano ZVI was dried by N2 gas and preserved from the oxidation by maintaining a thin layer of ethanol on the top of nano ZVI (Sun *et al.* 2006).

Degradation experiment

Degradation experiment was carried out to compare the efficiencies of nano ZVI and powder ZVI to eliminate PCP and TCE from synthetic aqueous solution. A PCP or TCE solution was prepared in deionized water at initial concentration of 100 mgL^1. The 100 mL of PCP or TCE solution was moved to 250 mL Erlenmeyer flask and then 1% (w/v) of commercial ZVI or NZVI was added. PCP or TCE degradation by commercial ZVI and nano ZVI was tested under different pH degrees. The pH of the solution was

adjusted by pH meter to the desired value (4 and 8) using HCL and NaOH solution. Flasks were covered and shacked at 150 rpm. PCP or TCE degradation was investigated under two different temperatures (25 and 40 °C). Changes in PCP or TCE concentration were measured at different periods (12, 24, and 36 hours of shaking). The experiments were performed in triplicate. The solution was then filtered and the residual of TCE concentration was determined at wavelength 520 nm according to the method of Tiwari, *et al.* (2013) while the residual of PCP concentration was determined according to the method of Chatterjee, *et al.*, (2001) at wavelength 555 nm using a spectrophotometer. The PCP or TCE removal percentage (R%) was calculated by the following equation:

$$Removal\% = [(C_i-C_e)/C_i] * 100$$

Where C_i and C_e mean the PCP and TCE concentrations at the initial time and at equilibrium
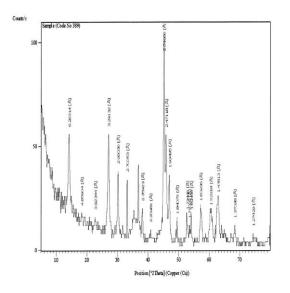

Fig. 1. XRD of Synthesized NZVI Particles

(µg/ml), respectively.

The sample was titrated for chloride content using the silver nitrate titration method.

RESULTS AND DISCUSSION

1. Characteristics of Synthesized NZVI Particles

Fig: 1. XRD analysis of nano ZVI was synthesized from borohydride reduction method. As well as indicated crystalline structure of the particles. Here test was done by the X- Ray diffraction and sample was done using the difractometer. X-Ray diffraction pattern was recorded from 10°-80°. The diffract grams is in agreement with the XRD pattern of NZVI. The fig (1) also observed that some undesired peaks had been seen, due to the impurity phase present in the sample. The broad peak revealed the existence of an amorphous phase of iron. The characteristic broad peak at 20 of 45° indicated that the zero valent iron was predominantly present in the sample.

2. Effect of pH on PCP and TCE degradation

The pH was also one of the important factors in the chlorinated organic pollutants (TCE or PCP) degradation by NZVI and ZVI (Figs. 2 and 3). Results

explained that acidic media were more perfect for declination of chlorinated pollutants and performance increased when pH was less than 3. These data was agreeing with Rasheed *et al.*, 2011 they stated that most of the organic pollutants were increased effectively at higher pH values in the nZVI. The results showed the degradation rate of chlorinated organic pollutants by nZVI and Fe powder improved at lower pH, this result due to adsorb the chlorinated pollutants onto the iron particles surface more readily. At higher pH condition, iron is change to insoluble structure $Fe(OH)_2$ and the deposition formed on the iron surface that reducing the efficiency of surface adsorption. Also at higher pH media, chlorinated compound and Fe particles are negatively charged that causing repulsive between them (Liu *et al.*, 2012). On the other hand, at acidic conditions is done acid washing on metallic surfaces, broadly. These reactions, reduces passivation of Fe particles and metallic surfaces with Facilitating soluability of these hydroxides (Shu *et al.*, 2007).

Effect of temperature on of PCP and TCE degradation

The effect of temperature on the degradation of chlorinated organic pollutants (PCP and TCE) by using NZVI and ZVI powder was studied at temperature of 25 °C and 40 °C. According to Figs. 4 and 5, chlorinated compound degradation increased with increasing temperature of the reaction solution. The degradation efficiencies of PCP by NZVI and ZVI powder were reached 92.8% and 62.1% for 25 °C while 100% and 79% for 45 °C after 36 hour of reaction time, respectively. The degradation efficiencies of TCE by NZVI and ZVI powder were reached 79.3% and 40.1% for 25 °C while 95.0% and 60.71% for 45 °C after 36 hour of reaction time, respectively. Data observed that the degradation rate of chlorinated organic pollutants is highly affected by the ambient temperature. Valsaraj (2000) mentioned the steps of pollutants degradation by iron particles, mass transfer of the pollutant to the Fe (0) surface, adsorption and chemical reaction of the pollutant on ZVI surface, desorption and mass transfer of the reaction products into the solution.

2. Effect of contact time and type of Iron on chlorinated organic pollutants degradation

Removal efficiency for chlorinated organic pollutants (PCP and TCE) at different periods of 12-36 hour was tested. Data observed that the ideal period for PCP and TCE degradation by iron partials were done in 36 hours. Therefore, degradation of PCP and TCE increased when the period increased (Fig. 6). This data was due to increment availability in the active bounding sites on the sorbent surface area (Engin *et al.*, 2007 and Konstantina *et al.*, 2007). Also, the results showed that NZVI was more effective to remove pollutants compared to ZVI powder. Degradation rate by NZVI was increased 21% for PCP and 34% for TCE compared with ZVI powder, due to high specific surface NZVI particle and higher capability of sorption pollutants compared with ZVI powder.
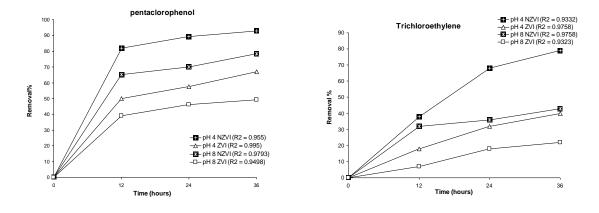
Fig. 2. The removal of chlorinated pollutants by NZVI or ZVI with different pH conditions at 25 °C temperature.
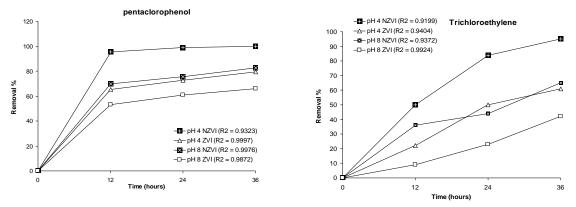

Fig. 3. The removal of chlorinated pollutants by NZVI or ZVI with different pH conditions at 40°C temperature.

3. Effect of NZVI on the Concentration of Chloride ion

Figure 7 shows the relation between chloride ions released from PCP or TCE degradation in the presence of NZVI or ZVI. Observed fig 7, the concentration of chloride ions remains unchanged at zero time, after that a gradually highly jumping in chloride ions concentration reached maximum at the 36 hours for PCP and TCE. The data observed that undetected chloride ions at zero time while it detected with low concentration at first time (12 hr) may be due to consumption of some ions for producing some reactive intermediates such as vinyl chloride and di-chloroethylene (DCE); thereby, these intermediates are very low levels and disappeared quickly (Liu *et al*. 2005).
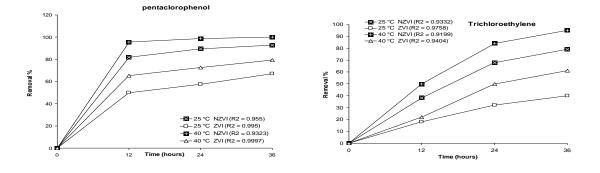

Fig. 4. The removal of chlorinated pollutants by NZVI or ZVI with different temperature conditions at pH 4.
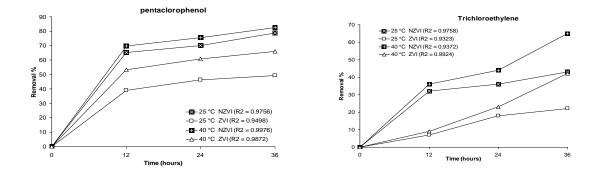
Fig. 5. The removal of chlorinated pollutants by NZVI or ZVI with different temperature conditions at pH 8.
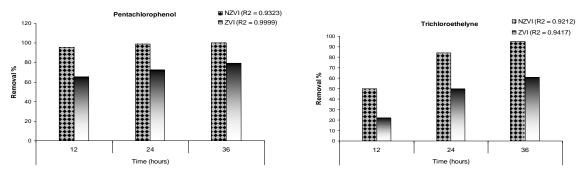

Fig.6. Effect of contact time and type of Iron on chlorinated organic pollutants degradation at 4 pH and 40 °C
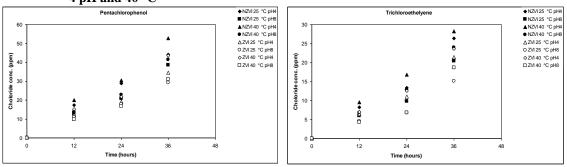

Fig. 7. Effect of NZVI on the Conc. of Chloride ion

Generally, Zerovalent iron (ZVI) can be used for the remediation of water contamination with chlorinated compounds. The results showed that both of ZVI powder and NZVI had effective to remove pollutants these data due to ZVI is a strong reducing agent and had active iron surface. Degradation by NZVI was more effective to remove pollutants compared to ZVI powder. These data due to the high specific surface area, nano sized ZVI-particles (nZVI) are more reactive than granular materials.

ZVI role in degradation

1- Oxidized ZVI particles after reaction with chlorinated organic pollutants (oxide films formed on the surface).

2- Lower chlorinated intermediate molecules.

3- Target chlorinated organic pollutants molecules diffuse through the solution and adsorb onto ZVI.

4- Electron transfer from ZVI to chlorinated organic pollutants molecules.

5- Chloride ion release

$Fe^0 + X\text{-}Cl + H^+ \rightarrow Fe^2 + X\text{-}H + Cl^-$

1) $Fe^0 \rightarrow Fe^{2+} + 2e^-$

2) $2H_2O \rightarrow 2H^+ + 2e^-$

3) $2H^+ + 2e^- \rightarrow H_2(g)$

4) $X\text{-}Cl + H^+ + 2e^- \rightarrow X\text{-}H + Cl^-$

CONCLUSION

The use of NZVI is a practical effective treatment technology for dechlorination of many organic chlorinated contaminants due to NZVI relatively high reactivity, inexpensiveness and low environmental impact. Thus, in future applications where NZVI is used to remediate sites contaminated with chlorinated organic pollutants, the efficiency can be greatly enhanced by maintaining a low pH value in the remediation zone.

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إزالة الملوثات العضوية المكلورة عن طريق برادة الحديد عديمة الشحنة ذات الحجم النانو من النظم المائية

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أصبحت تقنية النانو فى طليعة المجالات الأكثر أهمية اليوم وتستخدم على نطاق واسع لمعالجة الملوثات البيئية. تقيم هذه الدراسة فعالية استخدام برادة الحديد التجارية عديمة الشحنة وكذلك برادة الحديد المصنعة عديمة الشحنة ذات الحجم النانو فى التخلص من الملوثات العضوية المكلورة مثل البنتا كلوروفينول ، و التراى كلورو ايثيلين من النظم المائية وذلك تحت ظروف مختلفة. تم دراسة تأثير درجة الحموضة، ودرجة الحرارة، والوقت لتكسير وازالة الملوثات العضوية المكلورة. تم التعرف على برادة الحديد المصنعة عديمة الشحنة ذات الحجم النانو بواسطة جهاز الاشعة السينية. وتم قياس ايون الكلوريد لتتبع عملية تكسير وازالة المركبات العضوية المكلورة فى النظم المائية. وأظهرت النتائج أن أعلى نسبة ازالة لمركبات البنتا كلوروفينول ، و التراى كلورو ايثيلين وصلت الى 100 ، 95% على التوالى باستخدام برادة الحديد المصنعة عديمة الشحنة ذات الحجم النانو و ذلك تحت ظروف درجة حموضة منخفضة (pH 4) ، درجة الحرارة المرتفعة (C° 40) ، وزيادة وقت التفاعل (36 hr). كما أظهرت النتائج أن برادة الحديد المصنعة عديمة الشحنة ذات الحجم النانو كانت أكثر فعالية لإزالة الملوثات بالمقارنة مع استخدام برادة الحديد التجارية عديمة الشحنة . وقد ارتفع معدل ازالة تلك المركبات العضوية المكلورة بواسطة برادة الحديد المصنعة عديمة الشحنة ذات الحجم النانو الى 21٪ للبنتا كلورو فينول، 34٪ للتراى كلورو ايثيلين. وهكذا، يمكن استخدام برادة الحديد المصنعة ذات الحجم النانو فى التطبيقات المستقبلية لعلاج المواقع الملوثة بالمركبات العضوية المكلورة، ويمكن زيادة كفاءتها بشكل كبير من خلال المحافظة على قيمة انخفاض الرقم الهيدروجيني في المنطقة المعالجة.