Utilization of Zero Valent Iron (ZVI) Particles Produced from Steel Industry Waste for *In-Situ* Remediation of Ground Water Contaminated with Organo-Chlorine Pesticide Heptachlor

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ABSTRACT: Treatment of ground water contaminated with halogenated pesticides is a challenging task. This paper focuses on preparation, characterization and treatment of heptachlor by iron particles synthesized from steel industry waste (S-ZVI). The BOF sludge, which is dumped in landfills, is an iron rich source and was used as the source material for S-ZVI synthesis. The vital step was reducing agent sodium borohydride optimization and a high dose of 3.5g/10mL of dose was required for production of S-ZVI. The average particle size for S-ZVI and after modifying using surfactant PAA (5%) was 1660 nm and 300 nm, respectively. Crystalline structure of S-ZVI and a diverse chemical composition was found with high contents of Na, Ca and Mg. Reduction of heptachlor was studied in batch reactors using S-ZVI, PAA modified S-ZVI, Tween 20 modified S-ZVI and pure ZVI. After 48h, the reduction efficiency of heptachlor, by various forms of ZVI, was found to be 87%, 89%, 75 % and 93% respectively. The observed dechlorination rate constant of Heptachlor by PAA modified S-ZVI was found to be the highest (1.959/hr) followed by Tween 20 modified S-ZVI (1.106 /hr), unmodified S-ZVI (0.526 /hr) and pure ZVI (0.09 /hr). The Surface Area Normalised Rate constant (k_{SA}) were found to be 0.2884 L/hr/m^2, 0.1074 L/hr/m^2, 0.06606 L/hr/m^2 , and 0.000486 L/hr/m^2 for S-ZVI, PAA modified S-ZVI, Tween 20 modified S-ZVI, and pure ZVI respectively.

Key words: Heptachlor, Zero Valent Iron (ZVI), Blast Oxygen Furnace Sludge, Surfactant, Reductive Dehalogenation

INTRODUCTION

The availability of clean water is a matter of concern especially in developing nations where water supplies and treatment technologies are limited (Brame *et al.*, 2011). This paper focuses on remediation of groundwater contaminated with pesticides. Pesticides are bio-accumulative, relatively stable, dangerous and harmful because of their tissue degradation and carcinogenic nature (IARC, 1987) and hence require close monitoring. Residues of several organochlorine pesticides and insecticides like Hexachlorobenzene (HCB), Dichloro-diphenyl-trichloroethane (DDT), Aldrin, endosulfan and heptachlor were found in the ground water from rural areas in the Godavari river plain of Nanded district, India (Motekar, 2011). Occurrence of pesticides in dietary components like vegetables, fruits, milk is a serious matter of concern (John *et al.*, 2001; Bakore *et al.*, 2002). Heptachlor was first introduced as a contact insecticide in the USA in 1952 for foliar, soil and structural applications. Due to its highly stable structure heptachlor is classified as a

Persistent Organic Pollutant (POP). EPA has set an enforceable regulation for heptachlor, called a maximum contaminant level (MCL), at 0.0004 mg/L or 400 ppt (WHO, 1988).

Recently, nanoscale zero-valent iron (nZVI) is being studied for their potential application in in-situ remediation of groundwater (Tosco *et al.*, 2014). These particles can be injected in subsurface and can be transported in porpous media, has smaller particle size than traditional ZVI and high reactivity (El-Temsah and Joner, 2013). nZVI has been tested for reductive dehalogenation of several chlorinated organic contaminants like TCE, PCBs (Wang and Zhang, 1997; Lien and Zhang, 2001; Zhang, 2003) and removal of metals or metalloid contaminants like arsenic (Kanel *et al.*, 2006) and Cr(VI) from (Hu *et al.*, 2004). Bimetallic nZVI, containing small amounts of Palladium (Pd) or Nickel (Ni) are being used to remediate organochlorine pesticides (Zhang, 2003; Tian *et al.*, 2009). Though bimetallic nano particles are effective in degradation

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they suffer setback due to high cost and environmental concern (Mueller *et al.*, 2012). Magnetic attraction between nano iron particles causes the rapid aggregation of particles (Phenrat *et al.*, 2007), so various organic coatings are used nowadays like emulsions, polymers and polyelectrolytes that limit reactivity and increase the mobility of nano iron in the subsurface (Ponder *et al.*, 2000). Nowadays novel techniques are being explored to manufacture nano iron particles from waste material like steel mill waste (Kesavan and Azad, 2008) and tree leaf extract (Machado *et al.*, 2013). Steel industry waste like dust from Blast Furnace (Shen *et al.*, 2013) and pickling waste liquor (Fang *et al.*, 2011) has been used for preparation of nano scale iron particles for environmental remediation. The sludge produced in the steel industry, from the Basic Oxygen Furnace (BOF), has high percentage of iron. Hence, it was chosen as the starting material for the production of iron particles. This paper deals with the synthesis, characterization and application of micro sized particles of iron produced from BOF sludge of steel industry. These particles were modified by using various surfactants and utilized in degradation of organo-chlorine pesticide Heptachlor.

MATERIALS & METHODS

Chemicals used were Heptachlor (99+%, Dr. Ehrenstorfer GmbH), methanol (99%, Emplura), n-hexane (Merck HPLC Grade, Mumbai, India), HCl (AR Grade, Ranken Reagent), HNO_3 (AR Grade, Qualigens Fisher Scientific), 30% H_2O_2 (Ranbaxy Fine Chemicals Ltd.), Sodium Borohydride (Loba Chemie) and Iron(II) Sulfate Heptahydrate Crystals (Merck, India). The surfactants used were Poly acrylic acid (PAA) (National Chemicals, India) and Tween 20 (Sigma, Life Science). 1, 10 Phenenthroline Monohydrate (Merck, India) was the coloring agent used for iron estimation. All the chemicals used were of analytical grade. Sludge sample of the Basic Oxygen Furnace (BOF) of SAIL, Durgapur, India, was used in the study. Durgapur Steel Plant is situated at a distance of 158 km from Calcutta (now Kolkata), its geographical location is defined as 23° 27' North and 88°29' East. Digestion of the sludge sample was done using the standard digestion procedure of EPA method (3050B) (Guven & Akinci, 2010). The synthesis of sludge zero valent iron particles was carried out in a 500 mL three necked flask. One of the necks was used for blowing of nitrogen gas to achieve an anaerobic atmosphere during the synthesis; the other was used for the addition of sodium borohydride, the reducing agent, drop wise at 2mL/min using a pipette and the other for the glass rod to stir the solution. Approximately 10 mL of the acid digested sludge sample was taken

and 3.5 g of sodium borohydride/10mL of deionized water was slowly added forming iron particles. The particlers so formed were centrifuged at 14000 rpm for 10 minutes. The supernatant was removed and further centrifugation in ethanol was done and finally it was dried in the incubator at 27°C for almost 3 hours to obtain powdered iron particles which were stored in a vacuum dessicator to prevent its oxidation. Iron particles were prepared from ferrous sulphate also for comparison with sludge iron particles. 250 mL of both 0.04 M $FeSO_4.7H_2O$ and 0.08 M $NaBH_4$ aqueous solutions were prepared followed by purging of N_2 gas for 15 minutes. $NaBH_4$ solution was then added drop wise almost at 2mL/min to the $FeSO_4.7H_2O$ solution kept in the three neck flask with continuous stirring and purging of N_2 gas while synthesis. The resultant particles were separated, dried and stored in similar manner as described for sludge iron particles. The morphology of the synthesized particles was determined with a Scanning Electron Microscope and the composition was analyzed with an Energy Dispersive Spectrometer (SEM-EDX Analyser, JEOLJSM-6360). The Particle Size was analyzed using Malvern particle Size Analyser. Surface Area was determined by the nitrogen adsorption data by Brunauer–Emmett–Teller (BET Surface Area Analyser, Quantachrome Nova Win,version 10.01).

Batch experiments were conducted to investigate the reaction kinetics of the iron particles with pesticide heptachlor. The dechlorination of heptachlor was conducted in 20 mL vials mixed with a definite dose of iron particles. The pesticide aqueous solution was prepared by adding heptachlor dissolved in methanol so as to achieve and initial concentration of 550 µg/L. The filling of the aqueous solution of pesticide in the glass vials was done using a separating funnel purged with no head-space in each vial. The reaction vials were sealed with teflon rubber septa and mixed on a rotary shaker at 50 rpm. Controls without iron particles were prepared following the same procedure. Duplicates vials were kept for each time series. After the specified time, the vials were sacrificed for determination of pesticide concentration remaining in each vial. The oxidation reduction potential (ORP) and pH in the vials were monitored by a pH and ORP meter (Digital pH meter,Cyber Scan and Oaklan-Eutech Instruments, ORP Tester 10,10 BNC) as soon as the vials were taken out from the rotator. The total run time of the batch study was 48 hours with samples being withdrawn at an interval of 30 minutes, 1hour, 2 hours, 5 hours, 8 hours, 12 hours, 18 hours, 24 hours and 48 hours respectively. At specified time intervals, 250 µL aliquots of aqueous phase were withdrawn, from the batch reactors, using

a micro syringe pierced through the septa and was added to a GC auto sampler vial (Wheaton Science, USA) containing 880 µL *n*-hexane as solvent and sealed. The mixture was then thoroughly mixed on a vortex mixer for 30 min to ensure partitioning of heptachlor to the solvent phase. This method resulted in 97% extraction efficiency of heptachlor. The solvent was analyzed by a Gas Chromatograph (GC) equipped with Electron Capture Detector (ECD) (Thermo Scientific, Chemito, Ceres 800 Plus). Agilent (30 m x 0.25 mm ID) capillary column was used for separation of heptachlor. The carrier gas was chromatographic grade nitrogen. Sample injection volume was 1µL, in splitless mode, with the injector temperature set at 275°C and the detector set at 325°C. Separation was conducted with a temperature program that started oven temperature at 160°C and then ramped at 7°C/

min to 300°C. Four doses of iron particles (5g/L, 10g/L, 25g/L and 50g/L) were used and the dose with the maximum degradation efficiency was chosen for further kinetic studies. The iron particles were modified by using surfactant [Poly Acrylic Acid (20%) and Tween 20 (100%)], to study the impact of surface modification on reduction of pesticide.

RESULTS & DISCUSSION

The digested BOF sludge sample was analyzed using Atomic Absorption Spectrophotometer (AAS) (GBC Avanta, G53000) and its composition was found to be rich in iron content and hence quite perfect to be used as a starting material for synthesizing S-ZVI as shown in Table 1. A dose of 2.5 g of sludge was digested to be used for S-ZVI preparation. Initially the process of preparation of S- ZVI was done on the basis of

Table 1. Composition of Sludge Sample collected from Basic Oxygen Furnace (BOF) of SAIL, Durgapur, India

Element	Fe	Mg	Mn	Ca	Al	Si
Concentration (%)	38.9	1.7	0.2	14.8	1.7	3.1
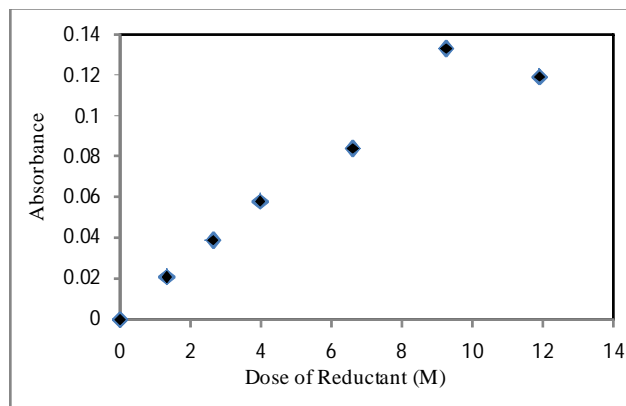
Fig. 1. Optimization of Reducing Agent Dose for S-ZVI production
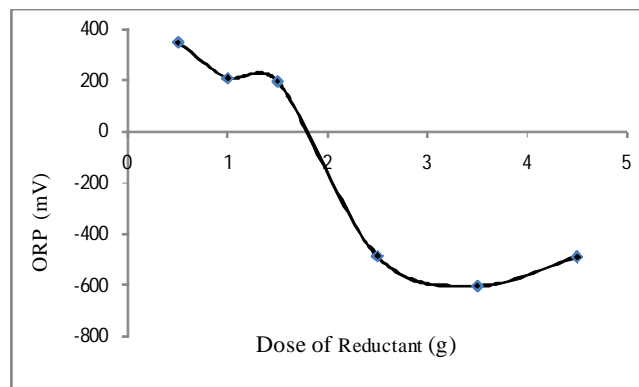
Fig. 2. Variation of Oxidation Reduction Potential (ORP) with Reducing Agent Dose
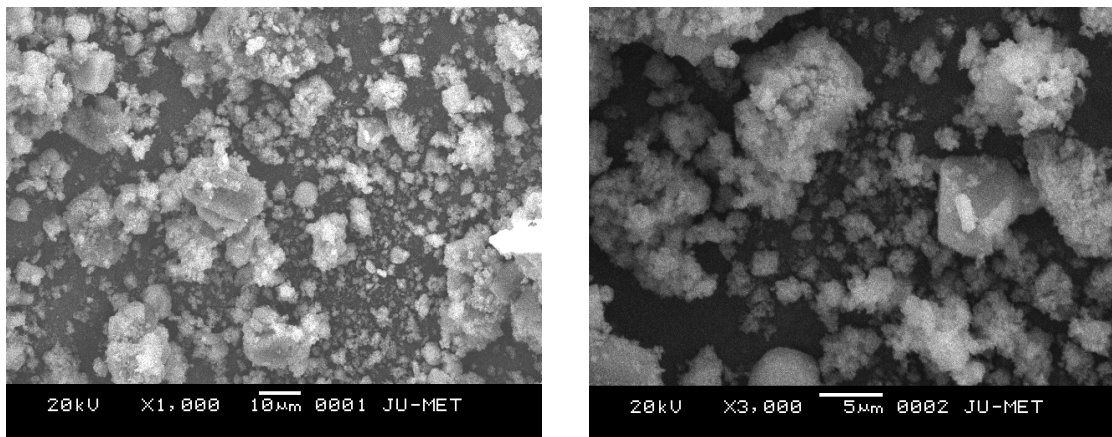
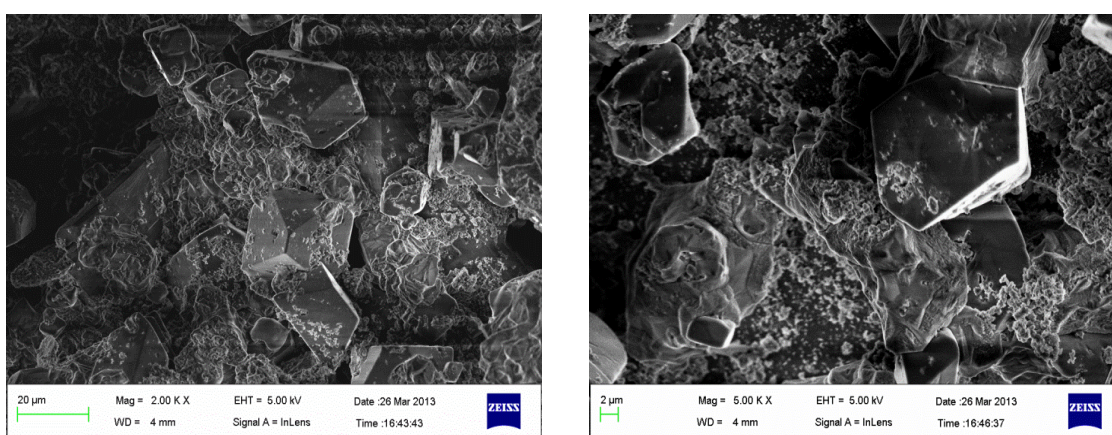**Fig. 3(a). SEM Images of S-ZVI at 1000X and 3000X magnification**

Fig. 3(b). SEM Images of S-ZVI at 2000X and 5000X magnification
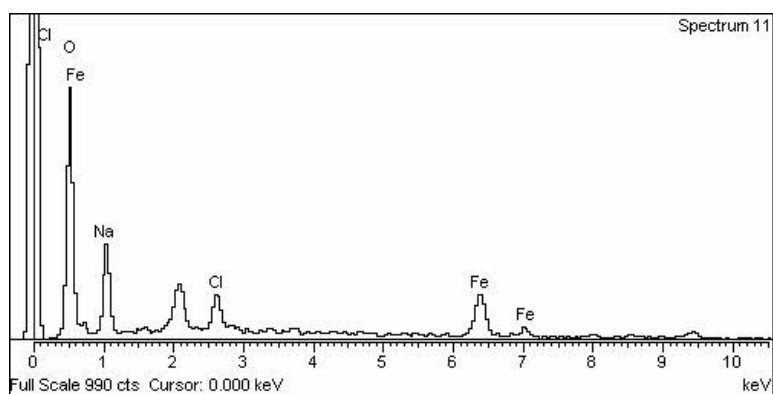

Fig. 4. EDX Analysis of Bare S-ZVI

standard protocol, taking 250 mL of acid digested sample and 250 mL of sodium borohydride as reducing agent, however the process failed to produce S-ZVI. The expected reason was the presence of other metals in the sludge sample which consumed the reducing agent preventing the formation of S-ZVI. To overcome this, the reducing agent concentration was increased and made 4 times the previous, which again lead to failure. No positive result was observed using 8 times and 16 times of sodium borohydride concentration too. Later, 10 mL of the acid digested sample and reducing agent concentration of 4.5g/10 mL of deionised water resulted in the formation of black S-ZVI particles immediately. A similar method was followed by previous researchers also (Kesavan and Azad 2008).
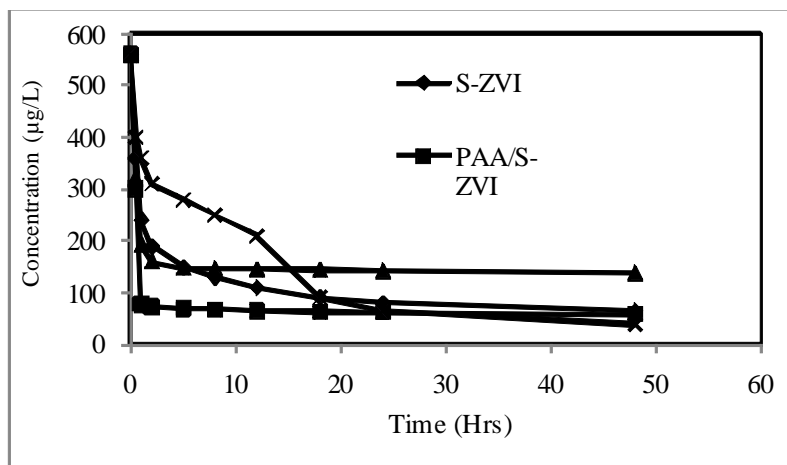
Fig. 5. Decline in heptachlor concentration with time during interaction with iron particles

Table 2. Comparison of K_{obs} and K_{SA} values

Reduction Rates	S-ZVI	PAA/S-ZVI	Tween 20/S-ZVI	Pure ZVI
Observed (k_{obs}) /hr	0.526	1.959	1.106	0.09
Surface Area Normalized (K_{SA}) L/hr/m^2	0.2884	0.1074	0.06606	0.000486

Table 3. Comparison of Observed Rate Constant (k_{obs}) values from literature for pure nZVI

Halogenated Organic Compound	K_{obs} value	Reference
Heptachlor	0.09/hr	Present Study
Hexachlorobenzene(HCB)	0.14 /hr	Shih *et al.*, 2009
HCB with bimetallic particles	0.23/hr	-do-
Tetrachloroethene	2.1/hr	Lien and Zhang, 2001
Trichloroethene	3.2/hr	-do-
TCE with nZVI in Fe/Pd alginate	6.11/hr	Kim *et al*, 2010

As the formation of S-ZVI took place using 4.5 g NaBH$_4$/10mL of deionised water, optimization of the amount of reducing agent was carried by using 0.5 g, 1.0g, 1.5g, 2.0g, 2.5g, 3.5g, and 4.5g of NaBH$_4$/10mL. The amount of S-ZVI formed was quantified using Orthophenenthroline method (Schrick *et al*. 2004). It was found that initially on increasing the amount of reducing agent, the amount of S-ZVI formed increased with maximum yield at 3.5 g NaBH$_4$/10mL (9.25 M) as shown in Fig. 1. So, 3.5g NaBH$_4$/10mL was chosen as the optimum dose for maximum yield. The particle size data also supports this dose yielding fine particles compared to other doses. The pH increased as the dose of sodium borohydride is increased probably due to reduction of water which resulted in formation of hydrogen and hydroxyl ions. The ORP reduced from +400 mV to -600 mV on the addition of 9.25 M NaBH$_4$ solution and thereafter it increased (Fig. 2). This can

be explained by the fact that the digested sludge contains silica which may combine with sodium in NaBH$_4$ solution and form sodium silicate. Sodium silicate is shown to hinder the corrosion process of iron (Lahodny *et al*., 1981). Hence in the initial stages of S-ZVI formation sodium borohydride is utilized in formation of iron whereas after the complete reduction of iron in sludge sample, excess sodium borohydride may be reacting with silica and forming sodium silicate, which hinders the corrosion of iron and hence the ORP values increased.

Characterization of S-ZVI

The average particle size for bare S-ZVI was found to be 1660 nm. The larger size of S-ZVI particles was due to agglomeration of the colloidal particles after the synthesis. This may not only reduce the mobility of particles but also reduce the reduction rates. The

BET-Surface area analysis result revealed a specific surface area of 0.3647 m^2/gm. Iron particles produced from FeSO$_4$.7H$_2$0 showed high surface area of 37.035 m^2/g with an average particle size of 1105 nm. The reason for getting low values of surface area for S-ZVI may be attributed to agglomeration of particles and higher values of size. Hence to overcome this problem, S-ZVI particles were modified using surfactants like PAA and Tween 20. The average particle size of PAA modified S-ZVI was found to be 303 nm. The presence of crystalline structure in the SEM image as shown in Fig. 3(a) & 3(b) suggests the presence of sodium silicates as Na content was found high too. Sodium silicates are the most commonly used commercially available alkali silicates. Ability of silicates to form gels or to react with multivalent metal ions in solutions or oxide surface prevents corrosion reaction (Asrar *et al.* 1998). However along with the presence of crystalline structure, small cotton like spherical mass deposits was found too which may be due to salt formation and deposition by impurities present in digested sludge samples. EDX analysis as shown in Fig. 4 suggests that apart from iron in both Fe^0 and Fe-O form, presence of Na salts, Ca was found. The source of Na salt could be from the reducing agent source (NaBH$_4$) reacting with some element in the sludge sample. Uses of Ca and Mg in steel industry are the probable sources of their presence in the sample.

To establish the optimum dose of S-ZVI for dehalogenation of heptachlor, concentration of iron particle was varied from 5g/L to 50 g/L. A dose of 50g/L, corresponding to highest degradation efficiency, was chosen as the optimum dose for further reduction of heptachlor using modified and unmodified ZVI. The probable reason for the requirement of such high dose could be the prevention of the reduction reaction due to the presence of silicates in the sludge sample. As the silicates reacted with Na present in NaBH$_4$ it formed sodium silicate, which was preventing the corrosion reaction. The concentration of heptachlor declined to 65 µg/L in 48 hrs as shown in Fig. 5. The initial pH of heptachlor solution was 6.57 which rose to 9.46 within 30 min and after which it remained constant. The pH values rose for the reduction of heptachlor with consuming H$^+$ ions. The inactive surface might be produced after the reduction reactions due to this pH change. It may be caused by the production of passivating oxide surfaces on S-ZVI which prevents further corrosion of particles and reduction in rates. The initial ORP value of around 154 mV decreased instantly to -428 mV after adding Fe particles. In blank samples the ORP values remained constant at 154 mV. This indicated that highly reducing conditions developed in the batch reactors which imparted the dechlorination of heptachlor. The reduction reactions

of S-nZVI with heptachlor followed pseudo first order reaction .The plot of ln (C/C$_O$) vs time resulted in observed reduction rates (k$_{obs}$) of 0.526 /hr. The surface area normalized reduction rate (k$_{SA}$) (at surface area of 0.3647 m^2/g) is 0.2884 L/hr/m^2. The percentage removal effeciency of Heptachlor was found to be 87 % at the end of 48 hours of reaction time.

Similar experiments were performed using surfactant modified S-ZVI. The concentration of heptachlor in batch reactor declined to 59 µg/L in 48 hrs leading to 89% reduction in 48 hours using Poly Acrylic Acid(PAA) modified S-ZVI. Here too the reduction followed a pseudo first order kinetics with an observed reduction rates (k$_{obs}$) which was 1.959 / hr. The surface area normalized reduction rate (k$_{SA}$) (at surface area of 0.3647 m^2/g) was 0.1074 L/hr/m^2. However, biodegradable surfactant Tween-20 modified S-ZVI did not prove to be very effective comparatively, where the concentration declined to 139 µg/L in 48 hours with a reduction of 75% from initial concentration. The observed reduction rates (k$_{obs}$) was 1.106 /hr and surface area normalized reduction rate (k$_{SA}$) (at surface area of 0.3647 m^2/g) was 0.06606 L/hr/m^2. To perform a comparative assessment pure ZVI (5 g/L) was used for the reduction of heptachlor. The concentration declined to 38.91 µg/L in 48 hrs with a reduction of 93% of heptachlor. The Observed reduction rates (k$_{obs}$) was 0.091 /hr and surface area normalized reduction rate (k$_{SA}$) (at surface area of 37.035 m^2/g) was 0.000486L/hr/m^2.In terms of reduction pure nZVI was found to be most effective.

S-ZVI had the highest surface area normalized rate constant followed by PAA modified S-ZVI, Tween 20 modified S-ZVI and pure ZVI. The degradation rates of interaction of halogenated organic compounds with nano zero valent iron has been compared with the rates of present study in Table 3. Comparing K$_{obs}$ values from literature, it can be inferred that K$_{obs}$ increases as the number of chlorine atom in the molecule increases because of the more recalcitrant structure of higher chlorinated compounds. Likewise, a value of 1.959 /hr for PAA modified S-ZVI suggests a high reaction rate for a bulky seven chlorine group heptachlor. But the surface area normalized rate was lowest for pure ZVI as it had extremely high surface area of 37.035 m^2/g whereas that of S-ZVI was as low as 0.3647 m^2/g due to the presence of large crystalline structure. This suggests that for same values of surface area, S-ZVI is the most reactive form.

CONCLUSIONS

The BOF sludge from steel industry is normally discarded in landfills and has high iron content of

around 40 % supported by the data from AAS analysis (Section 5.1) after acid digesting the sludge sample. This was chosen as the starting material for the synthesis of bare S-ZVI. The synthesis of S-ZVI was setback initially, so optimization of reducing agent sodium borohydride dose was done with 3.5g/10 mL as the optimized dose. The average size of laboratory synthesized PAA modified S-ZVI particles was around 303 nm compared to bare S-ZVI at 1660 nm showing that surfactant modification reduced agglomeration and particle size. The particles formed were nearly crystalline with a surface area of 0.3647 m^2/g. The XRD and SEM-EDX analysis of nanoscale Fe particles indicate the presence of mixed elements. EDX analysis suggested the presence of number of elements other than Fe. High Na content probably contributing to the crystalline structure and could be from reaction between the reducing agent sodium borohydride and elements in the sludge. Others, like Ca, and Mg are used in the steel industry mainly as flux. Structure of particles were mainly crystalline suggesting presence of Silica and small cotton like spherical mass deposits were found too which may be due to salt formation and deposition of impurities present in digested sludge samples. Batch experiments demonstrated that the sludge iron particles and pure ZVI particles could effectively dechlorinate Heptachlor. The reductive dechlorination of Heptachlor followed a pseudo first order kinetics. The reduction kinetics suggests that PAA modified S-ZVI had the fastest reaction kinetics (k_{obs} = 1.959 /hr) as well as high reduction efficiency of 89 %. The PAA modified S-ZVI resulted in 3.7 times increase in reaction rate over S-ZVI whereas the rate increased 1.8 times using Tween 20. Reduction efficiency for S-ZVI and Tween 20 modified S-ZVI was 86% and 75 % respectively. However the surface area normalised rate (K_{SA}) at 0.2884 L/hr/m^2 was highest for S-ZVI . Pure ZVI had the highest reduction efficiency of 93 % but slowest surface area normalized rate due to its high surface area. Hence, S-ZVI modified with surfactant like PAA can be recommended for in-situ remediation of groundwater contaminated by halogenated pesticide like heptachlor.

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