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Removal of Cr(VI) by Nanoscale Zero-valent Iron (nZVI) From Soil Contaminated with Tannery Wastes

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Abstract The illegal disposal of tannery wastes at Rania, Kanpur has resulted in accumulation of hexavalent chromium [Cr(VI)], a toxic heavy metal in soil posing risk to human health and environment. 27 soil samples were collected at various depths from Rania for the assessment of Cr(VI) level in soil. Out of 27 samples, five samples had shown significant level of Cr(VI) with an average concentration of 15.84 mg Kg^{-1}. Varied doses of nanoscale zero-valent iron (nZVI) were applied on Cr(VI) containing soil samples for remediation of Cr(VI). Results showed that 0.10 g L^{-1} nZVI completely reduces Cr(VI) within 120 min following pseudo first order kinetics. Further, to test the efficacy of nZVI in field, soil windrow experiments were performed at the contaminated site. nZVI showed significant Cr(VI) reduction at field also, indicating it an effective tool for managing sites contaminated with Cr(VI).

Keywords Nanoscale zero-valent iron · Hexavalent chromium · Tannery waste · Windrows

Leather production is a major industry in India and is a major source of pollution also. Kanpur, the largest and the most industrialized city in the state of Uttar Pradesh, sits on the bank of the Ganges River, 126 m above the sea level. Today Kanpur is better known for its leather industry. One neighborhood area, Jajmau, in the south eastern part of the city, near the south bank of River Ganga, is home to more than 350 tanneries. These tanneries daily produces large amount of solid toxic wastes/sludge with serious environmental impact during leather processing (Tarcan et al. 2010). The lack of stringent laws and treatment facilities has led to tannery wastes/sludge being dumped on temporary sites at Rania leading to the contamination of soil and ground water. This area has been used as a dumping ground for more than a decade. Land based disposal practices were practiced under the assumption that the dominant species in the tannery waste would be the thermodynamically stable Cr(III) species. However, significant levels of toxic Cr(VI) in ground water and surface water reported in the different parts of the world have raised critical questions on this kind of disposal practices (Belay 2010).

Different types of treatment technologies such as phytoremediation, microbial remediation, chemical reduction, physical sorption (using ion exchange resin, activated carbon etc.), membrane filtration (ultrafiltration, nanofiltration, reverse osmosis), soil flushing, electrokinetic removal etc. have been reported for the removal of Cr(VI) (Owlad et al. 2009). Recently the application of zero-valent iron nanoparticles (nZVI) has received considerable attention in the area of environmental remediation. nZVI has emerged as a potential technology for the remediation of surface water, ground water and soil contaminated with a wide array of organic (Elliott et al. 2009) as well as inorganic contaminants (Franco et al.

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2009; Flury et al. 2009). The high remediation efficiency of nZVI is mainly attributed to nZVIs high surface area to volume ratio, high levels of surface defects, high density of reactive surface sites and greater intrinsic reactivity of surface sites, which make the nanoparticles very reactive in degradation of the contaminants (Nurmi et al. 2005). A number of bench and field demonstrations have already been completed and documented in literature (Grieger et al. 2010). In our previous work, we have reported the use of nZVI for batch scale remediation of soil artificially spiked with Cr(VI) and demonstrated the high reduction potential of nZVI for Cr(VI) contaminated soil (Singh et al. 2011). In the present investigation, we have conducted the batch and field studies to test the efficacy of nZVI for the reduction of Cr(VI) present in soil contaminated with tannery waste.

Materials and Methods

Ferric chloride anhydrous ($FeCl_3$), sodium borohydride ($NaBH_4$), potassium dichromate ($K_2Cr_2O_7$) were obtained from CDH, India. 1, 5- diphenylcarbazide ($C_{13}H_{14}N_4O$) was procured from S.D. Fine Chemicals Ltd. India. Ethanol (C_2H_5OH) from Loba Chemie Pvt. Ltd, Perchloric acid ($HClO_4$, 72%), Nitric acid conc. (HNO_3, 70%) and acetone (CH_3COCH_3) were purchased from Merck, India. All chemicals used were of analytical reagent grade.

nZVI used in this study was synthesized in the laboratory by the reduction of $FeCl_3$ with $NaBH_4$. In brief, 0.2 M of $NaBH_4$ was added drop wise to the solution of $FeCl_3$ (0.05 M). Reaction mixture was shaken vigorously for half an hour. After that iron nanoparticles formed were separated, washed and then stored in ethanol. The particles had an average diameter of 26 nm with standard deviation of 16.9 nm. The nZVI particles consisted of elemental core of zerovalent iron and a shell of ferric oxyhydroxide (FeOOH) (Singh et al. 2011).

Khanpur, Rania in Kanpur, Uttar Pradesh is selected as study area in present work. It is located at latitude 26°24′40″N and longitude 80°05′57″E, at an elevation of 126 m from mean sea level. Rania is an industrial area having many large and small scale industries. The site selected for study had been used for many years as a dumping ground for the waste generated from leather industries. Basic chrome sulphate industries are the main generators of wastes in this area. Total 27 soil samples were collected from various depths (0–40 feet at an interval of 5 feet) of three sites (S_1, S_2 and S_3) from Rania on the basis of GPS (Global Positioning System) coordinates. All the samples were stored at 4°C in the laboratory until they were analyzed. Prior to analysis, soil samples were allowed to dry at room temperature, passed through a 2 mm sieve and homogenized. Soil samples were divided in two parts. One part is kept for metal analysis of soil and other one for batch experiments. Total Cr present in soil samples were determined by digesting the sample with 10 mL of digestion mixture (conc. HNO_3 + conc. $HClO_4$ in 5:1 ratio) in 250 mL Erlenmeyer flasks. The mixture was heated till the completion of digestion, filtered and then analyzed on atomic absorption spectrophotometer. Cr(VI) is estimated by colorimetric method specified in Method 7196A of USEPA (1, 5-diphenylcarbazide method). In brief, 200 μL of diphenyl carbazide solution and few drops of 0.1 N HCl were added to 1 mL of the sample. The solution was made up to the mark with distill water and then allowed to stand for 15 min. The absorbance was measured at a wavelength of 540 nm using Thermo spectronic GENESYS 10 UV scanning UV–Vis Spectrophotometer.

Out of 27 soil samples collected, five samples (three samples collected from 0, 5 and 10 feet of S_1 site and two samples collected from 0 and 5 feet of S_3 site) showing the presence of Cr(VI) were selected for batch experiments to investigate the efficacy of nZVI for the removal of Cr(VI) from tannery waste contaminated soil. Batch procedures include treating 1 g of soil sample with 10 mL of 0.01, 0.05, 0.10 and 0.15 g L^{-1} of nZVI in 15 mL centrifuge tubes. The reaction mixtures were continuously shaken at ambient temperature without any pH control. At predetermined time intervals (15, 30, 45 … 120 min.), reaction mixture was taken out, centrifuged and then the supernatant was analyzed for residual Cr(VI) by colorimetric technique. All the experiments were conducted in triplicates to ensure repeatability and accuracy. Control experiments with soil samples were also conducted under similar experimental conditions in the absence of nZVI. To study the trend of Cr(VI) percent reduction with different concentration of nZVI, the reaction mixture was allowed to react for 120 min with continuous shaking and then the samples were analyzed for Cr(VI). To determine the reaction kinetics of Cr(VI) removal, various concentration of nZVI (0.01, 0.05, 0.10, 0.15 g L^{-1}) were added to the soil sample [Cr(VI) initial concentration = 43.3 mg kg^{-1}] at a soil to solution ratio of 1 g:10 mL. At selected time intervals (15, 30, 45 … 120 min.), samples were taken out, filtered and tested for residual Cr(VI).

To check the efficacy of nZVI in field, two soil windrows (W_1 and W_2) were constructed at S_1 site (Cr(VI) conc. = 43.3 mg kg^{-1}). One windrow (W_1) was treated with nZVI and other one (W_2) was kept untreated. The windrows were trapezoidal in cross-section with the following dimensions: base = 2.2 m wide, top = 1.5 m wide, height = 1 m and length = 5.35 m. 5 g L^{-1} of nZVI was added in W_2 and was mixed properly. Once the nZVI was mixed, windrows were covered with perforated plastic sheets. Composite samples were collected from each windrow at 0, 5, 10, 15… 50 days for the analysis of residual Cr(VI) concentration.

Results and Discussion

Illegal dumping of tannery waste at the study area has resulted in contamination of the soil with hazardous Cr(VI) which may contribute to long term deterioration of ambient air, soil and water resources. The concentration profile of total Cr and Cr(VI) present at various depths of soil sampled from S_1, S_2 and S_3 sites are shown in Fig. 1. Mean Cr concentration found in all the collected soil samples were 64.35 mg kg^{-1} (range 26–236 mg kg^{-1}). The concentration of Cr in surface soil was found higher than the sub surface soil, although no definite trend was observed in the increase or decrease of the concentration of Cr with depth. Out of 27 samples, 5 samples (3 samples collected at 0, 5 and 10 feet of S_1 site and 2 samples collected at 0 and 5 feet of site S_3) showed significant presence of Cr(VI) with an average value of 15.84 mg kg^{-1}. The presence of elevated levels of Cr(VI) indicates considerable risk to environment and human health by direct contact with soil, ingestion, and inhalation in exposed area (Linos et al. 2011).

Results of the batch experiments conducted on Cr(VI) containing soil samples using different concentration of nZVI were shown in Fig. 2. All the experiments were carried out for a reaction period of 120 min. The Cr(VI) removal is calculated based on the final and initial concentration of Cr(VI) in the soil. The difference between the initial concentration of Cr(VI) in soil and final concentration found after the treatment is attributed to reduction by nZVI. This difference in concentration divided by the initial concentration in the soil represents Cr(VI) percent reduction. The results showed that addition of 0.10 g L^{-1} of nZVI resulted in reduction of Cr(VI) concentration below the permissible limit in all Cr(VI) containing samples within a time period of only 120 min (except in one sample of S_1 site which was reduced completely by 0.15 g L^{-1} of nZVI in the same reaction period) following pseudo first order kinetics (data not shown). These results are consistent with our previous work done on Cr(VI) reduction and immobilization (Singh et al. 2011). Cao and Zhang (2006) reported that the 1 g of nZVI reduces 84.4–109.3 mg Cr(VI) in ground water and 69.3–72.2 mg Cr(VI) in chromium ore processing residues. In a similar study conducted with soil spiked with 100 mg Kg^{-1} Cr(VI), 0.27 g L^{-1} of nZVI showed complete reduction (Singh et al. 2011). It was further noticed in batch experiments that the reduction of Cr(VI) in all cases increased with increase in nZVI concentration. Similar trend have been observed by others researchers (Franco et al. 2009; Singh et al. 2011) also. This effect may be attributed to the subsequent increase in number of surface reactive sites with the increase in nZVI concentration.

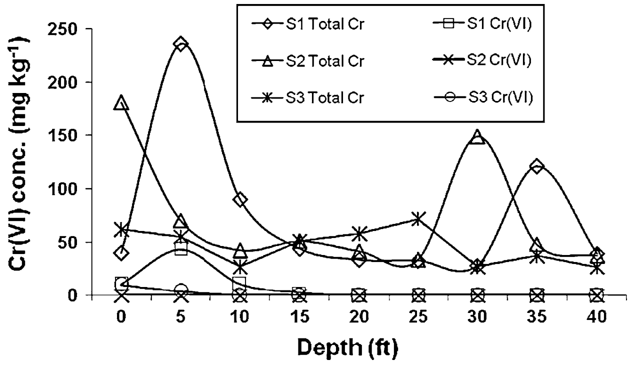

Fig. 1 Concentration of total Cr and Cr(VI) (mg Kg^{-1}) at various depths of soil sampled at S_1, S_2 and S_3 sites in Rania, Kanpur

Cr(III) is the most stable form of the element which occurs naturally in animals, plants, rocks, and soils. It has low mobility in aquatic system due to its low water solubility and is considered essential in trace concentration for the biological activities. On the contrary, Cr(VI) has high toxicity, solubility and mobility in the environment and is considered as carcinogenic, teratogenic and mutagenic. Removal of Cr(VI) by nZVI is based on reduction of chromium from hexavalent form [Cr(VI)] to trivalent form [Cr(III)], subsequently followed by precipitation of Cr(III) on the surface of nZVI in the form of a layer of chromium-iron oxides/hydroxides/oxyhydroxides. Cr(VI) percent reduction for 0.01, 0.05, 0.10, 0.15 g L^{-1} nZVI was found to be 14.54, 26.09, 86.83 and 100% in 120 min showing an increasing trend with the increasing concentration of nZVI (Fig. 3). However, retardation in percent reduction was noticed with the increase in the ratio of Cr(VI) and nZVI. This retardation is probably due to the formation of $Cr_xFe_{1-x}(OH)_3$ or $Cr_xFe_{1-x}(OOH)$ layer at the surface of nZVI, which serves as a passive layer and protects nZVI oxidation.

To check the efficacy of nZVI under field conditions, windrows experiment at contaminated field were carried out for 50 days. Treatment of windrow soil (W_1) with 5 g L^{-1} of nZVI resulted in 64% reduction in Cr(VI) concentration after 25 days which further reaches up to 99% on 40th day as compared to W_2 (untreated windrow) Fig. 4. The data obtained showed similar trend to our bench scale studies indicating the potential of nZVI for field scale remediation. These findings are further supported by the field scale remediation of Cr(VI) from groundwater using ZVI containing permeable reactive

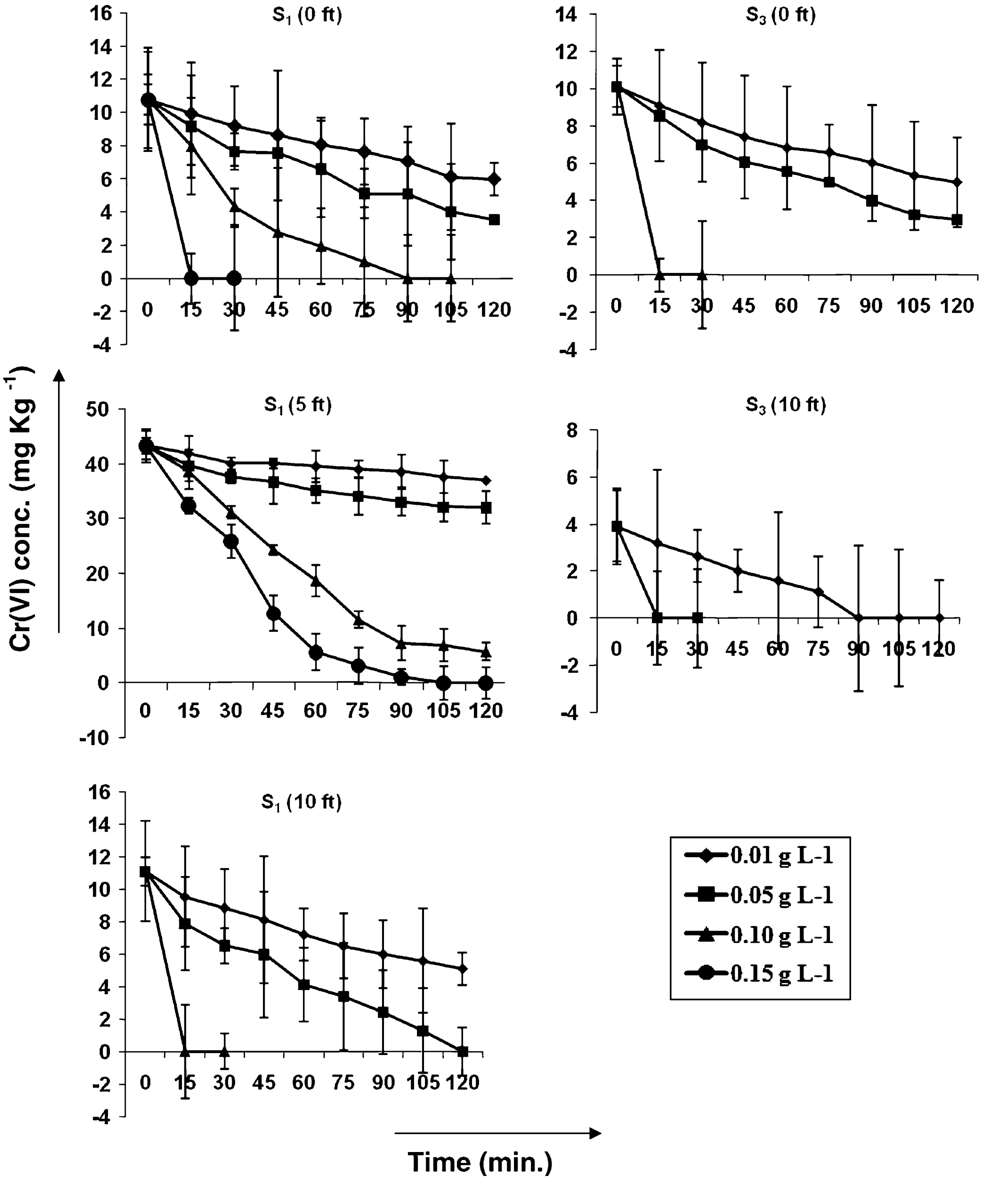

Fig. 2 Reduction of Cr(VI) by nZVI in tannery waste contaminated soil samples - S_1 and S_3 collected from Rania, Kanpur (*error bars* represents the standard deviation)

barriers (PRB) employed at various contaminated sites. Puls et al. 1999 used PRB for in situ remediation of groundwater contaminated from an old chrome-plating facility located on an US coast guard air base near Elizabeth city, NC and observed chromate reduction to less than 0.01 mg L^{-1}. Wilkin et al. 2005 also reported Cr(VI) reduction in groundwater from 1,500 µg L^{-1} to <1 µg L^{-1} by PRB installed at the US coast guard support center located near Elizabeth city, NC. Similar results were observed by Flury et al. 2009 in PRB installed at Willisau, Switzerland for in situ treatment of groundwater contaminated from wood preserving industries. However, the rate of Cr(VI) reduction depends on various environmental factors such as pH, alkalinity, organic matter, co-presence of other contaminants etc. (Lai and Lo 2008; Liu et al. 2008). Besides that the nature of mineral surface present at the site also regulates the rate of reduction (Buerge and Hug 1999).

Results obtained from this study suggest that nZVI has excellent potential for the remediation of Cr(VI) contaminated soil. Further the synthesis of nZVI is very simple with the requirement of only two common laboratory reagents and no special equipment is needed. Thus high reactivity and fast reaction kinetics of nZVI could provide an efficient, economic and environmental friendly remediation tool for sites contaminated with Cr(VI) containing tannery wastes. However additional work to determine the optimal environmental conditions for Cr(VI) reduction and precipitation is required for the better performance of nZVI under field conditions.

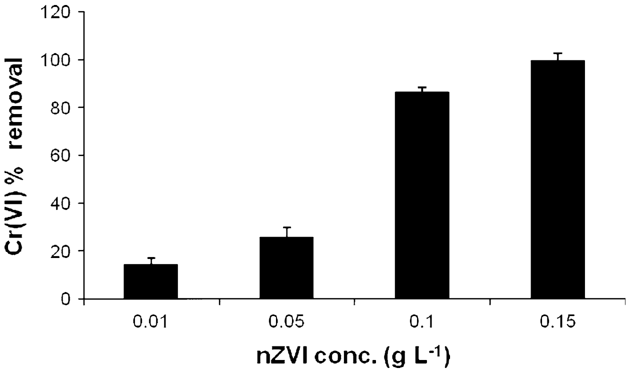

Fig. 3 Cr(VI) percent removal; Cr(VI) initial conc. = 43.3 mg Kg^{-1}; time = 120 min (*error bars* represents the standard deviation)

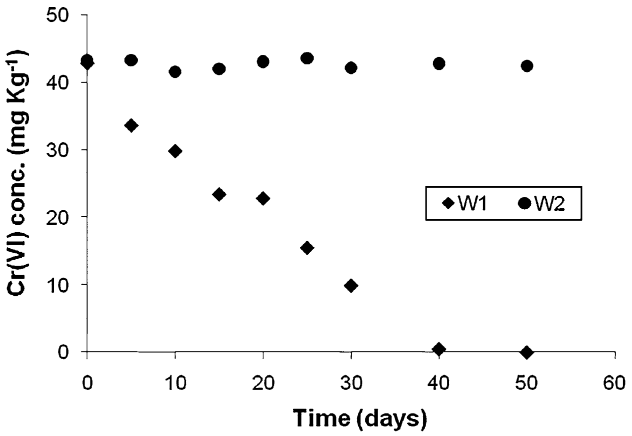

Fig. 4 Cr(VI) reduction in field using soil windrows: W_1 (treated) and W_2 (untreated); Cr(VI) initial conc. = 43.3 mg Kg^{-1}; time = 50 days

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References

Belay AA (2010) Impacts of chromium from tannery effluent and evaluation of alternative treatment options. J Environ Prot 1:53–58

Buerge IJ, Hug SJ (1999) Influence of mineral surfaces on chromium (VI) reduction by iron (II). Environ Sci Technol 33:4285–4291

Cao J, Zhang WX (2006) Stabilization of chromium ore processing residues (COPR) with nanoscale iron particles. J Hazard Mater 132:213–219

Elliott DW, Lien HL, Zhang WX (2009) Degradation of lindane by zerovalent iron nanoparticles. J Environ Engrg 135:317–324

Flury B, Eggenberger U, Mader U (2009) First results of operating and monitoring an innovative design of a permeable reactive barrier for the remediation of chromate contaminated groundwater. Appl Geochem 24:687–696

Franco DV, Da Silva LM, Jardim WF (2009) Reduction of hexavalent chromium in soil and ground water using zero-valent iron under batch and semi-batch conditions. Water Air Soil Pollut 197: 49–60

Grieger KD, Fjordbøge A, Hartmann NB, Eriksson E, Bjerg PL, Baun A (2010) Environmental benefits and risks of zero-valent iron nanoparticles (nZVI) for in situ remediation: risk mitigation or trade-off? J Contam Hydrol 118:165–183

Lai KCK, Lo IMC (2008) Removal of Cr(VI) by acid washed zero-valent iron under various groundwater geochemistry conditions. Environ Sci Technol 42:1238–1244

Linos A, Petralias A, Christophi CA, Christoforidou E, Kouroutou P, Stoltidis M, Veloudaki A, Tzala V, Makris KC, Karagas MR (2011) Oral ingestion of hexavalent chromium through drinking water and cancer mortality in an industrial area of Greece - an ecological study. Environ Health 10:50–57

Liu T, Tsang DCW, Lo IMC (2008) Chromium(VI) reduction kinetics by zero-valent iron in moderately hard water with humic acid: iron dissolution and humic acid adsorption. Environ Sci Technol 42:2092–2098

Nurmi JT, Tratnyek PG, Sarathy V, Baer DR, Amonette JE, Pecher K, Wang C, Linehan JC, Matson DW, Penn RL, Driessen MD (2005) Characterization and properties of metallic iron nanoparticles: spectroscopy, electrochemistry and kinetics. Environ Sci Technol 39:1221–1230

Owlad M, Kheireddine A, Daud WAW, Baroutian S (2009) Removal of hexavalent chromium contaminated water and wastewater: a review. Water Air Soil Pollut 200:59–77

Puls WR, Paul CJ, Powell RM (1999) The application of in situ permeable reactive (zero-valent iron) barrier technology for the remediation of chromate-contaminated groundwater: a field test. Appl Geochem 14:989–1000

Singh R, Misra V, Singh RP (2011) Synthesis, characterization and role of zero-valent iron nanoparticle in removal of hexavalent chromium from chromium-spiked soil. J Nanopart Res 13: 4063–4073

Tarcan G, Akinci G, Danisman AM (2010) Assessment of the pollution from tannery effluents upon waters and soils in and around Kula vicinity, Turkey. Water Air Soil Pollut 213: 199–210

Wilkin RT, Su CM, Ford RG, Paul CJ (2005) Chromium-removal processes during groundwater remediation by a zerovalent iron permeable reactive barrier. Environ Sci Technol 39:4599–4605