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# Surface modification of Nano zero Valente iron for improved reactivity and performance against hexavalent chromium - A ground water contaminant

**M Prasanthrajan and V Jayanthi**

### Abstract

A detailed survey and sampling were done at different locations of Tiruppur and Vellore to know the chromium contamination in ground water. The ground water samples of Vellore had chromium whereas water samples collected from Tiruppur had no traces of chromium. Nano zero Valente iron particles are highly suitable for ground water contaminant removal due to their small size and high reactivity nature. However the reactivity of iron decreases with time possibly due to formation of metal hydroxides or carbonates that partially passivity the surface. Iron surface loses reactivity on exposure to air as it is oxidized by atmospheric oxygen. NZVI modified with ascorbic acid by pre synthesis approach (A-nZVI) performed better and achieved 100% Cr (VI) removal in 30 minutes of reaction time under pH 4.0. The nZVI particles supported by ascorbic acid showed more stability than the bare nZVI. The size of the A-nZVI particles was in the range of 45 to 60 nm. The ground water collected from the bore wells of Walajahpet and Ranipet contained Cr (VI) in the range of 0.06 to 1.18 mg L<sup>-1</sup> and 0.08 to 0.72 mg L<sup>-1</sup> respectively. At a dose of 1.0 g A-nZVI/L, 100% of Cr (VI) (30 mg/L) removal was achieved in 30 minutes. Cr (VI) in the water samples collected from the contaminated wells of Vellore were also easily removed using A- nZVI.

**Keywords:** contaminant, ground water, hexavalent chromium, Nano zero Valent iron, reactivity

### Introduction

The large territories of modern cities are polluted by various components, including toxic pollutants. Ground water is one of the prime resources for human use without which survival of human mankind is not possible. Rapid industrial growth deteriorated the ground water quality to the nag end. Hence removing the common pollutants from ground water is highly essential. Nano Zero Valente Iron (nZVI) is a strong reducing agent which has got great potential in remediating most of the common contaminants in ground water. Surface modification of nZVI is a step ahead to improve its reactivity against ground water contaminants to convert toxic form to nontoxic in shorter period. After the reduction of pollutant, nZVI transforms into Fe<sup>2+</sup> and Fe<sup>3+</sup>, the naturally existing form of Iron, which is quite safer to the environment. Nano scale iron particles (between 50 to 300 nanometers in diameter) typically have surface areas up to 30 times greater than larger size powders or granular iron (Liu *et al.*, 2005) [3]. This results in nZVI that are 10 to 10,000 times more reactive, which makes it very suitable to react with heavy metals particularly hexavalent chromium, chlorinated alkenes such as perchloroethene (PCE) and trichloroethene (TCE). Over the decades, extensive use of chromium in tanning industries have resulted in chromium contaminated soil and ground water (Turick *et al.*, 1996) [6]. Hexavalent chromium is a major pollutant of groundwater in Vellore region of Tamil Nadu. Nano zero-Valente iron, an important natural reluctant of Cr (VI), is an option in the remediation of contaminated sites, transforming Cr (VI) to essentially nontoxic Cr (III). Originally, the zero Valente iron particles used for ground water remediation were on the millimeter size range. Decrease in particle size to the nanometer scale would increase the surface area per gram of ZVI particle by orders of magnitude. Contaminant removal from ground water by NZVI is surface mediated; therefore high surface area results in quick degradation of contaminants (Li *et al.* 2006) [2]. However unmodified NZVI particles have a strong tendency to aggregate, limiting their mobility and contaminant removal (Schrack *et al.* 2004; He and Zhao, 2005; Phenrat *et al.* 2007) [5, 1, 4].



Soil samples were also collected from the above said locations. For collecting soil sample, 'V' shape cut to a depth of 15 cm was made at each sampling spot and then the soil samples (about 500 g) were collected by scrapping the side walls of 'V' cut. The samples were collected in zip lock polythene cover and labeled properly. The collected soil samples were brought to the laboratory and shade dried at 25-30 °C for about 4 days. Then the soil samples were powdered using wooden hammer and sieved through 2mm brass sieve. The sieved soil samples were stored in the polybags with proper labels. Effluent samples (1 litre) were also collected from the effluent drainage path in 5 locations of Ranipet. The samples were collected in one litre polythene containers, properly labeled and brought safely to the laboratory and stored in the cold room at 4 °C.

#### Determination of hexavalent chromium in ground water samples

The concentration of hexavalent chromium in the ground water sample was determined by Diphenyl Carbazide (DPC) method. A known quantity of water sample (5 ml) was taken in 50 ml volumetric flask. In which, 10 ml of 1N sulphuric acid (AR Grade), 0.4 ml of orthophosphoric acid (AR Grade), and 4 ml of DPC reagents were added. Then the volume was made up to 50 ml using deionized water and allowed to stand for 20 minutes for the purple colour development. The optical density values of the samples were recorded within 30 minutes of colour development by UV-Visible Spectrometer (Schimadzu UV 1800) at 540 nm. The samples were compared with standard graph value. The standard graph was drawn by using chromium working standard solution 0, 0.5, 1.0, 1.5, and 2.0 ppm.

#### Determination of hexavalent chromium in soil samples

The concentration of Hexavalent chromium in the soil sample was determined by Diphenyl Carbazide method. One gram of soil and 25 ml of deionized water was taken in a polypropylene centrifuge tube and placed in the end-end shaker for 2hrs, after shaking; the suspension was centrifuged at 8000 rpm for 10 minutes and filtered through what man No. 42 filter paper. For analyzing hexavalent chromium 5 ml of filtrate sample was added with 10 ml of 1N sulphuric acid, 0.4 ml of ortho phosphoric acid, and 4 ml of DPC reagent. Then the volume was made up to 50 ml using deionized water and allowed to stand for 20 min for the purple colour development. The optical density values of the samples were recorded within 30 minutes of colour development by UV-Visible Spectrometer (Schimadzu UV 1800) at 540 nm. The samples were compared with standard graph value. The standard graph was drawn by using chromium working standard solution 0, 0.5, 1.0, 1.5, and 2.0 ppm.

#### Preparation DPC

The DPC reagent was prepared by dissolving 0.25 g 1, 5 – Di-Phenyl Carbazide and 4g Phthalic anhydride in 100 ml of 95% Ethyl alcohol (95 ml Ethyl alcohol and 5 ml distilled water). Diphenyl carbazide does not dissolve well in ethanol - water mixture, hence it has to be dissolved using magnetic stirrer. Then the DPC reagent was stored in a brown bottle by closing cap tightly and kept it in the refrigerator. The solution is stable for at least one month.

#### Preparation chromium standard stock solution

About 10 g of potassium dichromate was taken and dried in an oven at 1100 °C for several hours. A known quantity (2.829g) of oven dried of Potassium Dichromate ( $K_2Cr_2O_7$ , Analytical Reagent grade) was dissolved in deionized water and diluted to 1 litre, in a 1 litre volumetric flask. Then the flask was stopper and mixed well thoroughly by inverting the flask several times. This solution contains 1000  $\mu\text{g Cr}^{+6}/\text{ml}$  or 1000 ppm or 1000  $\text{mg L}^{-1}$ .

#### Preparation of $\text{Cr}^{6+}$ working standard solution

10 ml of the chromium stock standard solution (1000 ppm) were transferred into a 100 ml volumetric flask and diluted to the mark with deionized water. This solution contains 100  $\mu\text{g Cr}^{+6}/\text{ml}$ . Stopper the flask and inverted several times to mix the solution thoroughly. This working solution is always prepared fresh prior to use. From this desirable concentration of working standard solution (0.5, 1.0,

1.5, 2.0 ppm) can be prepared ( $V_1N_1=V_2N_2$ ). Desirable volume of each standard were taken in volumetric flask, in which 10 ml of 1N sulphuric acid (AR Grade), 0.4 ml of orthophosphoric acid (AR Grade), and 4 ml of DPC reagents were added. Then the volume was made up to 50 ml using deionized water and allowed to stand for 20 min for the purple colour development. All the ground water and soil samples collected from different locations of Vellore and Tiruppur districts were subject to hexavalent chromium analysis by DPC method.

#### Determination of total chromium

The concentration of total chromium in the ground water sample was measured by using an Atomic Absorption Spectrophotometer (AAS), for that the sample was digested with Aqua Regia ( $\text{HCl}:\text{HNO}_3$  3:1 ie. 3 parts of concentrated hydrochloric acid and 1 part of concentrated nitric acid). Ten ml of sample in an acid washed 100 ml conical flask was digested with 15 ml Aqua Regia on hot plate at 110 °C for 2 hrs until white slurry like substance is obtained. After that the conical flask was removed from the hot plate, cooled and 5 ml of distilled water was added and the content and boiled for few minutes. Finally the volume was made to 50 ml and kept it for overnight. Then the sample was filtered through What man No.42 filter paper. The total chromium present in the solution was measured in an Atomic Absorption Spectrophotometer (AAS), Perkin Elmer, A Analyst 400, using air-acetylene flame. The concentration of total chromium in the soil sample was measured by using an Atomic Absorption Spectrophotometer (AAS), for that the sample was digested with Aqua Regia ( $\text{HCl}$  &  $\text{HNO}_3$  of 3:1). One gram of soil sample in an acid washed 100 ml conical flask was digested with 15 ml Aqua Regia on hot plate at 110 °C for 2hrs until white slurry like substance is obtained. After that the conical flask was removed from the hot plate, cooled and 5 ml of distilled water was added to the content and boiled for few minutes. Finally the volume was made up to 50 ml and kept it for overnight. Then the samples were filtered through what man No.42 filter paper. The total chromium present in the solution was measured in an Atomic Absorption Spectrophotometer (AAS), Perkin Elmer, A Analyst 400, using air-acetylene flame.

#### Periodical sampling and monitoring of Cr (VI)

Based on the results obtained from the preliminary study, Walajahpet and Ranipet region were chosen for periodical sampling and for monitoring hexavalent chromium for about three months to know the exact trend of Cr (VI) load. In Walajahpet (Chennasamudram), five bore wells were chosen for collecting ground water samples. In Ranipet five bore wells were chosen at Chettithangal Village. About one litre ground water samples were collected from all the ten bore wells. The collected samples were brought to laboratory and analyzed for hexavalent chromium by DPC method.

#### Preparation of Surface modified nZVI

Nano zero Valente iron particles were synthesized by adding 0.25 M sodium borohydride drop wide (Flow rate 2.8 ml per minute) into a beaker containing 0.045 M  $\text{FeCl}_3$  (Wang and Zhang, 1997) [7] with vigorous stirring under nitrogen purging. The synthesized particles were tested against hexavalent chromium reduction under laboratory condition in reactor vial. In order to improve the reactivity, the surface of nZVI particles were successfully modified using Tiron, Sodium acetate and Ascorbic acid by pre synthesis approach. Excessive borohydride was added to accelerate the synthesis. Addition of the  $\text{NaBH}_4$  to the  $\text{FeCl}_3$  solution in the presence of vigorous magnetic stirring resulted in the rapid formation of fine black precipitated as the ferric iron reduced to nZVI and precipitated. The synthesized iron particles were then washed several times with deionized water and ethanol before use and stored in water containing 5% ethanol. The size distribution of the particles and surface morphology was investigated with the Scanning Electron Microscope operated at 25kV, magnification kx 56.99. To investigate the possibility of field application of surface modified nZVI particles, ground water samples collected from Vellore district containing chromium were tested using A-nZVI.

## Results and Discussion

The hexavalent chromium concentration in the ground water samples collected from Walajahpet ranged from Bdl to 1.38 mg L<sup>-1</sup>. The ground water collected from Ranipet recorded hexavalent chromium in the range of Bdl to 1.33 mg L<sup>-1</sup>. The ground water samples collected from Melvisharam, Arcot and Vellore regions had no hexavalent chromium (Table 1). The soil samples collected from Walajahpet region had Bdl to 55.37 mg kg<sup>-1</sup> of hexavalent chromium. The soil samples collected from Ranipet recorded 12.46 to 60.91 mg kg<sup>-1</sup> of hexavalent chromium. In Melvisharam, the soil hexavalent chromium concentration was in the range of 0 to 73.37 mg kg<sup>-1</sup>. Soil samples collected from Arcot and Vellore region had no hexavalent chromium (Table 2). The ground water and soil samples collected from Aandipalayam and Mangalam village of Tiruppur district had no hexavalent chromium. The total chromium concentration in the ground water samples collected from Walajahpet ranged 0 to 3.85 mg L<sup>-1</sup>. In Ranipet, the total chromium concentration of ground water samples ranged from 0 to 2.59 mg L<sup>-1</sup>.

In Melvisharam the total chromium concentration of ground water samples were in the range of 0 to 0.09 mg L<sup>-1</sup>. The ground water samples collected from Vellore and Arcot region had no chromium (Table 3). The soil samples collected from Walajahpet region had 13.85 to 147.75 mg kg<sup>-1</sup> of total chromium whereas the soil samples collected from Ranipet recorded 20.75 to 208.50 mg kg<sup>-1</sup> of total chromium. The total chromium concentration of soil samples collected from Melvisharam ranged from 0 to 140.60 mg kg<sup>-1</sup>. The soil samples collected from Arcot region had 0 to 56.9 mg kg<sup>-1</sup> of total chromium and Vellore region soil had no chromium (Table 4). The ground water samples collected from Aandipalayam, Tiruppur district recorded 0.67 mg L<sup>-1</sup> of total chromium. The soil samples collected from 25 locations of Aandipalayam had 0 to 65.65 mg kg<sup>-1</sup> of total chromium. Soil samples collected from Mangalam recorded 0 to 28.55 mg kg<sup>-1</sup> of total chromium. It is observed that the Walajahpet and Ranipet region of Vellore district were found to contain more of chromium both in ground water and soil.

**Table 1:** Hexavalent chromium concentration in the ground water samples collected from Vellore district

Sample	Hexavalent chromium concentration (mg L <sup>-1</sup> )					
	Walajahpet	Ranipet East	Ranipet West	Melvisharam	Arcot	Vellore
W1	0.55	0.44	Bdl	Bdl	Bdl	Bdl
W2	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
W3	Bdl	1.27	0.94	Bdl	Bdl	Bdl
W4	1.38	1.33	Bdl	Bdl	Bdl	Bdl
W5	0.83	Bdl	Bdl	Bdl	Bdl	Bdl
W6	Bdl	Bdl	1.00	Bdl	Bdl	Bdl
W7	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
W8	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
W9	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl
W10	0.55	Bdl	Bdl	Bdl	Bdl	Bdl
Range	Bdl to 1.38	Bdl to 1.33	Bdl to 1.00	Bdl	Bdl	Bdl

**Table 2:** Hexavalent chromium concentration in the soil samples collected from Vellore district

Sample	Hexavalent chromium concentration (mg kg <sup>-1</sup> )					
	Walajahpet	Ranipet East	Ranipet West	Melvisharam	Arcot	Vellore
W1	12.46	40.14	20.76	58.14	Bdl	Bdl
W2	6.92	30.45	22.15	63.68	Bdl	Bdl
W3	48.45	56.76	16.61	44.30	Bdl	Bdl
W4	55.37	30.45	12.46	73.37	Bdl	Bdl
W5	0.00	41.53	13.84	34.61	Bdl	Bdl
W6	12.46	33.22	60.91	31.84	Bdl	Bdl
W7	49.83	12.46	12.46	34.61	Bdl	Bdl
W8	48.45	35.99	16.61	48.45	Bdl	Bdl
W9	9.69	37.38	16.61	13.84	Bdl	Bdl
W10	52.60	34.61	13.84	Bdl	Bdl	Bdl
Range	Bdl to 55.37	12.46 to 56.76	12.46 to 60.91	Bdl to 73.37	Bdl	Bdl

**Table 3:** Total chromium concentration in the ground water samples collected from Vellore district

Sample	Total chromium concentration (mg L <sup>-1</sup> )					
	Walajahpet	Ranipet East	Ranipet West	Melvisharam	Arcot	Vellore
W1	1.37	1.33	Bdl	Bdl	Bdl	Bdl
W2	Bdl	0.45	0.01	Bdl	Bdl	Bdl
W3	Bdl	2.12	1.73	Bdl	Bdl	Bdl
W4	3.85	2.59	0.03	Bdl	Bdl	Bdl
W5	1.45	0.04	0.05	Bdl	Bdl	Bdl
W6	Bdl	0.03	1.50	Bdl	Bdl	Bdl
W7	0.25	0.05	0.02	Bdl	Bdl	Bdl
W8	Bdl	Bdl	0.14	Bdl	Bdl	Bdl
W9	Bdl	Bdl	0.02	Bdl	Bdl	Bdl
W10	1.68	0.04	0.06	0.09	Bdl	Bdl
Range	Bdl to 3.85	Bdl to 2.59	Bdl to 1.73	Bdl to 0.09	Bdl	Bdl

**Table 4:** Total chromium concentration in the soil samples collected from Vellore district

Sample	Total chromium Concentration (mg kg <sup>-1</sup> )					
	Walajahpet	Ranipet East	Ranipet West	Melvisharam	Arcot	Vellore
W1	38.25	72.20	70.25	86.20	56.90	Bdl
W2	36.25	40.00	52.45	90.10	37.50	Bdl
W3	74.10	94.50	52.60	68.90	Bdl	Bdl
W4	76.50	78.50	28.50	140.60	Bdl	Bdl
W5	13.85	59.00	29.50	64.00	Bdl	Bdl
W6	48.90	47.50	208.50	41.90	31.00	Bdl
W7	147.75	33.10	55.60	80.30	Bdl	Bdl
W8	73.60	55.40	28.70	70.80	Bdl	Bdl
W9	77.10	74.90	20.75	38.75	Bdl	Bdl
W10	65.25	47.00	31.80	Bdl	Bdl	Bdl
Range	13.85 to 147.75	33.10 to 94.50	20.75 to 208.50	Bdl to 140.60	Bdl to 56.90	Bdl

#### Periodical monitoring of hexavalent chromium concentration in the selected bore wells of Walajahpet

The hexavalent chromium concentration of ground water samples collected from five selected bore wells of Walajahpet was in the range of 0.33 to 1.18 mg L<sup>-1</sup>, 0.57 to 0.63 mg L<sup>-1</sup> and 0.06 to 0.14 mg L<sup>-1</sup> at three different period of sampling in one month interval. The hexavalent chromium concentration of ground water samples collected from five monitoring wells of Ranipet was in the range of 0.30 to 0.50 mg L<sup>-1</sup>, 0.50 to 0.72 mg L<sup>-1</sup> 0.08 to 0.15 mg L<sup>-1</sup> at three different period of sampling in one month interval. From this study it is clearly evidenced that the hexavalent chromium concentration of ground water samples of Walajahpet and Ranipet were in the range of above permissible limit (0.05 mg L<sup>-1</sup>) prescribed by World Health Organization.

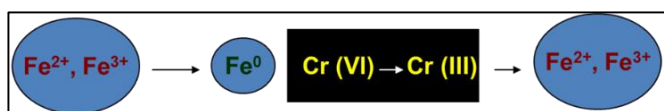
#### Reactivity test against Cr (VI) using A-nZVI

The nZVI and surface modified nZVI particles (A-nZVI) were tested against Cr (VI) reduction. NZVI modified with ascorbic acid by pre synthesis approach (A-nZVI) performed better and exhibited 100%

Cr (VI) removal in 30 minutes of reaction time under pH 4.0. The nZVI particles supported by ascorbic acid showed more stability than the bare nZVI. The size of the A-nZVI particles was in the range of 45 to 60 nm. Stable nZVI dispersion was maintained over extended periods of time. The appreciably smaller mean particle sizes and ability to remain in suspension should translate into improved subsurface mobility potential. Tiron-nZVI exhibited 88.27% Cr removal. Sodium acetate-nZVI showed 80.60% removal of chromium. Bare NZVI showed a potential of 80.13% Cr removal. The ground water collected from the selected wells of Walajahpet (Chennasamudram) and Ranipet (Chettithangal) contained Cr (VI) in the range of 0.06 to 1.18 mg L<sup>-1</sup> and 0.08 to 0.72 mg L<sup>-1</sup> respectively. From our study it is clearly evident that the Cr (VI) in the contaminated wells of Vellore can easily be removed by modified nZVI as it exhibited 100 percent removal of Cr (VI) @ 30 mg L<sup>-1</sup> in 30 minutes reaction time. The chromium removal was in the order of Ascorbic acid-nZVI < Tiron-nZVI < Sodium acetate-nZVI < nZVI (Bare).

**Table 5:** Adsorption potential of bare nZVI and modified nZVI against Hexavalent Chromium

Adsorbent	Initial concentration of Cr(VI) (mg L <sup>-1</sup> )	Final Concentration of Cr(VI) (mg L <sup>-1</sup> )	Removal Efficiency (%)	Maximum Cr (VI) removal efficiency (mg L <sup>-1</sup> ) per g of nZVI
Ascorbic acid-nZVI	30	0	100.00	130
Tiron-nZVI	30	3.52	88.27	52
Sodium acetate-nZVI	30	5.82	80.60	26
nZVI (Bare)	30	5.96	80.13	26

**Fig 2:** Image showing the A-nZVI**Fig 3:** Cr (VI) removal Mechanism

At a dose of 1.0 g A-nZVI/L, 100% of Cr (VI) (30 mg/L) removal was achieved in 30 minutes. The Cr (VI) removal efficiency decreased significantly with increasing pH. The reactivity was in the order ascorbic acid-stabilized nZVI > Tiron nZVI > Sodium acetate nZVI > Bare nZVI. Iron nanoparticles are good choice for the remediation of heavy metals in groundwater. Under ambient conditions, nZVI is fairly reactive in water and can serve as an excellent electron donor, which makes it a versatile remediation material.

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