

Removal of Hexavalent Chromium [Cr (VI)] from Spiked Soil Using Na Y (Nano Sodium) Zeolite Supported Zero Valent Iron Nanoparticles

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Abstract Soil remediation by nanoparticles has received increasing interests in recent years. The present work was conducted to investigate the feasibility of using new class of NC1 (Zeolite with ZVI nanoparticles) and NC2 (Na Y zeolite with ZVI nanoparticles) for *In situ* reductive immobilization of Cr (VI) in spiked soil. The spiked soil sample was subjected to XRD for the determination of crystallinity and average particle size. The size of the particle is 11.28 nm. The morphology of the nanoparticles was observed using SEM and FTIR. Batch experiments reported that the extend of Cr(VI) reduction was increased with increasing concentration of iron nanoparticles and inversely with initial Cr (VI) concentration as well as with decreasing pH (4 - 9). The efficiency of nanocomposites for Cr (VI) reduction was assessed in batch experiment and the results revealed that the rate of Cr (VI) reduction as a function of time showed a rapid reduction, it required 120 min to attain equilibrium for Cr (VI) reduction in NC2 and NC1 for spiked soil. In spiked soil, the maximum Cr (VI) reduction was achieved at an initial concentration of 200 mg kg⁻¹ in pH 5 with 6 mg kg⁻¹ of NC1 dosage whereas, 4 mg kg⁻¹ dosage for NC2. This study indicates that the zerovalent iron nanoparticles, especially those which were Na Y zeolite supported ZVI nanoparticles can yield high removal efficiency in the reduction of Cr (VI) spiked soil.

Keywords Zeolite, Na Y Supported ZVI Nanoparticles, XRD, SEM, FT-IR, Cr (VI) Reduction

1. Introduction

India is now at the mid point of its journey towards becoming a developed country by 2020. With the advancement of industrialization, agricultural and urban

activities, the levels of groundwater contamination have increased many folds in the last few decades. The environmental pollutants spread through different channels, many of which finally enter in to soil and groundwater (Rajaganapathy *et al.*, 2011). Chromium and its compounds have multifarious industrial use besides application in metallurgy they are extensively employed in finishing and processing of leather, producing refractory steel, drilling muds, electroplating cleaning agents, manufacturing catalysts, production of chromic acid and specially chemicals. These anthropogenic activities lead to widespread of Cr contamination in the environment, particularly soil and water (Achal *et al.*, 2011).

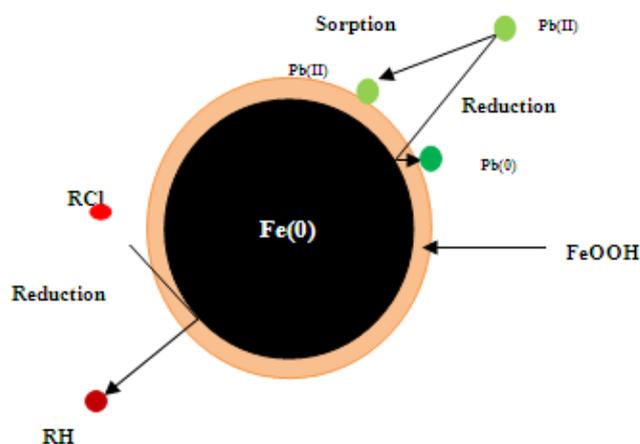
Chromium, essentially exists in two oxidation forms namely Cr (III) and Cr (VI). Over a narrow concentration range, Cr(III) is proved to be biologically essential to mammals as it maintains an effective glucose, lipid and protein metabolism, whereas Cr (VI) is reported to have toxic effect on humans and it is considered to be genotoxic and carcinogenic in nature (Cheuhan and Sankaramakrishnan, 2011). The Cr (VI) is acutely toxic, mutagenic and carcinogenic (Lee *et al.*, 2008). The permissible limit of Cr (VI) in industrial effluents is set at 0.5 mg/L by the Ministry of Environment and Forests (MoEF), by Government of India (Panda *et al.*, 2011).

Much research has focused on the remediation of Cr (VI) and many treatment processes have been developed. Environmental chemists and material scientists have always focused their attention on the development of cost-effective adsorbents which could be exploited for the effective removal of Cr (VI) from soil.

The ZVI nanoparticles has recently become the most common reducing agent for various applications due to its large surface areas, high surface reactivity, low cost, less toxicity and very effective for the transformation and detoxification of a wide variety of organic and inorganic

contaminants such as chlorinated hydrocarbons and toxic metallic ions in the environment. The ZVI nanoparticles properties associated with the potential to transform metal ions such as Cr, Ni, Zn, As, Cd, Ag, Pb (Cao and Zhang, 2006).

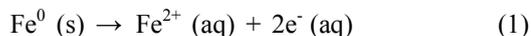
The ZVI nanoparticles is composed of a core which consists primarily of zero-valent or metallic iron while the mixed valent [*i.e.*, Fe (II) and Fe (III)] oxide shell is formed as a result of oxidation of the metallic iron (Figure 1). Iron typically exists in the environment as iron (II) and iron (III)-oxides and as such, ZVI is a manufactured material. Thus, far applications of ZVI have focused primarily on the electron-donating properties of ZVI nanoparticles. Under ambient conditions, ZVI nanoparticles are fairly reactive in water and can serve as an excellent electron donor, which makes it a versatile remediation material (Stumm and Morgan, 1995).



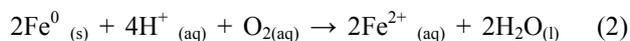
(The core consists of mainly ZVI and provides the reducing power for reaction with environmental contaminants. The shell is largely iron oxides/hydroxides formed from the oxidation ZVI and provides sites for chemical complex formation)

Figure 1. Core-shell structure for iron nanoparticles

The elemental iron slowly oxidizes to ferrous iron and releases two electrons. These electrons begin to function in a variety of reactions that lead to the transformation of target contaminants. Elemental iron can be oxidized by many substances in the environment in accordance with the following reaction (1).

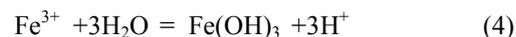


ZVI nanoparticles react with dissolved oxygen (DO) and water resulting in electrochemical/corrosion reactions that oxidize the iron (Zhang, 2003). As shown below, the Fe^0 becomes oxidized to ferrous iron (Fe^{2+}) ions and the electrons that are released become available to reduce other compounds according to following reaction (2).

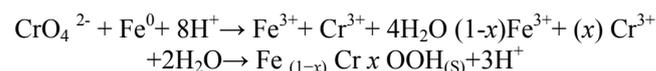


The fate of Fe^{2+} depends on the solution chemistry. In the presence of sufficient DO and other related oxidants, Fe^{2+} will be oxidized and form Fe^{3+} , which is subsequently precipitated into amorphous ferric hydroxides $\text{Fe}(\text{OH})_{3(\text{s})}$ or

ferrihydrate according to following reaction (3&4). The precipitates of these insoluble ferric hydroxides and oxyhydroxides may either localize close to the metallic iron surface or dissipate out into the bulk solution (Bang *et al.*, 2005)



ZVI nanoparticles can rapidly remove and/or reduce these inorganic ions and also have relatively higher capacity than conventional sorptive media and granular iron particles. In the Cr (VI) removal/reduction, the Cr (III) or Cr (III) hydroxide ($\text{Cr}(\text{OH})_3$) are steady product in the reaction. In fact, several investigators have reported that the removal mechanism involves reduction of highly soluble $\text{Cr}_2\text{O}_7^{2-}$ to sparingly soluble Cr (III) compounds at the surface of the iron. The $\text{Cr}(\text{OH})_3$ and mixed Cr (III)/ ($\text{Fe}(\text{OH})_3$) are precipitated on the iron surface. A range of ZVI nanoparticles and Fe (II) bearing materials promoted reduction and precipitation of Cr (VI). The net reactions of Cr (VI) reduction and co-precipitation of Cr (III) and Fe (III) are as follows,



Recently, interests on the adsorption of anions and neutral molecules by surface-modified zeolites are increased (Zhang *et al.*, 2002). Zeolites in their original form could adsorb only cations, but some heavy metals such as Cr and arsenic are present in cations, anions, non-ionized species (Sengupta, 2002).

Zeolites with a high Si/Al ratio have stronger solid acidity are more hydrophobic in their adsorption properties and more stable in acidic conditions. From the point of view, providing support for Fenton catalyst, ion exchange capacity, stability and adsorption properties for organic compounds are both important requirements. The Na Y zeolites (Si/Al ratio 2.8) have a three dimensional micropore structure, the large supercage of 1.2 nm and relatively small open window of 0.7 nm. This particular zeolite not only has favorable properties for ion exchange and immobility but also highly resistant to change in properties when exposed to an acidic environment (Eriksson, 2008).

In this work, a new class of NC1 (Zeolite with ZVI nanoparticles) and NC2 (Na Y zeolite with ZVI nanoparticles) prepared by ion exchange procedure, which were tested for their ability to reduce toxic hexavalent chromium [Cr (VI)] ions from spiked soil. Also, the influence of Cr (VI) and nanoparticles concentration, equilibrium period, variation in pH and temperature of solution on the efficacy of Cr (VI) removal was evaluated. Therefore, efforts were also made to investigate the reactivity of ZVI nanocomposite for remediation of Cr (VI) spiked soil.

2. Materials and Methods

2.1. Preparation of ZVI Nanoparticles

The ZVI nanoparticles were produced by reduction of ferric iron in the presence of sodium borohydride. These particles were prepared freshly each day by adding 0.16 M NaBH₄ aqueous solution drop wise to 0.1 M FeCl₃·6H₂O aqueous solution at ambient temperature and under atmospheric conditions.

2.2. Preparation of ZVI Nanocomposite Using Zeolite

Synthesis of Zeolite/ZVI nanoparticles composites with a size of approximately 79 nm and Si/Al=1.9 was synthesized according to Song (2005) with slight modification. To convert the sodium form of the zeolite into the H- form, 1.0 M NH₄NO₃ was added, stirred overnight and then calcined in air at 550°C for 12 h. HY (Zeolyst or nano) was added to 200 mL of nitrogen purged water and then 30 mL of a 1:2 mol ratio of FeCl₃:FeSO₄ was added drop wise in a glove bag under nitrogen. The composite materials were washed with water and ethanol, dried in an oven overnight at 368 K and then annealed under N₂ for 6 h at 723K.

2.3. Preparation of ZVI Nanocomposite Using Sodium Y Zeolite (Na Y Zeolite)

In ion exchange procedure, 1 g of FeSO₄·7H₂O and 0.5 g of NaY (Sodium nano) zeolite were mixed in 250 mL of deionized water. The liquid mixture was treated with ultrasound for 10 min and then stirred vigorously at ambient temperature for 30 min. The solution pH was around 4.5 during most of the treatment time. The pH value was slightly higher compared to initial pH 4 due to hydrolysis of the zeolite. The degree of Fe (II) oxidation to Fe (III) is minor and the possibility of any Fe (II) precipitation can be ignored in this study as the pH during ion exchange remained below 5. The solution was separated from the solid using a vacuum filtration flask with a 47 mm diameter membrane filter (0.45 μm). The solid was removed from the filter and placed in a three-neck flask containing 25 mL of deoxygenated and deionized water. Twenty five mL of a 1 M KBH₄ alkaline aqueous solution. The black solids formed were washed with deionized water to remove residual SO₄²⁻ ions. The whole aqueous solution reduction process was carried out in a nitrogen atmosphere.

2.4. XRD Measurement

The sample was drop-coated onto aluminium plate by just dropping a small amount of sample on the plate frequently and allowing to dry that finally prepared a thick coat of sample. The XRD measurement was performed on a Shimadzu, model LabX-XRD-6000 instrument operated at a voltage of 20 to 30 keV and a current of 30 mA with Cu K α radiation with a wavelength of 1.5409 Å.

2.4.1. Determination of Crystalline Size

Average crystallite size of Zeolite-supported ZVI nanoparticles was calculated using the Scherrer's formula.

$$D = k\lambda / \beta \cos\theta$$

D - Average crystallite size: K - Constant: λ- X-ray Wavelength: β - Angular FWHM of the XRD peak at the diffraction angle: θ- Diffraction angle

2.4.2. SEM Analysis

The thin film of the sample was prepared on a small aluminium plate by just dropping a very small amount of the sample on the plate, removing the extra solution using a blotting paper and then allowing the film on the plate to dry overnight. The analysis was performed on a SEM (Philips 41 OLS microscope), with accelerating voltage of 200 kV and counting time of 100s.

2.4.3. FT-IR Measurement

FT-IR measurement of sample was performed using Nicolet Avatar Model FT-IR spectrophotometer in a diffuse reflectance mode at a resolution of 4 cm⁻¹ in KBr pellets.

2.5. Batch Experiment for Cr (VI) Reduction in Spiked Soil

2.5.1. Preparation of Cr (VI) Solution

Stock solution (1000 mg/L) of Cr (VI) was prepared by dissolving 2.829 g of K₂Cr₂O₇ in 1000 ml of double distilled water. Experimental solutions of the desired concentrations were obtained by successive dilutions and Cr (VI) was determined *via* 1,5-diphenylcarbazide (DPC) colorimetric method by measuring the absorbance at a wavelength of 540 nm using UV-Vis spectrophotometer. 0.1M NaOH or HCl was used for the adjustment of pH and controlled by pH meter.

2.5.2. Effect of Equilibrium Period

Batch experiments were conducted using 500 ml conical flasks which were sealed with rubber cork and placed on a rotary shaker, set to 150 rpm at room temperature during the entire experiment period. All the flasks containing nanocomposite particles were purged with N₂. Each 100 g of soil having Cr (VI) concentration of 200 mg kg⁻¹ was taken in the flasks each containing nanocomposite dosage of 6.0 mg kg⁻¹ for NC1, while 4.0 mg kg⁻¹ for NC2. The mixture was equilibrated by shaking thoroughly in a shaker for different time intervals *viz.*, 0, 30, 60, 90, 120 and 150 min. At the end of the shaking period the reaction solution sampled by syringe. The sample was filtered immediately through 0.22 μm membrane filters for analysis.

2.5.3. Effect of Solute Concentration

The study was conducted at batch level in order to assess the effect of solute concentration for reduction of Cr (VI). Each 100 g of soil at varying concentrations *viz.*, 0, 100, 200, 300, 400 and 500 mg kg⁻¹ of Cr (VI) were introduced into flasks containing NC1 (6.0 mg kg⁻¹) and NC2 (4.0 mg kg⁻¹). The reaction mixture was shaken thoroughly for 120 min for reduction of Cr (VI). The sample was filtered immediately through 0.22 μm membrane filters and the filtrate was analyzed for remaining solute concentration.

2.5.4. Effect of Nanocomposite Dosage

Since, the nanocomposite dosage plays a major role in the reduction of Cr (VI), the effect of nanocomposite dosage on pollutant removal was investigated using batch technique described above. Different dosages of NC1 and NC2 viz., 0.0, 2.0, 4.0, 6.0, 8.0 mg kg⁻¹ were equilibrated with 100 g of soil (200 mg kg⁻¹ of Cr (VI)). The reaction mixture was shaken thoroughly for 120 min for reduction of Cr (VI). The sample was filtered immediately through 0.22 µm membrane filters and the filtrate was analyzed for remaining solute concentration.

2.5.5. Effect of pH

The study was conducted at batch level in order to assess the effect of pH for the reduction of Cr (VI). The dosage of NC1 (6.0 mg kg⁻¹) and NC2 (4.0 mg kg⁻¹) were introduced into flask containing 100 g of soil (200 mg kg⁻¹ of Cr (VI)). The reaction mixture was adjusted into different pH levels viz., 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and shaken thoroughly for 120 min. The sample was filtered immediately through 0.22 µm membrane filters and analysed for remaining solute concentration.

3. Results and Discussion

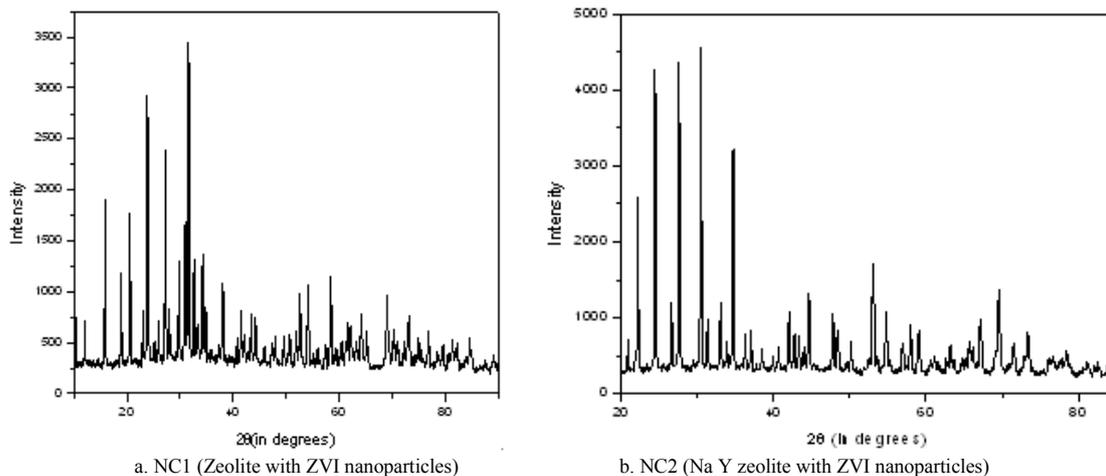


Figure 2. X-ray diffraction pattern

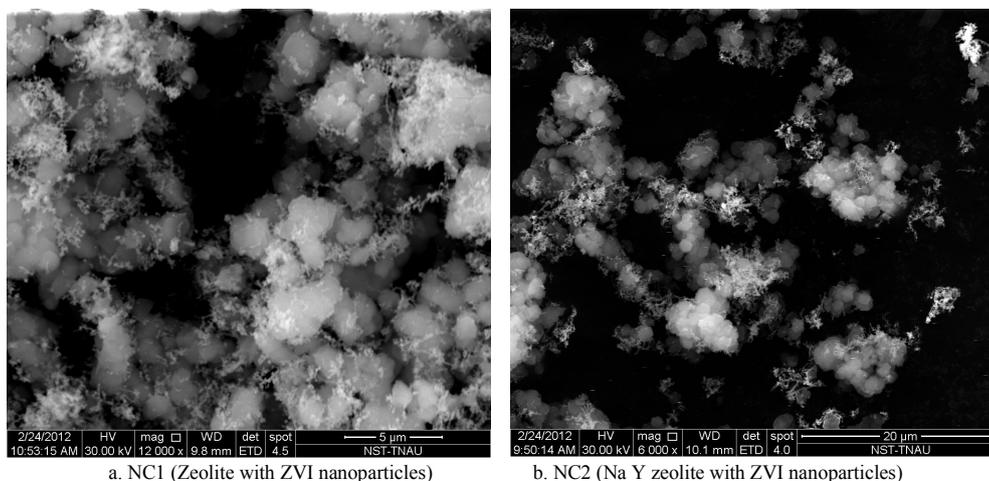


Figure 3. SEM images

3.1. X-ray Diffraction Analysis

X-ray diffraction was used to investigate the size and phase structure of ZVI nanoparticles. The exact nature of ZVI nanoparticles is identified by measuring the XRD spectrum of the samples (Fig.2).

The XRD pattern thus clearly shows that the ZVI nanoparticles are crystalline in nature. The sharpening of the peaks clearly indicates that the particles are nanoregime. The XRD pattern of NC2 is known to display peak at $2\theta = 44.8^\circ$, 65.1° and 82.4° corresponding to (110), (200) and (211) planes of body centered cubic $\alpha\text{-Fe}^0$, respectively (Wang *et al.*, 2010). The size of the nanoparticles varied based on the full width half maxima (FWHM) of the peak. The FWHM values of peaks get increased, the size of the nanoparticles get decreased. Chudasama *et al.* (2010) reported that the line broadening of the X-ray diffraction peaks is primarily due to the small particle size.

3.2. Scanning Electron Microscopy (SEM) Analysis

The result obtained from the SEM image gives a clear indication regarding the size and shape of the nanoparticles. SEM analysis reveals that the NC2 are predominately spherical and smooth than NC1 (Figure 3).

At low magnification, very large density of ZVI nanoparticles can be seen. Thus, ZVI nanocomposites are polydispersed and size ranged from 50 to 100 nm. The size distribution of the ZVI nanoparticles occurs within the range from 10 to 20 nm, the average size which is close to the result calculated from XRD. The images showed that the ZVI nanoparticles settle on the outer surface and the particles embedded within the pores of the zeolite and Na Y zeolite. This might be due to the high surface energy. Similar findings were reported by Wang *et al.* (2010).

3.3. EDAX Analysis

EDAX used for the elemental analysis or chemical characterization of a sample (Figure 4&5).The NC1 contains 44.98 per cent of O₂, 2.58 per cent of Na, 8.0 per cent of Al, 17.47 per cent of Si, 7.18 per cent of k and 19.79 per cent of Fe. NC2 contains 37.17 per cent of O₂, 3.09 per cent of Na, 8.19 per cent of Al, 17.58 per cent of Si, 9.44 per cent of K and 24.52 per cent of Fe.

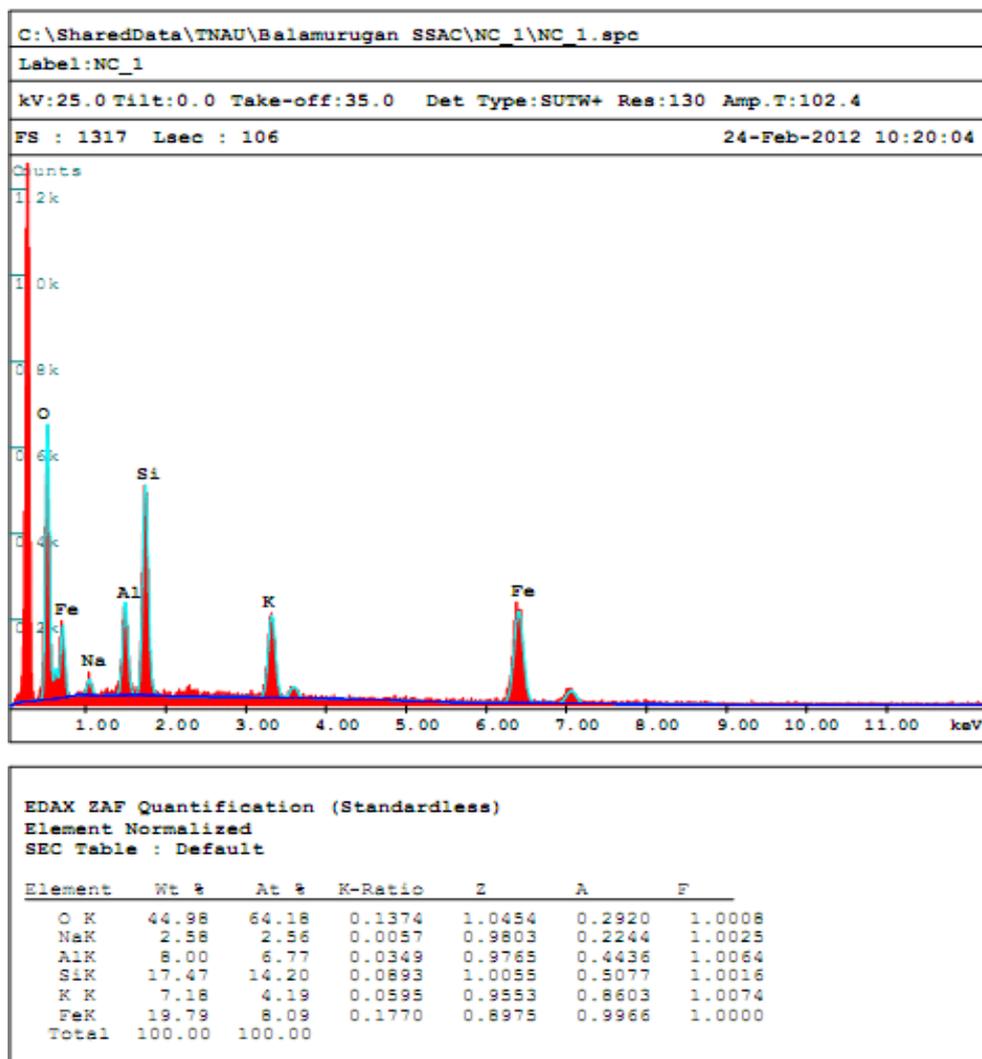


Figure 4. EDAX of NC1 (Zeolite with ZVI nanoparticles)

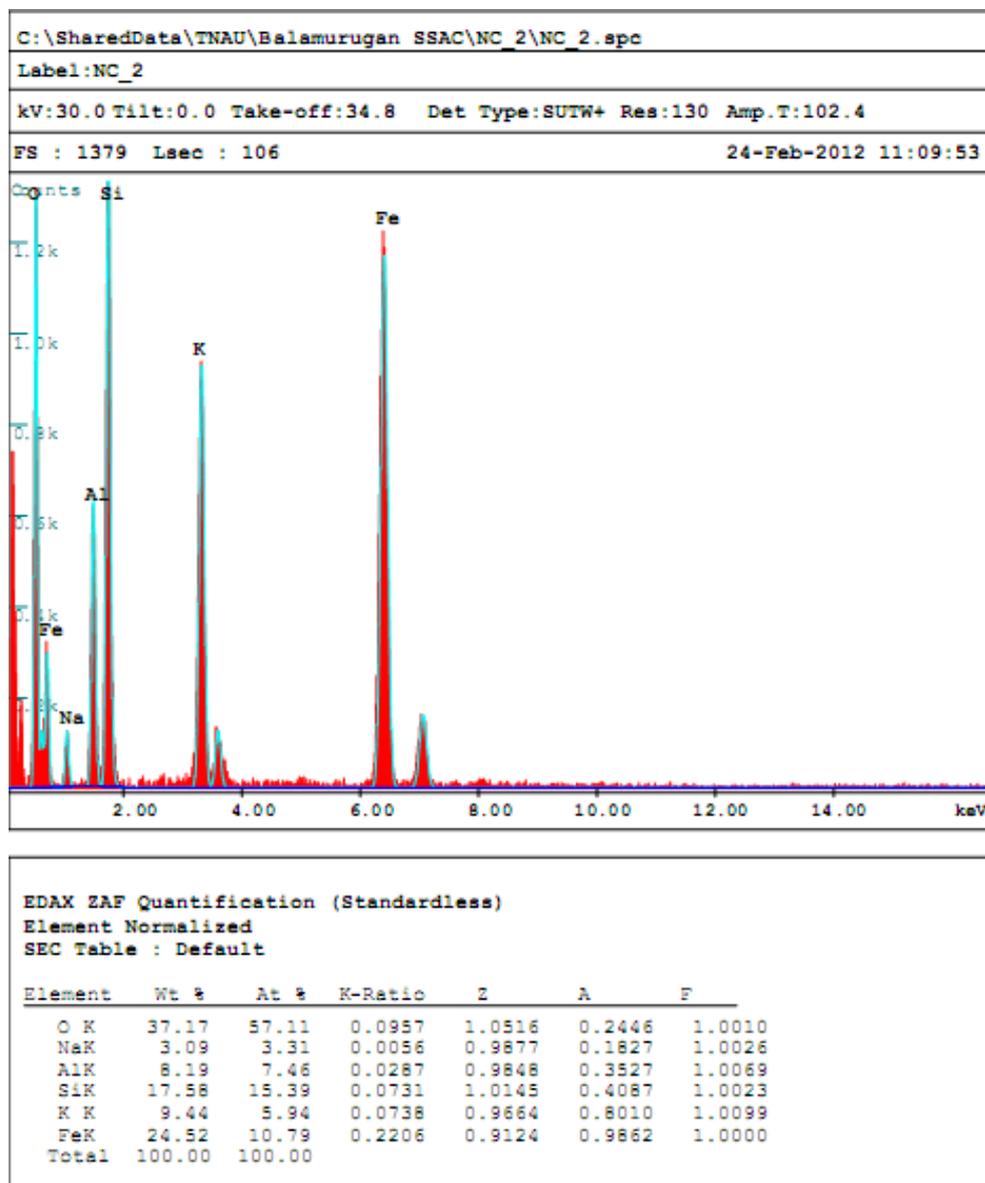


Figure 5. EDAX of NC2 (Na Y zeolite with ZVI nanoparticles)

3.4. FT-IR Spectroscopy Measurement

In this present investigation (Figure 6 & 7), the FT-IR spectrum of ZVI nanocomposites formed by zeolite and Na Y zeolite shows the absorption peaks in the regions between 3400 to 3200 cm^{-1} was characteristics of the hydroxyl (O-H) functional groups in alcohol and phenolic compounds (Singh *et al.*, 2011). Moreover, the peaks in the region between 3000 and 2850 cm^{-1} assigned to stretching vibration (-C-H-) of alkanes in the ZVI nanocomposites. Ashishkumar and Ramaprabhu (2011) also reported that the peaks at 3410 cm^{-1} indicate the O-H functional groups on the surface of nanoparticles.

The FT-IR spectra of ZVI nanoparticle spectra have bands at 1700-1780 and 2850-3000 cm^{-1} , which may be due to the

presence of hydrous components in the oxides. Abul *et al.* (2007) reported that the bands at 2870 cm^{-1} for carboxylate ion stretching, 2940 cm^{-1} for aliphatic C-H, C-H₂ and C-H₃ stretching, at 1725 cm^{-1} for C=O stretching of carboxylic acids. The weaker bands in the region of 1640 to 1550 cm^{-1} correspond to the bending vibration (N-H) of amide I (Shanker *et al.*, 2003). The peaks in the region between 1450 to 1375 cm^{-1} correspond to the bending vibration (-CH₃-) of alkanes. The large extent, band at the region of 1300 to 1000 cm^{-1} might be contributed to stretching vibration (C-N) of amines (Sathyavathi *et al.*, 2010). FT-IR spectra of nanocomposite also showed similar peak range as in ZVI nanoparticles. This confirms that the ZVI nanoparticles were attached on the surface of Zeolite and Na Y zeolite without any change in their functional groups.

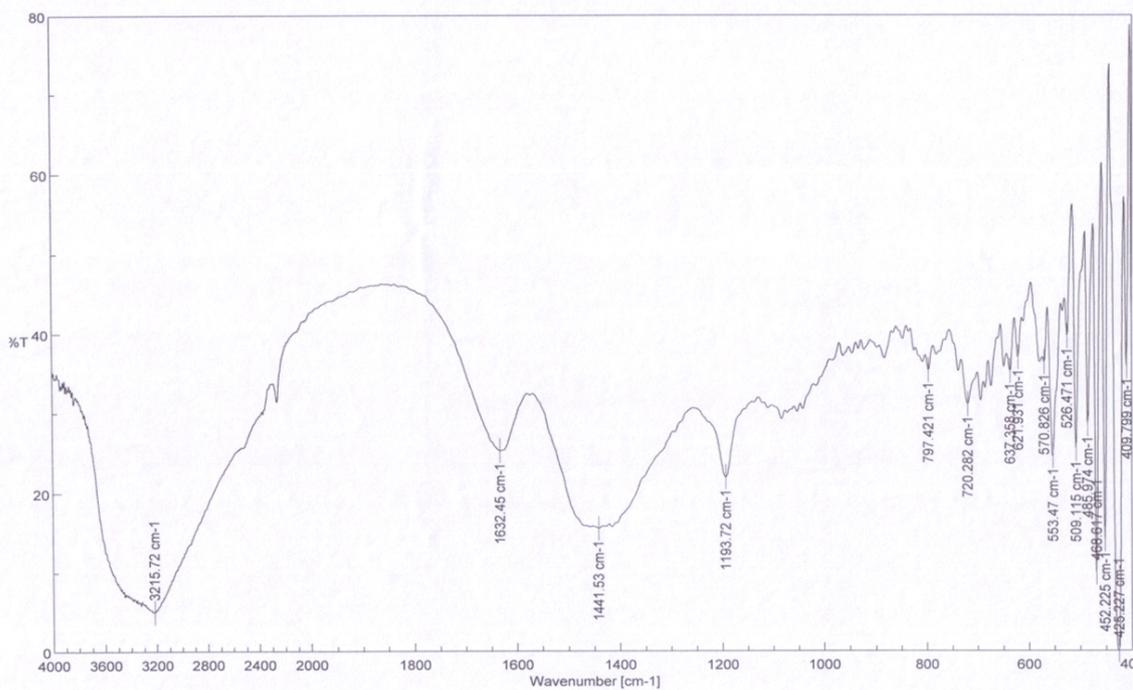


Figure 6. FT-IR spectrum NC1 (Zeolite with ZVI nanoparticles)

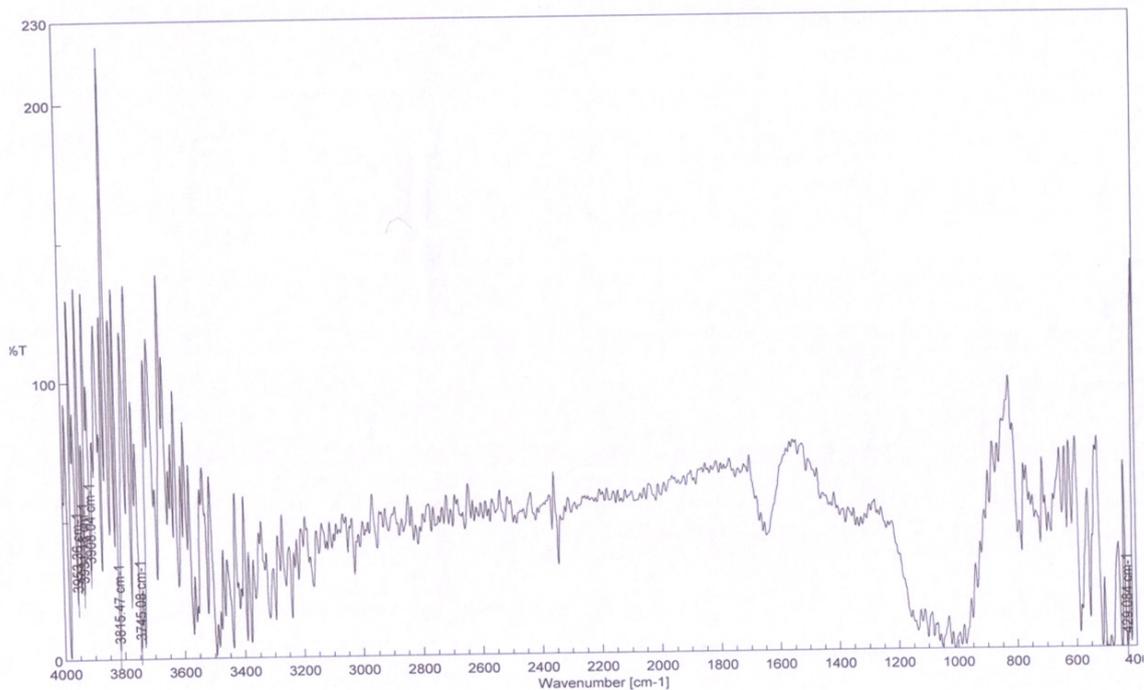
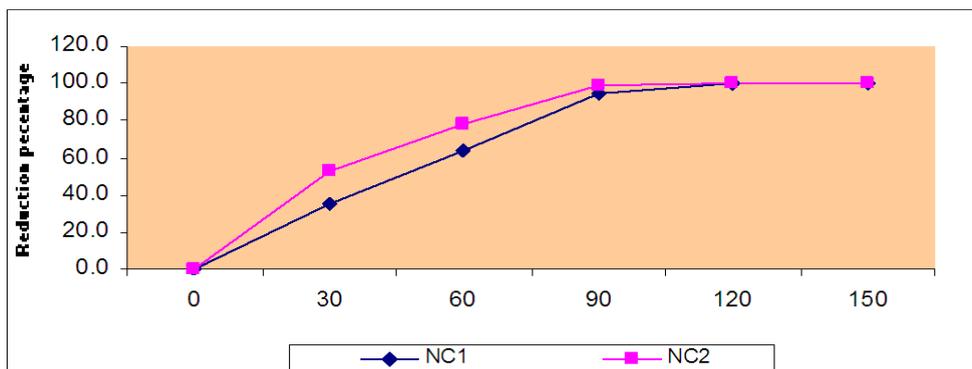
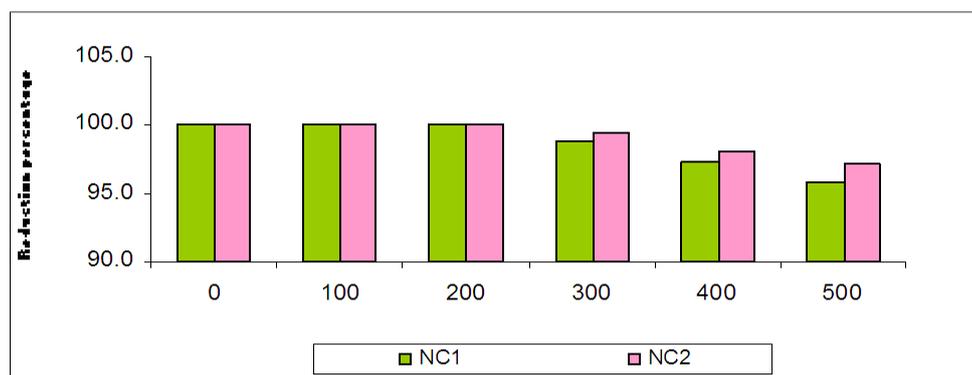


Figure 7. FT-IR spectrum NC2 (Na Y zeolite with ZVI nanoparticles)



NC1 - Nanocomposite 1; NC2 - Nanocomposite 2

Figure 8. Effect of equilibrium period on Cr (VI) reduction by nanocomposite for spiked soil



NC1 - Nanocomposite 1; NC2 - Nanocomposite 2

Figure 9. Effect of solute concentration on Cr (VI) reduction by nanocomposite for spiked soil

3.5. Cr (VI) Reduction Studies

3.5.1. Effect of Equilibrium Period

The relation between contact time and reduction efficiency of Cr (VI) shown in fig.8. The percentage reduction of Cr (VI) increased from 35.00 to 94.50 per cent in NC1 whereas, 52.5 to 99.3 in NC2 with increasing the contact time. The highest reduction efficiency was obtained at 120 min by NC1 and NC2, whereas at initial level the reduction efficiency was found to be minimum. The reason might be due to the primary Fe⁰ particles aggregates with zeolite and Na Y zeolite at initial equilibrium time. This results fall in line with the findings of Singh *et al.* (2011) and Wang *et al.* (2010).

3.5.2. Effect of Solute Concentration

The results showed (fig. 9) that the reduction efficiency of Cr (VI) decreased from 99.50 to 97.20 per cent in NC2 and 98.85 to 95.80 per cent in NC1 with increasing the initial Cr (VI) concentration from 0 to 500 mg kg⁻¹. The increasing concentration of Cr (VI) leads to reduce the reduction efficiency of ZVI nanoparticles owing to the absence of suitable catalytic surface (reactive sites) on ZVI nanoparticles.

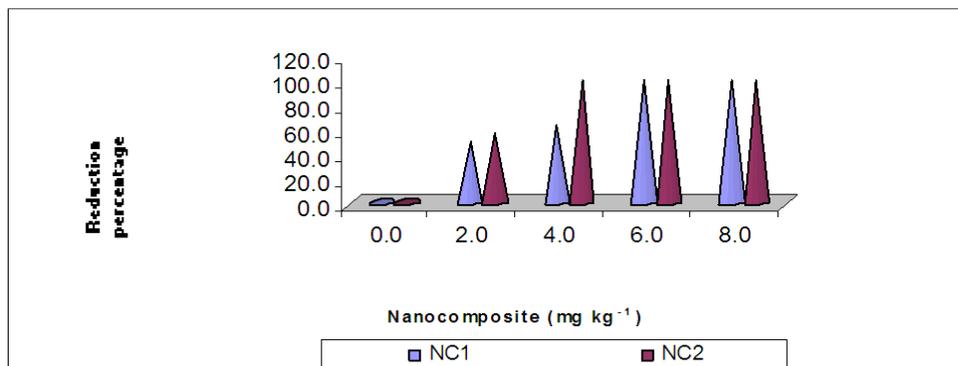
This is in accordance with the findings of Franco *et al.* (2009).

3.5.3. Effect of Nanocomposite Dosage

The relation between initial nanocomposite dosage and reduction efficiency of Cr (VI) is shown in figure 10. The percentage reduction of Cr (VI) increased from 56.50 to 100 per cent in NC2 and 50.4 to 100 per cent in NC1 when the nanocomposite dosage increased from 0.0 to 8 mg kg⁻¹. The Cr (VI) reduction efficiency increased with increase of nanocomposite dosage due to more surface area and reactive sites available for adsorption.

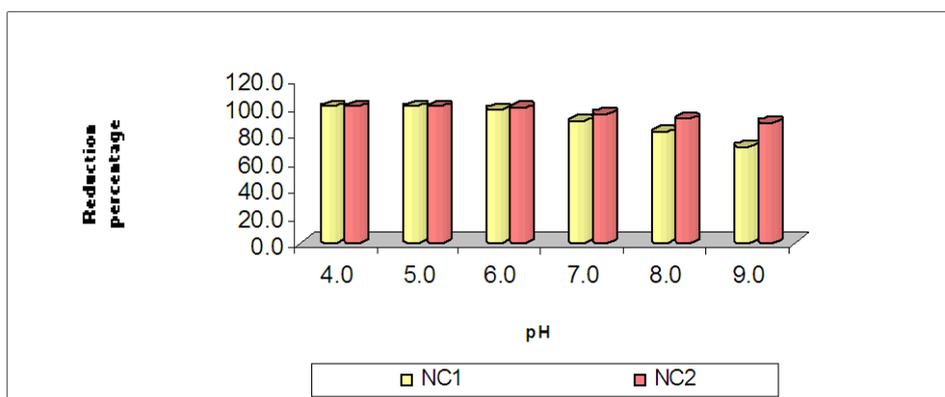
3.5.4. Effect of pH

The relation between initial pH of the solution and the reduction of Cr (VI) is shown in fig. 11. The percentage reduction of Cr (VI) decreased from 98.70 to 88.50 per cent in NC2 and 99.2 to 62.8 per cent in NC1 with increasing the initial pH. The highest reduction efficiency of Cr (VI) was achieved in pH 5. The reason may be due to production of more hydrogen ion combines with ZVI nanoparticles which favours the reduction of Cr (VI). This is in line with the findings of Rahmani *et al.* (2011).



NC1 - Nanocomposite 1; NC2 - Nanocomposite 2

Figure 10. Effect of nanocomposite dosage on Cr (VI) reduction for spiked soil



NC1 - Nanocomposite 1; NC2 - Nanocomposite 2

Figure 11. Effect of pH on Cr (VI) reduction by nanocomposite for spiked soil

4. Conclusions

Treatment of spiked soil containing hexavalent chromium was investigated under batch experiments using different zerovalent iron forms: NC1 (Zeolite with ZVI nanoparticles and NC2 (Na Y zeolite with ZVI nanoparticles). The results obtained from the experimental conditions support the conclusion that the concentration of Na Y zeolite with ZVI nanoparticles had significant effect on the reduction rate of Cr (VI) compared to zeolite with ZVI nanoparticles. The pH of the reaction mixture has a strong effect on the Cr (VI) reduction efficiency with increasing initial pH as well as with decreasing initial Cr (VI) concentration. Thus the results from the current research provides compelling evidence that the Na Y zeolite with ZVI nanoparticles may be used for *in situ* reductive efficacy of Cr (VI) contaminated spiked soil, which may lead to an innovative remediation technology is likely to be more cost effective and less environmentally disruptive.

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