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Research Article

Synthesis, characterization and application of zero valent iron nanoparticles for the removal of toxic metal hexavalent chromium [Cr(VI)] from aqueous solution

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Abstract

Hexavalent chromium is a heavy metal used in a variety of industrial applications which is highly toxic to humans, animals, plants and microorganisms. Moreover, it is a well-established human Carcinogen by the inhalation route of exposure and by the oral route of exposure. Therefore, it should be removed from contaminated waters. Its reduction to trivalent chromium can be beneficial because a more mobile and more toxic chromium species is converted to a less mobile and less toxic form. The reduction of hexavalent chromium [Cr(VI)] by nanoscale zerovalent iron (nZVI) has received considerable attention in recent years because of large surface to volume ratio. A considerable volume of research has been carried out in order to investigate the mechanism and kinetics of Cr (VI) reduction with nZVI, as well as the influence of various parameters controlling the reduction efficiency. This paper aims at synthesising zero valent iron nano particles by chemical reduction method using $FeCl_3.6H_2O$ with sodium borohydride ($NaBH_4$) as a reducer. The crystalline size of the nZVI particles was determined through XRD. Morphology of the particles was observed using SEM. The chromium stock solution was treated with nZVI by varying time and amount of nanoparticles in batch studies. And in the column studies, the chromium stock solution was treated with the scrap iron. The solution was then tested using UV-Vis spectrophotometer and the percentage removal of chromium was studied. The present experimental results revealed that Cr (VI) is considerably adsorbed on nZVI nanoparticles and it could be a cost effective method for the in situ remediation of Cr(VI).

Keywords: *nZVI- Zero valent iron nanoparticle, Cr(VI), SEM, XRD, UV-Vis spectrophotometer, scrap iron.*

1. Introduction

The field of nanotechnology is one of the most popular areas for current research and development in basically all technical disciplines. Nanotechnology is considered to be one of the most important advancements in science and technology in the past decade. At nano scale, materials exhibit unique properties that can be used for novel applications like magnetization. Additionally, nanotechnology derived products that reduce the concentrations of toxic compounds to sub-ppb levels can assist in the attainment of water quality standards and health advisories (Nora Savage *et al,* 2005). Nanoscale iron particles represent a new generation of environmental remediation technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. Nanoscale iron particles have large surface areas and high surface reactivity (Wei-xian Zhang *et al,* 2003). Research has shown that nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organo chlorine pesticides, and PCBs. Nanoparticle characterization is done by Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD). The particle size distribution of nZVI obtained in the study was 211.5 nm and was greatly influenced by the intensity and volume (Panturu *et al,* 2010). T he average iron particle diameter of nZVI particles ranges from 10-30 nm (Ponder *et al.* 2000). The particle size of iron nano particles ranged from tens to hundreds of nanometers (Sun *et al.* 2007).

Chromium (Cr) is a well-known heavy metal having wide range of applications in metal plating, leather tanning, metal corrosion inhibition, pigment production, and wood-preserving industries (Ritu Singh *et al,* 2003). The effluents from the industries contain Cr (III) and Cr (VI) at concentrations ranging from tenths to hundreds of

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mg/L. Chromium exists in primarily two-valence states, i.e., trivalent Cr (III) and hexavalent Cr (VI). Cr (III), a micronutrient important in the biological activity of insulin, is relatively stable and has low solubility in aqueous solution. In contrast, Cr (VI) is highly toxic, soluble, and mobile in the aquatic systems. Contact with chromium can result in severe health problems ranging from simple skin irritation to lung carcinoma. Therefore it should not be present in the leather fabrics. A variety of methods have been developed for the removal of chromium compounds from industrial wastewater. Moreover, Cr (VI) has been classified as a potential carcinogen, mutagen, and teratogen and has acute toxicity for different biological systems (Alebel *et al*, 2010). According to BIS (Bureau of Indian Standards), the maximum acceptable limit for Cr (VI) in drinking water is 0.05 mgL^{-1} (Ritu Singh *et al*, 2003).

Several techniques for Cr (VI) removal such as ion exchange, filtration, electrochemical precipitation, activated carbon adsorption, bioremediation, etc., have been reported in literature. However, these conventional methods are relatively expensive and complicated. In this context, zero-valent iron (Fe0) nanoparticle technology offers a potential advantage over conventional methods because of its unique physico-chemical properties, non-toxicity, and economy. A key advantage of this technique is its relative simplicity with the requirement of only two common reagents and no need for any special equipment. Furthermore, due to its nano size it can be injected and transported effectively into contaminated groundwater and aquifers for in situ treatment. The fate and transport of Fe0 nanoparticles in environment are greatly affected by the geochemical factors such as pH, dissolved oxygen, oxidation-reduction potential, and concentration of competing oxidants. Fe0 nanoparticles provide a high surface-to-volume ratio, which promotes mass transfer to and from the solid surface resulting in high potential for contaminant removal and degradation (R. Pratap Singh *et al*, 2003). As a strong reluctant, Fe0 nanoparticles can degrade a wide range of pollutants by adsorption and chemical reduction. Reduction of Cr (VI) by Fe0 nanoparticles has been investigated in various bench- and field scale studies. Fe0 rapidly reduces and immobilizes Cr (VI), accompanied by the formation of insoluble chromium compounds. In view of the above, Fe0 nanoparticles synthesized by borohydride reduction was tested for its potential to remove the Cr (VI) from contaminated ground water samples and also to determine the reaction kinetics involved in the process.

2. Materials and Methods

2.1 Preparation of nZVI

The chemicals used in this study such as $FeCl_3.6H_2O$, Sodium borohydride ($NaBH_4$) were of analytical grade. For the synthesis of nanoscale zero valent iron, 0.5406 g $FeCl_3.6H_2O$ was dissolved in a solution containing 24 ml ethanol and 6 ml distilled water and stirred well. 0.3783 g sodium borohydride was dissolved in 100 ml distilled water and added to the first solution drop wise (1drop/ 2 seconds). Slowly the solution turned to black colour. This solution mixture was stirred for 10 minutes before it was filtered under vacuum. The residue was washed thrice with 25 ml ethanol each time. The particles were dried at 50˚C in an oven overnight.

2.2 Treatment of water samples containing Cr (VI)

2.2.1 Preparation of Cr (VI) stock solution

Stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving 2.829 g of $K_2Cr_2O_7$ in 1000 ml of double distilled water. Experimental solutions of the desired concentrations 0.5 g/l, 1 g/l, 1.5 g/l, 2 g/l and 2.5 g/l of chromium were obtained by successive dilutions and Cr(VI) was determined by measuring the absorbance at a wavelength of 540 nm using UV-Vis spectrophotometer.

2.2.2 Batch Studies

The batch experiments for the reduction of Cr(VI) was performed in 250ml Erlenmeyer flasks into which synthesized nZVI particles were introduced, followed by the addition of $Cr_2O_7^{2-}$ aqueous solution. The reaction solution was stirred at a speed of 500 rpm and periodically sampled by glass syringe. The samples were filtered immediately through 0.2 μm membrane filters and analyzed for Cr(VI). The absorbance Starch stabilized Feo nanoparticles concentration used in this study was 0.05 g, 0.1 g, 0.15 g and 0.2 g.

2.2.3 Column Studies

Column experiment was carried out to investigate the removal efficiency of chromium by industrial iron chippings. The iron shaving can be considered to be zero valent iron (ZVI) because it is not oxidized. The iron shavings are obtained from local metal-processing shops. These were ground in a ball mill such that the material passes through a 2 mm screen and retains on 1 mm screen. Hexavalent chromium stock solution was prepared and column flow-through reduction experiments were conducted by passing synthetic Cr (VI) solution through a PVC column of 3 ft. height and 15 cm. internal diameter. The column is provided with a porous sieve of 1mm opening at the bottom and packed with scrap iron. Cr (VI) solution was passed drop by drop from top using a burette. After each trial, the bed was washed with distilled water. Column effluent samples were withdrawn with varied bed heights of 2 cm, 4cm, 6cm, 8cm, 10cm and with varied time and analysed.

3. Results and Discussion

3.1 Characterization

The oxidation states and phases of nZVI were checked using powder XRD with RigakuMiniflex 600. XRD pattern of stabilized nZVI samples was recorded over a 2θ range of 10 to 80˚. It was clear that the synthetic nZVI was in its zero valent state and no appearance of oxide/hydroxide shell formation was observed on the outer surfaces of the nZVI particles (Fig.3.1.1). The peak appearing at 2θ value of ~ 44.8° matches the value for nZVI reported in JCPDS (00-006-0696), indicated mainly the formation of nano iron in zero valent state.

SEM analysis was done using Cambridge Scanning Electron Microscope with EDAX attachment (CF). This instrument is used to determine the texture of crystal growth and could also indirectly used to measure the particle size of the materials. The scanning electron microscopy (SEM) image of synthesized nZVI particles is shown in the fig. 3.1.2 and 3.1.3. Results indicate that the synthesized nZVI particles show dendritic structure. Most of the nZVI particles are in nano scale (can be seen on the scale bar at the bottom right of the SEM image). Fig 3.1.2 shows evenly distributed dendritic particles approximately of 3μm in size, and Fig. 3.1.3, under higher magnification, confirms the dendritic shape and the size range of each particle. These structures increased the available surface area for reaction.

The solution was analysed using a Systronics UV-Visible Spectrophotometer-117.

The following figures show the SEM and XRD analysis results of nZVI:

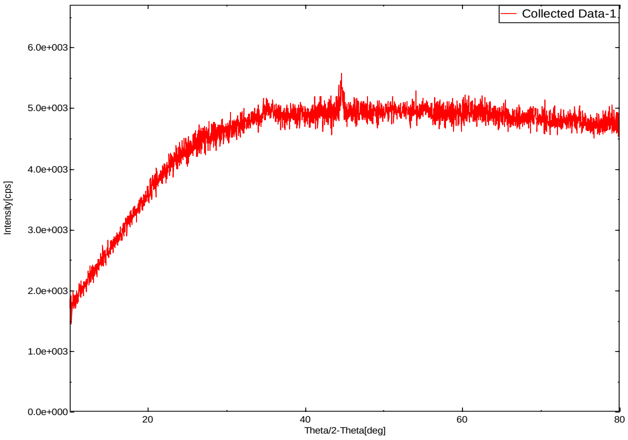

Fig. 3.1.1: XRD analysis of nZVI

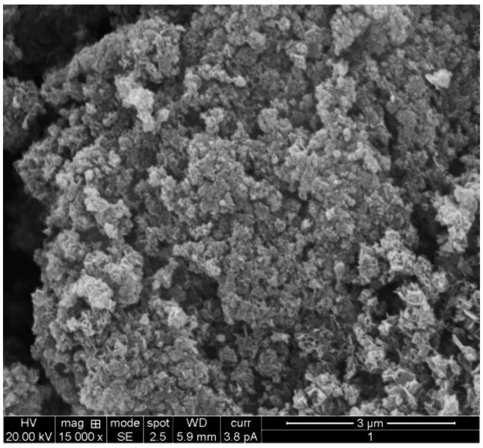

Fig. 3.1.2: SEM images of nZVI at 3 μm / 15000 X

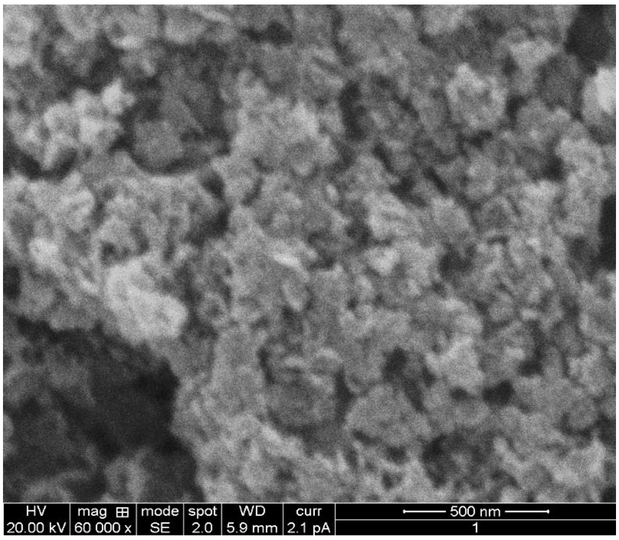

Fig. 3.1.3: SEM images of nZVI at 500 nm / 60000 X

3.2 Batch studies

The calibration curve was plotted by varying chromium concentration and noting down the absorbance values.

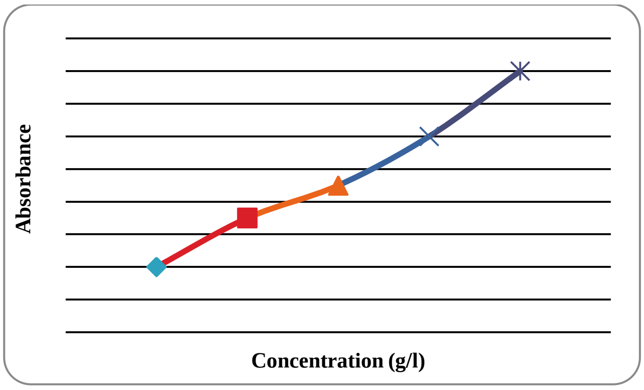

Figure 3.2.1: Calibration curve

Keeping the concentration of chromium constant, the amount of zero valent iron nanoparticles was varied and the optimum amount of zero valent iron nano particle was found out.

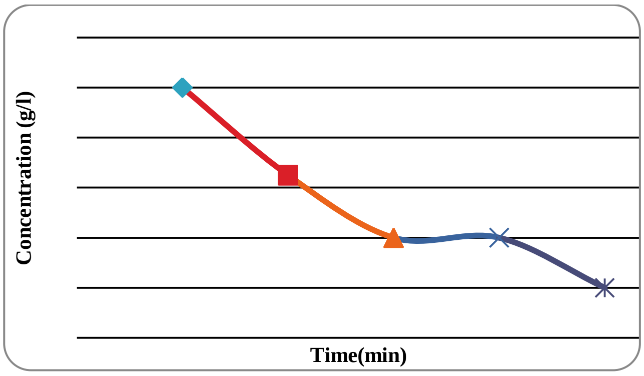

Fig. 3.2.2: Chromium: 0.5g/l, nZVI: 0.05g

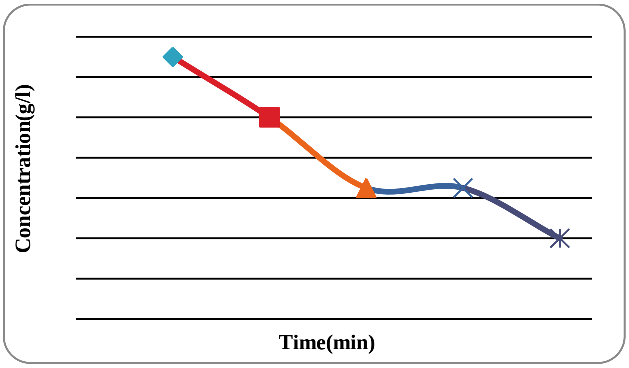

Fig. 3.2.3: Chromium: 0.5g/l, nZVI: 0.1g

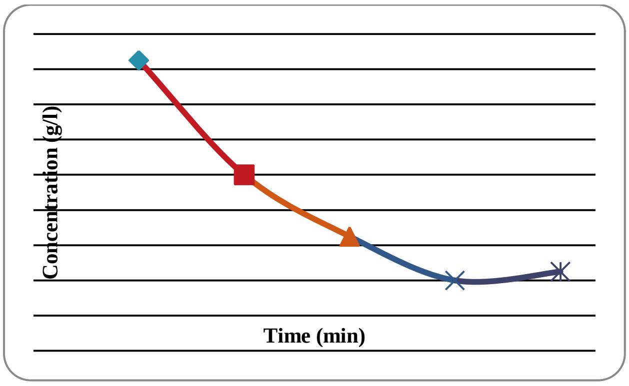

Fig. 3.2.4: Chromium: 0.5g/l, nZVI: 0.15g

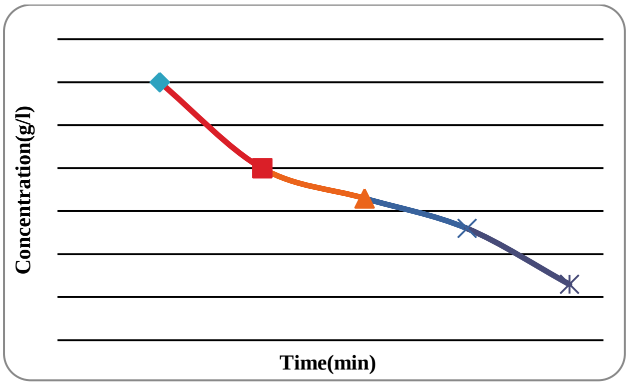

Fig. 3.2.5: Chromium: 0.5g/l, nZVI: 0.2g

From the above graphs, it was found that 0.05g nanoparticles gave highest % removal when compared with other amounts of nZVI i.e. 0.05, 0.1 g, 0.15 g and 0.2 g. Therefore 0.05 g nanoparticles were used to treat different concentrations of stock solutions and % removal v/s time graphs were plotted.

3.3 Study of % removal v/s time

The % removal v/s time values are calculated for different concentrations of chromium solution for 0.5 g of zero valent iron nanoparticles. The following graphs show the results:

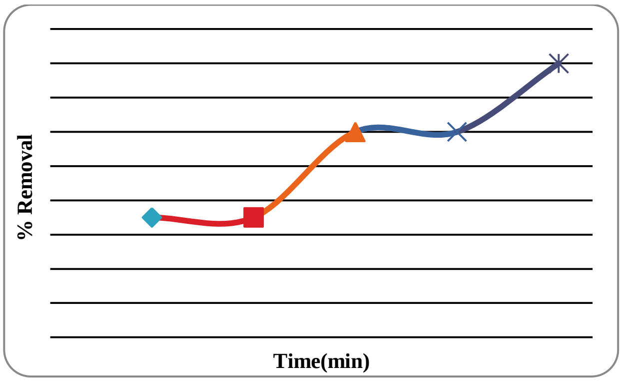

Fig. 3.3.1: nZVI: 0.05g, Cr (VI):0.1g/l

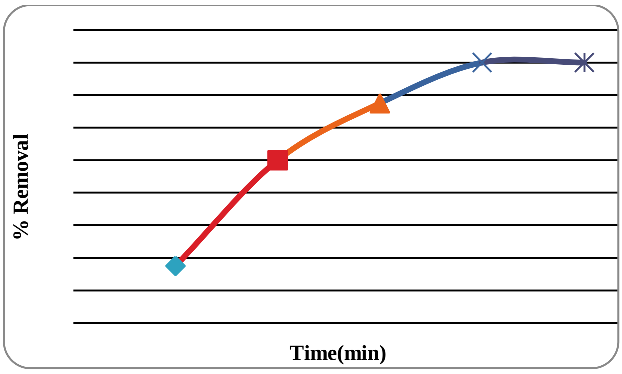

Fig. 3.3.2: nZVI: 0.05g, Cr (VI):0.2g/l

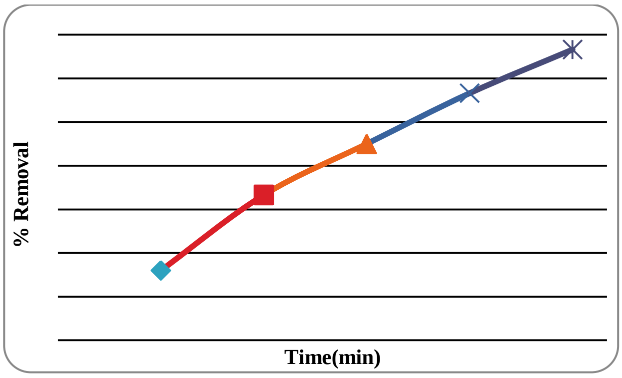

Fig. 3.3.3: nZVI: 0.05g, Cr (VI):0.3g/l

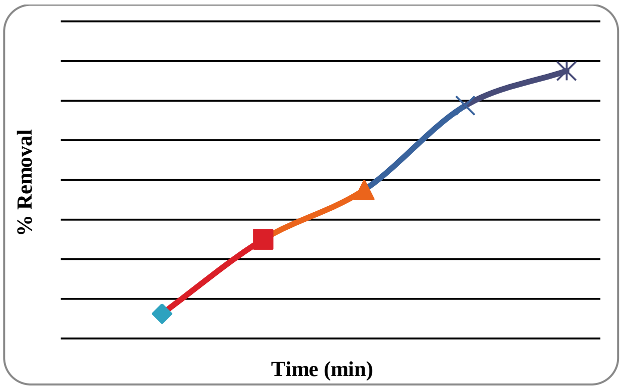

Fig. 3.3.4: nZVI: 0.05g, Cr (VI):0.4g/l

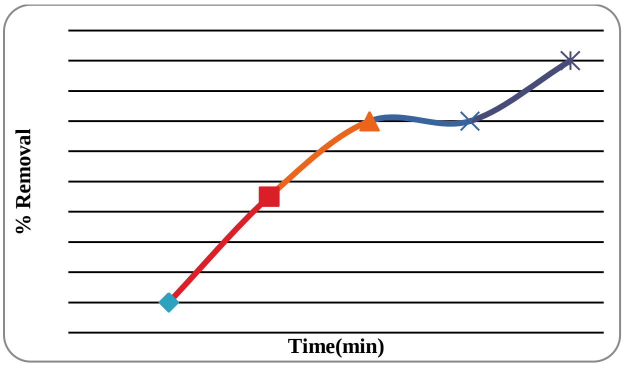

Fig. 3.3.5: nZVI:0.05g, Cr(VI):0.5g/l

% removal was calculated using the formula:

$$\%removal = \frac{C_0 - C}{C_0} x\, 100 \qquad (1)$$

Where C_0: concentration of Cr (VI) before adsorption (g/l).

C: concentration of Cr (VI) after adsorption (g/l).

From the above graphs, it was observed that the % removal was maximum at around 75 min.

3.4. Adsorption studies

The amount of adsorption capacity of nZVI nanoparticles on Cr (VI) reduction at an equilibrium state, q_e was calculated by

$q_e = (C_0 – C) \times V/M$ (2)

Where q_e (mg/g) is equilibrium adsorption capacity, C_0 and C are Cr(VI) concentration (mg/L) at an initial and equilibrium stage, respectively. V (L) is the volume of solution and M (g) is the mass of the adsorbent used.

Adsorption isotherm is fundamentally necessary to explain how solutes interact with adsorbent is therefore critical to the optimal use of adsorbents. The Freundlich isotherm model is employed in this study and the linearized form of the isotherm is as follows

$\log q_e = \log K_f + \log C$ (3)

where K_f and n are Freundlich constants.

Table 3.4: Adsorption isotherm constants for Cr(VI) reduction by nanoscale zerovalent iron

K_f	n	R^2
0.141	2.952	0.909

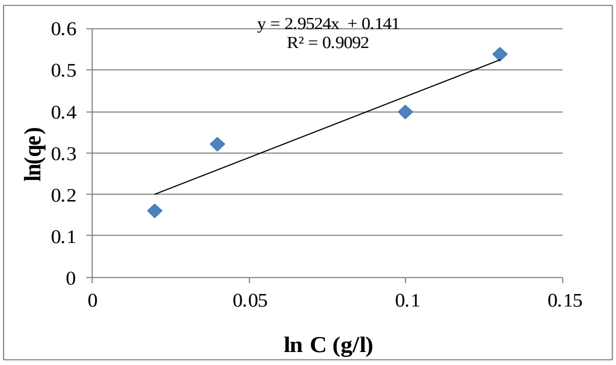

Fig. 3.4: Freundlich Isotherm

From the Fig. 3.4, the values for K and n are 0.141 and 2.952 respectively.

3.5 Column studies

In the Fig. 3.5.1, % removal of chromium was calculated and plotted against the bed height.

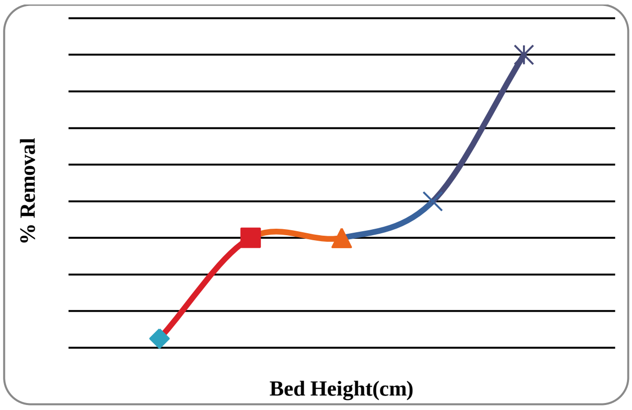

Fig. 3.5.1: % removal v/s bed height

It was observed that maximum % removal was seen for bed height of 10 cm. Then the chromium stock solution was passed through the column of bed height 10cm. The sample was collected at regular intervals of time and % removal was calculated.

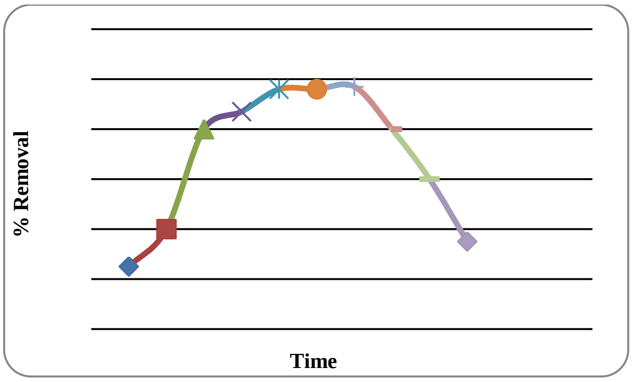

Fig. 3.5.2: column studies - % removal v/s time

From Fig. 3.5.2 it is observed that the % removal was maximum at around 105 min. The % removal then decreased along the curve.

4. Conclusion

Stable Fe0 nanoparticles were successfully synthesised in the laboratory using iron chloride and sodium borohydride. The particles were characterized with SEM and XRD. SEM Results indicate that the synthesized nZVI particles show dendritic structure and most of the nZVI particles are in nano scale. By XRD analysis, 2θ value of

~ 44.8° indicates the formation of nano iron in zero valent state .The characterization results clearly show that the present synthesis method would be useful to synthesize and could solve long pending stability issue of nZVI for its versatile applications in environmental remediation and water purification. The synthesized nano-zero valent iron material show dendritic texture of crystal growth. nZVI has several advantages such as low cost, easy preparation, and high reactivity compared to other metal nanoparticles. From the experimental results it was found that 0.05 gram nanoparticles gave highest % removal of Cr (VI) when compared to the other amounts of nZVI. Maximum % removal was found to be for 0.5 g/l chromium. Adsorption of Cr (VI) was found to fit Freundlich isotherm. In column studies, maximum % removal was found for bed height of 10cm. Maximum % removal of 97% was seen at time of 105 min. in column studies.

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