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Research Article

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A simple method for the determination of efficiency of stabilized Fe^0 nanoparticles for detoxification of chromium (VI) in water

Vemula Madhavi, Ambavaram Vijaya Bhaskar Reddy, Kalluru Gangadhara Reddy and Gajulapalli Madhavi*

Department of Chemistry, S. V. University, Tirupati, A.P., India

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ABSTRACT

Chromium is an important industrial metal used in various products/processes. Remediation of Cr contaminated sites poses both technological and economic challenges, as conventional methods are often too expensive and difficult to operate. Zero valent iron, an important natural reductant of Cr (VI), is an option in the remediation of contaminated sites, transforming Cr (VI) to essentially nontoxic Cr(III). In the present investigation, an attempt is made to study the efficiency of Fe^0 nanoparticles in remediation of Cr contaminated waters. Zero-valent iron (Fe^0) nanoparticles were synthesized, characterized, and were tested for removal of Cr (VI) from the water spiked with Cr (VI). Fe^0 nanoparticles were synthesized by ferrous sulphate by the reduction of sodium borohydride. The removal efficiency of unstabilised nano Fe^0 was compared with Carboxy Methyl Cellulose stabilized Fe^0 nano particles. It is observed that the CMC stabilizes the nanoparticles by accelerating the nucleation of atoms during the formation of Fe^0 nanoparticles and subsequently forms a bulky and negatively charged layer via sorption of CMC molecules on the Fe^0 nanoparticles, thereby preventing the nanoparticles from agglomeration. When a dose of 0.2 g/L of CMC-Fe^0 was used for a sample of Cr(VI) (40 mg/L) 100% degradation was observed but the degradation was only 50% when proceeded with unstabilised Fe^0 nano particles. The Cr (VI) removal efficiency was decreased significantly with increasing initial pH. Thus the Iron nanoparticles stabilized with CMC are of a good choice for the remediation of heavy metals in groundwater.

Key words: Agglomeration; conventional method; nucleation; remediation; stabilization; removal efficiency.

INTRODUCTION

Chromium has widespread industrial application, such as in textile dying, chemicals and pigments, wood preservation, tanning industries and electroplating for surface treatment, as well as finishing of metals, plastics and leather, etc. As a result of these applications, chromium enters in the effluent streams[1], thereby affecting the environment adversely. Cr(III) is an essential trace element needed for glucose metabolism in humans, plants and animals. It is relatively innocuous and immobile when compared to Cr (VI) compounds. Cr(VI) is extremely mobile in the environment and is toxic to humans, animals, plants, and microorganisms [2]. Because of its significant mobility in the subsurface environment, the potential risk of ground water contamination is high. The maximum concentration limit for chromium (VI) for discharge into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L.

Much research has been focused on the remediation of Cr (VI) and many treatment processes have been developed. Physico-chemical adsorption and ion exchange methods have been widely used for the remediation. The high cost and production of causing serious secondary pollution limit their use[3-4]. Many natural sorption techniques are also known to reduce Cr(VI),like clay, Zeolites etc.Sorption with surfactant based zeolite were used[5]. Bioremediation by strains of bacteria can effectively degrade Cr (VI) and is an economically favorable but the bactericidal toxicants at many waste sites would limit their growth and effectiveness[6]. Chemical reduction is known to remove Cr (VI) rapidly and effectively using reducing agent such as ferrous sulfate, sulfur dioxide, or sodium bisulfate, followed by precipitation as Cr (III). One of the disadvantages of this method is that they are expensive and release of H_2S leads to some other complications [7-8].

Fe^0 nanoparticles have long been used in the electronic and chemical industries due to their magnetic and catalytic properties. Now a days, use of Fe^0 nanoparticles is becoming an increasingly popular method for treatment of hazardous and toxic wastes and for remediation of contaminated water. Thus far, applications have focused primarily on the electron-donating properties of Fe^0. Under ambient conditions, Fe^0 is fairly reactive in water and can serve as an excellent electron donor, which makes it versatile remediation material.Fe^0 nanoparticles, due to their extremely high effective surface area, can enhance the reduction rates markedly. Nanoparticles are attractive for remediation of various contaminants because of their unique physiochemical properties, especially its high surface area over iron filings. Still today the main problem of nZVI based remediation technology is to synthesize air stable nZVI.Different chelating agents were used for stabilizing Fe0 like EDTA,DTPA,NTA,CDTA,HEDTA[9]. It was recognized that Fe^0 nanoparticles tend to rapidly agglomerate to form larger aggregates due to van der Waals and magnetic forces, rendering them undeliverable to the targeted contaminant locations[10]. To prevent aggregation of metallic nanoparticles, particle stabilization has been commonly practiced by attaching a stabilizer such as a soluble polymer or surfactant onto the nanoparticles [11]. The attached stabilizer molecules are designed to provide strong interparticle electrostatic and/or steric repulsions to overweigh the attractive Vander Waals and magnetic forces. To stabilize Fe^0 nanoparticles, two general strategies have been employed: (i) the application of stabilizers before the nanoparticles or aggregates are formed (pre-agglomeration stabilization) or (ii) to mechanically break down the formed nanoparticle agglomerates and add a stabilizer (post-agglomeration stabilization). Carboxy methyl cellulose, a “greener” for environmental applications, could apparently prevent agglomerated nanoparticles from becoming more reactive. It was proposed that CMC stabilizes the nanoparticles through the accelerating nucleation of Fe atoms during the formation of Fe^0 nanoparticles and, subsequently, forms a bulky and negatively charged layer via sorption of CMC molecules on the Fe^0 nanoparticles, thereby preventing the nanoparticles from agglomeration through electrosteric stabilization.

The present study describes the preparation of Fe^0 and CMC stabilized Fe^0 and compare their efficiencies in redox treatment study for the reduction of the hexavalent chromium present in water.

EXPERIMENTAL SECTION

Ferrous sulphate heptahydrated($FeSO_4.7H_2O$), sodium borohydride ($NaBH_4$), and potassium dichromate ($K_2Cr_2O_7$) were obtained from Merck, India. 1, 5-Diphenylcarbazide ($C_{13}H_{14}N_4O$) was procured from SD Fine Chemicals Ltd., India, sodium carboxy methyl cellulose (CMC) and ethanol (C_2H_5OH) from Merck, India. Fe^0 nanoparticles used for the study were synthesized in the laboratory by the reduction of $FeSO_4.7H_2O$ with $NaBH_4$.

The iron nanoparticles were synthesized by dropwise addition of stoichiometric amounts of $NaBH_4$ solution containing $FeSO_4{\cdot}7H_2O$ aqueous solution simultaneously with electrical stirring at ambient temperature. The ferrous iron was reduced to zero-valent iron according to the following reaction:

$$4Fe^{3+}_{(aq)} + 3BH^-_4 + 9H_2O \rightarrow 4Fe^0_{(s)}\downarrow + 3H_2BO_3 + 12H^+_{(aq)} + 6H_{2(g)}\uparrow$$

The Fe^0 nanoparticles were then rinsed several times with deionized water.

In the preparation of CMC-stabilized nanoparticles, $FeSO_{4.}7H_2O$ stock solution was added to CMC solution to yield a solution with desired concentration. Then the solution was allowed to form a complex with CMC. Here the addition of CMC serves as a dispersant and prevents the agglomeration of nanoparticles, thereby extends their reactivity. The $FeSO_4$ concentration used in this study was 1g/L and CMC concentration was 1% (w/w) of Fe[12]. In the next step Fe^{+2} is reduced to Fe^0 using stoichiometric amount of sodium borohydride solution at ambient temperature with vigorous stirring. $NaBH_4$ solids were dissolved in 0.1M NaOH because $NaBH_4$ is unstable in water and can quickly result in a loss of reducing capacity, addition of $NaBH_4$ to the $FeSO_4$ solution resulted in the rapid formation of fine black precipitate of CMC stabilized Fe^0 .

Figure 1. SEM image of Fe^0 nano particles without CMC.

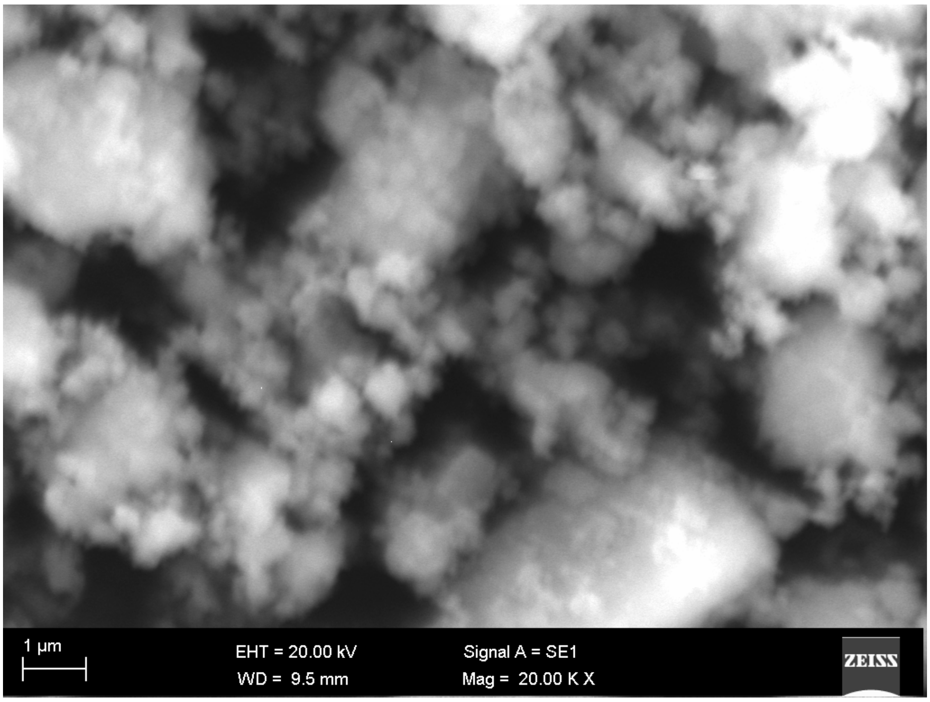
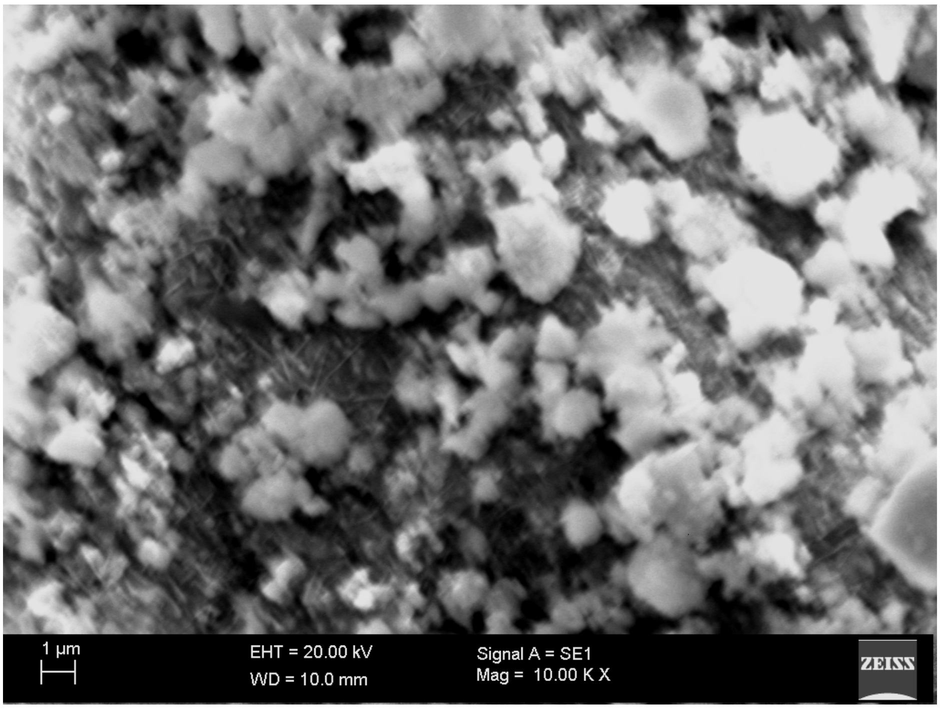


Figure 2 SEM image of Fe^0 nanoparticles with CMC



RESULTS AND DISCUSSION

Effect of nano Fe^0 particle concentration

Four Fe^0 nanoparticles concentrations were employed in this study. The increase of Fe^0 concentration greatly enhanced the removal efficiency. Total Cr (VI) was removed when the Fe^0 mass concentration was 0.4 g/L, but only 30% was removed when the Fe^0 mass concentration was 0.1 g/L.(Fig.3)It was observed in Fig.4 that at a dose of 0.1 g/L,of CMC-Fe^0 reduced total the concentrations of Cr(VI). Cr(VI) concentration decreased dramatically in the initial one minute, then slightly decreased in the later reaction. It was apparent that there was an initial sorption phase which appeared to be completed after 1 min.

Figure 3 Effect of Fe(0) nanoparticles concentration on the Cr(VI) removal

Conc. of Cr(VI) =40 mg/L

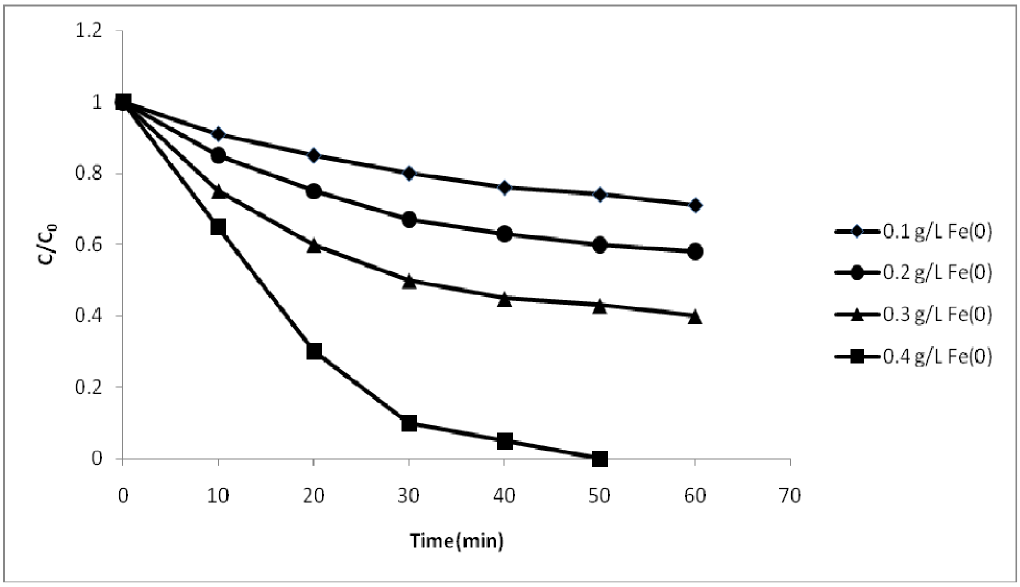
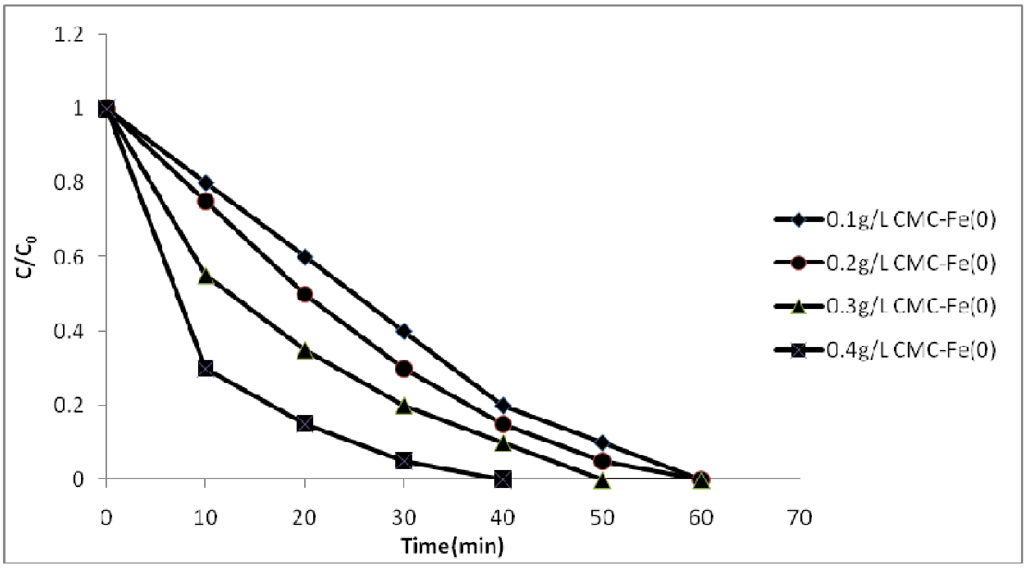


Figure 4 Effect of CMC-Fe(0) nanoparticles concentration on the Cr(VI) removal

Conc. of Cr(VI)=40 mg/L



Effect of contact time

The effect of contact time of unstabilised and CMC stabilized Fe^0 nano particles with Cr(VI) was studied(Fig.5).The reaction mixtures with 0.2 mg/L of nano particles with 40 mg/L of Cr(VI) were allowed to react for 1 h with continuous shaking. During the reaction, at predetermined time intervals (0, 10, 30… min), the reaction mixture was withdrawn and transferred to centrifuge tubes and centrifuged at 5,000 rpm for 10 min. This time was also included in total reaction period since the reaction has not stopped during centrifugation. The Cr(VI) was analyzed by the colorimetric technique.

Figure 5 Effect of contact time of unstabilized and CMC stabilized Fe(0) nano particles

Conc. Of Cr(VI)=40mg/L, Fe(0),CMC-Fe(0)=0.2g/L

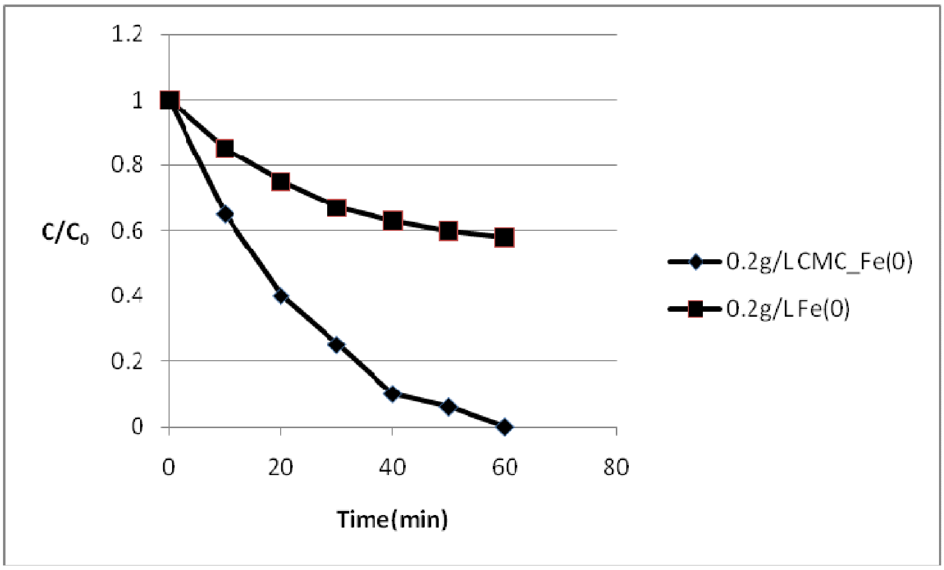
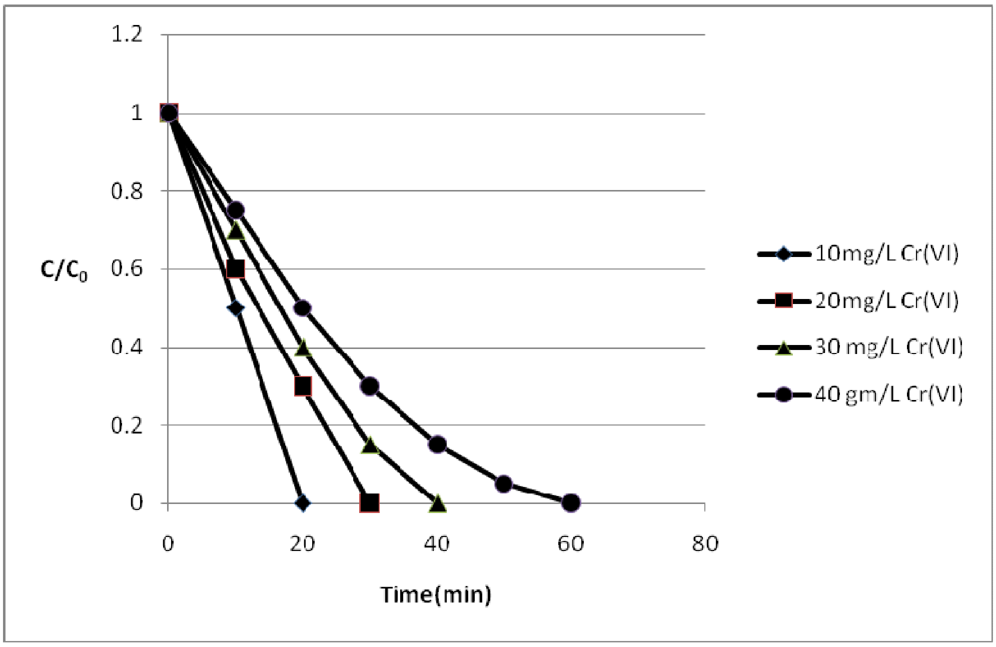


Figure 6 Effect on initial concentration of Cr(VI) on Cr(VI) removal efficiency

Conc. Of Cr(VI)=40 mg/L, conc. of CMC-Fe(0)=0.2g/L



Effect on initial Cr(VI) concentration

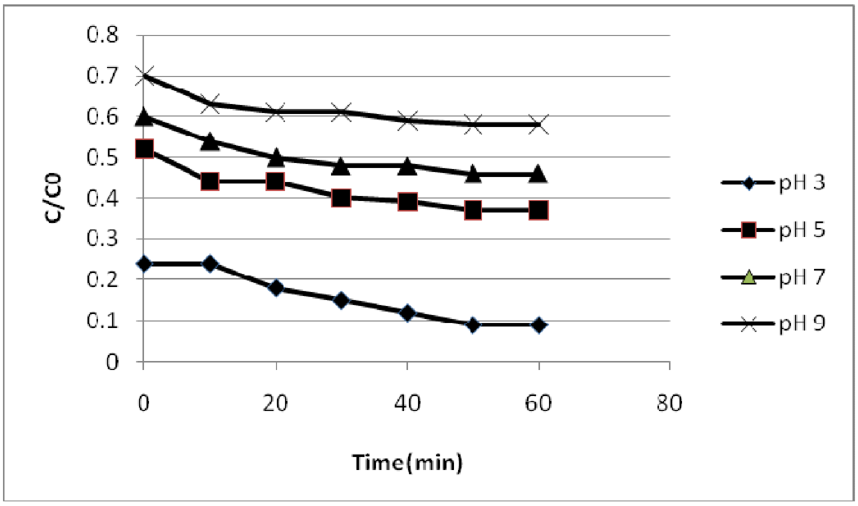
Fig.6 shows the results of batch experiments conducted at concentrations of 10 to 40 mg/L. It was observed that Cr(VI) removal efficiency was decreased when Cr(VI) was at higher concentration levels, there was a decrease of 50% in the Cr(VI) concentration of 40 mg/L, and 100 % decrease was observed with a concentration of 10 mg/L with 0.2 g/L Fe^0, but there was a decrease of 100% in Cr(VI) concentration with CMC stabilised Fe^0 nano particles at the same mass concentration even with 40 mg/L but the removal rate is prolonged.

Effect on initial pH value

The Cr(VI) removal efficiency increased significantly with decreasing pH,(Fig.7) mainly because in acid condition, the accelerated corrosion of Fe^0 enhanced the reaction rate. The experiments for analysis of Cr(VI) reduction involving CMC stabilized nano Fe^0 was carried out from pH 1 to10. Results obtained for both Fe^0 at different pH, indicate that the reduced chromium was totally converted into insoluble compounds even at pH 5 indicating that the Fe^0 nanoparticles were still with high reactivity.

Figure 7 Effect of initial pH on Cr(VI) removal efficiency

Conc. of Cr (VI) =40mg/L, Conc. of CMC-Fe (0) =0.2g/L



The above studies have shown that CMC can suppress the formation of the insoluble hydroxides containing Cr (III) due to its stabilizing properties[10]. In the present case (pH 5) the formation of a gelatinous precipitate (brown color) during remediation indicates the formation of an insoluble compound containing Cr (III)–Fe (III) and the hydrolyzed CMC. It was observed that in the pH conditions above 5 even the CMC could not able to control the formation of insoluble Cr(III) compounds. Thus better remediation was observed at and up to pH 5

CONCLUSION

The study reveals that Fe^0 nanoparticles play a key role in Cr(VI) removal through reduction and also in reducing the toxicity due to Cr. The CMC stabilized Fe^0 has higher removal efficiency. The factors like low pH, high concentration of CMC-Fe^0 and higher treatment times facilitate the removal efficiency. The study further suggests that the stabilized Fe^0 nanoparticles may be used for reduction of Cr(VI) contaminated water which may lead to an innovative remediation technology that is likely more cost effective and less environmentally disruptive.

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