Zero Valent Iron (ZVI) nanocomposite for the removal of hexavalent chromium from aqueous solution

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Abstract -A new class of nano scale zero valent iron (nZVI) particles supported on activated carbon (AC) were synthesized and the feasibility of using nanocomposite (AC+nZVI) for the removal of Cr(VI) in water was investigated through laboratory batch test. Nanocomposite was synthesized by impregnating carbon with ferrous sulfate followed by chemical reduction with NaBH4. The XRD and SEM examinations applied for determination of particle size and characterization of produced nanoparticles. Batch experiments were performed to investigate the effects of initial Cr(VI) concentration, nanocomposite concentration, pH of solution and contact time variation on the removal efficiency of Cr(VI). The chromium removal efficiency was found to be increased with decrease in initial pH of solution and increased with nanocomposite dosage and contact time. Nanocomposite presented an outstanding ability to remove Cr(VI) due to large surface area, low particle size and high surface activity. The iron nanoparticle technology may thus offer an economically and environmentally sustainable and unique solution to one of the most vexing environmental problems.

Index Terms- Nanocomposite, Hexavalent chromium, Removal efficiency, Environment, Safety
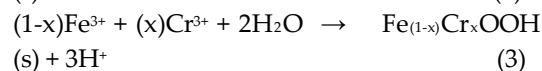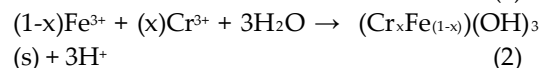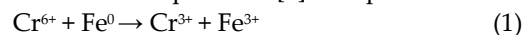
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1 INTRODUCTION

Chromium is a common pollutant found in a variety of industrial effluent, including those from the textile, leather tanning, electroplating and metal finishing industries. Chromium may be found in solution in various chemical forms viz., trivalent and hexavalent. The toxicity caused by hexavalent chromium is high and therefore its removal from effluent is necessary. The hexavalent form has been considered to be more hazardous due to its carcinogenic properties [1]. Various technologies are currently available to remove Cr (VI) including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis [2].

These methods are non-economical and have many disadvantages such as incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require disposal or treatment. In contrast, the use of reduction agent is one of the preferred methods for removal of heavy metals because

of its efficiency and low cost [3]. For this purpose in recent years, investigations have been carried out for the effective removal of various heavy metals from solution using nano zero valent iron (nZVI) as reduction agent.

The mechanisms of Cr (VI) reduction by Fe^0 is a cyclic and consists of multiple reactions of electrochemical corrosion [4]. The reduction rate of Cr (VI) by Fe^0 produces ferric ion (Fe (III)) and chromium ion (Cr (III)) (equation 1). Chromium (III) may be removed through the precipitation or co-precipitation in terms of mixed Fe (III) and Cr (III) hydroxide as shown in equation 2 [5] or equation 3.

$$Cr^{6+} + Fe^0 \rightarrow Cr^{3+} + Fe^{3+} \qquad (1)$$

$$(1-x)Fe^{3+} + (x)Cr^{3+} + 3H_2O \rightarrow (Cr_xFe_{(1-x)})(OH)_3 (s) + 3H^+ \qquad (2)$$

$$(1-x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \rightarrow Fe_{(1-x)}Cr_xOOH (s) + 3H^+ \qquad (3)$$

Direct application of nZVI particle in water treatment system may cause fast loss of nZVI particle and iron pollution due to its tiny particle size. Hence, it is necessary to load nZVI particle onto supporting materials for the treatment of pollutant. Herein, we have developed a new strategy, employing a carbon supported nZVI particle.

The objective of this study was to prepare AC supported nZVI and to test its performance for chromium removal from contaminated water. AC was used as the supporting material due to its excellent properties in mechanical strength and porous

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structures. The effects of various parameters such as initial chromium concentration, nanocomposite dosage, pH and contact time on chromium removal were also assessed.

2 MATERIALS AND METHODS

2.1 Chemicals

The reagents used in this study (FeSO₄, activated carbon, ethanol, acetone, K₂Cr₂O₇, HCl, NaOH and NaBH₄) were reagent grade and deionized water used in all preparations.

2.2 Preparation of nanocomposite

One gram of dry based carbon was equilibrated with 30 mL of 1.0 M N₂-purged ferrous sulfate solution for 3 hours. The slurry was diluted by five times using a mixture of ethanol and deionized water (v / v 1:1). 100 mL of 0.2 M NaBH₄ was then added in a drop wise manner (1.0 mL min⁻¹) into the slurry at 25 °C with magnetic stirring and N₂ bubbling. Ferrous iron (Fe^{2+}) was reduced according to the following reaction [6].

$$2Fe^{2+} + BH_4^- + 2H_2O = 2Fe^0 + BO_2^- + 2H_2 + 4H^+$$
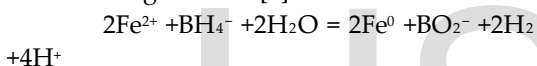
After 30 min of agitation, the activated carbon supported nZVI particle was separated from the mixture and washed with acetone for three times followed by vacuum dried at 60 °C and stored in a N₂- purged desiccator. The vacuum dried samples were used for characterization [7].

2.3 Characterizations of prepared nanocomposite

X-Ray Diffractometer (XRD) Shimazdu, model LabX-XRD-6000 was used to study the crystallinity of the nanocomposite. A Scanning Electron Microscopy (SEM) JEOL, model JSM-6390 was used to investigate the surface morphology of prepared nanoparticles.

2.4 Batch experiments

Batch experiment was conducted to evaluate the effect of the following parameters on the removal of Cr (VI) by carbon supported nZVI particles: initial solution pH, initial chromium concentration, nanocomposite concentration and contact time. A solution of K₂Cr₂O₇ with the concentration of 1000 ppm in deionized water was used as stock solution of Cr (VI). Experimental solutions of Cr (VI) were obtained by dilution from a stock solution (1000 ppm) into deionized water and 0.1 M NaOH or HCl was used to adjustment of pH and controlled by pH meter. In batch experiments, 100 ml of known concentration of solution were performed in 250 ml Erlenmeyer flask fitted with rubber cork. The experiments were done by different concentration of nanocomposite (0, 0.5, 1, 2, 3 and 4 g L⁻¹), initial Cr (VI) concentration (25, 50, 75 and 100 mg L⁻¹) and initial pH (3, 4, 5, 6, 7, 8, 9 and 10) in different time interval (0, 10, 20, 30, 40 50 and 60 min). All the experiments were performed in triplicate and carried out in a thermostatically controlled shaker at 250 rpm agitation speed and 25°C of constant temperature. After given period of time the sample filtered through 0.22 μm membrane filter and analyzed for Cr (VI). The residual Cr (VI) was analyzed by using 1,5-diphenylcarbazide and by UV-Vis spectrophotometer, (ELICO-SL-150) at a wavelength of 540 nm [8].

3 RESULTS AND DISCUSSION

3.1 Characterizations of nanocomposite

The XRD diffractogram of the nanoparticle had only a characteristic 2θ value of 48.6° was found (Fig.1). These diffraction patterns indicate that the iron present in the sample is mainly in its zero-valent state and all zero-valent irons are in a single-phase cubic closet-packed structure. The other broad peaks 28° and 46° were characteristics of graphite crystallite of AC.

The SEM images of the nanoparticle are shown in fig.2. It can be seen that the supported nZVI particles in the pores of AC are needle shaped and the particle size is approximately 11-20 nm. It can be also seen that the spherical-like white nZVI particles were crystalline in nature and these particles were well-dispersed in the AC matrix. However, as for nanocomposite lots of nZVI particles not only deposited on the surface, but also in the mesopores and macrospores of AC. Similar, observation has also been reported by other investigators in carbon supported zero valent iron particles[7].
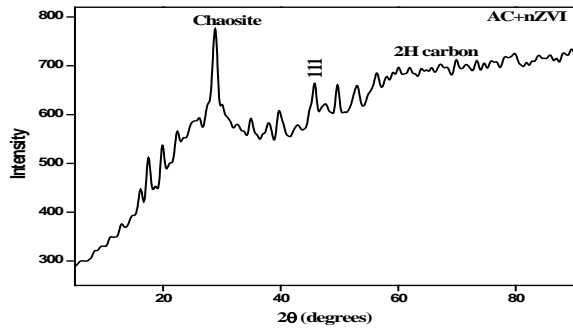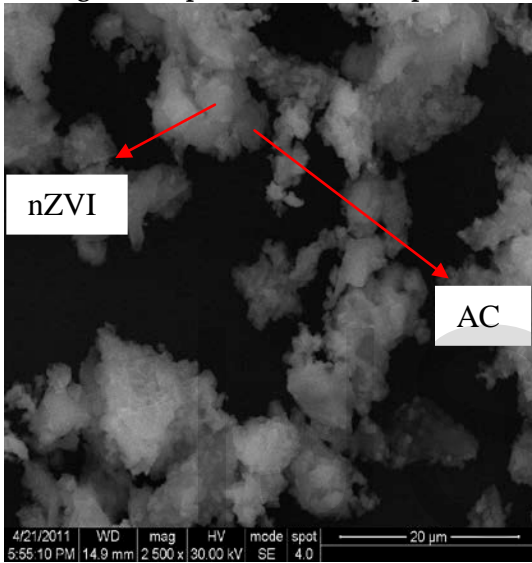
Fig. 1 XRD pattern of nanocomposite

Fig. 2 SEM microimage of nanocomposite

3.2 Effect of contact time on chromium removal

Contact time is one of the effective factors in batch studies. In this stage, all of the parameters except contact time, including temperature (25°C), nanocomposite dose (2 g L^{-1}), pH (3), initial chromium concentration (75 mg L^{-1}) and agitation speed (250 rpm) were kept constant. The effect of contact time on chromium removal efficiency showed in fig. 3. The results showed that after 40 minutes of contact time, over 98.9 percent of Cr (VI) in the solution has been removed by nanocomposite (Table.1). Considering the removal efficiency of Cr (VI) with contact time, it can be concluded that 40 minutes of contact time is enough to remove over than 98 per cent of Cr (VI) in solution and 50 minutes of contact time is enough for complete removal. It showed that the rate of uptake was rapid in the early

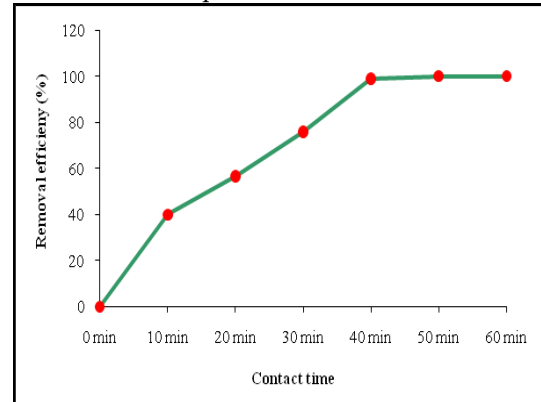stages but gradually decreased and became constant when equilibrium was reached.

Fig.3 Effect of contact time on the removal of Cr (VI)

(Temperature = 25 ^{0}C, agitation speed = 250 rpm, initial Cr (VI) concentration= 75 mg L^{-1}, nanocomposite = 2 g L^{-1}, pH = 3)

Table 1. Effect of contact time on chromium removal by nanocomposite

Sl No.	Equilibrium period (min)	Residual Cr (VI)* concentration (mg L^{-1})	Removal percentage
1	0	75.0	0.0
2	10	45.0	40.0
3	20	32.6	56.5
4	30	18.1	75.9
5	40	0.77	98.9
6	50	BDL	100.0
7	60	BDL	100.0

**Constant factors:** Temperature=25 ^{0}C, agitation speed = 250 rpm, nanocomposite dosage - 2 g L^{-1}, pH - 3, Cr concentration: 75 mg L^{-1}

BDL- Below Detectable Level

3.3 Effect of initial chromium concentration on chromium removal

The concentration of Cr (VI) in solution determines the toxicity of the solution. Therefore, the effect of initial concentration of Cr (VI) on the removal efficiency of Cr (VI) by nanocomposite was investigated. The experiments were done with variable initial chromium concentration (25, 50, 75 and 100 mg L^{-1}), constant temperature (25 °C), pH (3), agitation speed (250 rpm), contact time (40 minutes) and 2 nanocomposite dose (2 g L^{-1}). The Cr (VI) removal efficiency after different contact times

were calculated and plotted against contact times (Fig.4). As in table. 2, chromium removal efficiency increased inversely with the concentration of initial Cr (VI), 93.2 per cent at concentration of 100 mg L^{-1} and 100 per cent at concentration of 25 mg L^{-1}. In case of low chromium concentrations, the ration of the initial number of moles of chromium ions to the available surface area of adsorbent is large and subsequently the fractional adsorption becomes independent of initial concentration. However, at higher concentrations, the available sites of adsorption become fewer and hence the percentage removal of metal ions which depends upon the initial concentration decreases [9].
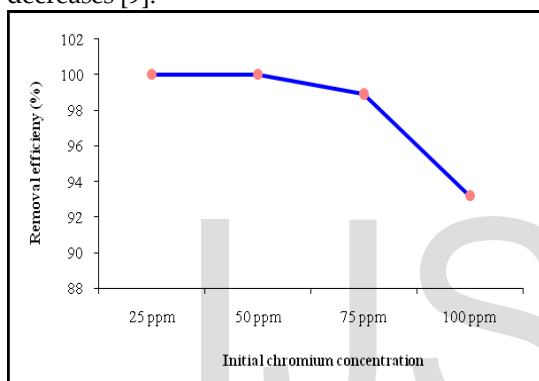
Fig.4 Effect of initial chromium concentration on the removal of Cr(VI)

(Temperature = 25 ^{0}C, agitation speed = 250 rpm, pH = 3, nanocomposite = 2 g L^{-1}, contact time = 40 minutes)

Table 2. Effect of initial chromium concentration on chromium removal by nanocomposite
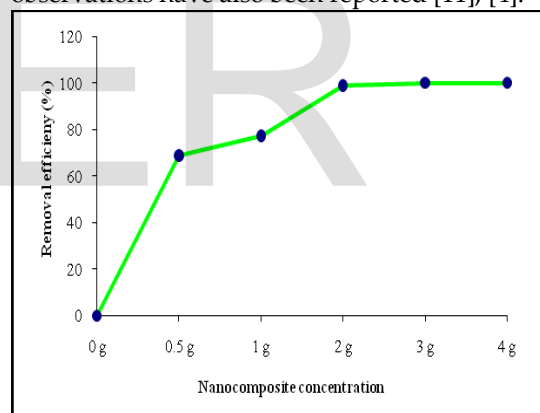
Sl No.	Initial Cr (VI) concentration (mg L^{-1})	Residual Cr (VI)* concentration (mg L^{-1})	Removal percentage
1	25	BDL	100.0
2	50	BDL	100.0
3	75	0.77	98.9
4	100	6.80	93.2

Constant factors: Temperature = 25 ^{0}C, agitation speed = 250 rpm, nanocomposite dosage - 2 g L^{-1}, pH- 3, time: 40 min
BDL- Below Detectable Level

3.4 Effect of nanocomposite dose on chromium removal

At this stage, to optimize the nanocomposite dose for the removal of Cr (VI) from the solution, batch studies were done under the conditions described at previous stage with constant temperature of 25^{0}C, agitation speed of 250 rpm, pH of 3, initial Cr (VI) concentration of 75 mg L^{-1}, contact time of 40 minutes and variable nanocomposite dose (0.5, 1, 2, 3 and 4 g L^{-1}).

The removal efficiency of Cr (VI) against the amount of nanocomposite used was shown in fig.5. According to the results, 2 g L^{-1} of nanocomposite is enough for more than 98 per cent removal of Cr (VI) with the high initial concentrations of up to 75 mg L^{-1} (table.3). It can be seen that the chromium removal efficiency increased with increase in nanocomposite dose, since contact surface of adsorbent particles increased and it would be more probable for $HCrO_4^-$ and $Cr_2O_7^-$ ions to be adsorbed on adsorption sites and thus adsorption efficiency increased [10]. Similar observations have also been reported [11], [4].

Fig.5 Effect of nanocomposite concentration on the removal of Cr (VI)

(Temperature = 25 ^{0}C, agitation speed = 250 rpm, initial Cr (VI) concentration= 75 mg L^{-1}, pH = 3, contact time = 40 minutes)

Table 3. Effect of nanocomposite on chromium removal

Sl. No	Nano composite (g L^{-1})	Residual Cr (VI) * concentration (mg L^{-1})	Removal percentage
1	0.0	75.0	0.0
2	0.5	23.5	68.9

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3	1.0	19.3	77.2
4	2.0	0.77	98.9
5	3.0	0.0	100.0
6	4.0	0.0	100.0

Constant factors: Temperature = 25 ^{0}C, agitation speed = 250 rpm, Cr concentration: 75 mg L^{-1}, pH - 3, time: 40 min

BDL- Below Detectable Level

3.5 Effect of pH on chromium removal

The effect of pH was determined by studying removal of Cr (VI) at temperature of 25^{0}C, agitation speed of 250 rpm, initial Cr (VI) concentration of 75 mg L^{-1}, contact time of 40 minutes with nanocomposite dose of 2 g L^{-1} over a pH range of 3 to 10. The experimental results on the effect of pH on chromium removal efficiency were presented in Fig. 6.

The percentage removal of Cr (VI) decreased from 98.3 to 33.2 per cent with increasing the initial pH (table.4). The pH dependence of metal adsorption can largely be related to type and ionic state of the functional group present in the adsorbent and also to the metal chemistry in the solution [12]. In lower pH, the dominant form of Cr (VI) is $HCrO_4^-$ and the surface of the adsorbent is positively charged. By increasing of pH, the $HCrO_4^-$ species shifts to other forms CrO_4^{2-} and $Cr_2O_7^{2-}$. The decrease in adsorption of Cr (VI) by increasing the pH is due to the competition between the anions CrO_4^{2-} and OH^- [13]. Similar observations have been reported too [14].
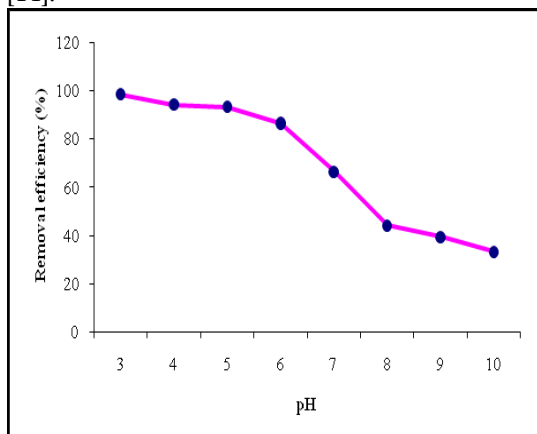
Fig.6 Effect of pH on the removal of Cr (VI)
(Temperature = 25 ^{0}C, agitation speed = 250 rpm, initial Cr (VI) concentration= 75 mg L^{-1},

nanocomposite = 2 g L^{-1}, contact time = 40 minutes)

Table 4. Effect of pH on chromium removal by nanocomposite

Sl No.	pH	Residual Cr (VI) * concentration (mg L^{-1})	Removal percentage
1	3	1.24	98.3
2	4	4.40	94.1
3	5	5.13	93.1
4	6	10.2	86.4
5	7	25.3	66.3
6	8	42.1	43.9
7	9	45.6	39.2
8	10	50.1	33.2

Constant factors: Temperature = 25 ^{0}C, agitation speed = 250 rpm, nanocomposite dosage - 2 g L^{-1}, Cr concentration: 75 mg L^{-1}, time: 40 min

BDL- Below Detectable Level

4 CONCLUSIONS

Nanocomposite found to be suitable adsorbent for the removal of Cr (VI) from aqueous solution. The adsorption was found to be strongly dependent on contact time, initial Cr (VI) concentration, pH and nanocomposite dose. The removal efficiency of Cr (VI) was increased by increasing the nanocomposite amount and was decreased by increasing chromate initial concentration. The uptake of chromium was maximum at 40 minutes of contact time and this is enough to remove more than 98 per cent of chromate ions from aqueous solution. The pH of the aqueous solution is crucial to the adsorption of Cr (VI) possibly because the presence of various Cr (VI) species and the surface charge of adsorbent. However, the removal efficiency increased significantly with decreasing initial pH. Finally, the results revealed that the nanocompostie is a faster and cost effective solution for treating chromium in aqueous solutions.

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