

## Effects of physicochemical factors on Cr(VI) removal from leachate by zero-valent iron and $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles

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### ABSTRACT

The effects of nanoparticle dosage, initial hexavalent chromium concentration, pH value, reaction temperature, and initial concentration of humic acid (HA) on chromate (CrO<sub>4</sub><sup>2-</sup>) removal from landfill leachate by nanoscale zero-valent iron (NZVI) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles were examined in the present investigations. The Cr(VI) removal rate decreased as the initial Cr(VI) concentration and the reaction temperature increased, whereas corresponding removal rate by NZVI was higher than that of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The optimum pH for the removal of Cr(VI) by NZVI was found to be 5.0 and more than 99.0% of Cr(VI) was removed within 5 h. However, the removal rate by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> decreased as pH increased. Presence of HA resulted in substantial reduction in the rate and extent of Cr(VI) removal by NZVI, whereas Cr(VI) removal rate by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> did not significantly decrease as HA concentration increased from 0.5 g/L to 3.0 g/L. Increasing the dosage of nanoparticles enhanced the rate constant and the removal of Cr(VI) by NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> followed pseudo-first-order reaction kinetics. The information should be very useful for the successful application of NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> for the treatment of groundwater or raw wastewater.

**Key words** | hexavalent chromium, humic acid, nanoscale zero-valent iron

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### INTRODUCTION

As detailed by numerous researchers, if not handled properly landfill leachate can be a serious environmental problem through the discharge heavy metals (HMs) (Poon & Chen 1999). Chromium is one of the common HMs in landfill leachate. For example, it has been reported that in central Taiwan, there are more than 300 landfills with high concentrations of Cr in leachate, typically containing 0.6–20.0 mg Cr/L (Fan *et al.* 2006; Peng *et al.* 2006). Chromium is a potential carcinogen and can cause both short term and long term adverse effects to humans, animals, and plants. The U.S. EPA maximum contaminant level for chromium in drinking water is 0.1 mg/L (Code of Federal Regulations). Chromium in natural water exists in two stable states, hexavalent (Cr(VI)) and trivalent (Cr(III)). Cr(VI) exists primarily as salts of H<sub>2</sub>CrO<sub>4</sub>, HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> depending on the pH. H<sub>2</sub>CrO<sub>4</sub> predominates at pH less than 1.0, HCrO<sub>4</sub><sup>-</sup> at pH between 1.0 and 6.0, and CrO<sub>4</sub><sup>2-</sup> pH above about 6.0. At pH > 3.5,

hydrolysis of aqueous Cr(III) yields trivalent chromium hydroxyl species (CrOH<sup>2+</sup>, Cr(OH)<sub>2</sub><sup>+</sup>, Cr(OH)<sub>3</sub> and Cr(OH)<sub>4</sub><sup>-</sup>) (Mohan & Pittman 2006). Cr(VI) species such as chromate (CrO<sub>4</sub><sup>2-</sup>, HCrO<sub>4</sub><sup>-</sup>) and dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>) are highly soluble and mobile in aqueous solution and are of great environmental concern.

Due to the extremely small particle size, large surface area, and high reactivity, NZVI and hematite ( $\alpha$ ,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles have been introduced into water treatment processes to remove numerous heavy metals with a much higher efficiency than normal iron powders (Ponder *et al.* 2000; Cao & Zhang 2006; Kanel & Choi 2007; Magalhães *et al.* 2009).

We believe that hexavalent chromium (Cr(VI), e.g. as chromate CrO<sub>4</sub><sup>2-</sup>) undergoes a reductive reaction in NZVI systems that involves reduction of dissolved chromate (CrO<sub>4</sub><sup>2-</sup>) to insoluble Cr(III) followed by precipitation of Cr(OH)<sub>3</sub> or coprecipitation of Cr(III) with Fe(III)

oxides/hydroxides (Li *et al.* 2008). It is well known that Fe(III) oxide/hydroxide sorption plays an important role in the procedure. Fe<sub>2</sub>O<sub>3</sub> nanoparticles have also been used for Cr(VI) removal from wastewater, especially because of its superior catalytic activity and the large specific surface area of the nanoparticles. Some studies have shown the performance and mechanism of Cr(VI) adsorption by maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles (Hu *et al.* 2005). Various magnetic nanoparticles have been used for removal of Cr(VI) and the adsorption capacities followed the order: MnFe<sub>2</sub>O<sub>4</sub> > MgFe<sub>2</sub>O<sub>4</sub> > ZnFe<sub>2</sub>O<sub>4</sub> > CuFe<sub>2</sub>O<sub>4</sub> > NiFe<sub>2</sub>O<sub>4</sub> > CoFe<sub>2</sub>O<sub>4</sub> (Hu *et al.* 2007). Recently, tar decomposed on the hematite surface and reacted with  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to produce carbon/Fe composites, which showed high activity to reduce Cr(VI) in aqueous medium (Magalhães *et al.* 2009). However, despite the successful application of NZVI and hematite nanoparticles in removing various contaminants from the water systems, there have not been extensive and comparative studies reporting effects of environmental factors on the removal of Cr(VI) from landfill leachate using both NZVI and hematite nanoparticles. As such, to look for a cheaper and more effective adsorbent for Cr(VI) removal, NZVI and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles were considered.

In this work, experiments were conducted to study the effects of physicochemical factors including nanoparticles loading, initial concentration of Cr(VI), pH value, reaction temperature, and initial concentration of HA on chromate (CrO<sub>4</sub><sup>2-</sup>) removal. Kinetics of Cr(VI) removal was also studied and the Cr(VI) removal performances were compared between NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles under different conditions. The main objectives of our research were to (1) characterize NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (2) compare Cr(VI) removal performances between NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles, and (3) study kinetics of Cr(VI) removal from landfill leachate.

## EXPERIMENTAL METHODS

NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were obtained from Nanjing Emperor Nano Material Co. Ltd. NZVI particles were pretreated with citric acid to eliminate their surface passivator. Briefly, NZVI was soaked with citric acid

(3.5%, w/w) solution for 24 h with mild stirring at ambient temperature. Solids were washed with deionized water and anhydrous ethanol at least two times, and finally dried at 50°C. The whole process was carried out in a nitrogen atmosphere.

All experiments were performed using a dilute simulated landfill leachate, and final concentrations of Cr(VI) and HA in the solution were 20 mg/L and 1.0 g/L, respectively. The pH value of the leachate was 6.7.

Effects of initial concentration of Cr(VI) (20, 50, 100, 200 mg/L), pH values (3.0, 4.0, 5.0, 6.0, 7.0, and 8.0), reaction temperature (20, 25, 30, and 35°C), and initial concentration of HA (0.5, 1.0, 2.0, and 3.0 g/L) on the removal of Cr(VI) were studied. Kinetics of Cr(VI) removal by NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were performed using leachate (20 mg/L Cr(VI)) treated with varying NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> solid concentrations (0.5, 1.0, 2.0, and 3.0 g/L). These studies were conducted using the procedure reported by Ponder *et al.* (2000). All experiments were performed in duplicate.

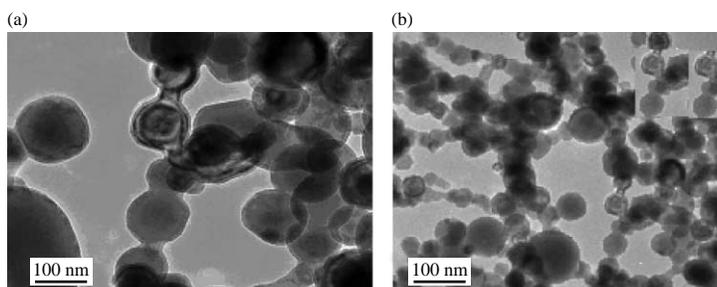
## ANALYTICAL METHODS

Morphological analyses of NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were performed by transmission electron microscope (TEM) using a Tecnai G2F20 microscope (Li *et al.* 2008). The specific surface areas ( $S_{\text{BET}}$ ) of NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> were measured by Brunauer–Emmett–Teller (BET) N<sub>2</sub> method. Zeta potentials of NZVI and hematite nanoparticles were determined using a micro-electrophoresis instrument (JS94G<sup>+</sup>, Zhongchen, China). The concentration of HA was measured using a UV/visible spectrophotometer UV-2800 at 254 nm (Tufenkci *et al.* 2006). For the solution containing chromate, the applied wavelength was 230 nm to avoid interference. The Cr(VI) concentration in the solution was determined using the spectrophotometer and by the diphenylcarbazine method (GB/T7467-1987, China).

## RESULTS AND DISCUSSION

### TEM characterization

TEM images of NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> are shown in Figure 1. Figure 1(a) shows that NZVI has very thin layers of oxide



**Figure 1** | TEM image of p-NZVI (a) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (b). (The scale bar represents 100 nm).

shells with distinguishable gray or dark portions inside due to Fe. The main compound on the NZVI surface was iron ferrihydroxide (Cao & Zhang 2006). The particles are nearly spherical in shape and uniform in size with a mean diameter of 65.3 nm. It was also observed from Figure 1(a) that NZVI formed a chainlike, aggregated structure because of its natural magnetism. Figure 1(b) revealed that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were multidispersed with an average diameter of around 30 nm and also formed a chainlike structure because of its natural magnetism. The specific surface areas of NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles are 32.8 and 58.6 m<sup>2</sup>/g.

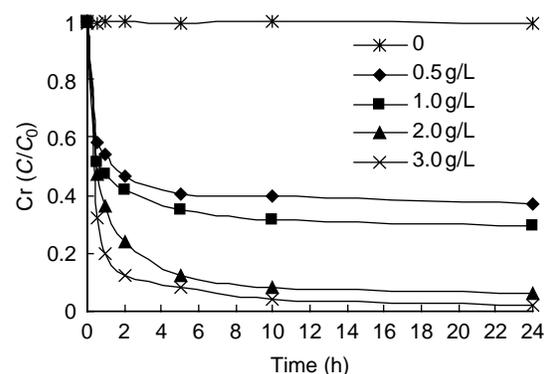
## Effects of physicochemical factors on Cr(VI) removal from leachate

### Effect of nanoparticle dosage on Cr(VI) removal

The effect of nanoparticle dosages (0.5, 1.0, 2.0, and 3.0 g/L) on the rate of removal of the Cr(VI) (20 mg/L) was investigated using the leachates at an initial pH value of 6.7 (Figures 2 and 3). Increasing amounts of NZVI resulted in a faster and more extended removal of the Cr(VI) from the aqueous phase. At a concentration of 0.5, 1.0, 2.0, and 3.0 g/L NZVI, more than 54%, 58%, 76% and 87% of the Cr(VI) in solution was removed within 2 h (Figure 2). In comparison, when  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was applied, removals were 57.2%, 63.5%, 82.5% and 88.0%, respectively for the four concentrations (Figure 3). Cr(VI) removal rate by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was a little higher than by NZVI. This is mainly due to an increase in the dosage of NZVI and hematite nanoparticles that can lead to an increase in total available active sites for Cr(VI). Hence, about 20% more Cr(VI) removal is achieved when the dosage of NZVI and hematite nanoparticles is increased from 1.0 g/L to 2.0 g/L. However,

for a fixed Cr(VI) dosage, the total Cr(VI) available to NZVI and hematite nanoparticles is limited when the dosage of NZVI and hematite nanoparticles is excess. Hematite nanoparticles may aggregate together as the dosage increases, however, the aggregation does not appear to NZVI due to the pre-treatment of NZVI. As a result, the removal rate increases 11% when the dosage of NZVI increases from 2.0 to 3.0 g/L. When hematite was applied, the removal rate only increases 5.5%.

After 2 h, the Cr(VI) concentration decreased slowly in the leachate exposed to NZVI; otherwise, the adsorption equilibrium had been achieved in the leachate treated by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Similar phenomena have been observed by the other researchers (Burris *et al.* 1995; Mohapatra *et al.* 2009). An initial fast rate of Cr(VI) disappearance from aqueous solution exposed to NZVI is due to the physical adsorption and the reductive reactions. Following this, the precipitation of Cr(OH)<sub>3</sub> or coprecipitation of Cr(III) with Fe(III) oxides/hydroxides contribute to the slow removal rate of Cr (Li *et al.* 2008). Electrostatic repulsion and ion exchange were the main mechanisms during the adsorption of



**Figure 2** | Reduction of Cr(VI) for various NZVI dosages.

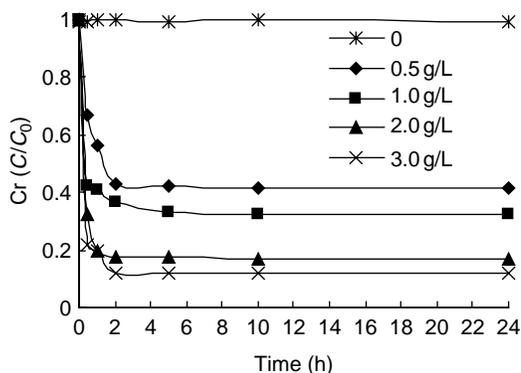


Figure 3 | Reduction of Cr(VI) for various  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> dosages.

Cr(VI) onto  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Hu *et al.* 2005). Since nearly all of the adsorption sites of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exist on the exterior of the adsorbent, it is easy for the adsorbate to access the active sites. Hence, the rapid adsorption of Cr(VI) is perhaps due to external surface adsorption (Hu *et al.* 2006). This result may help to explain the kinetics behavior detailed in part 3.3.

#### Effect of initial Cr(VI) concentration on Cr(VI) removal

One hundred milliliters of 20, 50, 100, and 200 mg/L Cr(VI) leachates were mixed with 1 g/L of nanoparticles, respectively. The effect of initial Cr(VI) concentration on Cr(VI) removal from leachate is shown in Figures 4 and 5.

It can be seen that the rate of Cr(VI) uptake was initially quite high and a much slower subsequent removal process led gradually to an equilibrium condition. The equilibrium time for the removal of Cr(VI) by NZVI was about 5 h, while it about  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was only 2 h. NZVI could not only adsorb Cr(VI) but also reduce it, so the more equilibrium time for NZVI may be attributed to repeat adsorption - reduction process. The quicker adsorption of Cr(VI) onto  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is due to external surface adsorption.

After 24 h, at initial concentrations of 20, 50, 100, and 200 mg/L, the removal rate of Cr(VI) by NZVI was found to be 99.7%, 92.0%, 91.7%, and 78.9%, respectively. In contrast, for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, it was 86.5%, 77.0%, 69.3%, and 57.0%, respectively. Further, the similar shape of the curves at each initial concentration indicates that the removal rate of Cr(VI) decreases with an increase of the initial Cr(VI)

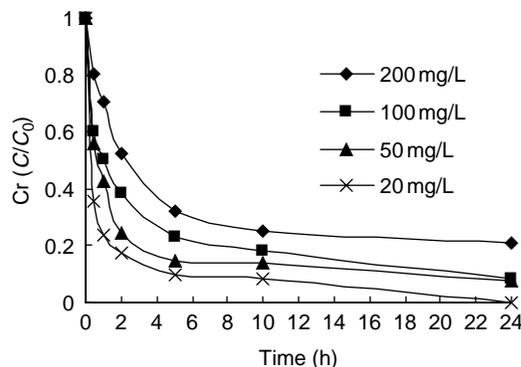


Figure 4 | Effect of initial Cr(VI) concentration on the removal of Cr(VI) by NZVI.

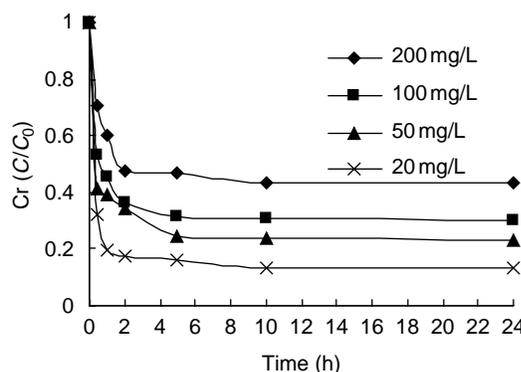


Figure 5 | Effect of initial concentration of Cr(VI) on the removal of Cr(VI) by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

concentration. Corresponding removal rates by NZVI are higher than by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. This is mainly due to the fact that for a fixed adsorbent dosage, the total available adsorption sites are limited leading to a decrease in percentage removal of adsorbate corresponding to an increased initial adsorbate concentration (Hiemstra & Van-Riemsdijk 1999).

#### Effect of pH values on Cr(VI) removal

Chromium removal rate was investigated as a function of solution pH and results are shown in Figure 6. When the leachates were exposed to NZVI for 5 h with increasing pH of 3.0, 4.0 and 5.0, the removal rates increased. However, as the pH was further increased from 5.0 to 8.0, the removal efficiency decreased gradually. Similar findings have been reported by Li *et al.* (2008). The hydrolysis reaction of citric acid on the surface of NZVI will lead to the dissolution of citric acid, that facilitates the reaction between NZVI and Cr(VI). When the pH of the solution is below 5, it might

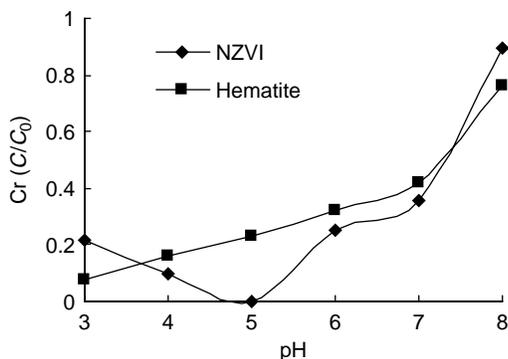


Figure 6 | Effect of pH values on the removal of Cr(VI).

prevent the citric acid from hydrolysis. Hence Cr(VI) removal at pH = 3.0 was less than that at pH = 5.0. In the removal of Cr(VI), an anion is preferred at low pH because the hydrous surface is more positively charged at lower pH (Mohapatra *et al.* 2009). The electrostatic attraction between the positive charges of NZVI and the negatively charged chromate anion facilitates the adsorption of Cr(VI) and enhances the reduction of Cr(VI) to Cr(III) (Geng *et al.* 2009).

In the case of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), the removal rate decreased with an increase of pH values. The result is in agreement with previous studies (Alowitz and Scherer 2002; Hu *et al.* 2006). Since the surfaces of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) are generally covered with hydroxyl groups that vary in forms at different pH, with an increase in pH, the higher concentration of OH<sup>-</sup> ions in the mixture will apparently compete with Cr(VI) species (CrO<sub>4</sub><sup>2-</sup>) for adsorption sites (Hu *et al.* 2006). Further, the leachates contain a certain amount of HA, which will induce the aggregation of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles and increase the aggregation size from pH 3 to 8 (Illes & Tombacz 2006). Hence, the acidity of the leachate has a major influence on the removal process.

In order to better understand the effect of pH on removal, the zeta potential of nanoparticles was measured and the results are shown in Figure 7. NZVI pre-treated with citric acid is positively charged at pH < 4.8. The zeta potential of non pretreated-NZVI was positive when pH was higher than the isoelectric point (IEP) of 8.1 (Sun *et al.* 2007). The pre-treated NZVI had a negative charge over a much wider pH range, likely as a result of the dissociation

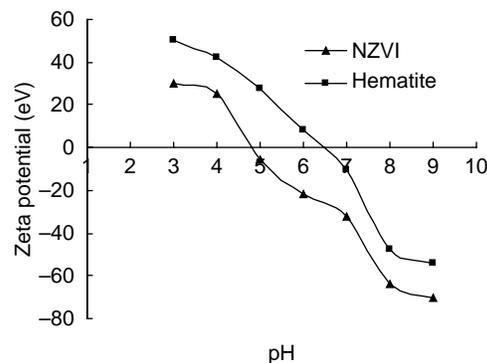


Figure 7 | Zeta-potential as a function of solution pH: NZVI and Hematite.

of carboxylic acid groups on the citric acid molecules. The zeta-potential of hematite decreased as pH increased and the IEP occurred at around pH 6.4. This IEP value agreed closely with reported values for magnetite (Pang *et al.* 2007). This result may help to explain the effect of pH on the removal of Cr(VI). CrO<sub>4</sub><sup>2-</sup> predominates and the surface of NZVI and hematite is negatively charged at pH above ~6.5, where the electrostatic repulsion between CrO<sub>4</sub><sup>2-</sup> and NZVI/hematite is adverse to the removal of Cr(VI).

#### Effect of reaction temperature on Cr(VI) removal

The effect of the temperature on the Cr(VI) removal was investigated at four different temperatures, i.e. from 20°C to 35°C. Figure 8 compares Cr(VI) removal rates between NZVI and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) at different temperatures. The results indicated that the reaction temperature effects the Cr(VI) removal by NZVI and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), and had a greater impact of hematite

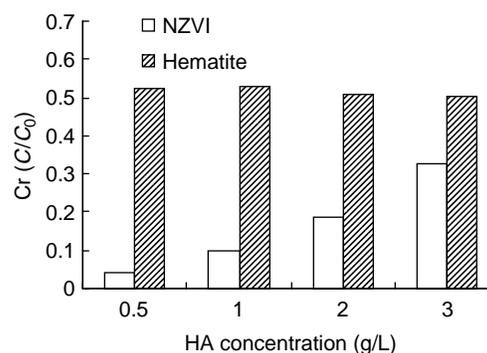


Figure 8 | Effect of reaction temperature on the removal of Cr(VI).

( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The mechanism may be explained as follows: both the removal of Cr(VI) by NZVI and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) are exothermic type reaction (Altundogan *et al.* 2000; Hu *et al.* 2005) and increasing the medium temperature is not conducive to the adsorption of Cr(VI). Otherwise, an increase in the temperature is favorable for the transfer of electrons from NZVI to Cr(VI). As a result, a fraction of Cr(VI) in the solution might be reduced to Cr(III) as the reaction time increases. Hence Cr(VI) removal rates using NZVI were higher than those using hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). The Cr(VI) removal rates using NZVI are less affected by temperature. When the wastewater is at higher temperature (<35°C), NZVI would be the preferred choice.

#### Effect of initial concentration of HA on Cr(VI) removal

The effect of HA on the removal of Cr(VI) was studied in the presence of varying HA concentrations, and the results are presented in Figure 9. Using NZVI to remove Cr(VI), the removal rate decreases with increasing initial HA concentration. HA adversely affects Cr(VI) removal from the leachate. A similar result was obtained by Rosa *et al.* (2003). HA has a high adsorption affinity for Cr, which prevents the removal of Cr by reducing the concentration of the available Cr. HA are organic polyelectrolytic ligands, which have a better ability to chelate iron ions or oxide surface and will reduce reactive sites of NZVI available to Cr(VI) (Gu *et al.* 1994).

In the case of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), removal rates of Cr(VI) were lower than those using NZVI, whereas they

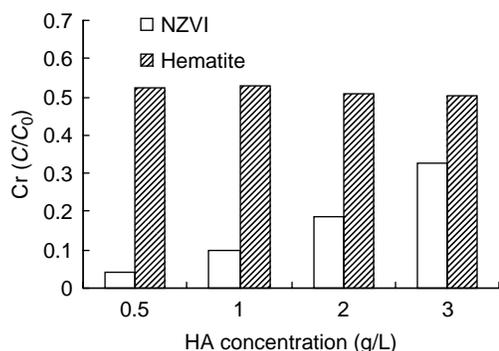


Figure 9 | Effect of initial concentration of HA on the removal of Cr(VI).

did not decrease markedly as the initial concentration of HA increased. HA have a better ability to chelate hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), which reduces reactive sites of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> available to Cr(VI) (Gu *et al.* 1994). Besides, HA might form aggregates on the surface of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which would prevent  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> from adsorbing Cr(VI) (Tsang *et al.* 2009). Hematite can adsorb the HA entirely, if only small amount of organic matter was added into the solution. The capacity of adsorption HA is limited and HA concentrations from 0.5 g/L to 3.0 g/L may exceed the limit at the given condition, and therefore increasing the concentration of HA did not reduce reactive sites of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> available to Cr(VI).

#### Kinetics of Cr(VI) removal by NZVI and $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

Dependence of initial nanoparticles dosages on the rate constant was studied under the given conditions and the results are presented in Tables 1 and 2. It is observed that the rate constant of Cr(VI) removal increased with an increase of the initial NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> dosages.  $k_{\text{obs}}$  ranged from  $6.6 \times 10^{-3}$  at an initial NZVI dosage of 0.5 g/L to  $26.1 \times 10^{-3}$  at 3.0 g/L (Table 1). In contrast, it ranged from  $7.2 \times 10^{-3}$  to  $30.4 \times 10^{-3}$  when  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was used (Table 2). It follows that increasing the dosage of

Table 1 | Effect of initial NZVI dosages on Cr(VI) removal.  $k_{\text{obs}}$  is the rate constant. (Experimental condition: initial Cr(VI) concentration: 20 mg/L; mixing with a constant temperature bath shaker at 160 rpm; initial pH 6.7; 20°C)

NZVI dosages (g/L)	$k_{\text{obs}}$ (min <sup>-1</sup> )	$r^2$	$t_{1/2,\text{obs}}$ (min)
0.5	$6.6 \times 10^{-3}$	0.953	30
1.0	$8.3 \times 10^{-3}$	0.962	30
2.0	$22.2 \times 10^{-3}$	0.960	30
3.0	$26.1 \times 10^{-3}$	0.98	30

Table 2 | Effect of initial  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> dosage on Cr(VI) removal.  $k_{\text{obs}}$  is the rate constant. (Experimental condition: initial Cr(VI) concentration: 20 mg/L; mixing with a constant temperature bath shaker at 160 rpm; initial pH 6.7; 20°C)

$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> dosages (g/L)	$k_{\text{obs}}$ (min <sup>-1</sup> )	$r^2$	$t_{1/2,\text{obs}}$ (min)
0.5	$7.2 \times 10^{-3}$	0.983	30
1.0	$15.6 \times 10^{-3}$	0.987	30
2.0	$28.1 \times 10^{-3}$	0.990	30
3.0	$30.4 \times 10^{-3}$	0.996	30

nanoparticles increased the surface area and reactive sites, so the rate constant was enhanced (Morgada *et al.* 2009). However,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has a more Brunauer-Emmett-Teller (BET) area than that of NZVI, and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> may have more reactive sites, which leads an increase of  $k_{\text{obs}}$ . At the given condition, Cr(VI) removal rate by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is greater than it by NZVI in the initial 1 h, so  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is more suitable to remove the higher concentration of Cr(VI) in the short term.

The data were examined using a pseudo-first-order reaction kinetics expression (Alowitz & Scherer 2002):

$$\text{rate} = -\frac{d[C]}{dt} = k_{\text{obs}}[C] \quad (1)$$

where  $C$  is the concentration of Cr(VI) (mg/L) in solution at  $t$  minute and  $k_{\text{obs}}$  is the pseudo-first-order rate constant of Cr(VI) (min<sup>-1</sup>). Integrating of Equation (1) and then solving natural logarithms of the equation results in:

$$\ln \frac{C}{C_0} = -k_{\text{obs}}t \quad (2)$$

where  $C_0$  is the initial concentration of Cr(VI) (mg/L) in solution. As can be seen,  $\ln(C/C_0)$  displayed a good linearity about the reaction time within the ranges of 0–60 minutes ( $R^2 > 0.90$ ), and the removal of Cr(VI) by NZVI and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> followed pseudo-first-order reaction kinetics (Figures 10 and 11). In all cases, the regression line did not go through the origin, indicating that the adsorption may play an important role in the Cr(VI) dissipation. Similar phenomena have been observed by other researchers (Illes & Tombacz 2006; Geng *et al.* 2009).

Using the data of the part 3.2.4, the apparent activation energy ( $E_a$ ) is obtained by plotting  $k_{\text{obs}}$  against the temperature. The leachate was exposed to NZVI and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>),  $E_a$  value was 28 and 16 kJ/mol, respectively. Pilling *et al.* reported that  $E_a$  values in a range of 10–21 kJ/mol has been attributed to be a physical process (Pilling & Seakins 1995). Otherwise, an  $E_a$  value more than 21 kJ/mol may be attributed to chemically controlled processes. It can be concluded the reduction of Cr(VI) to Cr(III) by NZVI is chemically controlled and the removal of Cr(VI) by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is physically controlled.

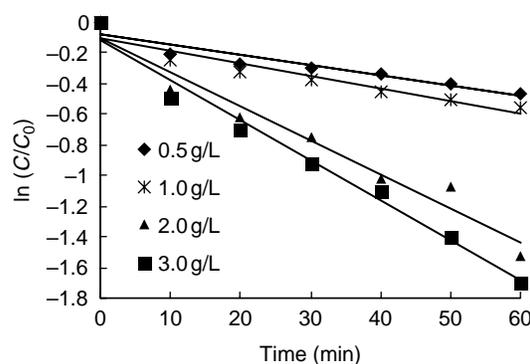


Figure 10 | Pseudo-first-order rate constant for removal of Cr(VI) for various NZVI dosages.

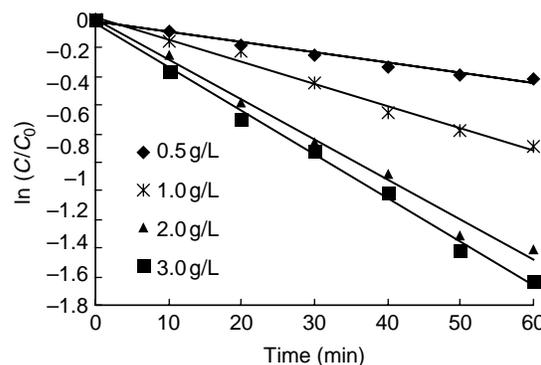


Figure 11 | Pseudo-first-order rate constant for removal of Cr(VI) for various  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> dosages.

## CONCLUSIONS

The following conclusions can be drawn from this study.

- (i) The removal rate of Cr(VI) decreased with the increase in the initial Cr(VI) concentration. Corresponding removal rates by NZVI are higher than those by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The removal efficiency was highly pH dependent. The optimum pH for the removal of Cr(VI) by NZVI was found to be 5.0 and more than 99.0% of the compound was removed within 5 h. The removal rate using  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> decreased with an increase in pH value. The reaction temperature adversely affected the Cr(VI) removal using NZVI and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), and had a greater impact on hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>).
- (ii) HA significantly suppressed Cr(VI) removal by NZVI from the leachate and the removal rate decreased with an increase of initial HA concentration. HA had

a greater adverse impact on hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), however, the removal rate did not significantly decrease as HA concentration increased from 0.5 g/L to 3.0 g/L.

- (iii) Increasing the dosage of nanoparticles enhanced the rate constant.  $k_{\text{obs}}$  ranges from  $6.6 \times 10^{-3}$  at an initial NZVI dosage of 0.5 g/L to  $26.1 \times 10^{-3}$  at 3.0 g/L. In the case of  $\alpha\text{-Fe}_2\text{O}_3$ , it ranges from  $7.2 \times 10^{-3}$  to  $30.4 \times 10^{-3}$ . The removal of Cr(VI) by NZVI and  $\alpha\text{-Fe}_2\text{O}_3$  followed pseudo-first-order reaction kinetics. Cr(VI) to Cr(III) by NZVI is chemically controlled and the removal of Cr(VI) by  $\alpha\text{-Fe}_2\text{O}_3$  is physically controlled.

Information related to the effects of environmental factors on the removal rates of chromate ( $\text{CrO}_4^{2-}$ ) is important to assess the applicability of iron nanoparticles for the treatment of groundwater or raw wastewater such as landfill leachate.

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