

*Ind. Eng. Chem. Res.* **2008**, *47*, 2131-2139

# **Stoichiometry of Cr(VI) Immobilization Using Nanoscale Zerovalent Iron (nZVI): A Study with High-Resolution X-Ray Photoelectron Spectroscopy (HR-XPS)**

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CY09D018

Date: 21-03-2009

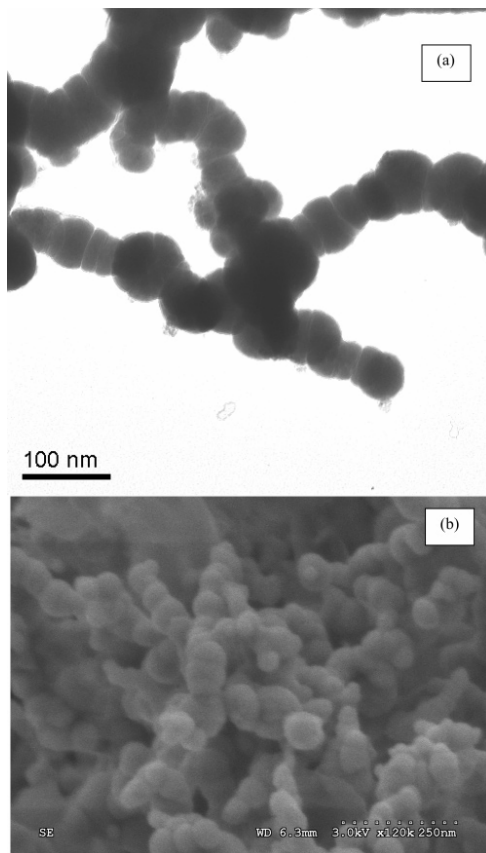
## **Abstract:**

- In the pH range of 4 to 8, the nZVI has a chromium removal capacity ranging from 180 to 50 mg Cr/g nZVI. Under similar conditions, microscale iron particles (100 mesh) typically have a capacity of less than 4 mg Cr/g Fe.
- Characterizations with high-resolution X-ray photoelectron spectroscopy (HRXPS) indicate that Cr(VI) is to Cr(III), which is subsequently incorporated into the iron oxyhydroxide shell of nZVI and form alloy-like Cr-Fe hydroxides with a representative formula approximating  $(\text{Cr}_{0.67}\text{-Fe}_{0.33})(\text{OH})_3$  or  $\text{Cr}_{0.67}\text{Fe}_{0.33}\text{OOH}$ . The Cr-Fe hydroxide shell is relatively stable and serves as a sink for Cr-(VI).

## Introduction

1. Chromium is used in industrial processes such as electroplating, leather tanning and mineral extraction, and as a common ingredient used in protective coatings, pigments, and stainless steel.
2. Maximum contaminant level (MCL) for total chromium in drinking water is set at 0.1 mg/L.
3. Stable oxidation states for Cr are +6 and +3. Cr(+3) state salts are mostly having less solubility.
4. Chromium is a potential carcinogen and is highly toxic to humans, animals, and plants.

5. Cr(+6) can be reduced with oxalate, citrate, hydrogen sulphide at lower rates.
6. Zerovalent iron (ZVI) is an excellent electron donor and reductant for environmental applications because iron is readily available, inexpensive, and nontoxic.
7. NZVI can also be used to remediate halogenated organic compounds and metal ions. The nZVI particles are in the size range of 1-100 nm. A representative particle size is around 50-60 nm.
8. TEM images also show that the nanoparticles tend to form much larger (e.g., microscale) aggregates in the absence of surface-active dispersants.



1. Reaction kinetics and mechanisms are apparently complicated and not well understood.
2. The reaction rate typically depends on
  - (a) the total surface area
  - (b) the initial concentrations of both nZVI, and the contaminants of concern.
  - (c) solution chemistry such as solution pH and presence of other oxidants such as oxygen and nitrate.
3. In this study, experiments are conducted on the use of nZVI for Cr(VI) treatment over wide ranges in terms of chromium concentration and solution pH and analysed with HR-XPS.

**Figure:** Images of zerovalent iron nanoparticles prepared by the reduction of Fe(III) with sodium borohydride: (a) a TEM micrograph, and (b) a SEM

## Materials and Methods

### Synthesis of nzvi:



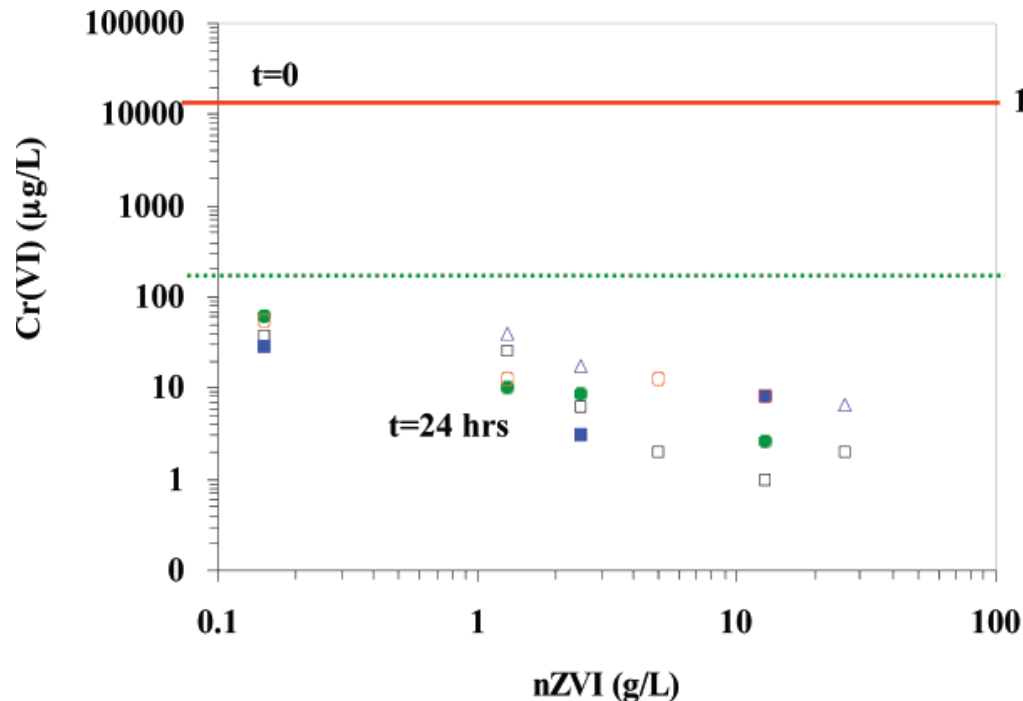
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Washed with alcohol, and stored in 5% alcohol until used

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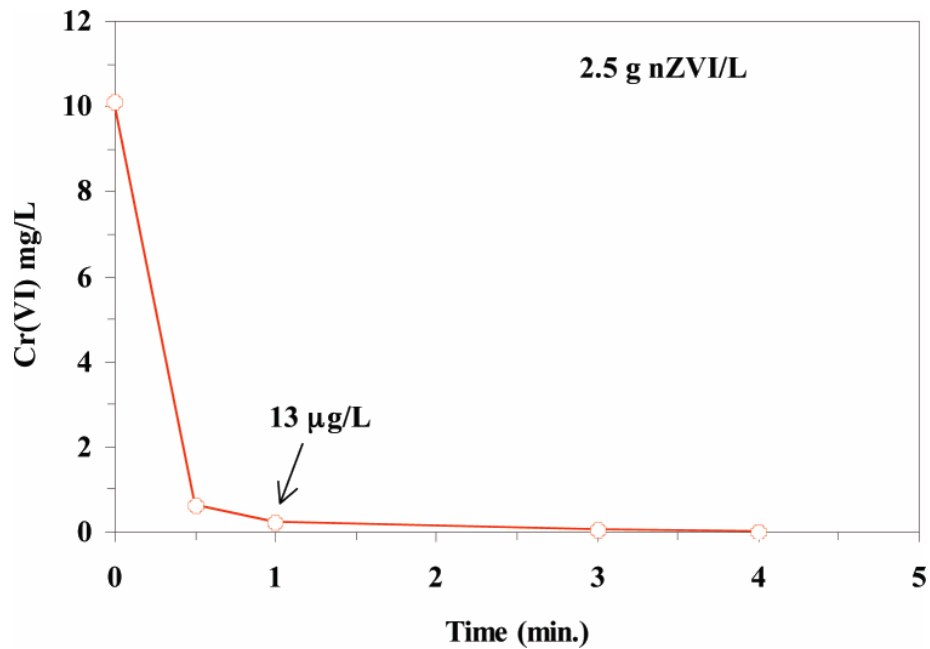
Size of the 80% of the particles is less than 100 nm

- They performed batch experiments using 10-2000 mg/L Cr(+6) and 0-25 g/L NZVI, with a shaking rate 300 rpm.
- Total Chromium was determined using atomic absorption (AA) spectroscopy.
- Chromium (VI) concentration was measured using the 1,5-diphenylcarbohydrazide method. This method is insensitive to Cr(III).
- UV-vis absorption measured at 542 nm.

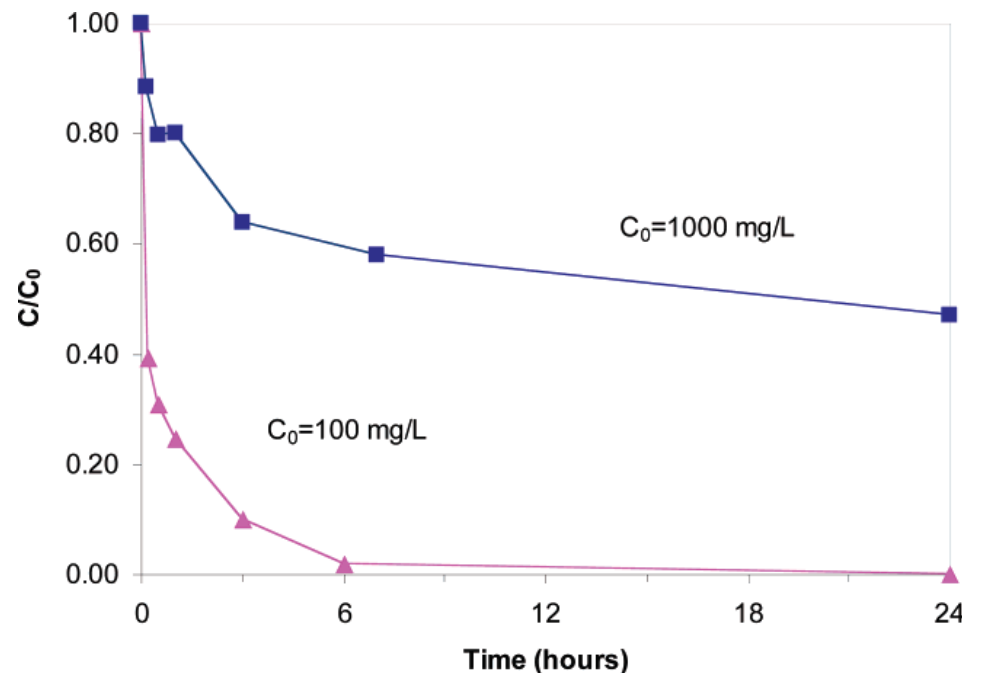


- 0-25 g/L NZVI
- Minimum 0.2 g/L NZVI
- Allowed level is 100 micro gram/L

**Figure:**Residual chromium in the aqueous phase after 24 h of reaction with nZVI. The initial Cr (VI) concentration was 10 900  $\mu\text{g/L}$ . The solution pH was 11. The data were obtained from several different batch experiments over a period of 4 weeks.



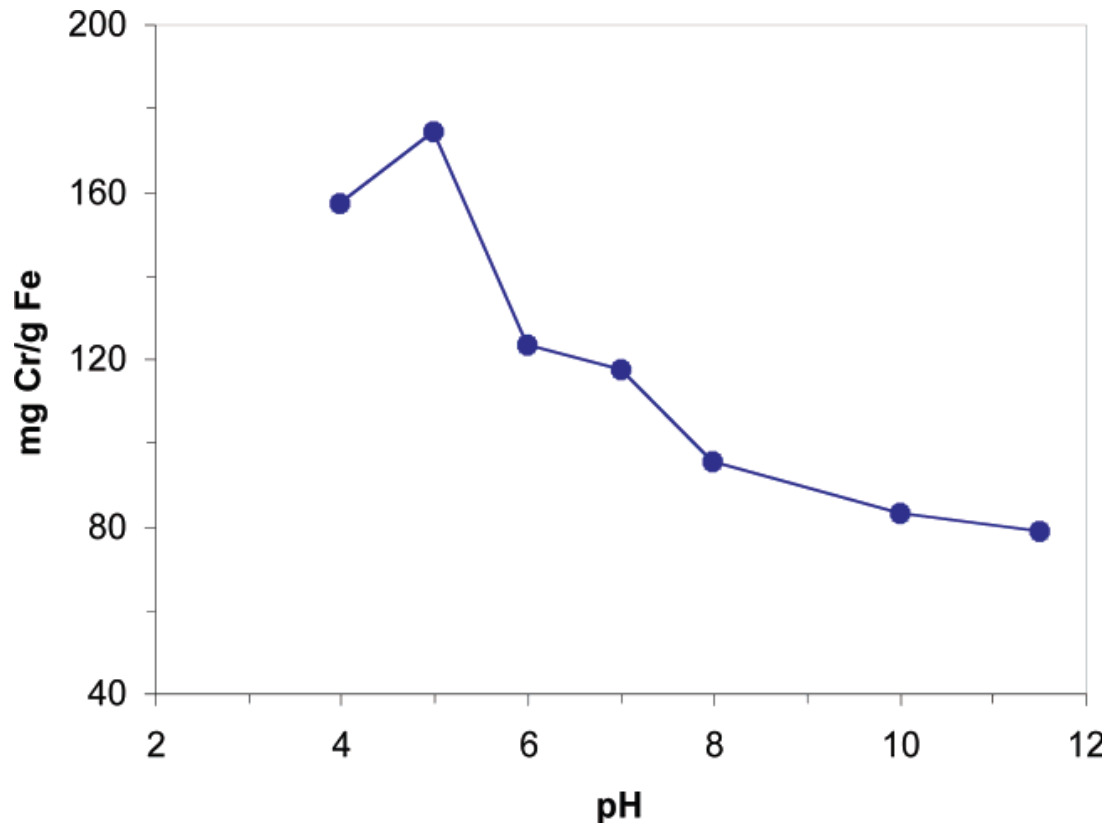
**Figure:** Concentration trend of Cr(VI) in the aqueous phase as a function of time. The initial Cr(VI) concentration was 10 900  $\mu\text{g/L}$ . The solution pH was 11. The nZVI dose was 2.5 g/L.



**Figure:** Concentration trends of Cr(VI) in the aqueous phase as a function of time. The initial Cr(VI) concentrations were 100 and 1000 mg/L. The Nzvi dose was 5.0 g/L.



## Effect of P<sup>H</sup> on removal of Cr(+6)



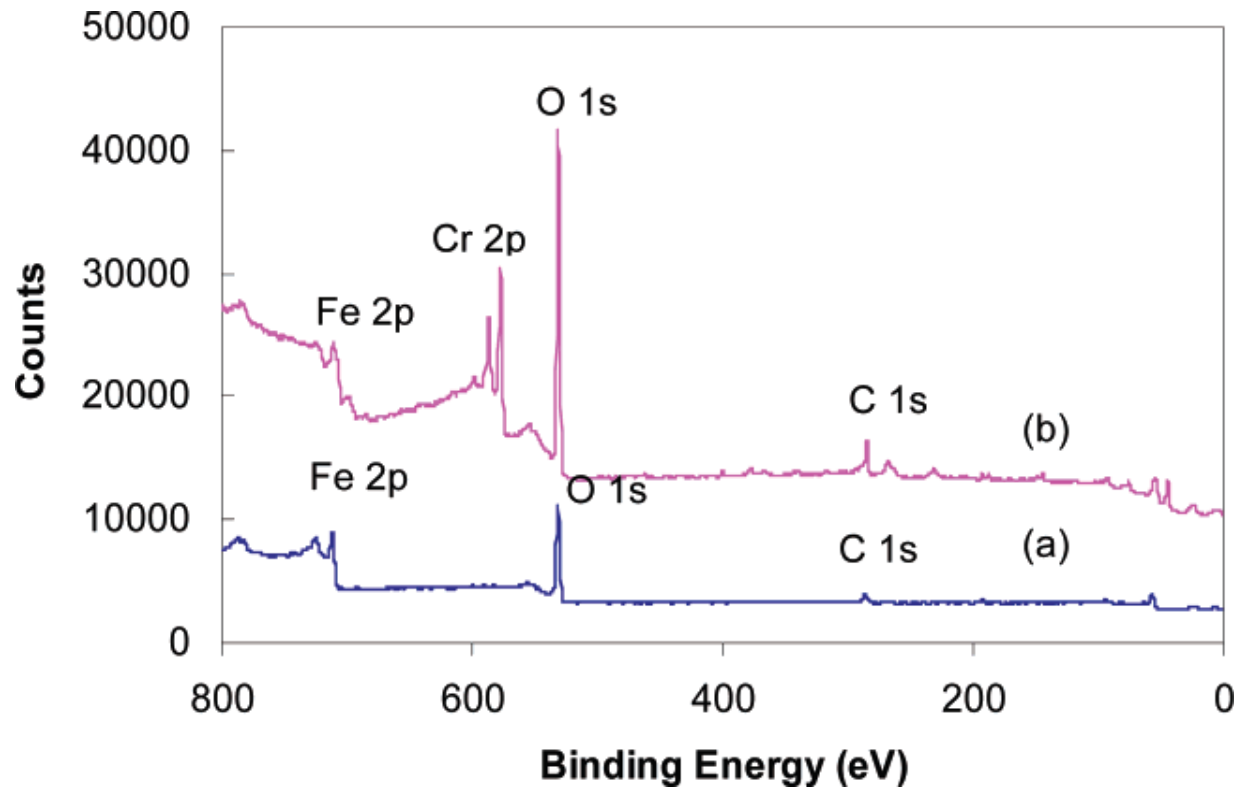
**Figure:** Removal of Cr(VI) by ZVI as a function of solution pH. The initial concentration of Cr(VI) was 1000 mg/L and ZVI loading was 2.5 g/L.

<u>P<sup>H</sup></u>	<u>Capacity to remove</u>
5.0	179 mg/g Fe
11.5	80 mg/g Fe

**P<sup>H</sup> increases, capacity decreases**

### Reasons:

- The iron oxidation and Cr(VI) reduction reactions are favored at low P<sup>H</sup>.
- In the sorption of Cr(VI), an anion is preferred at low P<sup>H</sup> because the hydrous surface is more positively charged at lower P<sup>H</sup>.<sup>9</sup>



**Figure:** XPS survey for iron nanoparticles of (a) freshly prepared and (b) after reacting with 1000 mg/L Cr for 10 min. ZVI loading was 5.0 g/L.

- The nZVI was exposed to 1,000 mg/L Cr(VI) for 10 min, 1 h, 3 h, and 24 h.

## **XPS Studies of the Chromium on Iron Nanoparticles:**

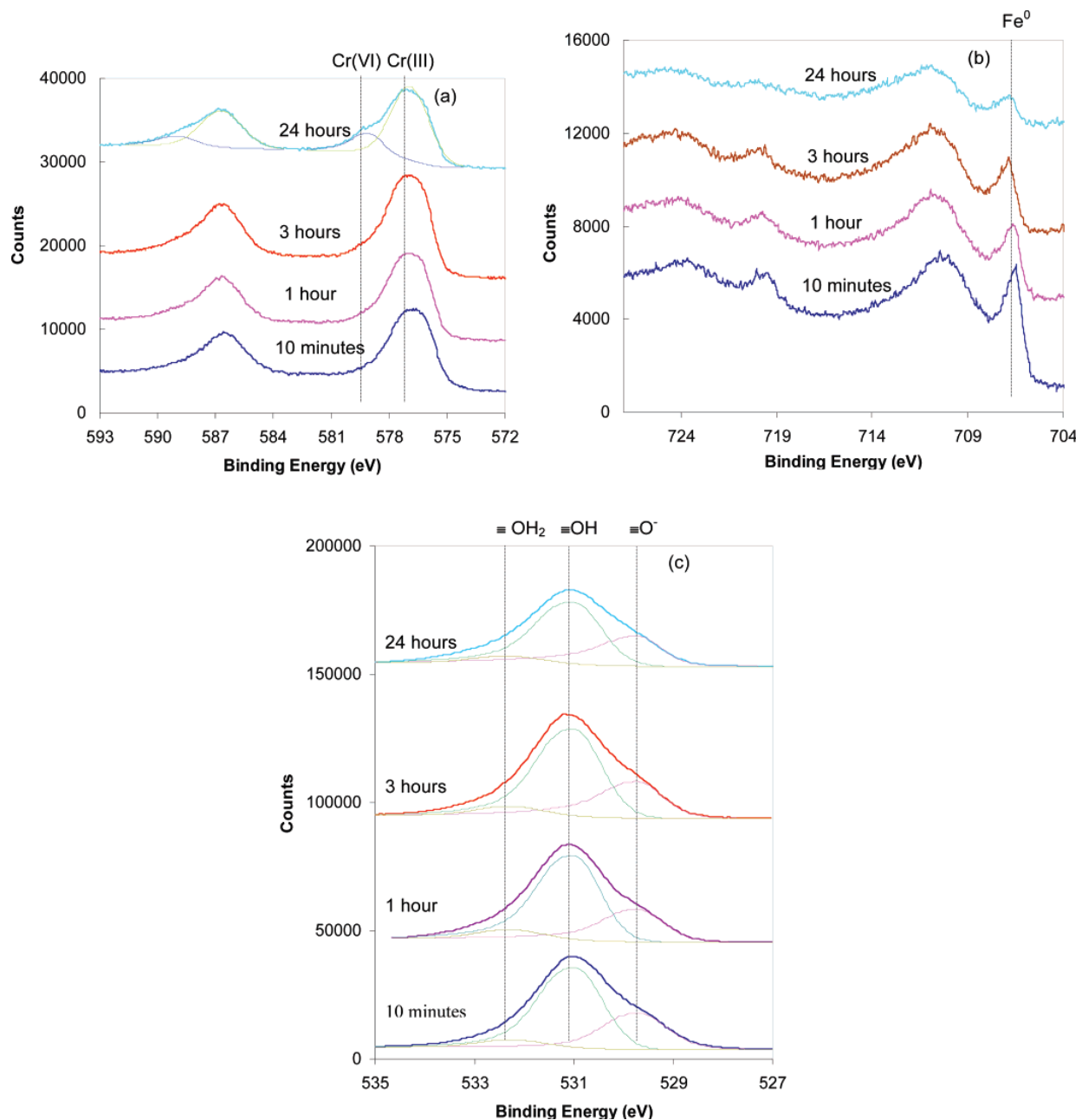
It explains,

- (1) Which elements are present at the nZVI surface,
- (2) What chemical or valence states of these elements are present, and
- (3) How much of each chemical state of each element is present.
- (4) The photoelectron peaks for the chromium 2p<sub>3/2</sub> and 2p<sub>1/2</sub> centers at 576.9 and 586.7 eV, may be due to Cr<sub>2</sub>O<sub>3</sub> or Cr(OH)<sub>3</sub>.
- (5) The spin-orbit splitting is 9.8 eV. FWHM is 3.0 eV.

The photoelectron peak generated from Cr(VI) compounds is much sharper with a fwhm at 2.1 eV and has higher binding energies (579 eV for chromium 2p<sub>3/2</sub>) and smaller 2p spin-orbit split (9.3 eV), indicates uptake of Cr(+6).

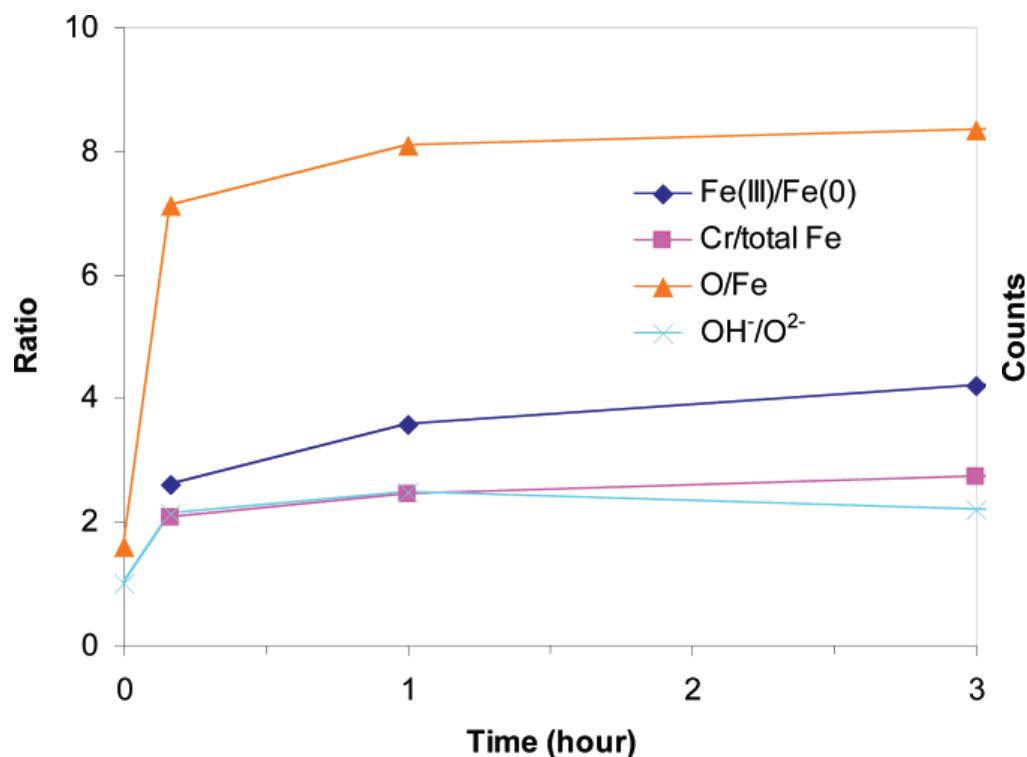
## To decide $\text{Cr}_2\text{O}_3$ (or) $\text{Cr}(\text{OH})_3$ :

- For  $\text{Cr}_2\text{O}_3$ ,  
Cr  $2p_{3/2}$ : 576.3, 577.6, 578.9, and shake up peak 587.9 eV  
Cr  $2p_{1/2}$  586.1, 587.0, and 588.7 eV
- The seven peaks are fitted with fwhm at 1.4 eV, and the area fractions are 29.3%, 29.1%, 7.9%, 2.4%, 13.7%, 13.6%, and 4.0%, respectively.
- A **sharp** peak at **530 eV for  $\text{O}^-$**  and a small hump at 532 eV for the adsorbed  $\text{H}_2\text{O}$ .  
In contrast,  **$\text{Cr}(\text{OH})_3$**  has a peak centering at **531 eV for  $\text{OH}$** .
- For  $\text{Cr}(\text{OH})_3$ , one can expect the peak area ratio of  $\text{OH}/\text{O}^-$  increase with time and also with solution pH.
- The shoulder at 719 eV could be the result of two overlapping components: the shakeup satellite  $2p_{3/2}$  for oxidized iron and  $2p_{1/2}$  for zerovalent iron

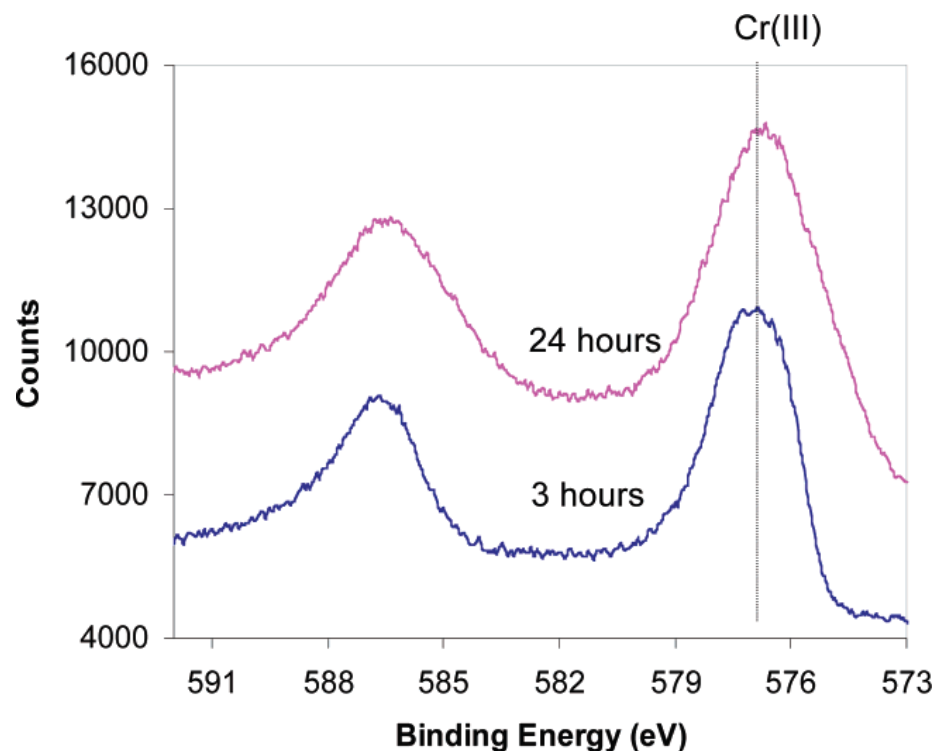


**Figure :** High-resolution XPS survey of (a) chromium 2p, (b) iron 2p, and (c) oxygen 1s of nZVI after reacting with 1000 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for 10 min, 1 h, 3 h, and 24 h, respectively.

## Stoichiometry of Cr(VI) Immobilization:

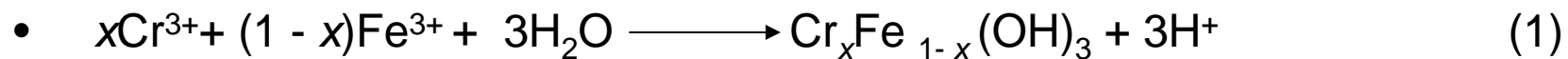


**Figure:** XPS photoelectron peak area ratios for Fe(III) to Fe(0), total chromium to total iron, total oxygen to total iron, and OH<sup>-</sup> to O<sup>2-</sup> at different time intervals.



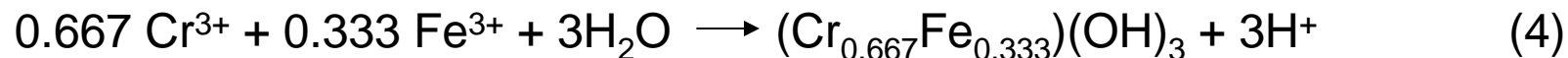
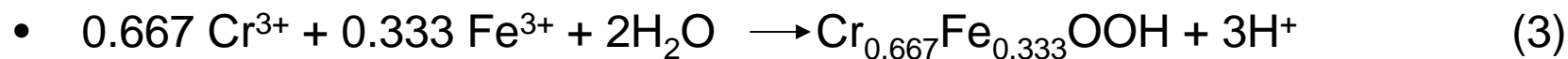
**Figure:** High-resolution XPS survey of chromium 2p for nZVI reacting with 100 mg/L K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> for 3 and 24 h

- In previous work, they postulated based upon the solution chemistry that Cr(III) is incorporated onto the surface FeOOH structure and generates  $(\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3$  or  $\text{Cr}_x\text{Fe}_{1-x}\text{OOH}$  at the surface ( $0 < x < 1$ ).

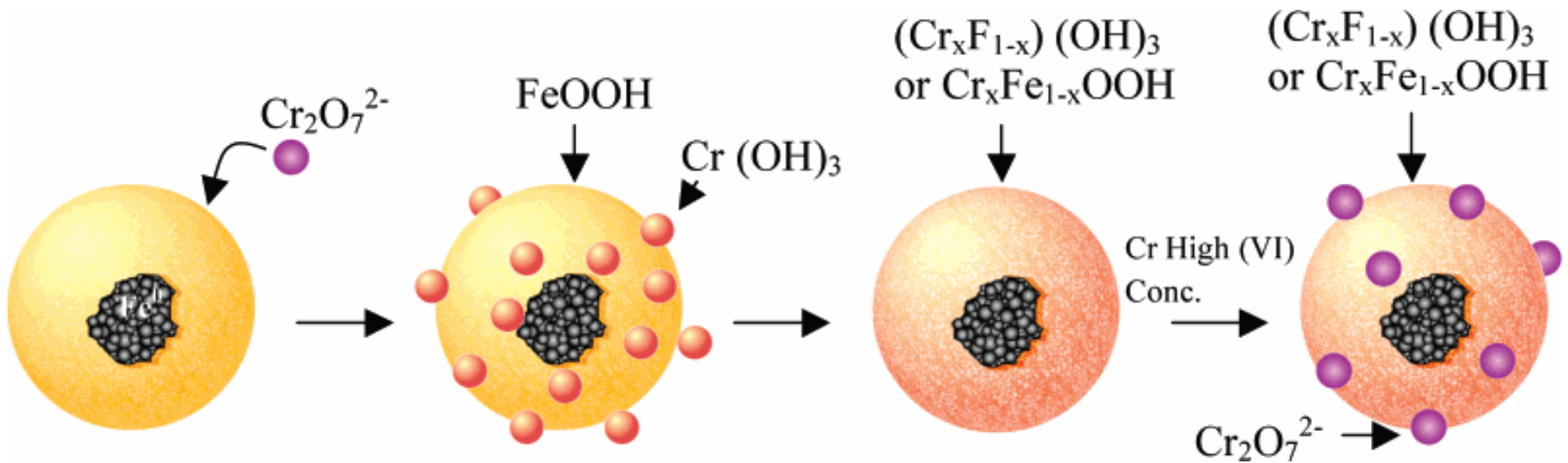


- Elemental ratios were obtained by comparing the products of each peak area and atomic sensitivity factors.

- As shown in Figure, the surface chromium to iron ratio after 3 h is approximately 2. Accordingly the value of  $x$  is approximately 0.667:

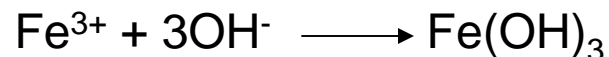


- Reaction 3 generates an oxygen to iron ratio of 6.0, whereas reaction 4 has an oxygen to iron ratio at 9.0. The measured oxygen to iron ratio as shown in Figure is approximately 8.

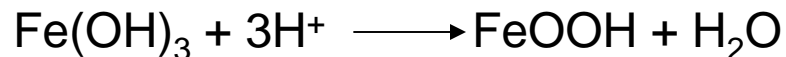


**Figure 10.** Conceptual model for chromium immobilization with nZVI

- In aqueous phase,  $\text{Fe}^{3+}$  reacts with  $\text{OH}^-$  or  $\text{H}_2\text{O}$  to form hydroxide or oxyhydroxide:



Subsequent dehydration of  $\text{Fe}(\text{OH})_3$  generates  $\text{FeOOH}$



- The existence of a mixture of  $\text{FeOOH}$  and  $\text{Fe}(\text{OH})_3$  is thus consistent with the chemistry of iron oxides in water



- Due to increase in the formation of  $\text{Cr}_{0.667}\text{Fe}_{0.333}\text{OOH}$  and  $(\text{Cr}_{0.667}\text{Fe}_{0.333})(\text{OH})_3$  layer on nZVI, increases the resistance for the electron transfer from Fe0 to Cr(VI).
- Because of the sorption of  $\text{Cr}_2\text{O}_7^{2-}$ , with 24 h reaction time, the area ratio of O/Fe increases and OH-/O<sup>2-</sup> decreases slightly compared to that of a shorter reaction time.
- The existence of Cr(VI) on the nZVI surface occurs only at high concentrations of Cr(VI) in the solution or at low concentrations of nZVI.
- Oxidation (i.e., corrosion) of iron can be shielded (inhibited) by the formation of Fe-Cr (alloying).

**Thank you**