

# Environmental Application of Biogenic Magnetite Nanoparticles to Remediate Chromium(III/VI)-Contaminated Water

Kim Y. And Roh Y.

Department of Earth and Environmental Sciences, Chonnam National University, 61186, Gwangju, Korea

\*corresponding author:

e-mail: rohy@jnu.ac.kr

**Abstract** The physicochemical characteristics of biogenic minerals, such as their high specific surface area and high reactivity, as well as the presence of a bacterial carrier matrix make them interesting for various applications, for instance as catalysts, adsorbents, oxidants or reductants. The objective of this study was to examine the efficiency of biogenic magnetite nanoparticles (BMNs) produced by metal-reducing bacteria in removing chromium. Interactions between ionic Cr(III/VI) and BMNs were examined under different solution pH (pH 2 to pH 12) using different dose of BMNs (0 to 6 g/L). Chemically synthesized magnetite nanoparticles (CMNs) were used in experiments for comparison. Results showed that BMNs had higher Cr(VI) removal efficiency (100%) than CMNs (82%) with reaction time of 2 weeks. The lower the pH of Cr-contaminated solution and the longer the reaction time, the higher the Cr(VI) removal efficiency. The Cr(VI) removal efficiency by BMNs in Cr-contaminated groundwater was about 94% after reaction time of 2 weeks. BMNs coated with organic matter were more effective to lead adsorption of Cr(III) with electrostatic interaction (82%) and to prevent oxidation of Fe(II) within the magnetite structure than CMNs (13%). These results indicate that BMNs could be used to decontaminate ionic chromium in environmental remediation technologies.

**Keywords:** Chromium, Remediation, Groundwater, Magnetite, Nanoparticle

## 1. Introduction

Chromium (Cr) is present in the environment primarily in two oxidation states: Cr(III) and Cr(VI). While trivalent Cr(III) is only toxic at high concentrations, hexavalent Cr(VI) is a strong oxidizer which is toxic to humans and the environment at  $\mu\text{g/L}$  concentrations. Cr(III) exists primarily as a cation (e.g.,  $\text{Cr}^{3+}$ ,  $\text{Cr}(\text{OH})^{2+}$ ) in solution while Cr(VI) exists primarily as an anion (e.g.,  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ) depending on the pH (Guertin *et al.*, 2005). Iron containing minerals are considered to be beneficial for chromium treatment in aqueous solutions because minerals are predominantly available in nature. They play key roles in elemental recycling in the environment. Coupled Fe(II)–Fe(III) redox is considered to be highly attractive due to enhanced electron-transfer mediator in the remediation

process for heavy metals or radionuclides (Baig *et al.*, 2014). Consequently, Fe(II)-containing minerals including pyrite, siderite, magnetite and mackinawite have widely been investigated for Cr(VI) removal (Erdem *et al.*, 2004; Mullet *et al.*, 2004). Among them, magnetite has been evaluated as a novel adsorbent for heavy metals because combining nanoparticles adsorption and the magnetic separation technique is space-saving, cost-effective, simple-to-use, and environmentally-sound compared to the present treatment technologies (Hu *et al.*, 2005). Biogenic minerals have good physicochemical characteristics such as high specific surface area, high reactivity, and the presence of bacterial carrier matrix, making them useful for various applications. For instance, they can be used as catalysts, adsorbents, oxidants, and reductants (Hennebel *et al.*, 2009). A few research studies have reported that biogenic magnetite nanoparticles (BMNs) are successful in reducing Cr(VI) (Telling *et al.*, 2009; Crean *et al.*, 2012). However, the sorption efficiency of heavy metals by biogenic magnetite under various experimental conditions has not been studied in details yet. Therefore, the objective of this study was to determine the efficiency of BMNs produced by metal-reducing bacteria in removing Cr(III/VI) removals from aqueous solutions under different solution pH (pH 2 to pH 12) using different doses of BMNs (0 to 6 g/L) at room temperature.

## 2. Experimental

### 2.1. Preparation of magnetite nanoparticles and characterization

Biogenic magnetite nanoparticles (BMNs) were synthesized using metal-reducing bacteria with 40 mM akaganeite as an electron acceptor and 10 mM glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) as an electron donor in 100 ml of growth media according to method described previously (Kim *et al.*, 2011). Metal-reducing bacteria (Geocha-1) were enriched from the intertidal flat sediments of Suncheon in the Jeonnam province of South Korea. For comparison, chemically synthesized magnetites (CMNs) were prepared using co-precipitation method (Mascolo *et al.*, 2013) and used for experiments. Mineralogical characteristics of the magnetite precursor, akaganeite, and transformed phases by microbial processes were examined using X-ray

diffraction (XRD) and transmission electron microscopy (TEM) with energy dispersive X-ray (EDS) analyses. X-ray diffraction analysis was performed using an X'Pert PRO (PANalytical, Netherlands) equipped with Cu K $\alpha$  radiation (40 kV, 20 mA) at a scan speed of 5  $\theta$ /min. TEM analysis was conducted on a Phillips Tecnai F20 (Philips, Netherlands) at accelerating voltage of 200 kV to determine the morphology and elemental composition of the synthesized magnetite nanoparticle. The surface area of the magnetite nanoparticle was measured using a Brunauer–Emmett–Teller (BET) surface area analyzer (ASAP-2020M, Micromeritics, USA).

### 2.2. Chromium (III/VI) removal

Cr(III)- and Cr(VI)-contaminated solutions were prepared by dissolving 50 mg/L CrCl $_3$ ·6H $_2$ O and CrK $_2$ O $_4$  in distilled water, respectively. Cr(III/VI) removal experiments were performed in 50 mL conical tubes. To examine the Cr removal by BMNs, 0.3 g of BMNs was added into the 50 mL of Cr(III)- or Cr(VI)-solution (pH=7) in a conical tube. To create comparison, Cr(III/VI) removal efficiencies by CMNs without the addition of nanoparticles were examined. All samples in the conical tube were shaken at 150 rpm to ensure complete mixing at room temperature. The reaction time was in the range from 0.5 to 366 h. During experiments, 1 mL of suspension was withdrawn with a 3 mL syringe at 30 min, 1 h, 24 h, 48 h, and 366 h and filtered through 0.2  $\mu$ m filter to determine the rate of Cr(III/VI) removal by BMNs or CMNs. Effects of pH on Cr removal by BMNs were evaluated by adding 0.1 g of BMNs into 50 mL of Cr(VI)-solution with different pH (ranging from pH 2 to pH 12). For analysis, 1 mL of suspension was withdrawn with a 3 mL syringe at 48 h and then filtered through 0.2  $\mu$ m filter. The pH value of Cr(VI) solution was adjusted to pH 2, 4, 7, 10, and 12 with 0.5 M HCl or 0.5 M NaOH. No buffer was added in these experiments. In order to evaluate *in-situ* applicability, natural groundwater dissolved various inorganic nutrients was used as Cr(VI)-contaminated groundwater (pH 7.8; initial Cr(VI) concentration at 50 mg/L) spiked with CrK $_2$ O $_4$ . The groundwater collected from a military field range in Yonchon-gun, Gyeonggi-do, Korea was composed of the following cations and anions: Mg $^{2+}$  (8.34 mg/L), Ca $^{2+}$  (59.33 mg/L), Na $^{+}$  (17.58 mg/L), K $^{+}$  (2.69 mg/L), Cl $^{-}$  (39.05 mg/L), NO $_3^{-}$  (5.38 mg/L), SO $_4^{2-}$  (9.05 mg/L), Al $^{3+}$  (0.22 mg/L), Cd $^{2+}$  (0.003 mg/L), Cu $^{2+}$  (0.064 mg/L), Fe $^{2/3+}$  (0.039 mg/L). The groundwater based test was performed using different doses (1 to 8 g/L) of BMNs in 50 mg/L Cr(VI) for 2 weeks.

### 2.3. Analytical methods

Chromium concentrations were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on Optima 8300 (Perkin-Elmer, USA) in accordance with the standard method. Elemental composition and chemical oxidation state of surface and near-surface species were investigated with X-ray photoelectron spectroscopy (XPS) using Multilab 2000 (VG Inc., UK). Mineralogical characteristics of magnetite

nanoparticles were observed by XRD and TEM-EDS analyses with same processes as mentioned above.

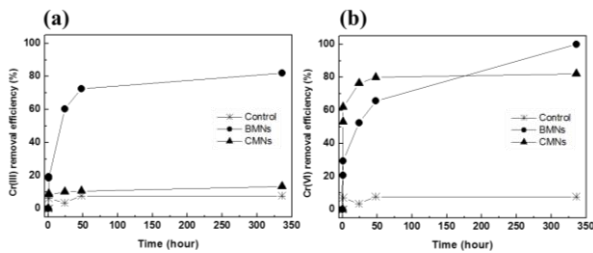
## 3. Results and discussion

### 3.1. Biogenic magnetite nanoparticles

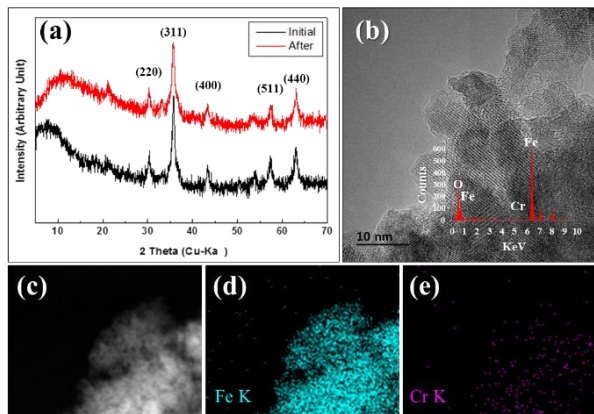
The bacterial consortium (Geocha-1) reduced akaganeite ( $\beta$ -FeOOH) to magnetite (Fe $_3$ O $_4$ ). These BMNs were spherical in shape with size of around 5-15 nm in diameter. BMNs synthesized by bacteria were coated with organic materials that had a functional group such as carboxyl (-COO $^{-}$ ). They are regarded as extracellular polymeric substances (EPSs) due to microbial metabolism (Kim *et al.*, 2011). The surface area of freeze-dried BMNs was measured at 101 m $^2$ /g, which was similar to that (103 m $^2$ /g) of biogenic magnetite nanoparticles formed by *Geobacter* species in previous study (Iwahori *et al.*, 2014). The point of zero charge, pH $_{pzc}$ , of these BMNs was around 6.8.

### 3.2. Cr(III) and Cr(VI) removal

Fifty milliliters of 50 mg/L solutions as Cr(III) and Cr(VI) contaminants were reacted with 0.3 g BMNs or CMNs at pH 7. The effect of time on the removal efficiency of Cr(III/VI) by magnetite nanoparticles is shown in Fig. 1. As results, Cr(VI) was removed by both CMNs and BMNs (Fig. 1b). Over 50% of Cr(VI) was removed by CMNs during the first 30 min of reaction time and additional 20% was removed after the 30 min of reaction time. However, Cr(VI) removal efficiency by BMNs was gradually increased as reaction time was increased. Lower Cr(VI) removal efficiency by BMNs than that by CMNs was continued until at 48 h after reaction. After reaction time of 2 weeks, BMNs finally showed higher Cr(VI) removal efficiency (100%) than CMNs (approx. 82%). Thus, about 40% of Cr(VI) was removed additionally by BMNs after 48 h of reaction, while only a small portion of additional removal (about 5%) was achieved by CMNs after 24 h of reaction time. Such slower removal rate of Cr(VI) by BMNs compared to that by CMNs might be attributed to organic matter on BMNs. It might have prevented oxidation of Fe(II) within the magnetite structure in aqueous solutions. In effect, lower amount of Fe leaching (0.2 g/L) from BMNs compared to that (11.2 g/L) from CMNs was observed after 48 h of reaction in Cr(VI)-solution based on ICP-AES analysis (wavelength of 238.2 nm). Baig *et al.* (2014) have revealed that high capacity of Cr(VI) reduction-adsorption in aqueous solution is dependent on the release of Fe(II) from magnetite which is oxidized into Fe(III), resulting in reduction from Cr(VI) to Cr(III). After 48 h of reaction, nanoparticles recovered showed XRD peaks without mineralogical changes during contact time with Cr(VI) (Fig. 2a). Also, TEM-EDS results of the nanoparticles showed Cr adsorption on surface of the particles (Fig. 2). Results of EDS revealed that the weight % of Cr adsorbed onto the surface of BMNs was lower (1.2 wt.%) than that adsorbed onto the surface of CMNs (1.6 wt.%).

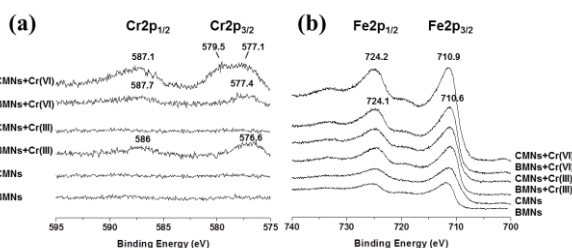


**Figure 1.** Effect of reaction time on removal of Cr(III) (a) and Cr(VI) (b) by BMNs and CMNs



**Figure 2.** XRD patterns (a), TEM-EDS images (b), backscattered electron image (c), STEM-EDS elemental spot map of Fe (d), and STEM-EDS elemental spot map of Cr (e) for BMNs treated Cr(VI)-contaminated water.

To further understand the interaction between Cr(VI) and BMNs, after reaction with Cr(VI) for 48 h, the sample was analyzed by XPS. XPS spectra of C 1s, Fe 2p core level give further proof on the chemical structure of BMNs coated with organic matter (Fig. 3). Before reaction with Cr, the Fe 2p<sub>3/2</sub> peaks appeared at 710.2 and 710.5 eV in BMNs and CMNs, respectively, indicating that Fe is present as Fe<sub>3</sub>O<sub>4</sub> (Cornell and Schwertmann, 2003). BE values at ~710 eV are reported for Fe(II)/Fe(III) oxides. Values of ~711 to ~712 eV are more consistent with values for Fe(III) hydroxide phases (Asami and Hashimoto, 1977).



**Figure 3.** Cr 2p (a) and Fe 2p (b) XPS spectra of CMNs and BMNs treated Cr(III/VI).

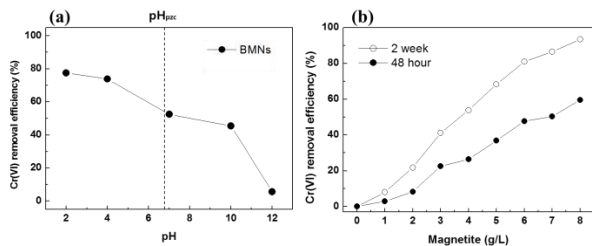
In particular, the C 1s peak at 288.5 eV belonging to carboxylate (–COO<sup>–</sup>) moiety (Zhang *et al.*, 2006) was detected in BMNs, but not in CMNs (data not shown). XPS spectra of chromium from the adsorbent surface after reacting with Cr(III/VI)-solutions are shown in Fig. 3. Fe 2p<sub>3/2</sub> peaks slightly shifted at 710.6 and 710.9 eV in BMNs and CMNs, respectively. The increase of binding energy of Fe 2p<sub>1/2</sub> has been previously suggested as oxidation of Fe(II) to Fe(III) or substitution of Cr(III) for Fe(III) in Cr-

substituted magnetite (Hu *et al.*, 2005; Manjanna and Venkateswaran, 2002). However, further experimental evidences are needed. The deconvolution of the Cr 2p photoelectron peak indicates the existence of at least two Cr chemical species as Cr(VI) and Cr(III). In previous studies, XPS spectra have revealed peaks at ~577 eV for Cr(III) and at ~579 eV for Cr(VI) (Aronniemi *et al.*, 2005). The BE values of the Cr 2p<sub>3/2</sub> peak on BMNs reacted with Cr(III/VI)-solutions and on CMNs reacted with Cr(VI) fall within 576.6 to 577.4 eV. This can be attributed to Cr(III) which corresponds to species that participates in Cr<sub>2</sub>O<sub>3</sub>, CrO(OH), or Cr(OH)<sub>3</sub>. In particular, CMNs reacted with Cr(VI) has shown a peak at 579.5 eV corresponding to Cr(VI) as CrO<sub>4</sub><sup>2–</sup> ion or in CrO<sub>3</sub> (Palloukis *et al.*, 2004). This indicates that Cr is adsorbed onto CMNs as Cr(III) and Cr(VI), suggesting that some adsorbed Cr(VI) anions are reduced to Cr(III) on the surface of CMNs. Adsorbed Cr(VI) on BMNs are dominantly observed as Cr(III) reduced phases. In comparison to BE values reported in previous studies, the lower BE value of 576.6 eV for BMNs reacted with Cr(III)-solution in this study is more comparable to Cr(III) oxides, while the slightly higher values of other samples with BE values of 577.1–577.4 eV are more consistent with Cr(III) hydroxides (Asami and Hashimoto, 1977). However, CMNs reacted with Cr(III) showed no Cr peak, indicating no adsorption during the process. Consequently, these results showed that both magnetites had a high capacity of Cr(VI) adsorption-reduction in aqueous solution. However, CMNs had rapid reaction by Fe(II) oxidation while BMNs showed high efficiency in the long run, indicating that main mechanisms involved in adsorption-reduction were different. These results indicated that Cr(VI) in solution might have been adsorbed onto the surface of CMNs and then reduced to Cr(III) by redox process (Peterson *et al.*, 1997). However, BMNs is a little bit more complicated because it is related to organic complex which might have originated from extracellular polymeric substances (EPS).

### 3.3. Effect of pH for Cr(VI) removal

As results of experiments using different pH solutions, the lower the pH of contaminated solution, the higher the Cr(VI) removal efficiency. The uptake of Cr(VI) by BMNs for 48 h was highly dependent on pH (Fig. 4). The maximum removal efficiency using BMNs was about 77.5% for initial Cr(VI) concentrations of 50 mg/L at pH=2. The amount of Cr(VI) removed from solution was decreased with increasing pH. The removal efficiency was less than 50% at pH > 7. When pH was less than pH<sub>pzc</sub>= 6.8, the surface of BMNs was protonated and the positively charged surface attracted Cr(VI) ions. The variation in removal efficiency at different pH values may be attributed to affinities of BMNs for different species of Cr(VI) existing at acidic pH values, namely H<sub>2</sub>CrO<sub>4</sub>, HCrO<sub>4</sub><sup>–</sup>, CrO<sub>4</sub><sup>2–</sup>, and Cr<sub>2</sub>O<sub>7</sub><sup>2–</sup> (Manuel *et al.*, 1995). Optimum adsorption occurred at pH < 4 (Fig. 4 (a)). With increase in pH, the amount of Cr(VI) removal was decreased because of higher concentration of OH<sup>–</sup> ions present in the reaction mixture which might have competed with Cr(VI) species for the adsorption site (Hu *et al.*, 2005). At pH >

$pH_{pzc}=6.8$ , BMNs surface was negatively charged, thus increasing electrostatic repulsion with negatively charged Cr(VI) species. However, there is neither complete removal (100%) of Cr(VI) at strong acidic pH value (pH = 2), nor complete remain (100%) of Cr(VI) at high pH (pH = 10). Thus, it implies that some other factors might have played a role. In addition the presence of organic matters on BMNs was probably preventing Fe(II) oxidation from the magnetite during short time and leading continuous reactions to achieve high efficiency of Cr(VI) removal during long-term period (Fig. 4 (b)).



**Figure 4.** Cr(VI) removal efficiency by BMNs at different pH values of solutions (a), different reaction time in Cr(VI)-contaminated groundwater (b).

Ion exchange is also expected to occur under alkaline condition. According to Dimitri *et al.* (2000), when affinity of  $CrO_4^{2-}$  with mineral is higher than that of  $OH^-$ ,  $CrO_4^{2-}$  can exchange with  $OH^-$  from the surface of hydrolyzed mineral at high pH. Therefore, Cr(VI) removal by BMNs might be affected by functional organic matter coated on particles, redox reaction, surface charge, and ion affinity depending on pH.

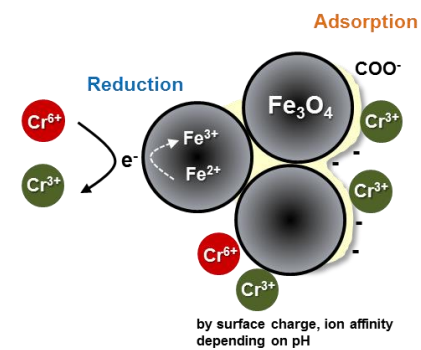
### 3.4. Effect of common ions on Cr(VI) removal

In order to evaluate *in-situ* applicability, various inorganic nutrients dissolved in natural groundwater were used as Cr(VI)-contaminated groundwater. The presence of common ions coexisting with Cr(VI) in groundwater might compete for available adsorption sites. Although not all solutes will compete for the exact same adsorption sites, the presence of other solutes might reduce the adsorption of any given solute to some degree (Hu, *et al.*, 2005). In Cr(VI)-contaminated groundwater, main cations were  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $Al^{3+}$ ,  $Cu^{2+}$ , and  $Fe^{2/3+}$  while the main anions were  $Cl^-$ ,  $NO_3^-$ , and  $SO_4^{2-}$ . As a result, Cr(VI) removal efficiency by BMNs in groundwater was about 94% after 2 weeks of reaction (Fig. 4 (b)). The Cr(VI) removal efficiency in groundwater was slightly lower compared to that using Cr(VI)-solution in distilled water (100%). However, such small competitive influence of these ions could be negligible for *in-situ* remediation (Hu, *et al.*, 2005). As shown in Fig.5, the longer the reaction time, the higher the Cr(VI) removal efficiency.

## 4. Conclusion

Despite high Cr(VI) removal efficiency in acidic contaminated solution, BMNs were relatively stable at pH range of 2 to 10. Therefore, they might be used in most natural and wastewater. BMNs coated with organic matters

were effective to lead adsorption of Cr(III) with electrostatic interaction, and to prevent fast oxidation of Fe(II) within the magnetite structure enhancing Cr(VI) reduction efficiency in the long-run. These results indicate that the coupled adsorption and reduction reactions on BMNs for Cr(VI) removal are accomplished by two reaction sites of mineral surface and functional organic layers (Fig. 5). In addition, Cr(VI) removal using BMNs may be affected by surface charge and ion affinity depending on pH. Therefore, BMNs as functional magnetite-organic complex nanoparticles may be effective for long-term *in-situ* remediation for Cr-contaminated sites with various pH ranges by minimizing the loss of its magnetic recoverability. It also has high potential to applicability for riding heavy metals in environmental remediation technologies.



**Figure 5.** Schematic illustration of the mechanism of Cr(III/VI) removal by biogenic magnetite nanoparticles.

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