Characteristics and kinetics of hexavalent chromium reduction by gallic acid in aqueous solutions

ZiFang Chen, YongSheng Zhao and Qin Li

ABSTRACT

Gallic acid (GA) is a naturally occurring plant polyphenol compound. Experiments were conducted to study the kinetics and effects of pH, temperature, irradiation, and initial hexavalent chromium (Cr(VI)) concentration on Cr(VI) reduction by GA. Results indicated that Cr(VI) could be reduced to chromium oxide (Cr(III)) with GA in a wide range of pH values from 2.0 to 8.5. The reaction followed a pseudo-first-order kinetic model with respect to Cr(VI) and GA in acid conditions (pH 2.0–5.0). However, the reaction did not follow the pseudo-first-order kinetic model at pH 6.5 and 8.5. Removal efficiencies and reaction rate constants of Cr(VI) significantly increased with decreasing pH value and increasing temperature. The effect of irradiation on Cr(VI) reduction increased with increasing pH, and irradiation improved the removal efficiency of Cr(VI) by 11.29% at pH 6.5. At pH 2.0, nearly all molar ratios of GA required for the reduction of Cr(VI) were 1:2 (±0.1) under different initial Cr(VI) concentrations; however, the molar ratios of GA required for the reduction of Cr(VI) were 1:1.29, 1:1.43, and 1:1.69, respectively, when the initial Cr(VI) concentrations were 10, 25, and 50 mg/L at pH 5.5.

Key words | gallic acid, hexavalent chromium reduction, influence factor, kinetics

ZiFang Chen
YongSheng Zhao (corresponding author)
Qin Li
Key Laboratory of Groundwater Resources and
    Environment,
Ministry of Education,
Jilin University,
Changchun 130021,
China
E-mail: zhaoyongsheng@jlu.edu.cn

INTRODUCTION

Chromium contamination is a significant environmental problem worldwide. In China, chromium is one of the most common pollutants at hazardous waste sites and is considered a priority pollutant by the Environmental Protection Agency (Edward et al. 2002; Liu et al. 2014). Extensive distribution of this pollutant in the environment is from natural and anthropogenic sources, particularly industrial pollution sources, such as the refractory industry, wood preservation, leather tanning processes, and electroplating industries (Miretzky & Cirelli 2010). In general, chromium can exist in nine different valence states ranging from -2 to $+6$, but trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) are the two predominant forms because of their stability in natural environments (Saputro et al. 2014). Nakayama et al. (1981) reported that the distribution of chromium species in natural waters was 25–40% for inorganic Cr(VI), 10–20% for inorganic Cr(III), and 45–60% for Cr(III) complexed with dissolved organic carbon.

The toxicity of chromium is directly relevant to its chemical species and the total concentration of all species in the natural environment. Hexavalent chromium is a strong oxidizing and mobile agent, and is highly toxic and carcinogenic to animals and humans (Machado et al. 2014; Tsopmo et al. 2014). In contrast, Cr(III) is relatively less toxic and less mobile in the environment, and a small amount of Cr(III) is biologically essential to mammals because it maintains an effective metabolism (Guru et al. 2008). Trivalent chromium tends to precipitate or bind to the surface of the medium. Compared with Cr(III), Cr(VI) can easily move through sediment and enter aquifers to contaminate groundwater (Cundy et al. 2008). The discharge of Cr(VI) to surface water is regulated to below 0.5 mg/L by the Ministry of Environmental Protection in China, while total Cr, including Cr(III) and Cr(VI), is regulated to below 1.5 mg/L. Given that the valence states of chromium determine its toxicological effects and physico-chemical properties, such as mobility and transport behavior, reduction of Cr(VI) to Cr(III) is one of the major routes for remediation of chromium-contaminated environmental sites (Palmer & Wittbrodt 1991).

The common methods for removing Cr(VI) from soil and water are bioremediation and chemical reduction. Bioremediation of Cr(VI) was performed in some contaminated sites by using bacterial strains to enzymatically reduce this metal (Oliver et al. 2003; Krishna et al. 2005; Jeyasingh

et al. 2010; Molokwane *et al.* 2013). However, bactericidal toxicants or indigenous microorganisms found in contaminated sites would suppress the growth and actual effectiveness of these bacterial strains (Focardi *et al.* 2013; Chirwa *et al.* 2013). Chemical reduction can significantly reduce Cr(VI) to Cr(III), thereby reducing the toxicity of the contaminated environment. In chemical reduction, conventional reductants include zero-valent iron-based reagents (Chen *et al.* 2011; Qiu *et al.* 2012; Fu *et al.* 2014), ferrous-based mixed reagents (Ludwig *et al.* 2007; Chen *et al.* 2012; Henderson *et al.* 2013), and sulfur-based reagents (Chrysochoou *et al.* 2012; Ali *et al.* 2013; Sun *et al.* 2013). However, some reductants are suppressed or are ineffective under the actual conditions in contaminated sites, whereas other reductants may introduce additional environmental problems, such as secondary pollution.

Some naturally occurring organic compounds and environment-friendly organic molecules have been considered for the removal of Cr(VI) from aqueous solutions. Arakawa *et al.* (1993) reported that Cr(VI) was efficiently reduced using alkaline extracts from dead leaves. Okello *et al.* (2012) demonstrated that quercetin and other flavonoids were safe and effective reductants that could quickly reduce Cr(VI) to Cr(III). Xu *et al.* (2004) reported that vitamin C could be used in the effective remediation of Cr(VI) contaminated soils and groundwater at a wide range of pH levels with or without sunlight. Like flavonoids, gallic acid (GA) is a simple polyphenol, widely present in plants and fruits, which is considered one of the precursors of humic substances and is non-toxic to the environment, acting as a free radical scavenger in industry (Asnaashari *et al.* 2014; Lu *et al.* 2006). Nakayasu *et al.* (1999) compared the rate of reduction of Cr(VI) using humic substances containing GA and tannic acid and evaluated the chemical species of chromium after the reduction of Cr(VI) by GA in strong acidic conditions, which did not conform with the pH range in the natural environment.

Gallic acid could reduce Cr(VI) to Cr(III) because the phenolic hydroxyl group has the characteristics of easy oxidation, and the mechanism is that Cr(VI) acts as an electrophile that readily accepts electrons from the phenolic hydroxyl group of GA; it is reduced to Cr(III) and the phenolic hydroxyl group to a quinone (Elovitz & Fish 1995; Nakayasu *et al.* 1999; Xu *et al.* 2007; Eslami *et al.* 2010). However, few studies have investigated the characteristics of the reaction on the reduction of Cr(VI) with GA. In this article, the reaction of Cr(VI) reduction with GA was studied using potassium dichromate solution as a model contaminant. We aimed to evaluate the kinetics of Cr(VI) reduction with respect to Cr(VI) with GA concentration and the effects of various parameters such as pH, temperature, irradiation and initial Cr(VI) concentration. Furthermore, the molar ratio of GA required for the reduction of Cr(VI) was discussed under different pH values.

MATERIALS AND METHODS

Reagents

GA and diphenylcarbazide were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Potassium dichromate, sulfuric acid (98%), phosphorus acid (85%), sodium hydroxide, glacial acetic acid, and anhydrous sodium carbonate were supplied by a chemical plant (Beijing Chemical Works, Beijing, China). Folin–Ciocalteu reagent was purchased from Beijing Dingguo Changsheng Biotechnology Co., Ltd (Beijing, China). All the chemicals were of analytical pure grade and were used as received without any pretreatment. For the experiment, deionized water prepared with Milli-Q Direct (Merck Millipore, Billerica, MA, USA) was used.

Experimental methods

The GA solution was prepared by dissolving 0.12 g of GA into deionized water and subsequently diluting it to 2,000 mL to obtain a 60 mg/L GA solution. The Cr(VI) solution was prepared by dissolving a certain amount of potassium dichromate in deionized water and subsequently diluting it to 1,000 mL to obtain 20, 50, and 100 mg/L Cr(VI) solutions, respectively. The reactions were conducted in 250 mL brown reaction bottles. Reaction mixtures were obtained by collecting 100 mL of Cr(VI) solution (20 mg/L), adjusting the pH value, and adding 100 mL GA solution (60 mg/L) unless otherwise specified. The initial pH of the solution was adjusted with sulfur solution (0.5 M) and sodium hydroxide solution (1.0 M).

Four groups of experiments were established to determine the effects of pH, temperature, irradiation, and initial Cr(VI) concentration on Cr(VI) reduction by GA. To study the effect of pH on Cr(VI) reduction, the pH values used were 2.0, 3.0, 4.0, 5.0, 6.5, and 8.5 (± 0.1), respectively. To study the effect of temperature, experiments with pH levels of 2.5 and 5.5 were performed at different temperatures, namely, 10, 20, and 30 °C (± 1 °C). To study the effect of irradiation, brown reaction bottles and transparent reaction bottles were used under unfiltered light. To study the effect of initial Cr(VI) concentration, Cr(VI) at initial concentrations of 10, 25, and 50 mg/L was reacted with GA at 30 mg/L (0.175 mmol/L), at pH levels of 2.5 and 5.5. At regular time

intervals, 1.0 mL of the mixture solution was collected to determine Cr(VI), and another 5.0 mL of the solution was used to determine GA. All experiments were conducted in a temperature-controlled room at $20 \pm 1\,^{\circ}C$ unless otherwise specified. Each experiment was repeated thrice.

Analytical methods

Hexavalent chromium was measured by the spectrophotometric method at 540 nm using the diphenylcarbazide method after the dilutions. Total chromium was determined by flame atomic absorption spectrometry. The Folin–Ciocalteu method was used to measure the concentration of GA at 765 nm by ultraviolet spectrophotometer (Singleton *et al.* 1999). The pH and temperature were determined using Hach DR900 (Hach Company, Loveland, CO, USA). Instruments used in the experiment included UNIC 7200 visible spectrophotometer (Uinco (Shanghai) Instrument Co. Ltd, Shanghai, China), Shimadzu AA-6300 atomic absorption spectrophotometer (Shimadzu Corp., Kyoto, Japan), and WFZUV-2802H ultraviolet spectrophotometer (Uinco (Shanghai) Instrument Co. Ltd, Shanghai, China).

Kinetics model

Previous studies have demonstrated that the overall reaction of Cr(VI) could be characterized by the pseudo-first-order kinetics model (Wittbrodt *et al.* 1995; Nakayasu *et al.* 1999; Park *et al.* 2007), and the rate model can be expressed as follows:

$$v = \frac{dc}{dt} = -k_{obs}c \tag{1}$$

where v is the reaction rate, c is the Cr(VI) concentration, and k_{obs} is the pseudo-first-order rate constant. Equation (1) can be integrated to calculate Equation (2) as follows:

$$\ln c = \ln c_0 - k_{obs}t \tag{2}$$

Thus, half-time ($t_{1/2}$) is calculated via Equation (3):

$$t_{1/2} = \frac{\ln 2}{k_{obs}} \tag{3}$$

where c_0 is the initial Cr(VI) concentration, and t is the reaction time.

However, the k_{obs} values depend on the concentration of Cr(VI) and GA. Therefore, Elovitz & Fish (1994, 1995)

developed an empirical rate expression based on the reaction of Cr(VI) reduction with phenols, and the reaction rate can be expressed as follows:

$$v = \frac{dc}{dt} = -k_{ArOH}c \times c_{GA} \tag{4}$$

where c_{GA} is the GA initial concentration, and k_{ArOH} $(M^{-1} \cdot h^{-1})$ is the empirical second-order rate constant; k_{obs} is calculated by combining Equations (1) and (4) as follows:

$$k_{obs} = k_{ArOH} \times c_{GA} \tag{5}$$

RESULTS AND DISCUSSION

Effect of pH on Cr(VI) reduction

The relationship between the Cr(VI) reduction reaction and the different pH values is shown in Figure 1. The removal efficiencies of Cr(VI) were 100, 100, 64.01, 38.81, 16.08, and 16.12% at different pH values. GA could reduce Cr(VI) to Cr(III) in a wide range of pH values (2.0–8.5). The initial pH had a significant effect on the reduction of Cr(VI) by GA (Figure 1). At pH $\leq$ 3.0, the removal efficiency of Cr(VI) was 100% within 56 hours. Decreasing pH level resulted in lower reaction time in the mixture solution (the reaction time is the contact time when Cr(VI) concentration was indeclinable in the reaction system). When pH was >3.0, the removal efficiency of Cr(VI) reduction decreased in the aqueous solution.

According to the experimental data, the reaction rate of Cr(VI) reduction by GA could be described by the
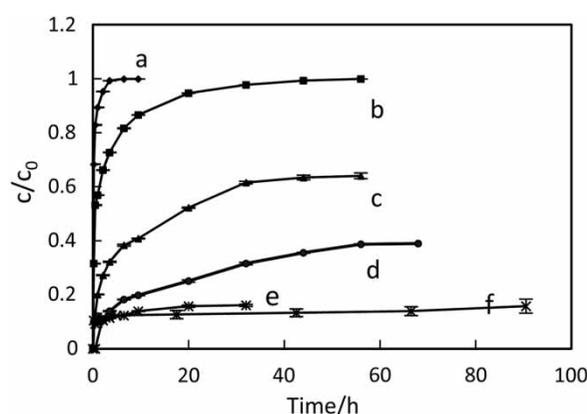

Figure 1 | Effect of pH on Cr(VI) reduction: (a) pH 2.0, (b) pH 3.0, (c) pH 4.0, (d) pH 5.0, (e) pH 6.5, and (f) pH 8.5.

pseudo-first-order kinetic model at pH < 5.0. This result was consistent with the conclusion of Nakayasu et al. (1999). However, the reaction could not be described by the pseudo-first-order kinetic model because R^2 was <0.5 at pH levels of 6.5 and 8.5, indicating that [H$^+$] is insufficient in the reaction solutions. Table 1 summarizes the rate constants at different pH values. These rate constants indicated that the k_{ArOH} increased by 125.9, 54, and 9.19 times with decreasing initial pH from 5.0 to 4.0, 3.0, and 2.0, respectively. The pH level plays an important role in the reduction of Cr(VI) by GA, and low pH levels promote Cr(VI) reduction. Therefore, the reduction rate of Cr(VI) was increased with decreasing pH value, and the removal efficiency was higher under acidic conditions than under neutral or weak alkaline conditions.

In the experiments, the pH was measured after the reaction. The solution pH changed from initial pH values (2.0, 3.0, 4.0, 5.0, 6.5, and 8.5) to 2.1, 3.2, 5.96, 6.35, 6.71, and 7.28, respectively. Results illustrated that Cr(VI) reduction with GA would result in increasing pH in acidic conditions because [H] participated in the reaction and combined with oxygen ions to generate [H$_2$O]. At pH 8.5, the pH was decreased in the reaction system. This may be explained because GA is a trihydroxybenzoic acid, a type of organic acid, which could be hydrolyzed in solution.

Effect of temperature on Cr(VI) reduction

To explore the effect of temperature on Cr(VI) reduction by GA, two groups of experiments were conducted in brown reaction bottles at different temperatures. At pH 2.5, the reaction times were 22, 9.5, and 6 hours when the reaction temperatures were 10, 20, and 30 °C, respectively (Figure 2(a)). Increasing the reaction temperature could shorten the reaction time in the mixture solution. At pH 5.5, the contact time when Cr(VI) concentration was indeclinable in the reaction system was more than 170 hours at different temperatures, which was longer than the reaction time at pH 2.5. The removal efficiencies of Cr(VI) were 47.62%, 55.35, and 58.13% when the reaction temperatures were 10 °C, 20 °C, and 30 °C, respectively (Figure 2(b)). Increasing the reaction temperature could improve the removal efficiency of Cr(VI) when [H$^+$] was insufficient in the reaction solution.

The reaction rate of Cr(VI) reduction by GA followed a pseudo-first-order kinetics model because the correlation coefficient (R^2) was greater than 0.85 at different temperatures. Low pH could improve the reaction rate constants of the Cr(VI) reduction under different temperature conditions (Table 2). The k_{ArOH} increased by 0.61 and 2.68 times at pH 2.5 and by 0.25 and 0.344 times at pH 5.5 when the reaction temperature was adjusted from 10 °C to 20 °C and 30 °C, respectively (Table 2). Increasing the temperature could improve the reaction rate of the Cr(VI) reduction, thereby implying that high temperature could increase the number of activated molecules and could promote Cr(VI) reduction. Therefore, temperature has a significant effect on the reduction of Cr(VI), and increasing

Table 1 | Rate constant and half-time of Cr(VI) reduction at different pH values

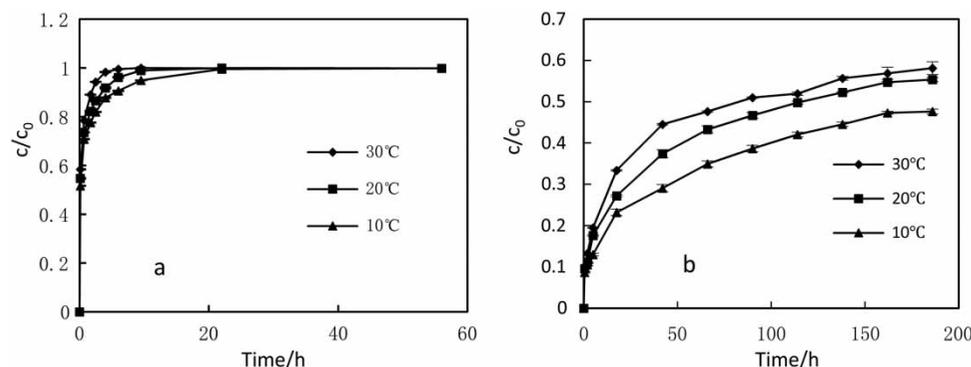| pH	c_{GA}/mmol/L	$10^3 k_{\mathrm{obs}}$/h^{-1}	k_{ArOH}/M^{-1}h^{-1}	$t_{1/2}$/h	R^2
2.0	0.175	951.6	5437.7	0.7	0.9455
3.0	0.175	103.6	592.0	6.7	0.9747
4.0	0.175	17.3	98.9	40.1	0.8531
5.0	0.175	7.5	42.9	92.4	0.9225
6.5	0.175	5.1	29.1	135.9	0.4912
8.5	0.175	1.0	5.7	693.1	0.4135

Figure 2 | Effect of temperature on Cr(VI) reduction at pH 2.5 and 5.5: (a) pH 2.5; (b) pH 5.5.

Table 2 | Rate constant and half-time of Cr(VI) reduction at different temperatures

pH	T/°C	c_{GA}/mmol/L	$10^3 k_{obs}$/h^{-1}	k_{AroH}/M^{-1}h^{-1}	$t_{1/2}$/h	R^2
2.5	30	0.175	756.7	4324.0	0.9	0.9851
	20	0.175	324.4	1853.7	2.1	0.9913
	10	0.175	200.9	1148.0	3.4	0.9987
5.5	30	0.175	4.3	24.6	161.2	0.858
	20	0.175	4.0	22.9	173.3	0.8915
	10	0.175	3.2	18.3	216.6	0.9115

the temperature could improve the reaction rate and improve the removal efficiency of Cr(VI) during Cr(VI) reduction by GA.

In addition, activation energy (E_a) was evaluated from the rate constant study by plotting $\ln(k_{obs})$ versus 1/T(K). The activation energy for reduction under 293, 303 313 K was found to be 47.16 kJ mol^{-1}.
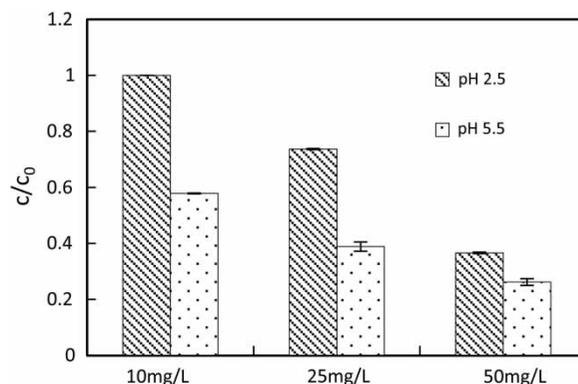
Effect of irradiation on Cr(VI) reduction

The effect of irradiation on the reduction of Cr(VI) by GA was studied with unfiltered sunlight. The effect of irradiation was negligible when the pH was ≤3.0 (Table 3). However, the effect of irradiation gradually increased with increasing pH value and when the pH was >3.0. At pH 6.5, irradiation could improve the removal efficiency of Cr(VI) by 11.29% in the reaction of Cr(VI) reduction by GA. Irradiation catalyzed the reaction of Cr(VI) and GA, and improved the removal efficiency of Cr(VI) at pH >3.0. This finding implies that irradiation promoted electron transfer between the phenolic hydroxyl group and Cr(VI) in the reaction (Yurkow *et al.* 2002; Mytych *et al.* 2003).

Effect of initial Cr(VI) concentration on Cr(VI) reduction

To determine the effect of initial Cr(VI) concentration on the reduction of Cr(VI) by GA, studies were conducted with different initial Cr(VI) concentrations (10, 25, and 50 mg/L) at pH 2.5 and 5.5 (Figure 3). At pH 2.5, the

Table 3 | Removal efficiency of Cr(VI) with or without irradiation units (%)

pH	2.0	3.0	4.0	5.0	6.5	8.5
Dark	99.87	99.87	64.01	38.81	16.08	16.12
Sunlight	99.87	99.87	70.81	48.85	27.37	38.42
△	0	0	6.80	10.04	11.29	12.30

Figure 3 | Effect of initial Cr(VI) concentration on Cr(VI) reduction.

removal efficiencies of hexavalent chromium were 99.87%, 73.65%, and 36.63%, however, the molars of GA required for the reduction of Cr(VI) are 0.095, 0.170, and 0.171 mmol/L, respectively (initial GA concentration 0.175 ± 0.01 mmol/L). So, the molar ratios of GA required for the reduction of hexavalent chromium were 1:2.02, 1:2.08, and 1:2.06 (±0.2), respectively, under the different initial Cr(VI) concentrations. However, the removal efficiencies of Cr(VI) were 57.82%, 38.86%, and 26.22%, and the molars of GA required for the reduction of Cr(VI) are 0.086 mmol/L, 0.123 mmol/L, and 0.169 mmol/L, respectively. The corresponding molar ratios of GA required for the reduction of Cr(VI) were 1:1.29, 1:1.43, and 1:1.69 (±0.2) at pH 5.5, respectively.

The effect of the initial Cr(VI) concentration on Cr(VI) reduction by GA differed with various pH levels. At pH 2.5, the initial Cr(VI) concentration had little effect on the Cr(VI) reduction, but the removal amount of Cr(VI) per unit time increased with increasing initial Cr(VI) concentration based on the nearly similar reaction time. The molar ratio of GA required to reduce Cr(VI) was approximately 1:2, that is, each molecule of GA offers six electrons to the reaction. The H$^+$ played an important role in the reaction, and sufficient H$^+$ might eliminate the effect of different initial Cr(VI) concentrations on the Cr(VI) reduction. At pH 5.5, the molar ratio of GA required for the reduction of Cr(VI) gradually decreased with increasing initial Cr(VI) concentration. This may be explained because higher initial Cr(VI) concentration could provide more activated molecules, thereby improving the reaction moles of Cr(VI) when the number of hydrogen ions was insufficient (at pH 5.5). This result is similar to phenols oxidation reactions at different pH levels (Elovitz & Fish 1995). Therefore, the reaction involved in the Cr(VI) reduction by GA was complicated because of the different molar ratios

of GA required for the reduction of hexavalent chromium under different conditions.

CONCLUSION

Reduction of Cr(VI) by GA was studied using potassium dichromate solution as the target contaminant. Gallic acid is a non-toxic substance and a naturally occurring reductant that could reduce Cr(VI) to Cr(III) in a wide range of pH values, thereby reducing the toxicity of Cr(VI)-contaminated aqueous solutions. The reaction followed a pseudo-first-order kinetics model with respect to Cr(VI) and GA at pH ≤ 5.0. The pH and temperature significantly affected the reduction of Cr(VI). A decrease in pH value or an increase in temperature could accelerate the reaction rate and significantly improve removal efficiency. Irradiation with unfiltered sunlight could improve the removal rate of Cr(VI) at pH > 3.0. The effect of the initial Cr(VI) concentration was dependent on the pH value, and a high initial Cr(VI) concentration can promote Cr(VI) reduction with a unit of GA when H^+ is insufficient in the aqueous solution (pH 5.5). On the contrary, a different Cr(VI) concentration has no effect on molar ratios of GA required for the reduction of Cr(VI) at pH 2.5.

ACKNOWLEDGEMENTS

REFERENCES

Ali, S., Farooq, M. A., Hussain, S., Yasmeen, T., Abbasi, G. H. & Zhang, G. P. 2013 Alleviation of chromium toxicity by hydrogen sulfide in barley. *Environmental Toxicology and Chemistry* **32**, 2234–2239.

Arakawa, H., Tsushima, M., Kishi, M. & Watanabe, N. 1993 Reduction of chromium(VI) by water-extracts from withered oak leaves. *Chemistry Letters* **22**, 2113–2116.

Asnaashari, M., Farhoosh, R. & Sharif, A. 2014 Antioxidant activity of gallic acid and methyl gallate in triacylglycerols of Kilka fish oil and its oil-in-water emulsion. *Food Chemistry* **159**, 439–444.

Chen, C. P., Juang, K. W. & Lee, D. Y. 2012 Effects of liming on Cr(VI) reduction and Cr phytotoxicity in Cr(VI)-contaminated soils. *Soil Science and Plant Nutrition* **58**, 135–143.

Chen, J., Xiu, Z., Lowry, G. V. & Alvarez, P. J. 2011 Effect of natural organic matter on toxicity and reactivity of nano-scale zero-valent iron. *Water Research* **45**, 1995–2001.

Chirwa, E. M. N., Venter, I. & Wienand, H. 2013 Biological Cr(VI) immobilisation in saturated aquifer zone using culture inoculated soil columns *Water Science and Technology* **67**, 2321–2329.

Chrysochoou, M., Johnston, C. P. & Dahal, G. 2012 A comparative evaluation of hexavalent chromium treatment in contaminated soil by calcium polysulfide and green-tea nanoscale zero-valent iron. *Journal of Hazardous Materials* **201–202**, 33–42.

Cundy, A. B., Hopkinson, L. & Whitby, R. L. D. 2008 Use of iron-based technologies in contaminated land and groundwater remediation: a review. *Science of the Total Environment* **400**, 42–51.

Edward, J. H., Yurkow, J., Samantha, M. & Su, W. 2002 Photochemical reduction of hexavalent chromium in glycerol-containing solutions. *Environmental Pollution* **117**, 1–3.

Elovitz, M. S. & Fish, W. 1994 Redox interactions of Cr(VI) and substituted phenols: kinetic investigation. *Environmental Science & Technology* **28**, 2161–2169.

Elovitz, M. S. & Fish, W. 1995 Redox interactions of Cr(VI) and substituted phenols: products and mechanism. *Environmental Science & Technology* **29**, 1933–1943.

Eslami, A. C., Asanphan, W. P., Wagner, B. A. & Buettner, G. R. 2010 Free radicals produced by the oxidation of gallic acid: an electron paramagnetic resonance study. *Chemistry Central Journal* **4**, 15–18.

Focardi, S., Pepi, M. & Focardi, S. E. 2013 Microbial reduction of hexavalent chromium as a mechanism of detoxification and possible bioremediation applications. In: R. Chamy & F. Rosenkranz (eds) *Bioremediation – Life of Science*, Rijeka, Croatia.

Fu, F., Dionysiou, D. D. & Liu, H. 2014 The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. *Journal of Hazardous Materials* **267C**, 194–205.

Guru, M., Venedik, D. & Murathan, A. 2008 Removal of trivalent chromium from water using low-cost natural diatomite. *Journal of Hazardous Materials* **160**, 318–323.

Henderson, A. D. & Demond, A. H. 2013 Permeability of iron sulfide (FeS)-based materials for groundwater remediation. *Water Research* **47**, 1267–1276.

Jeyasingh, J., Somasundaram, V., Philip, L. & Bhallamudi, S. M. 2010 Bioremediation of Cr(VI) contaminated soil/sludge: experimental studies and development of a management model. *Chemical Engineering Journal* **160**, 556–564.

Krishna, K. R. & Philip, L. 2005 Bioremediation of Cr(VI) in contaminated soils. *Journal of Hazardous Materials* **121**, 109–117.

Liu, H., Bruton, T. A., Doyle, F. M. & Sedlak, D. L. 2014 In situ chemical oxidation of contaminated groundwater by persulfate: decomposition by Fe(III)- and Mn(IV)-containing oxides and aquifer materials. *Environmental Science & Technology* **48**, 10330–10336.

Lu, Z., Nie, G., Belton, P. S., Tang, H. & Zhao, B. 2006 Structure-activity relationship analysis of antioxidant ability and neuroprotective effect of gallic acid derivatives. *Neurochemistry International* **48**, 263–274.

Ludwig, R. D., Su, C. M., Lee, T. R., Wilkin, R. T., Acree, S. D., Ross, R. R. & Keeley, A. 2007 In situ chemical reduction of Cr(VI) in groundwater using a combination of ferrous sulfate and sodium dithionite: A field investigation. *Environmental Science & Technology* **41**, 5299–5305.

Machado, T. C., Lansarin, M. A. & Matte, N. 2014 Reduction of hexavalent chromium: photocatalysis and photochemistry and their application in wastewater remediation. *Water Science and Technology* **70**, 55–61.

Miretzky, P. & Cirelli, A. F. 2010 Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. *Journal of Hazardous Materials* **180**, 1–19.

Molokwane, P. E. & Chirwa, E. M. N. 2013 Modelling biological Cr(VI) reduction in aquifer microcosm column systems. *Water Science and Technology* **67**, 2733–2738.

Mytych, P., Karocki, A. & Stasicka, Z. 2003 Mechanism of photochemical reduction of chromium(VI) by alcohols and its environmental aspects. *Journal of Photochemistry and Photobiology A: Chemistry* **160**, 163–170.

Nakayama, E., Tokoro, H., Kuwamoto, T. & Fujinaga, T. 1981 Dissolved state of chromium in seawater. *Nature* **290**, 768–770.

Nakayasu, K., Fukushima, M., Sasaki, K., Tanaka, S. & Nakamura, H. 1999 Comparative studies of the reduction behavior of chromium(VI) by humic substances and their precursors. *Environmental Toxicology and Chemistry* **18**, 1085–1090.

Okello, V. A., Mwilu, S., Noah, N., Zhou, A., Chong, J., Knipfing, M. T., Doetschman, D. & Sadik, O. A., 2012 Reduction of hexavalent chromium using naturally-derived flavonoids. *Environmental Science & Technology* **46**, 10743–10751.

Oliver, D. S., Brockman, F. J., Bowman, R. S. & Kieft, T. L. 2003 Microbial reduction of hexavalent chromium under vadose zone conditions. *Journal of Environmental Quality* **32**, 317–324.

Palmer, C. D. & Wittbrodt, P. R. 1991 Process affecting the remediation of chromium contaminated sites. *Environmental Health Perspectives* **92**, 25–40.

Park, D., Yun, Y. S., Ahn, C. K. & Park, J. M. 2007 Kinetics of the reduction of hexavalent chromium with the brown seaweed Ecklonia biomass. *Chemosphere* **66**, 939–946.

Qiu, X., Fang, Z., Yan, X., Gu, F. & Jiang, F. 2012 Emergency remediation of simulated chromium (VI)-polluted river by nanoscale zero-valent iron: Laboratory study and numerical simulation. *Chemical Engineering Journal* **193–194**, 358–365.

Saputro, S., Yoshimura, K., Matsuoka, S., Takehara, K., Narsito, Aizawa J. & Tennichi, Y. 2014 Speciation of dissolved chromium and the mechanisms controlling its concentration in natural water. *Chemical Geology* **364**, 33–41.

Singleton, V. L., Orthofer, R. & Lamuela-Raventos, R. M. 1999 Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. *Methods in Enzymology* **299**, 152–178.

Sun, W. Y., Shen, W., Wang, Q. Y., Ding, S. L. & Su, S. J. 2013 Adsorption of chromium (VI) from aqueous solution onto aluminum pillared pyrolusite leaching residue. *Fresenius Environmental Bulletin* **22**, 2645–2650.

Tsopmo, A., Gao, Q. & Baakdah, M. M. 2014 Reduction of hexavalent chromium by digested oat bran proteins. *Food Chemistry* **153**, 171–176.

Wittbrodt, P. R. & Palmer, C. D. 1995 Reduction of Cr(VI) in the presence of excess soil fulvic acid. *Environmental Science & Technology.* **29**, 255–263.

Xu, G. R., In, M. Y., Yuan, Y., Lee, J. J. & Kim, S. 2007 In situ spectroelectrochemical study of quercetin oxidation and complexation with metal ions in acidic solutions. *Bulletin of the Korean Chemical Society* **28**, 889–892.

Xu, X. R., Li, H. B., Li, X. Y. & Gu, J. D. 2004 Reduction of hexavalent chromium by ascorbic acid in aqueous solutions. *Chemosphere* **57**, 609–613.

Yurkow, E. J., Hong, J., Min, S. & Wang, S. 2002 Photochemical reduction of hexavalent chromium in glycerol-containing solutions. *Environmental Pollution* **117**, 1–3.