

RESEARCH ARTICLE

**Hexavalent Chromium Reduction
by Water-Soluble Antioxidants**

*Chemical Sciences
Journal, Vol. 2012:
CSJ-88*

Hexavalent Chromium Reduction by Water-Soluble Antioxidants

D Kim¹, J Om², C Kim^{3*}

¹ Lambert High School, Suwanee, GA, USA.

² Aqua Vectors, Inc., Halesite, NY, USA.

³ School of Science and Technology, Georgia Gwinnett College, Lawrenceville, GA, USA.

*Correspondence to: Chulsung Kim, ckim@ggc.edu

Accepted: Nov 16, 2012; Published: Nov 24, 2012

Abstract

Coffee and black tea, two common beverages, were investigated as potential electron donors to reduce Cr(VI) to Cr(III). Antioxidant capacity experiments showed that both coffee and black tea are strong antioxidants that provide electrons. When 2 grams of either fresh coffee or black tea were applied to 25 mL of 20 mg/L Cr(VI) solution, all of the Cr(VI) disappeared within 10 minutes. When, instead of using fresh coffee and black tea, residue collected after brewing was applied to the Cr(VI) solution, most of the Cr(VI) disappeared with the used black tea within 3 hours, and approximately 75% of the Cr(VI) was removed with the used coffee within the 8-hour reaction period. The research confirmed that coffee and black tea are excellent, ecofriendly natural electron donors to remediate Cr(VI)-contaminated water without any harmful chemicals. Used coffee and black tea can also be recycled as potential electron providers for Cr(VI) detoxification technology.

Keywords: Hexavalent chromium; coffee; black tea; remediation.

1. Introduction

Coffee and tea are the most widely consumed beverages in the world, other than water [1, 2]. Green and black teas are the most common teas in the world [3], with black tea consumption much higher than green tea: black and green teas make up approximately 80.0% and 19.5%, respectively, of total tea consumption in the United States [4]. Coffee is another leading beverage in the United States, and approximately 54% of those 18 years or older in the US population drink coffee every day, at an average rate of three cups per day [5]. Both coffee and black tea have been considered as great source for antioxidants which are reducing agents. These antioxidants protect essential human body components from the reactive oxygen species by providing electrons to those electron seekers that are continuously produced through metabolism [6]. Although tea has long been well known as the leading antioxidant beverage, a recent study showed that coffee is in fact the leading antioxidant resource for Americans, not because of its high antioxidant capacity but because of its high consumption [7].

Chromium is the 21st most common element in the Earth's crust, with various oxidation states [8]. Among them, hexavalent [Cr(VI)] and trivalent [Cr(III)] chromium are commonly found in nature. Due to its two oxidation states, it has a dual face with respect to health effects. Trivalent chromium [Cr(III)] is an essential nutrient for mammals, aiding normal metabolism and having low solubility. Despite the positive health effects of Cr(III), Cr(VI) is a very soluble element and a potential carcinogen [9]. Due to these two distinguishing toxicity and solubility properties of Cr(VI) and Cr(III), reduction of Cr(VI) to Cr(III) has been applied as a remediation technology for Cr(VI)-contaminated water. Various reducing agents, such as iron compounds [10, 11], small organic compounds [12], hydrogen sulfide gas [13], and microorganisms [14, 15], have been studied and applied to remediate Cr(VI)-contaminated water.

In this research, efforts have been made to study the potential application of two common antioxidant-containing substances, coffee and black tea, for the remediation of Cr(VI)-contaminated wastewater. Bench-top experiments were performed to investigate hexavalent chromium reduction by both fresh and used coffee and black tea. The primary benefits of the proposed technology include a) the application of non-toxic, environmentally friendly reducing agents for Cr(VI) reduction, and b) the creation of a potential recycling method for used coffee and black tea.

2. Methods

Bench-top experiments were conducted in order to study the effect of fresh and used coffee and black tea on the reduction of Cr(VI). Stock solution of 1,000 mg/L Cr(VI) was prepared using potassium dichromate (K₂Cr₂O₇), and the solution was stored in an amber bottle. Fresh hexavalent chromium solution (20 mg/L) was prepared for each

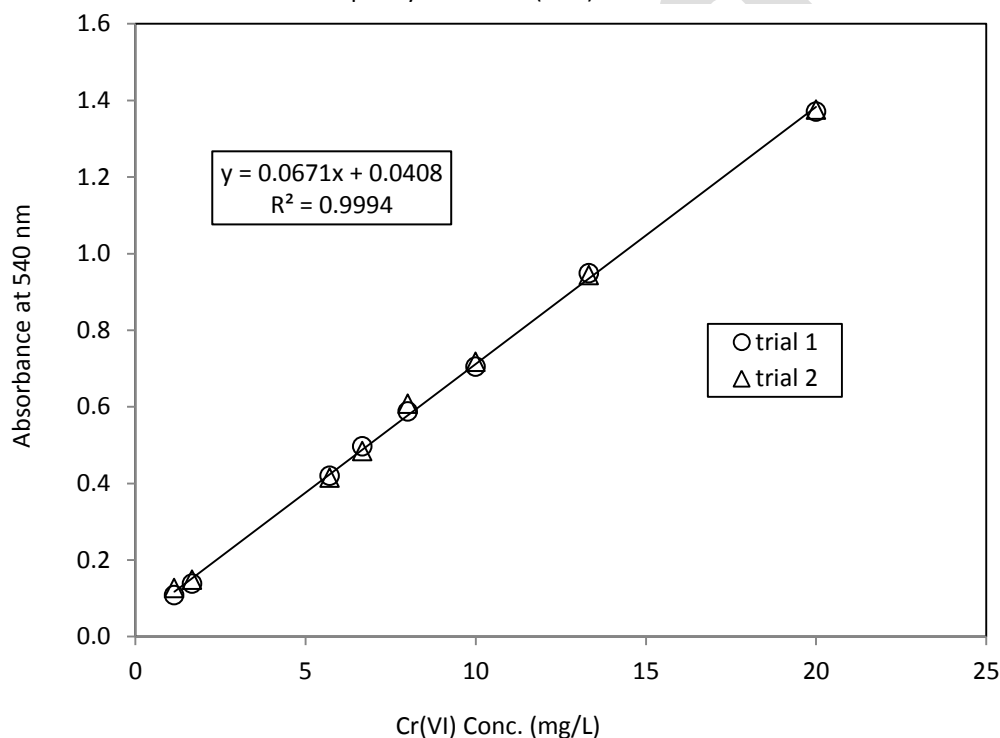
experiment, and the concentration of Cr(VI) was determined using a slightly modified diphenylcarbazide (DPC) colorimetric method [16] controlling the pH with phosphate buffer. The concentration of Cr(VI) was determined by measuring absorbance at 540 nm using a spectrophotometer (Vernier VIS-NIR). All chemicals used for this research were ACS grade or higher, and the DPC solution was prepared with acetone. All prepared solutions were stored in amber bottles and kept in a refrigerator. Fresh DPC solution was prepared every two weeks or when the solution turned pinkish in color. Solution pH was measured using an IQ 150 pH meter (IQ Scientific Instruments Inc.).

Cr(VI) concentration as a function of time was monitored in the presence of fresh or used coffee and black tea. The mass-to-volume ratio of the introduced amount of coffee or black tea to the 20 mg/L of Cr(VI) solution was 2g/100mL. The solution of Cr(VI) with either coffee or black tea was prepared in a 125 mL Erlenmeyer flask, which was swirled during the reaction period using a flat form shaker (Innova 2000, New Brunswick Scientific). Samples were taken from the flask, followed by filtering using Fisher P4 filter paper before determining the amount of Cr(VI) in the solution. All the experiments were performed at room temperature and duplicated.

3. Results and Discussion

In a prior study of the Cr(VI) reduction by coffee and black tea, the standard curve was developed (Figure 1). As shown in Figure 1, the two trials showed very consistent results and the regression line was obtained based on the average values.

Figure 1: Standard curve for hexavalent chromium [Cr(VI)] in mg/L using slightly modified diphenylcarbazide (DPC) method.

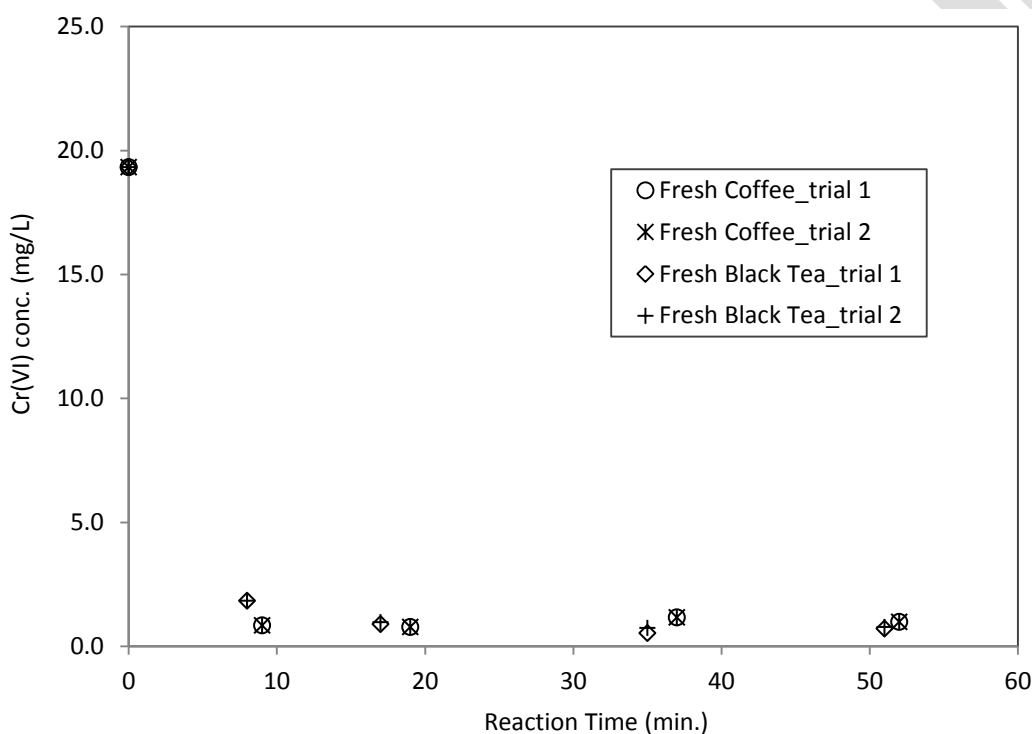


Preliminary tests confirmed that the color of tea and coffee did not effect on the absorbance of Cr(VI)-DPC complexes. Therefore, in this research, all Cr(VI) concentration in the experimental solutions was determined using the regression equation shown in Figure 1.

The Cr(VI) disappearance rate as a function of time in the presence of either fresh coffee or tea was also performed and the results are shown in Figure 2. The ratio of fresh coffee or black tea mass to hexavalent chromium [Cr(VI)] solution volume was $\left(\frac{0.5 \text{ grams of fresh coffee or black tea}}{25 \text{ mL of Cr(VI) solution}}\right)$ and the initial Cr(VI) concentration was targeted for 20 mg/L. As shown in the Figure 2, both fresh coffee and black tea have strong

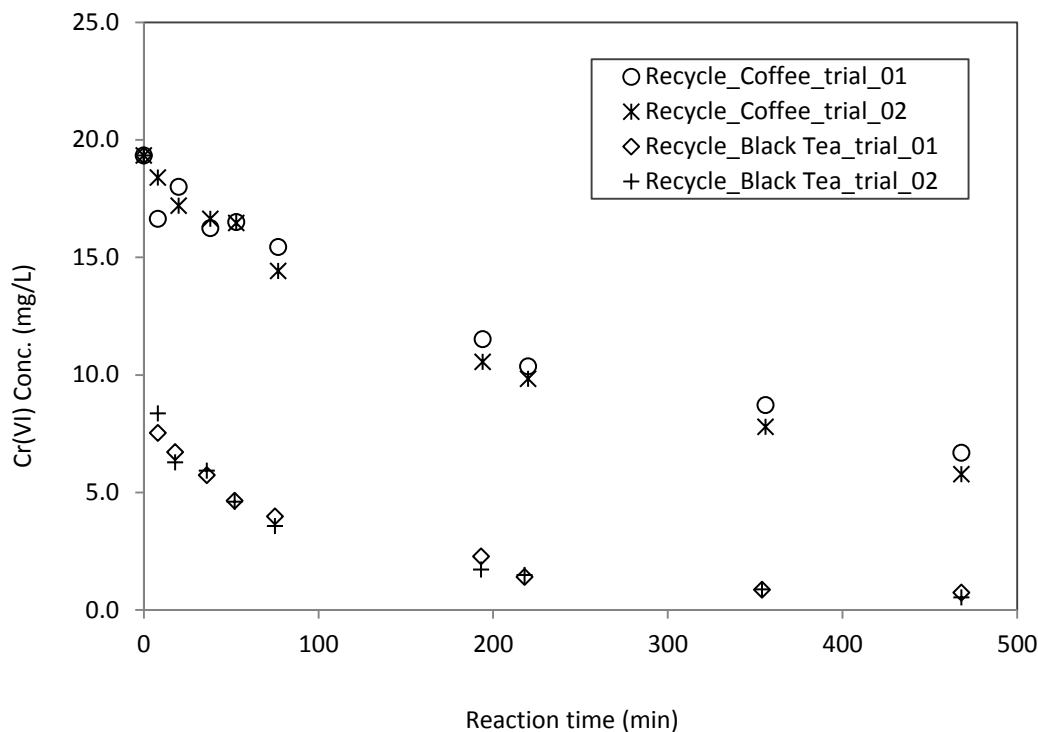
reduction capacities with respect to Cr(VI) which were disappeared instantly. The initial dissolved amount of Cr(VI) for this specific experiment was 9.61 micromole (0.5 mg), which requires 28.8 micromole of electrons to be fully reduced to trivalent chromium [Cr(III)]. The available electrons could be come from the instantly dissolved various antioxidants from coffee and black tea indicating that those antioxidants play as reducing agents proving electrons to Cr(VI). The initial pH of the Cr(VI) 20 mg/L solution was 6.6 ± 0.2 and as the reaction underwent, the pH changed to 5.6 ± 0.2 which was very close to the pH values of prepared coffee and tea. While no buffer was introduced in this reaction, the pH of the Cr(VI) reduction reaction was likely controlled by the introduced coffee and black tea within the reaction pH range between 5.6 and 6.6.

Figure 2: Hexavalent chromium [Cr(VI)] disappearance rate in the presence of either fresh coffee or tea as a function of time.



Additional experiments were performed with the used coffee and black tea. Black tea from used tea bags and coffee after brewing were collected and air dried. Hexavalent chromium [Cr(VI)] reduction experiments in the presence of used coffee and black tea were performed using the same procedures as those with fresh coffee and black tea. The Cr(VI) reduction as a function of reaction time with used coffee and black tea are shown in Figure 3. As shown in Figure 3, the used coffee and black tea are strong enough to reduce dissolved Cr(VI). The used black tea has a higher reducing capacity than the used coffee. Most of the Cr(VI) disappeared within three hours in the presence of used black tea, whereas with used coffee, approximately 25% of the initial Cr(VI) still remained after 8 hours of reaction time. There should be two factors that play important roles for the reduction of Cr(VI) in the presence of used coffee or black tea; a) the total available amount of antioxidants in coffee and black tea, and b) dissolution rate of the available antioxidants from coffee and tea. Because the antioxidant capacity of black tea is higher than that for coffee [10], the used black tea may show higher reducing capacity of Cr(VI) than used coffee. However, with the very limited information about the dissolution rate of those available antioxidants from coffee and black tea, it is difficult to identify the effects of dissolution rate on the Cr(VI) reduction by used coffee or black tea.

Figure 3: Hexavalent chromium [Cr(VI)] disappear rate in the presence of used coffee and tea as a function of time. (The ratio of mass to volume of Cr(VI) solution was $\left(\frac{0.5 \text{ grams of used coffee or black tea}}{25 \text{ mL of Cr(VI) solution}}\right)$; initial Cr(VI) concentration was targeted for 20 mg/L)



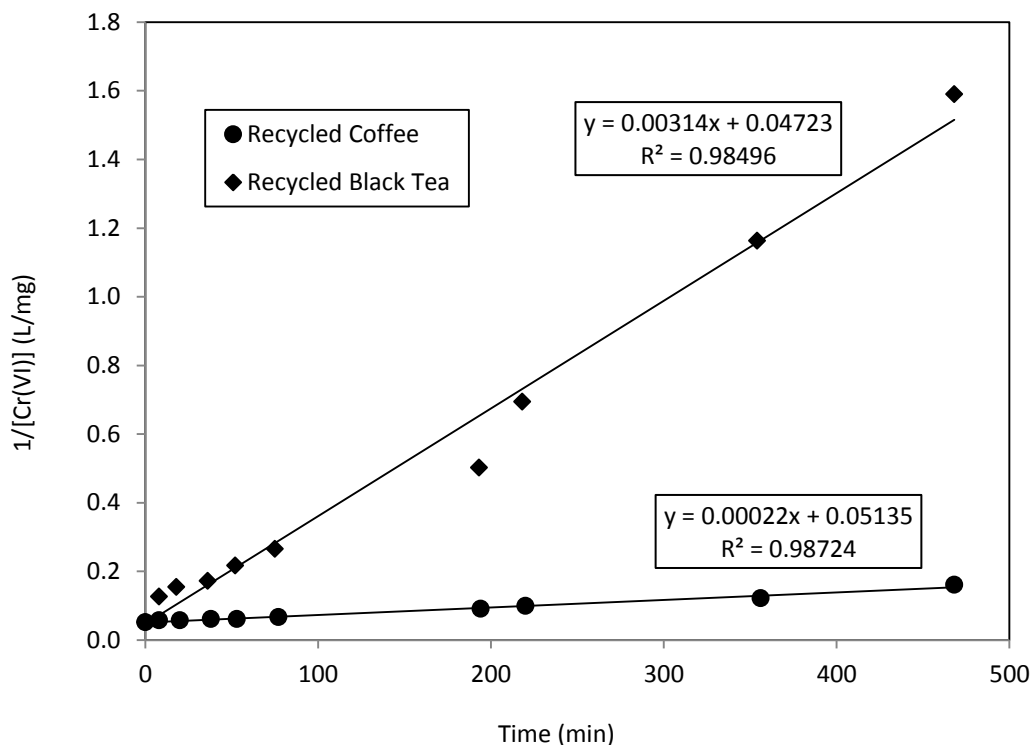
Regarding the Cr(VI) disappearance rate in the presence of used coffee and black tea as a function of time, pseudo second-order rate constants were determined, as shown in Figure 4. The determined pseudo second-order reaction rate constants (k_{obs}) for Cr(VI) in the presence of used coffee and black tea were 0.00022 and $0.0031 \text{ min}^{-1} \text{ L mg}^{-1}$, respectively. It should be noted that while the pseudo second-order reaction rates obtained in this research were well fitted to the Cr(VI) reduction rates with used coffee and black tea, this is only the general, integrated exemplification for the reaction rate. There should be various dissolved antioxidants and potential non-antioxidant electron donors available from the used coffee and black tea, and each dissolved species has different reaction rate with Cr(VI), resulting in different rate constant. The obtained pseudo second-order reaction rate, however, could be valuable information for predicting the Cr(VI) disappearance rate in the presence of used coffee and black tea. In summary, coffee and black tea are non-toxic, environmentally friendly reducing agents that could be used to remediate toxic hexavalent chromium [Cr(VI)]-contaminated water.

4. Conclusion

Hexavalent chromium reduction by used coffee and black tea was investigated. The conventionally prepared coffee and black tea showed significant amounts of antioxidant capacity. The research also showed that these antioxidants have strong relationship with Cr(VI)-reducing capacity. When 0.5 gram of fresh coffee or black tea was introduced to 25 mL of 20-mg/L Cr(VI) solution, most of the Cr(VI) was reduced within 10 minutes. When the residue after brewing coffee and black tea were collected, air dried, and introduced to the Cr(VI) solution, this used coffee and black tea also showed Cr(VI) reduction capacity, although the Cr(VI) disappearance rate was significantly dropped from the ones with fresh coffee and black tea. Most of the Cr(VI) disappeared in the presence of used black tea within 3 hours, while approximately 75% of the Cr(VI) was reduced in the presence of used coffee after 8 hours. The research observations clearly showed that both used coffee and black tea are excellent

candidates as reducing agents to remediate hexavalent chromium [Cr(VI)]-contaminated water. Most importantly, the reducing agents introduced in our research were non-toxic, ecofriendly, biodegradable food wastes.

Figure 4: Pseudo second order Cr(VI) reduction rate in the presence of used coffee and black tea (The figure was plotted based on the second order integration method expression as $\frac{1}{[Cr(VI)]_t} = k_{obs}t + \frac{1}{[Cr(VI)]_0}$. The pseudo second order rate constants (k_{obs}) for used coffee and black tea are 0.00022 and $0.0031 \text{ min}^{-1} \text{ L mg}^{-1}$.)



Competing Interests

Authors do not have any competing interests regarding this published work.

Authors' Contributions

DK performed experiments and collected data. The initial draft was also prepared by DK. JO oversaw the project and analyzed the data. CK supported Cr(VI) determination method, reviewed the draft and finalized the manuscript.

References

1. USDA, Agricultural Research Service. Brewing up the latest tea research. [<http://www.ars.usda.gov/is/ar/archive/sep03/tea0903.htm>]
2. Harvard School of Public Health. The nutrition source; Healthy beverage guidelines. [<http://www.hsph.harvard.edu/nutritionsource/healthy-drinks/healthy-drinks-full-story/index.html#level-2>]
3. Karori SM, Wachira FN, Wanyoko JK, Ngure RM, 2007. Antioxidant capacity of different types of tea products. African Journal of Biotechnology, 6(19): 2287–2296.
4. The Tea Association of the USA, Tea fact sheet. [<http://www.teausa.com/index.cfm/14655/tea-fact-sheet>]
5. Harvard School of Public Health, Coffee by the numbers. [<http://www.hsph.harvard.edu/multimedia/flash/2010/coffee/facts.html>]
6. Gliszcznsk-Swiglo A, 2006. Antioxidant activity of water soluble vitamins in the TEAC (trolox equivalent antioxidant capacity) and the FRAP (ferric reducing antioxidant power) assays. Food Chemistry, 96(1): 131–136.

7. Vinson, JA, 2005. Polyphenols: Total Amounts in Foods and Beverages and US per Capita Consumption [abstract], 230th National Meeting of American Chemical Society, AGFD 10.
8. Barnhart J, 1997. Occurrences, uses, and properties of chromium. *Regulatory Toxicology and Pharmacology*, 26(1): S3-S7.
9. Gaggelli E, Beti F, D'Amelio N, Gaggelli N, Valensin G, Bovalini L, *et al.*, 2002. Metabolic pathways of carcinogenic chromium. *Environmental Health Perspectives*, 110(5): 733–738.
10. Ponder SM, Darab JG, Mallouk TE, 2000. Remediation of Cr(VI) and Pb(II) aqueous solutions using supported, nanoscale zero-valent iron. *Environmental Science and Technology*, 34: 2564–2569.
11. Bond D, Fendorf S, 2003. Kinetics and structural constraints of chromate reduction by green rusts. *Environmental Science and Technology*, 37: 2750–2757.
12. Deng B, Stone AT, 1996. Surface-catalyzed chromium(VI) reduction: the TiO₂-Mandelic acid system. *Environmental Science and Technology*, 30: 463–472.
13. Lan Y, Deng B, Kim C, Thornton EC, Xu H, 2005. Catalysis of elemental sulfur nanoparticles of chromium(VI) reduction by sulfide under anaerobic conditions. *Environmental Science and Technology*, 39: 2087–2094.
14. Masood F, Malik A, 2001. Hexavalent chromium reduction by *Bacillus* sp. Strain FM1 isolated from heavy-metal contaminated soil. *Bulletin of Environmental Contamination and Toxicology*, 86: 114–119.
15. Batool R, Yrjala K, Hasnain S, 2012. Hexavalent chromium reduction by bacteria from tannery effluent. *Journal of Microbiology and Biotechnology*, 22(4): 547–554.
16. APHA; AWWA; WPCF, 1998. Metals. In *Standard methods for the examination of water and wastewater*. 20th edition. Edited by Clesceri LS, Greenberg AE, Eaton AD. Washington, DC: American Public Health Association, 3/65 – 3/70.