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Application of ferrous iron containing minerals to remove Hexavalent chromium from soil

Mahdieh Khorshid[1*], Shahin Oustan[1], Norsatollah Najafi[1], Alireza Khataee[2]

[1] *Department of Soil Science, Faculty of Agriculture, University of Tabriz, Iran*

[2] *Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Iran*

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Abstract

In this research, the removal of hexavalent chromium from three Cr (VI)-spiked soils by different Fe (II) containing minerals (phlogopite, biotite, magnetite and pyrite) was investigated. The soils received Cr (VI) in two levels (100 and 500 mg Cr (VI) kg^{-1} soil) and then were subjected to several wetting and drying cycles for one month. A batch experiment was carried out in the mineral amended soils (5 and 10 g kg^{-1}) for 1 and 4 weeks. Significant differences ($p<0.01$) were observed between the Cr (VI) removal efficiency of the amendments. On average, pyrite removed Cr (VI) from the soils 18%, 29% and 37% more efficient than magnetite, biotite and phologopite, respectively. Increasing the amendment dosage and contact time had more or less little effect on the Cr (VI) removal efficiency. The mean Cr (VI) removal efficiencies were 5.43±0.87, 14.65±1.93 and 40.87±5.46% for soils 1, 2 and 3, respectively. According to the results obtained soil characteristics, particularly pH and organic carbon, play dominant role both in self and amendment-induced removal efficiencies of Cr (VI).

***Corresponding Author:** Mahdieh Khorshid ✉ m.khorshid@tabrizu.ac.ir

Introduction

Chromium is ranked one of the top 20 environmental contaminants on the list of hazardous substances (ATSDR, 2014). Two stable oxidation forms of chromium, Cr (III) and Cr (VI), exists in natural environments. Hexavalent form (Cr (VI)) is soluble, mobile, toxic and carcinogenic, while trivalent form (Cr (III)) is an essential micronutrient for humans and insoluble in media with pH values greater than 5.5 (Kantar *et al.*, 2015). Therefore, reduction of Cr (VI) to Cr (III) and its subsequent precipitation, is of great importance for remediation of Cr (VI)-contaminated soils and ground waters. In aqueous solutions, Cr (VI) is mainly present as monomeric forms of $H_2CrO_4^o$, $HCrO_4^-$ (bichromate) and CrO_4^{2-} (chromate). These oxyanions are highly mobile and severely affect the environment (Palmer and Wittbrodt, 1991; Richard and Bourg, 1991). Reduction of Cr (VI) can be accomplished either chemically or biologically using reducing agents (USPEA, 2000). The rate of Cr (VI) reduction strongly depend on the reductant type, pH and other co-existing chemical components (Zhitkovich, 2011). Immobilization of Cr (VI) by using ferrous sulfate has been known for years (Kostarelos *et al.*, 2009; Di Palma *et al.*, 2015). However, some Fe (II) containing minerals could be particularly important for Cr (VI) reduction. Reduction of Cr (VI) to Cr (III) is coupled with oxidation of Fe (II) to Fe (III) and then rapid precipitation of Fe (III)–Cr(III) hydroxide (Equation 2) or Fe (III)–Cr (III) oxyhydroxide solid solutions (Equation 3), which considerably decreases the possibility of any reaction back to forming Cr (VI) (Özer *et al.*, 1997).

$$HCrO_4^{2-} + 3Fe^{2+} + 7H^+ \rightarrow 3Cr^{3+} + 3Fe^{3+} + 4H_2O \quad (1)$$
$$(1\text{-}x)Fe^{3+} + xCr^{3+} + 3H_2O \rightarrow Cr_xFe_{1-x}(OH)_3 + 3H^+ \quad (2)$$
$$(1\text{-}x)Fe^{3+} + xCr^{3+} + 2H_2O \rightarrow Cr_xFe_{1-x}(OOH) + 3H^+ \quad (3)$$

Eary and Rai (1989) investigation on Cr (VI) reduction by hematite and biotite and founded the reduction takes place in the solution phase rather than in the solid-liquid interface. Jung and Lee (2005), Jung *et al.*, (2007) observed Cr (VI) was transformed to Cr (III) coupled with the oxidations of Fe (II) to Fe (III) in magnetite surface. Several studied have been done on the Cr (VI) reduction by pyrite under acidic conditions (Chon *et al.*, 2006; Lin and Huang, 2008).

Most of previous studies have been focused on Cr (VI) reduction by ferrous iron containing minerals in soilless systems and little research has been done in soil environment. The aim of this study was to compare the efficiency of some Fe (II) containing minerals including magnetite, pyrite, biotite and phlogopite to remove Cr (VI) as a function of soil type, Cr (VI) concentration, reductant dosage and contact time.

Materials and methods

Materials

A natural single crystal of pyrite was obtained from Mazraeh mines located in the northeast of Ahar, Iran. Phlogopite and biotite were prepared from Kara-Bag mine in Urmia and Iran Minerals Production and Supply Company, respectively. Magnetite was purchased from Sigma Aldrich Company. All other reagents with analytical grade, obtained from Merck Chemical Company, Germany.

Soil Samples

Three medium textured soil samples were collected from the upper layer (0 to 20-cm) of the agricultural fields in East Azerbaijan (the alkaline soil, namely soil 1) and Gilan (the neutral soil, namely soil 2 and the slightly acid soil, namely soil 3) provinces in northwest and north of Iran, respectively. The soils were air dried and then ground and sieved to <2 mm. Some physical and chemical characteristics of the soils were measured. Soil $pH_{1:1}$ (McLean, 1982), soil texture (Gee and Bauder, 1986), organic carbon (OC) content (Nelson and Sommers, 1982), calcium carbonate equivalent (CCE) (Allison and Moodie, 1965), cation exchange capacity (CEC) (Chapman, 1965), easily reducible Mn (Gambrell and Patrick, 1982). The exchangeable Cr (VI) concentration of the soils was determined using the James and Bartlett method (1983). The Cr (VI) concentration was determined by the diphenylcarbazide colorimetric method (USEPA, 1992) in filtered samples by measuring the absorbance at 540 nm using a spectrophotometer (HACH, DR 2000).

Experimental Procedure

One kg of each soil was mixed thoroughly with proper amounts of K_2CrO_4 to obtain Cr (VI) concentrations of 0, 100 and 500 mg kg^{-1}. The spiked soil samples were kept at room temperature for one month. The moisture content of the soils was maintained in field capacity (FC) condition by periodical watering. Then, soils were left to air dry. Thereafter, the soils were gently grounded to pass through a 2-mm sieve and stored in plastic bags until use. To reach the desired ionic strength, 45 ml of a 0.03 M KCl solution was added to 5.00 g of air dried Cr (VI) spiked soil and left to stand for 24 hour to equilibrate (Kantar *et al.* 2008). After pre-equilibration, the suspensions were amended with 0 (control), 5 and 10 g kg^{-1} soil of different amendments including pyrite, magnetite, biotite and phlogopite (all passed through a 200 mesh sieve). These suspensions were shaken at 120 rpm for one and four weeks at 25°C. Then, 5 mL of buffer solution (0.8 M KH_2PO_4/0.8 M K_2HPO_4) was added to the suspensions. The pH of the extraction solution was adjusted to 7.2 (James and Bartlett, 1983). Finally, the suspensions were shaking at 120 rpm for 2 h and passed through a Whatman 42 filter paper. Aliquots of the soil extracts were used for Cr (VI) concentration determination.

Calculations

The Cr (VI) removal percentages in the control soils (R_c) were calculated as follows (Choppala *et al.*, 2013):

$$R_c = \frac{Cr_0 - Cr_{exch.}^{control}}{Cr_0} \times 100 \qquad (4)$$

Where, Cr_0 is the concentration of Cr(VI) (mg kg^{-1}) added to the soils and $Cr_{exch}^{control}$ is the exchangeable Cr (VI) (mgkg^{-1}) of the control soils after incubation period.

The Cr (VI) removal percentages in the amended soils (R_a) were calculated as follows:

$$R_a = \frac{Cr_{exch.}^{unamended} - Cr_{exch.}^{amended}}{Cr_{exch.}^{unamended}} \times 100 \qquad (5)$$

where, $Cr_{exch.}^{unamended}$ and $Cr_{exch.}^{amended}$ are the concentration of Cr (VI) (mg kg^{-1}) in the control and amended soils, respectively after shaking times.

Results and discussion

Properties of the Soils

Some physical and chemical properties of the soils used in the study are presented in Table 1. The soils varied in OC, pH and CCE. The soil 1 was alkaline (pH 8.15) with less than 10 g kg^{-1} OC, and moderately calcareous (68 g kg^{-1}), while soils 2 and 3 are neutral (pH = 7.05) and slightly acidic (pH = 6.1) and contain 19.5 and 35 g kg^{-1} OC, respectively. Both of the later soils were free of calcium carbonate.

Table 1. Characteristics of the investigated soils.

Soil No.	$pH_{1:1}$	Easily reducible Mn (mg kg^{-1})	Texture	CEC (cmol$_c$ kg^{-1})	OC (g kg^{-1})	CCE (g kg^{-1})
1	8.15	207	Sandy clay loam	14.4	9	68
2	7.05	323	Loam	20.7	19.5	nil
3	6.10	196	Silty loam	42.3	35	nil

CEC: cation exchange capacity, OC: organic carbon, CCE: calcium carbonate equivalent.

The Cr (VI) removal percentage in the control soils (R_c)

Three soils used in this study illustrated different efficiencies of Cr (VI) self-removal. The Cr (VI) removal percentages from the control soils (R_c), when various Cr (VI) concentrations spiked, are showed in Table 2. The removal percentage decreased with increasing concentration of Cr (VI) and values ranged from 13% to 100%. The Cr (VI) self-removal in soil 3 was greater than two other soils. This soil completely removed Cr (VI) at the100 and 500 mg Cr (VI) kg soil^{-1} within a period of 4 weeks. For this reason, soil 3 was spiked with 1000 mg Cr (VI) kg soil^{-1}. Both lower pH and higher organic matter content may be responsible for the complete removal of Cr (VI) in this soil. Soil organic matter has been recognized as an effective Cr (VI) reductant, particularly at low pH values as shown in the Equation 6 (Losi *et al.*, 1994; Wittbrodt and Palmer, 1995 or Banks *et al.*, 2006).

$$3CH_2O \text{ (organic matter)} + 4CrO_4^{2-} + 5H^+ + 2H_2O \rightarrow 4Cr(OH)_3(s) + 3HCO_3 \quad (6)$$

Table 2. The removal percentage of Cr (VI) in the control soils (R_c values).

Soil No.	Initial Cr(VI) (mg kg^{-1})	Removal Cr(VI) (%)
1	100	41
	500	13
2	100	91
	500	66
3	100	100
	500	100
	1000	96

As it is obvious from the above equation, the Cr (Vl) reduction increases with increasing soil organic carbon content as well as the decreasing soil pH. The lowest content of organic carbon and highest pH was found in soil 1, therefore, the least self-removal of Cr (VI) was occurred in this soil. As a conclusion, the residual Cr (VI) concentration in the control soils depends on organic carbon content and pH. Bartlett and Kimble (1976), Jardine *et al.,* (2007), Xiao *et al.*, (2012) demonstrated that Cr (VI) in the soil was favorably reduced by soil organic matter under acid and neutral conditions.

The Cr (VI) removal efficiency in the amended soils (R_a)

Fig. 1. shows the Cr (VI) removal efficiency in the three Cr (VI)-spiked soils at four levels of Fe (II) containing minerals (pyrite, magnetite, biotite, phlogopite) in 2 dosages (5 and 10 g kg^{-1}) after 1 and 4 weeks. The results from the soils spiked with 100 and 500 mg Cr (VI) kg^{-1}soil revealed that significant ($p<0.01$) decreases in removal Cr (VI) efficiency by amendments were detected with increasing Cr (VI) spiked. This indicates that there are limited reactive surface site on minerals. Graham and Bouwer (2012) reported [Cr (VI)]/[pyrite reactive sites] has a important role on Cr (VI) reduction.

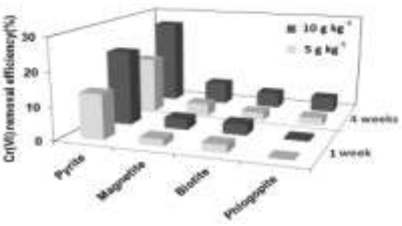

Fig. 1. (a)

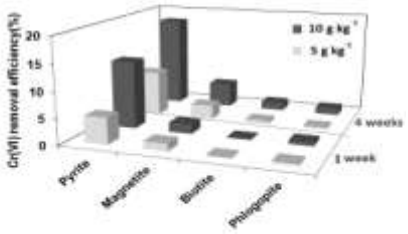

Fig. 1. (b)

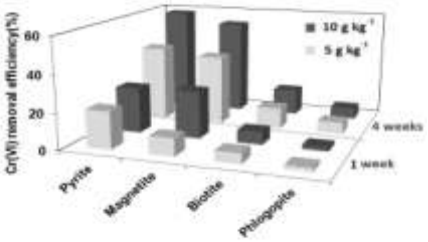

Fig. 1. (c)

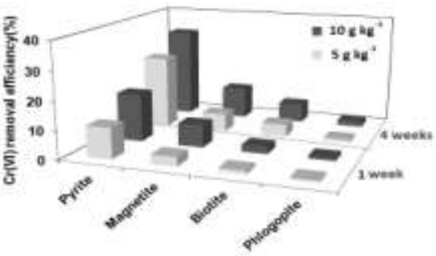

Fig. 1. (d)

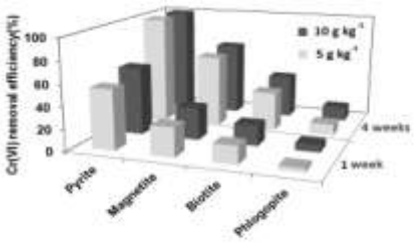

Fig. 1. (e)

Fig. 1. The Cr (VI) removal efficiency in three Cr (VI)-spiked soils amended with four Fe (II) containing minerals (pyrite, magnetite, biotite, phlogopite) at 2 dosages (5 and 10 g kg^{-1}) after 1 and 4

weeks a) soil 1: 100 mg Cr (VI) kg^{-1}, b) soil 1: 500 mg Cr (VI) kg^{-1}, c) soil 2: 100 mg Cr (VI) kg^{-1}, d) soil 2: 500 mg Cr (VI) kg^{-1}, e) soil 3: 1000 mg Cr (VI) kg^{--1}.

Although the four amendments were able to remove Cr (VI) from soils, significant differences ($p<0.01$) in the Cr (VI) removal efficiency were observed between amendments. Pyrite showed remarkably higher Cr (VI) removal efficiency than other minerals. Pyrite at dosage of 5 g kg^{-1} could completely remove Cr (VI) from soil 3 in 4 weeks. The Cr (VI) removal efficiency by amendments followed: pyrite> magnetite> biotite> phologopite. Duncan test indicated that in all of the soils pyrite and phologopite were, respectively, the strongest and the weakest amendments (Table 3). On average, the efficiency of pyrite for Cr (VI) removal was 18%, 29% and 37% higher than magnetite, biotite and phologopite, respectively. Although there is no clear agreement on the reaction mechanism involved in Cr (VI) reduction by pyrite, it is approved that the reduction of toxic Cr (VI) to non-toxic Cr (III) species, coupled with the oxidation of Fe (II) to Fe (III) and disulfide (S_2^{2-}) to sulfate (SO_4^{2-}) on the pyrite surface as well as in aqueous phase (Mullet *et al.*, 2007; Lin and Huang, 2008; Graham and Bouwer, 2012):

Cr (VI)+ pyrite → Cr (III) + Fe(III)+ SO_4^2.

Table 3. The Duncan's mean comparison test for Cr (VI) removal efficiency.

		pyrite		magnetite		biotite		phlogopite	
Dosage(g kg^{-1})		5	10	5	10	5	10	5	10
Soil No	1	11.12^b	19.97^a	2.14^{cd}	4.17^c	1.37^d	2.47^{cd}	1.03^d	1.19^d
	2	24.78^b	33.21^a	14.51^c	24.54^b	7.10^{cd}	7.60^{cd}	2.56^d	2.82^d
	3	77.56^a	81.34^a	46.58^b	48.90^b	26.19^c	29.43^c	7.00^d	9.95^d

Doubling dosages of pyrite, magnetite, biotite and phlogopite form 5 to 10 g kg^{-1} increased the Cr (VI) removal efficiency by 8, 5, 2 and 1%, respectively. Despite the less than expected results, these increases were significant at $p<0.01$ as illustrated by the analysis of variance. Additionally, the Cr (VI) reduction by the minerals proceed considerably over time in three soils and significant differences ($p<0.01$) were observed between the minerals. By increasing the contact time from 1 to 4 weeks, the efficiency of pyrite, magnetite, biotite and phlogopite for Cr (VI) reduction increased by 22, 19, 9 and 3%, respectively.

Results revealed the importance of soil characteristics particularly pH and organic carbon in Cr (VI) self-removal efficiency. Also, three soils under study showed vast variation in mean Cr (VI) removal efficiency using the ferrous iron containing minerals. The corresponding values were 5.43±0.87, 14.65±1.93 and 40.87±5.46% for soils 1, 2 and 3, respectively. Increasing pH of the soils causes severe oxidation of mineral surfaces and forming passivated surfaces. Kantar *et al.* (2015) using pyrite as a reducing agent observed much slower rate of Cr (VI) reduction under alkaline than acidic conditions. On the other hand, soil organic carbon may increases Cr (VI) reduction by the minerals through: 1) forming highly soluble Cr (III) and Fe (III) complexes and decreasing surface oxidation products, 2) increases dissolving of Fe (II) from mineral and subsequently reduced Cr (VI) to Cr (III) (Kantar *et al.*, 2014).

Conclusion

The results revealed the significant effect of soil native pH values and organic matter contents on Cr (VI) removal percentages in the control soils. The Cr (VI) removal percentage was high in the soil with Low pH and high organic carbon. All fe (II) containing minerals employed in this study indicated ability for removal of Cr (VI) from the different Cr-spiked soils, however differences in the Cr (VI) removal efficiency were significant ($p<0.01$) between minerals. The Cr (VI) removal efficiency by amendments followed: pyrite> magnetite> biotite> phologopite. Soil type was the important factor in Cr (VI) removal efficiency by minerals. Cr (VI) removal efficiency increased with increasing contact time and decreased with increasing initial Cr (VI) concentrations.

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