



## Reduction of chromium toxicity by applying various soil amendments in artificially contaminated soil

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### Original Article

#### Abstract

Six soil amendments including municipal solid waste compost (MSWC), coal fly ash (CFA), rice husk biochar prepared at 300°C (B300) and 600°C (B600), zerovalent iron (Fe<sup>0</sup>), and zerovalent manganese (Mn<sup>0</sup>) were evaluated to determine their ability to reduce mobility of chromium (Cr) in a Cr-spiked soil. The Cr-spiked soil samples were separately incubated with selected amendments at 2 and 5% [weight by weight (W/W)] for 90 days at 25 °C. The efficacy of amendment treatments was evaluated using desorption kinetic experiment and sequential extraction procedure. Results showed that applications of various amendments had significant effects on desorption and chemical forms of Cr. Addition of amendments considerably decreased mobility factor (except for CFA<sub>5%</sub>) of Cr compared to the control treatment. The addition of Fe<sup>0</sup>, MSWC, and B300 to soil significantly decreased Cr release, compared to other amendments. The lowest Cr desorption was achieved by Fe<sup>0</sup> at 5%. Application of B600 and CFA increased soil pH and caused the oxidation of Cr(III) to Cr(VI). Based on the obtained highest values of coefficient of determination (R<sup>2</sup>) and lowest values of standard error (SE) of the estimate, the two first-order reaction model could be best fitted for describing Cr release in soil samples. In general, from the practical view, Fe<sup>0</sup>, MSWC, and B300 treatments are effective in Cr immobilization, while application of Fe<sup>0</sup> at 5% was the best treatment for stabilization of Cr. Therefore, these treatments can be recommended for the immobilization of Cr from polluted soil.

**KEYWORDS:** Stabilization, Chromium, Amendments, Desorption Kinetic

**Date of submission:** 16 Aug 2014, **Date of acceptance:** 22 Sep 2014

**Citation:** Saffari M, Karimian N, Ronaghi A, Yasrebi J, Ghasemi-Fasaei R. **Reduction of chromium toxicity by applying various soil amendments in artificially contaminated soil.** J Adv Environ Health Res 2014; 2(4): 251-62.

#### Introduction

Soil pollution by heavy metals is a major problem in many countries. Chromium is a heavy metal, the concentration of which considerably increases in the environment due to industrial activities. Chromium exists in multiple valence states in the environment, but the most common forms are trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. The mobility

of Cr in soil depends on its oxidation state.<sup>1</sup> The toxicity and mobility of Cr(VI) is higher than Cr(III) in soil.<sup>1</sup> Hence, the stabilization of Cr principally deals with the reduction of Cr(VI) to Cr(III).

Chemical stabilization techniques are used to reduce heavy metals mobility in the soil using contaminant-immobilizing amendments. The use of immobilizing amendments in polluted soils as a remediation procedure can reduce mobility and bioavailability of heavy metals by adsorption, complex formation, or (co)precipitation process. Previous researches

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have reported that Cr(VI) is reduced to Cr(III) by soil organic matter and  $Fe^{2+}$ .<sup>1</sup> On the other hand, Cr(III) can be oxidized to Cr(VI) by manganese oxides<sup>2,3</sup> and alkaline resources (such as coal fly ash) that increase soil pH above neutral.<sup>4,5</sup>

Currently, there are no common methodologies to assess chemical stabilization efficiency. Nevertheless, several methods were used to estimate the soil stabilization efficiency of various amendments in heavy metals stabilization in soils, such as sequential extraction method, leaching test, and adsorption-desorption experiments. The mobility of heavy metals is controlled by the sorption and desorption characteristics of soil.<sup>6</sup> The desorption technique of heavy metals in soil can be related to their mobility and toxicity.<sup>7</sup> In addition, sequential extraction procedures can be useful in monitoring the stabilization process of heavy metals in soil. A typical sequential procedure starts with a weak solvent, followed by a stronger solvent in order to sequentially solubilize various operationally defined metal fractions; exchangeable (EX), carbonate-bound (Car), reducible [Mn-oxide-bound (Mn-OX)], oxidisable [amorphous and crystalline Fe-oxide-bound (FeA-Ox and FeC-Ox)], and residual metal fractions.<sup>8</sup> The Ex and Car fractions are considerably mobile, while other fractions are less mobile in soil. Several extractants were used for the evaluation of heavy metal mobility in soils and sediments using batch methods.<sup>9,10</sup> Acidic solutions, dilute salt solutions, and complexing agents are usually used as extractants.<sup>9,11</sup>

Application of inappropriate amendments may increase the mobility of heavy metals in

soil. In addition, very few researches have been performed on Cr stabilization due to the low reactivity of its common species in soil. Therefore, the present study was conducted to recognize appropriate amendments for Cr stabilization by chemical stabilization technique in soil. The main objectives of this study were to evaluate the influence of coal fly ash (CFA), municipal solid waste compost (MSWC), two types of rice husk biochar (B300 and B600), zerovalent iron ( $Fe^0$ ), and zerovalent manganese ( $Mn^0$ ) on release and chemical form of Cr in contaminated calcareous soil in order to reduce the risk of increasing of Cr in the environment.

## Materials and Methods

Surface (0–30 cm) soil samples were collected (fine, mixed, mesic, Fluventic Calcixerepts) from Shiraz, Fars Province, Iran. Selected chemical and physical properties were determined using standard methods.<sup>12</sup> Plant available form of heavy metals was extracted using diethylene triamine pentaacetic acid (DTPA). Total content of heavy metals were determined using 4M  $HNO_3$  and measured using an atomic absorption spectrometer (Shimadzu AA-670, Shimadzu Corp., Kyoto, KYT, Japan).<sup>13</sup> In order to determine the concentration of Cr(VI), alkaline digestion was applied (0.5 mol/l NaOH + 0.28 mol/l  $Na_2CO_3$ ) and the amount of Cr(VI) was measured using the colorimetric method with 1,5-diphenylcarbazide (DPC) at a wavelength of 540 Nm.<sup>14</sup> Cr(III) amount was calculated by subtracting Cr(VI) from total Cr. The selected properties of soil are presented in table 1.

**Table 1. Selected chemical and physical properties of studied soil**

Property	Value	Property (mg/kg)	Value
pH	7.8	Soluble Fe in DTPA	4.1
CCE (%)	39.5	Soluble Cu in DTPA	0.9
Sand (%)	27	Soluble Mn in DTPA	5.6
Clay (%)	35	Soluble Cr in DTPA	1.6
OM (%)	1.4	Soluble Cr in $NaNO_3$	2.8
CEC (Cmol(+)/kg)	15.8	Total Cr	109.0
EC (dS/m)	0.65	Cr(VI)	8.5

CCE: calcium carbonate equivalent; OM: organic matter; CEC: cation-exchange capacity; EC: electrical conductivity; DTPA: diethylene triamine pentaacetic acid

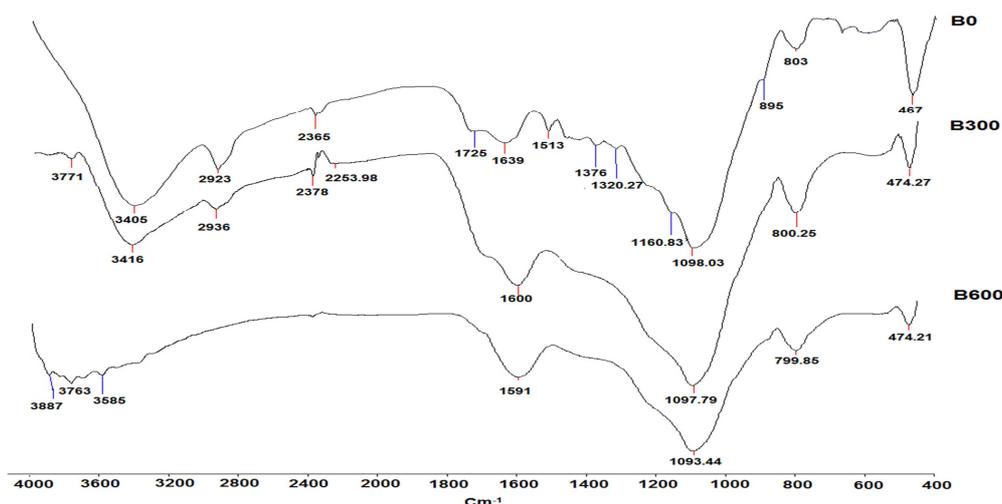
Various amendments were used for their abilities to decrease Cr mobility in Cr-spiked Soil; CFA, MSWC, rice husk biochar prepared at 300°C (B300) and 600 °C (B600), zerovalent iron (Fe<sup>0</sup>), and zerovalent manganese (Mn<sup>0</sup>). CFA and MSWC were collected from Zarand Coal Washing Factory and the Recycling and Municipal Solid Waste Compost Factory of Kerman, Iran, respectively. Biochar was prepared at 300 °C and 600 °C from rice husk. Husk samples (covered with aluminum foil) were

placed in a furnace for 4 hours to produce biochar. Zerovalent iron (Fe<sup>0</sup>, 99.5%, in the form of iron grit) and zerovalent manganese (Mn<sup>0</sup>, 99.5%, in the form of manganese grit) were used in the present study. The selected properties of the used amendments are presented in table 2. In addition, fourier transform infrared spectroscopy (FT-IR) (Spectrum RXI, PerkinElmer Inc., Waltham, MA, USA) was used for the recognition of the morphology and structure of the produced biochar (Figure 1).

**Table 2. Selected chemical composition of amendments**

Amendments	Chemical properties				
CFA	SiO <sub>2</sub> (%) <sup>*</sup>	Al <sub>2</sub> O <sub>3</sub> (%) <sup>*</sup>	TiO <sub>2</sub> (%) <sup>*</sup>	Fe <sub>2</sub> O <sub>3</sub> (%) <sup>*</sup>	CaO (%) <sup>*</sup>
	46.47	27.32	0.90	6.73	4.56
	BaO (%) <sup>*</sup>	SrO (%) <sup>*</sup>	MgO (%) <sup>*</sup>	K <sub>2</sub> O (%) <sup>*</sup>	Na <sub>2</sub> O (%) <sup>*</sup>
	0.15	0.14	2.32	3.42	0.82
	SO <sub>3</sub> (%) <sup>*</sup>	P <sub>2</sub> O <sub>5</sub> (%) <sup>*</sup>	Mn <sub>3</sub> O <sub>4</sub> (%) <sup>*</sup>	pH	C (%) <sup>**</sup>
4.60	4.60	0.82	9.1	67	
MSWC	H (%) <sup>**</sup>	n (%) <sup>**</sup>	O (%) <sup>**</sup>	-	-
	3.80	3.92	0.96	-	-
	pH	EC (dS/m)	OM (%)	Cu (mg/kg)	Zn (mg/kg)
	7.40	19.36	38.00	19	28
	Fe (mg/kg)	Mn (mg/kg)	Pb (mg/kg)	Cd (mg/kg)	Ni (mg/kg)
25.00	11.00	13.30	0.28	1.2	
B300	pH	EC (dS/m)	C (%) <sup>**</sup>	H (%) <sup>**</sup>	n (%) <sup>**</sup>
	6.20	13.10	41.57	2.11	1.52
B600	8.70	21.20	48.99	1.55	Trace

<sup>\*</sup>Determined by X-ray fluorescence (XRF) analyzer; <sup>\*\*</sup>Determined by CHN analyzer; CFA: Coal fly ash; MSWC: Municipal solid waste compost



**Figure 1. FTIR spectra of rice husk before (B0) and after pyrolysis (B300 and B600) [X-axis and Y-axis are wavenumber (cm<sup>-1</sup>) and transmittance (%), respectively]**

**Table 3. Experimental design for incubation experiment**

Treatment	Amendment (applied rate) (%)	Treatment	Amendment (applied rate) (%)
S1	MSWC (2)	S7	B600 (2)
S2	MSWC (5)	S8	B600 (5)
S3	CFA (2)	S9	Fe <sup>0</sup> (2)
S4	CFA (5)	S10	Fe <sup>0</sup> (5)
S5	B300 (2)	S11	Mn <sup>0</sup> (2)
S6	B300 (5)	S12	Mn <sup>0</sup> (5)

CFA: Coal fly ash; MSWC: Municipal solid waste compost

**Table 4. Summary of the sequential extraction procedure used in this study**

g soil: ml solution	Extracting solution	Shaking time (h)	Chemical form of Cr	Symbol
10:40	1 m Mg(NO <sub>3</sub> ) <sub>2</sub>	2	Exchangeable	EX
10:40	1 m NaOAc (pH = 5 CH <sub>3</sub> COOH)	5	Carbonate-bound	Car
10:20	0.7 m NaOCl (pH = 8.5)	0.5 in boiling water	Organically-bound*	Om
5:50	0.1 m NH <sub>2</sub> OH.HCl (pH = 2 HNO <sub>3</sub> )	0.5 in boiling water	Mn-oxide-bound	Mn-OX
5:50	0.25 m NH <sub>2</sub> OH.HCl + 0.25 m HCl	0.5 at 50°C in water	Amorphous Fe-oxide-bound	FeA-Ox
5:50	0.2 m (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 0.2 m H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> + 0.1 MC <sub>6</sub> H <sub>8</sub> O <sub>6</sub>	0.5 in boiling water	Crystalline Fe-oxide-bound	FeC-Ox

\* Two times extraction

For the incubation experiment, soil samples were placed in plastic and Cr(VI) was added at the rate of 500 µg/g as K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. Selected amendments were added to each soil sample separately, at two levels [2 and 5% weight by weight (W/W)] (Table 3), and each soil sample was mixed thoroughly. The soil samples were incubated for 90 days at 25 °C. Moisture was preserved at field capacity (FC). After incubation, samples were air-dried and used for Cr desorption and fractionation study.

Soil Cr was fractionated to 7 fractions using the Singh et al.<sup>15</sup> method. Table 4 provides an outline of the Singh et al.<sup>15</sup> procedure. Residual forms (Res) were calculated by subtracting the sum of 6 fractions from total Cr. Cr mobility was evaluated using a mobility factor<sup>16</sup>, and calculated according to the following equation:

$$(Ex + Car / \text{sum of fractions}) \times 100$$

Desorption kinetics of Cr(VI) was studied by means of batch-type experiments; 5 g of each soil sample, in triplicate, was placed in polyethylene tubes and extracted separately with 25 ml of two extractants: 0.01 m Ethylenediaminetetraacetic acid (EDTA) at pH 7.0 and 25 ml of 0.01 m NaNO<sub>3</sub>. Samples were shaken for periods of 0.08

to 102.25 hours (0.08, 0.25, 0.58, 1.25, 2.25, 4.25, 8.25, 16.25, 30.25, 54.25, and 102.25 hour) at 25 ± 2°C, and then, centrifuged immediately at 2500 rpm. The supernatants were filtered through filter paper and Cr concentration was determined using an atomic absorption spectrometer.

A two first-order kinetic model was used as an approximate method for describing Cr desorption. A two first-order reaction model can divide Cr into 3 fractions<sup>9,10</sup>, Q<sub>1</sub>, Q<sub>2</sub>, and Q<sub>3</sub> as follows:

$$q = Q_1(1 - e^{-k_1t}) + Q_2(1 - e^{-k_2t})$$

$$Q_3 = q_{\text{total}} - Q_2 - Q_1$$

where q represents amount of Cr released at time t, Q<sub>1</sub> (mg/kg) is labile fraction, readily extractable, associated to the rate constant k<sub>1</sub>, and Q<sub>2</sub> (mg/kg) is moderately labile fraction, less extractable, associated to the rate constant k<sub>2</sub>, Q<sub>3</sub> (mg/kg) is Cr fraction, which is not extractable, and q<sub>total</sub> is the total concentration of Cr in the soil.

This model was tested by the coefficient of determination (R<sup>2</sup>) and standard error (SE) of estimate.

The SE was calculated as follows:

$$SE = \left[ \frac{\sum(E - E')^2}{n - 2} \right]^{0.5}$$

where E and E' are the measured and calculated amounts of Cr release in soil at time t, respectively, and n is the number of measurements. The regression of nonlinear procedure and other statistical analyses were calculated by Microsoft Excel 2007 (Microsoft Corp., Redmond, WA, USA).

## Results and Discussion

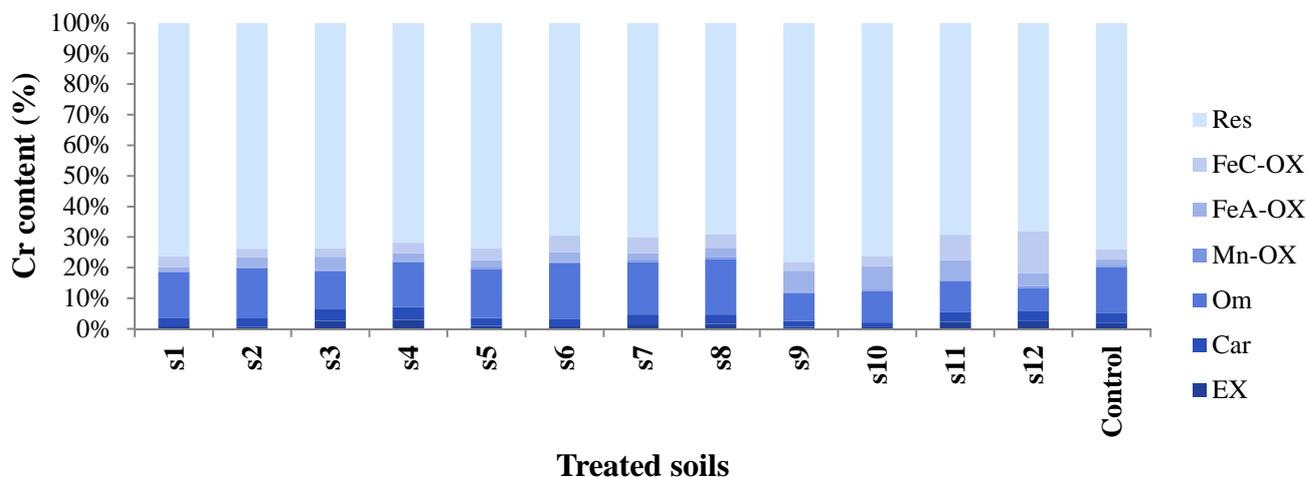
### Characterization of biochar amendments

According to the results of biochar analysis, elimination of unstable compounds at higher temperatures caused biochar to have higher percentages of carbon (C) but much lower hydrogen (H) and nitrogen (N) contents (Table 2). Increased pyrolysis temperature led to increased pH (from 6.2 to 8.7) and EC (from 13.1 to 21.2 dS/m). Figure 1 shows the FTIR spectra of rice husk before pyrolysis (B0), B300, and B600. The sharp peak at 3405 and 3416  $\text{cm}^{-1}$  in B0 and B300, and the weak peaks at around 3585  $\text{cm}^{-1}$  in B300 and B600 are due to hydroxyl group (-OH) stretching and functional group of phenols. The peaks at 2923 and 2936  $\text{cm}^{-1}$  seen in B0 and B300 are ascribed to aliphatic C-H deforming vibration and functional group of alkanes. These functional groups disappear at temperatures higher than 600 °C. The weak band at 1725  $\text{cm}^{-1}$  for B0, which disappears at temperatures higher than B300, is assigned to C=O stretching in the carbonyl group and neutral functional group of aldehydes. The weak band at around 1640  $\text{cm}^{-1}$  for B0 is due to the presence of C=C stretching (functional group of alkenes). The weak band at 1539  $\text{cm}^{-1}$  for B0 indicates the presence of N-O asymmetric stretch (nitro compounds). This band disappears at temperatures higher than 300°C indicating the volatilization of nitrogen forms. The band at around 1600  $\text{cm}^{-1}$  for B300 and B600 indicates the presence of aromatic C=O ring stretching (likely -COOH) or aromatic C=C stretching. This band is stronger in B600 compared to B300; therefore,

pH was higher in biochar produced in high temperature than in low temperature. The weak bands at 1320 and 1376  $\text{cm}^{-1}$  in B0 indicate the presence of the N-O asymmetric stretch (nitro compounds). This band disappears at temperatures higher than 300°C indicating the volatilization of nitrogen forms. The band at around 1090  $\text{cm}^{-1}$  is due to aliphatic ether, alcohol C-O, or aromatic stretching in cellulose and hemicelluloses. In general, the results from FTIR analysis showed that the functional groups, such as carboxylic bonds and aromatic C = O ring stretching (likely -COOH), were higher in B600 than B300, which increased its pH.

### Chemical fractions of Cr affected by amendments

Application of various amendments had considerable effects on chemical forms of Cr (Figure 2). Sequential extraction experiment showed that Cr was mostly bound to Res in soil samples. This finding is in agreement with observations by others.<sup>17-19</sup> Among the chemical forms of heavy metals, EX fraction usually determines the real environmental risk. Hence, the amount of EX form could be used to assess the effect of the amendments on Cr immobilization. According to the results, the chemical form of EX was significantly decreased when soils were amended by MSWC, B300, or Fe<sup>0</sup> at application rates of 2% and 5%. Organic matter and iron can convert Cr(VI) to less soluble Cr(III) through a reduction process.<sup>1</sup> In addition, coprecipitation with Fe hydrous oxide, which has low mobility in soil, can decrease EX fraction in treated soil by Fe<sup>0</sup>.<sup>20</sup> Furthermore, there was no statistically significant difference between B600 treatment and control in the EX fraction. On the other hand, CFA and Mn<sup>0</sup> treatments significantly increased Ex fraction of Cr. Kim and Dixon reported that manganese oxides can increase the mobility of Cr by oxidizing Cr(III) to Cr(VI) in soil.<sup>21</sup> In addition, alkaline materials, like CFA, which increase soil pH to above neutral, can oxidize Cr(III) to Cr(VI) and increased Cr mobility.<sup>4,5</sup> In general, the reduction in EX form of Cr in amended soil followed the sequence of Fe<sup>0</sup> > MSWC > B300 > B600 > Mn<sup>0</sup> > CFA. The addition of amendments also had effects on other Cr fractions in soil samples.



**Figure 2. Percentages of various fractions of Cr in amended soil**

Fe<sup>0</sup>, MSWC, and B300 treatments significantly decreased Car fraction. The Car fraction characterizes the most mobile and bioavailable form.<sup>22</sup> Hence, the decreasing of Car fraction in treated soil showed that these amendments are able to increase Cr stabilization. Pantsar-Kallio et al. reported that organic materials can reduce Fe(III) to Fe(II), which in turn, reduces Cr(VI) to Cr(III).<sup>4</sup> Other amendments did not have a significant effect on Car fraction. Mn<sup>0</sup> treatments showed the highest percentage of Car form, especially at high rates (5%). Application of organic sources (B300, B600, and MSWC) considerably increased mean of Om fraction compared to the control soil. The Mn-OX fraction was less affected by soil amendments, while the FeC-OX and FeA-OX fractions in amended soils (especially soils treated by Mn<sup>0</sup> and Fe<sup>0</sup>) increased (except for MSWC treatment in FeC-OX fraction) compared to the control soil. The mobility of heavy metals depends on their chemical fractions. In the control soil, the mobility factor was 5.24%. The mobility factor in S1-S12 samples was 3.72, 3.55, 6.50, 7.45, 3.71, 3.25, 4.94, 4.94, 2.63, 2.14, 5.87, and 6.61, respectively. The lowest mobility factor is associated with application of Fe<sup>0</sup> especially at a high rate (5%). These results confirm the effectiveness of Fe<sup>0</sup> in stabilizing of Cr in contaminated soils, as previously reported by Mench et al.<sup>23</sup> and Kumpiene et al.<sup>3</sup> In general, Fe<sup>0</sup>

treatment was superior to other amendments in reducing Cr mobility in fractionation experiment.

#### Desorption kinetic of Cr affected by amendments

Figures 3 and 4 show the trends in cumulative Cr desorption in soil samples by EDTA and NaNO<sub>3</sub>. The obtained trend from Cr desorption using both extractants showed that extractions induced a two-step release process (biphasic pattern); initial quick release at the beginning (4.25 hours) and followed by a slow reaction, until the curve appeared flat and obtained equilibrium (30.25 hours). Kirpichtchikova et al. reported that the short-term elimination of metals is dominated by the most labile fractions, while the long-term removal is determined by the replenishment of the labile pool from more recalcitrant fractions.<sup>24</sup> The biphasic pattern of the desorption of heavy metals has also been reported by others.<sup>9,25,26</sup> The time of reaching equilibrium was almost similar in untreated and treated soil samples. On the one hand, it seems that in the first stage of desorption (slow release), Cr release is related to the mobile fractions (EX and Car fractions) with lower bonding energy.<sup>27</sup> On the other hand, the Cr extracted in the second stage is related to the less mobile forms.<sup>28</sup> The results showed that the total amount of Cr released by 0.01 m NaNO<sub>3</sub> was higher than that by 0.01 m EDTA. The Cr

released by 0.01 m  $\text{NaNO}_3$  varied from 3.98 to 39.74 mg/kg and by 0.01 m EDTA it ranged from 4.593 to 25.29 mg/kg. The highest amount of desorbed Cr was observed in the control soil with 39.74 and 25.29 mg/Cr kg soil using 0.01 m  $\text{NaNO}_3$  and 0.01 m EDTA, respectively. The lowest amount of desorbed Cr was observed in the  $\text{Fe}^{0}_{5\%}$  treatment with 3.98 and 4.59 mg/Cr kg soil using  $\text{NaNO}_3$  and EDTA, respectively. Application of  $\text{Fe}^0$  at the rates of 2 and 5% considerably decreased Cr release by 89.97% and 79.11%, respectively, compared to the control soil, in the 0.01 m  $\text{NaNO}_3$  media. Addition of  $\text{Fe}^0$

also significantly decreased Cr release by 81.84% and 51.35% at levels of 2 and 5%, respectively, in the 0.01 m EDTA media. Kumpiene et al. used zerovalent iron for stabilization of Cr and showed that the application of  $\text{Fe}^0$  decreased Cr concentrations in leachates (by 45%), soil pore water (by 94%), and plant shoots (by 95%).<sup>3</sup> Application of  $\text{Mn}^0$  decreased Cr release by 5.2 and 9% at the rates of 2 and 5%, respectively, in the 0.01 m  $\text{NaNO}_3$  media. Cr release in  $\text{Mn}^0$ -treated soil samples decreased by 0.45 and 6.1% at the rates of 2 and 5%, respectively, in the 0.01 m EDTA media.

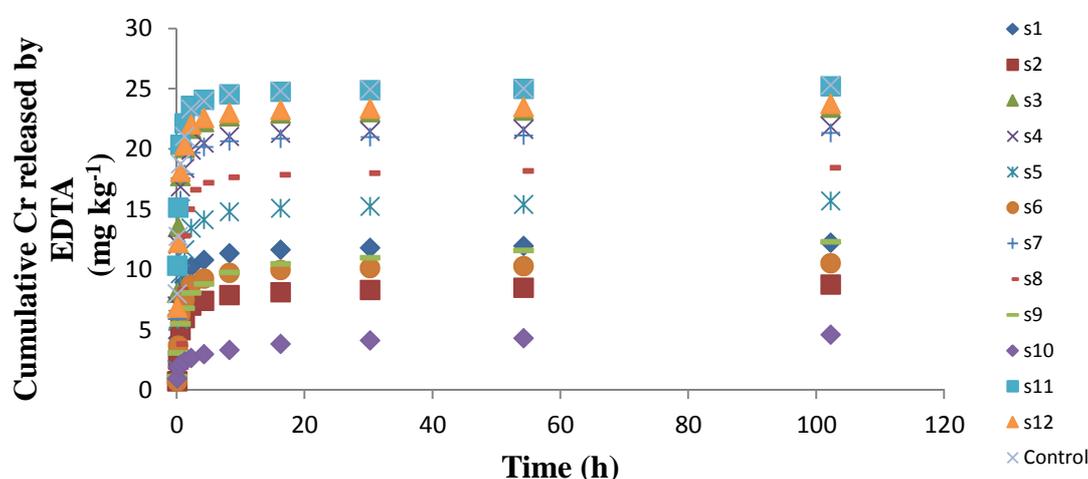


Figure 3. Variation of Cr desorption by 0.01 m EDTA in time in treated soils

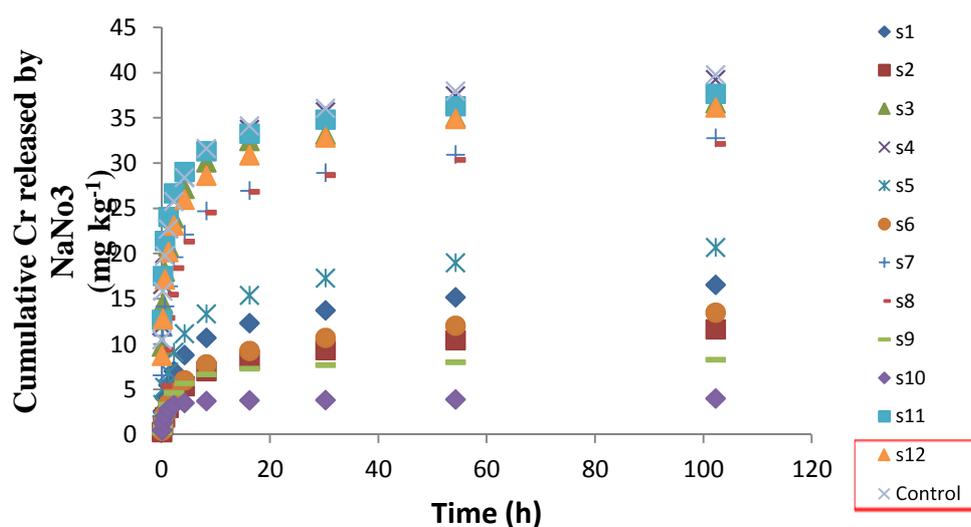


Figure 4. Variation of Cr desorption by 0.01 m  $\text{NaNO}_3$  in time in treated soils

The results indicated that  $Mn^0$  could not decrease Cr release efficiently, because manganese oxides can increase mobility of Cr by transformation of Cr(III) to Cr(VI) in soil.<sup>20</sup> The application of 2 and 5% MSWC led to reduction of Cr desorption by 58.35 and 70.71% in the 0.01 m  $NaNO_3$  media, and 51.69 and 65.44% in the 0.01 m EDTA media, respectively. Increasing soil organic matter increased sorption sites for Cr. Addition of CFA at the rates of 2 and 5% decreased Cr release by 7.8 and 1.3% in 0.01 m  $NaNO_3$  media, and 7.4 and 13.6% in 0.01 m EDTA media, respectively. Application of CFA as an alkaline material could not decrease Cr release efficiently. Increasing soil pH followed by application of CFA led to the transformation of Cr(III) to Cr(VI).<sup>4,5</sup> Treatment with B600 at the rates of 2 and 5% decreased Cr release by 17.5 and 19.1% in 0.01 m  $NaNO_3$  media and 15.6 and 27.1% in 0.01 m EDTA media, respectively. Desorption of Cr significantly decreased when soil samples were amended using B300 at application rates of 2 and 5%. The application of 2 and 5% B300 led to reduction of Cr desorption by 48 and 66.1% in 0.01 m  $NaNO_3$  media, and 15.66 and 27.14% in 0.01 m EDTA media, respectively. The results clearly show that the application of B600 and CFA increased soil pH, and thus, increased the oxidation of Cr(III) to Cr(VI) and could not considerably decrease Cr mobility. The results also illustrated that the application of amendments at high levels (5% W/W) could provide a suitable condition for Cr adsorption. Therefore, the application of amendments at 5% (W/W) is more effective than at 2% (W/W) in reduction of Cr availability. Generally,  $Fe^0$ , MSWC, and B300 treatments were superior to the  $Mn^0$ , CFA, and B600 in the stabilization of Cr in desorption experiment. According to the desorption results,  $NaNO_3$  extracted greater amounts of Cr from the soil samples compared to EDTA. Jalali and Sajadi Tabar reported that EDTA was not the best choice for identifying kinetic differences,<sup>9</sup> but provides an upper limit of metal mobility

and can be a valuable parameter in predicting long-term transfer in soils.<sup>29</sup> Hence, using 0.01 m  $NaNO_3$  media is preferred to 0.01 m EDTA media in the investigated operating conditions. The two first-order reaction model was used for metal speciation in soil and sediment samples.<sup>9,10,30</sup> This model exhibited biphasic reaction; rapid extraction followed by slow extraction of metal. Hence, it was expected that this model could be described the Cr desorption. The parameters of the two first-order reaction model ( $Q_1$ ,  $K_1$ ,  $Q_2$ ,  $K_2$ ,  $R^2$ , SE, and  $Q_1/Q_2$ ) are presented in tables 5 and 6. Based on the obtained highest values of  $R^2$  and lowest values of SE of the estimate, the two first-order reaction model could be best fitted for describing Cr release in soil samples. The results show that the values of  $Q_2$  (less extractable) in amended soil samples (except for soil treated with B600 and  $Mn^0$  in 0.01 m EDTA, and by CFA in 0.01 m  $NaNO_3$ ) were lower than  $Q_1$  (readily extractable fraction) compared to the control soil. The higher amount of  $Q_2$  in some amended soil samples compared to the control soil confirmed the positive effect of amendment in Cr stabilization. The assumption is that the fractions of Cr determined with the two first-order reaction model is correlative with fractionation of Cr derived from the fractionation method. Hence, the simple correlation coefficient ( $r$ ) was estimated for relationships among parameters of the two first-order reaction model and chemical forms of Cr (tables 7 and 8). There was a significant positive correlation between  $Q_1$  and  $K_1$ , EX, Mn-Ox, and FeC-Ox, between  $Q_2$  and  $K_2$ , Ex, Car, and  $K_2$ , and between  $K_2$  and Car in 0.01 m EDTA media. In addition, there was a positive significant relationship between  $Q_1$  and  $Q_2$ , EX, and Car, between  $K_1$  and Car, between  $Q_2$  and Ex, Car, and  $K_2$ , and between  $K_2$  and FeC-Ox in 0.01 m  $NaNO_3$ . Jalali and Sajadi Tabar found a significant correlation between  $Q_2$  and acid malic with Om, inorganic precipitates fraction, and Res fractions of Nickel.<sup>9</sup> Brunori et al. noticed that  $Q_1$

could be related to Ex fraction and part of Om fraction,  $Q_2$  could be related to the Om residual and inorganic precipitates fraction, and  $Q_3$  could be related to residual fraction.<sup>31</sup>

The results of correlation coefficients between

chemical forms of Cr and parameters of the two first-order reaction model confirmed the hypothesis of Brunori et al.<sup>31</sup> based on positive correlation between  $Q_1$  and mobile fractions (EX and Car) especially in 0.01 m NaNO<sub>3</sub> media.

**Table 5. Estimated parameters of the two first-order reaction model used to describe release kinetics of Cr with 0.01 m EDTA**

Value	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	Control
$Q_1$	2.808	1.891	9.318	5.863	3.837	2.409	13.635	13.290	7.650	2.199	12.489	16.195	13.544
$K_1$	0.189	0.106	0.919	0.523	0.257	0.179	5.500	3.631	1.896	7.108	14.573	5.189	7.661
$Q_2$	9.140	6.647	13.630	15.581	11.513	7.873	7.307	4.763	4.298	2.224	12.153	7.114	11.266
$K_2$	2.415	1.942	8.739	5.915	2.533	2.261	0.712	0.442	0.064	0.084	1.416	0.704	0.901
$R^2$	0.996	0.994	0.995	0.994	0.996	0.992	0.996	0.997	0.994	0.992	0.988	0.995	0.991
SE	3.429	2.539	4.835	4.682	4.412	3.027	4.930	4.660	3.516	1.101	4.715	5.432	5.660
$Q_1/Q_2$	0.307	0.284	0.684	0.376	0.333	0.306	1.866	2.790	1.780	0.989	1.028	2.276	1.202

$Q_1$ : Readily extractable (mg/Kg);  $K_1$ : Constant rate related to  $Q_1$  (1/min);  $Q_2$ : less extractable (mg/Kg);  $K_2$ : Constant rate related to  $Q_2$  (1/min);  $R^2$ : coefficient of determination; SE: standard error

**Table 6. Estimated parameters of the two first-order reaction model used to describe release kinetics of Cr with 0.01 m NaNO<sub>3</sub>**

Value	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	Control
$Q_1$	6.969	5.391	16.667	19.431	8.927	5.549	15.314	13.888	5.289	3.555	15.365	16.593	17.920
$K_1$	1.200	0.543	8.697	9.655	1.217	0.649	4.982	4.264	0.736	1.421	0.170	0.123	0.128
$Q_2$	9.205	6.331	17.879	17.751	11.333	7.974	15.806	16.592	2.869	3.518	20.494	17.982	19.916
$K_2$	0.050	0.033	0.192	0.143	0.049	0.035	0.101	0.116	0.069	0.002	9.741	5.470	7.113
$R^2$	0.993	0.997	0.940	0.978	0.994	0.997	0.983	0.988	0.998	0.989	0.997	0.981	0.983
SE	5.198	3.876	8.710	8.713	6.446	4.414	8.374	8.740	2.848	1.179	7.893	8.898	9.321
$Q_1/Q_2$	0.757	0.852	0.932	1.095	0.788	0.696	0.969	0.837	1.843	1.010	0.750	0.923	0.900

$Q_1$ : Readily extractable (mg/Kg);  $K_1$ : Constant rate related to  $Q_1$  (1/min);  $Q_2$ : less extractable (mg/Kg);  $K_2$ : Constant rate related to  $Q_2$  (1/min);  $R^2$ : coefficient of determination; SE: standard error

**Table 7. Simple correlation coefficients (r) between parameters of the two first-order reaction model of Cr desorption, extracted by EDTA, with Cr fractions**

	$Q_1$	$K_1$	$Q_2$	$K_2$
$K_1$	0.558*	-	-	-
$Q_2$	0.089	-0.037	-	-
$K_2$	-0.178	-0.409	0.743**	-
EX	0.657*	0.298	0.632*	0.465
Car	0.518	0.037	0.768**	0.578*
Om	-0.203	-0.383	0.108	0.067
Mn-Ox	0.626*	0.349	0.056	-0.312
FeA-Ox	0.032	0.474	-0.419	-0.239
FeC-Ox	0.576*	0.427	-0.045	-0.278
Res	-0.167	0.013	-0.277	-0.233

\*Correlation is significant at the 0.05 level; \*\*Correlation is significant at the 0.01 level;  $Q_1$ : Readily extractable (mg/Kg);  $K_1$ : Constant rate related to  $Q_1$  (1/min);  $Q_2$ : less extractable (mg/Kg);  $K_2$ : Constant rate related to  $Q_2$  (1/min);  $R^2$ : coefficient of determination; EX: Exchangeable; Car: Carbonate-bound; Om: Organically-bound Mn-OX: Mn-oxide-bound; FeA-Ox: Amorphous Fe-oxide-bound; FeC-Ox: Crystalline Fe-oxide-bound; Res: Residual forms

**Table 8. Simple correlation coefficients (r) between parameters of the two first-order reaction model of Cr desorption, extracted by NaNO<sub>3</sub>, with Cr fractions**

	Q <sub>1</sub>	K <sub>1</sub>	Q <sub>2</sub>	K <sub>2</sub>
K <sub>1</sub>	0.520	-	-	-
Q <sub>2</sub>	0.952**	0.360	-	-
K <sub>2</sub>	0.480	-0.397	0.604*	-
EX	0.921**	0.509	0.878**	0.494
Car	0.914**	0.617*	0.866**	0.292
Om	-0.020	0.172	0.060	-0.381
Mn-Ox	0.457	-0.158	0.519	0.433
FeA-Ox	-0.277	-0.211	-0.298	0.207
FeC-Ox	0.334	-0.311	0.407	0.576*
Res	-0.383	-0.444	-0.453	0.084

\* Correlation is significant at the 0.05 level; \*\* Correlation is significant at the 0.01 level; Q<sub>1</sub>: Readily extractable (mg/Kg); K<sub>1</sub>: Constant rate related to Q<sub>1</sub> (1/min); Q<sub>2</sub>: less extractable (mg/Kg); K<sub>2</sub>: Constant rate related to Q<sub>2</sub> (1/min); R<sup>2</sup>: coefficient of determination; EX: Exchangeable; Car: Carbonate-bound; Om: Organically-bound Mn-OX: Mn-oxide-bound; FeA-Ox: Amorphous Fe-oxide-bound; FeC-Ox: Crystalline Fe-oxide-bound; Res: Residual forms

## Conclusion

Stabilization of heavy metals is a cost effective soil remediation method, which is used to reduce the mobile contaminant fraction in soil by low-cost and widely available amendments. In the present study, 6 types of soil amendments were investigated for their abilities to reduce Cr mobility in soil; CFA, MSWC, rice husk biochar prepared at 300°C (B300) and 600°C (B600), zerovalent iron (Fe<sup>0</sup>) and zerovalent manganese (Mn<sup>0</sup>). The stabilization of Cr in Cr-spiked soil is assessed by sequential extraction and desorption kinetic methods. According to the results, addition of amendments in soil samples considerably decreased mobility factor (except for CFA<sub>5%</sub>) of Cr compared to the control samples. Addition of Fe<sup>0</sup>, MSWC, and B300 in soil samples decreased Cr release considerably more than other amendments, compared to control treatment. The lowest Cr desorption was achieved by Fe<sup>0</sup> at the rate of 5%. According to the desorption results, NaNO<sub>3</sub> extracted greater amounts of Cr from the soil samples compared to EDTA. Hence, the use of 0.01 m NaNO<sub>3</sub> media is preferred to 0.01 m EDTA media in the investigated operating conditions. The results clearly illustrate that the application of B600 and

CFA increased soil pH, and thus, increased the oxidation of Cr(III) to Cr(VI). Based on the obtained highest values of R<sup>2</sup> and lowest values of SE of the estimate, the two first-order reaction model could be best fitted for describing Cr release in soil samples. In general, from the practical view, Fe<sup>0</sup>, MSWC, and B300 treatments are effective in Cr immobilization, while application of Fe<sup>0</sup> at the rate of 5% (W/W) was the best treatment for stabilization of Cr in polluted soil. Further research is required in order to evaluate the synergetic effects of selected amendments on Cr stabilization.

## Conflict of Interests

Authors have no conflict of interests.

## Acknowledgements

The authors would like to thank Shiraz University for providing research facilities and the two anonymous reviewers for their valuable suggestions.

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