



# Cobalt sorption–desorption behavior of calcareous soils from some Iranian soils



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## ABSTRACT

Little research has been done to study the role of soil parameters in cobalt (Co) retention, release and the processes involved in calcareous soils of arid and semi-arid regions. We studied the Co sorption and desorption capacity of various calcareous soils using batch technique. The sorption and desorption behavior of Co varied greatly among the studied soils. The sorbed fraction ranged from 92.3% to 97.2% and from 51.0% to 71.8%, when 5 and 200 mg Co l<sup>-1</sup>, was added to the soil samples, respectively. Cobalt sorption curves were well fitted with Langmuir, Freundlich, and linear equations. The values of the distribution coefficients obtained from linear equation ranged from 9.5 l kg<sup>-1</sup> to 23.4 l kg<sup>-1</sup>. Desorption experiments resulted in a Co recovery ranged from 3.6% to 11.4%, indicating a low desorption of Co from soils. The results of the geochemical modeling indicated that under low Co addition, the solutions were undersaturated with respect to Co(OH)<sub>2(am)</sub>, Co(OH)<sub>2(c)</sub>, Co<sub>3</sub>(PO<sub>4</sub>)<sub>2(s)</sub>, CoCl<sub>2(s)</sub>, CoHPO<sub>4(s)</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O<sub>(s)</sub>, and CoO<sub>(s)</sub>, whereas under higher Co addition, the solutions were undersaturated with respect to Co(OH)<sub>2(am)</sub>, CoCl<sub>2(s)</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O<sub>(s)</sub>, CoO<sub>(s)</sub>, CoHPO<sub>4(s)</sub>, and saturated with respect to Co<sub>3</sub>(PO<sub>4</sub>)<sub>2(s)</sub>, and CoCO<sub>3(s)</sub>. The hysteresis indices indicated that desorption of freshly sorbed Co with 0.01 M CaCl<sub>2</sub> was hysteretic in all soils and low mobility and leaching potential of freshly sorbed Co can be expected from these calcareous soils. Statistical correlations revealed that Co sorption and desorption onto the soils were influenced by the presence of CaCO<sub>3</sub> in soils. These findings suggested that calcareous soils are able to retain strongly Co in which the movement of Co in the soil profile would be negligible. Thus, little risk of groundwater contamination can be expected with Co in these calcareous soils.

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## 1. Introduction

Cobalt (Co), a divalent heavy metal is a micronutrient and adequate availability of Co is required for crop production. It is essential element for both human and animal health (Smith and Carson, 1981; Wendling et al., 2009). On the other hand, elevated concentrations of Co have a deleterious impact for crop production and can increase the risk of Co fluxes from soils to aquifers and surface water bodies (Khan et al., 2014). Previous studies have indicated threat of Co to the ecosystem, agro-system and people's health (Marr et al., 1998; Padmavathiamma and Li, 2007; Blust, 2011; Gray and Eppinger, 2012; Lotfy and Mostafa, 2014). Understanding the process governing the sorption and desorption of Co in soils is essential for predicting the transfer of Co from the solid phase to the liquid phase. In addition, the sorption reactions of heavy metals are the most important chemical processes affecting the

behavior and bioavailability of heavy metals in soils and play an important role in environmental aspects of heavy metals management (Alloway, 1995). Sorption–desorption isotherms are much used to characterize the retention of heavy metals in soil (McLaren et al., 1986; Gray et al., 1998, 1999; Vega et al., 2006; Covelo et al., 2007). Some works have been carried out to investigate the sorption of Co on minerals or oxides such as sorption of Co by several oxides: Fe<sub>3</sub>O<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub> (Tewari et al., 1972; Tewari and Lee, 1975), compacted bentonite (Eriksen et al., 1999), calcium-montmorillonite (Nagy and Koínya, 1998), alumina (Wang et al., 2002), bentonite (Yu et al., 2006; Khan et al., 1996), goethite (Angove et al., 1999; Fischer et al., 2007), montmorillonite (Chen and Lu, 2008), solid phases (Payne et al., 2009) bentonite, alumina and silica (Li et al., 2009), peat and algae treated peat (Lourie and Gjengedal, 2011), and alginate beads and nano-graphite encapsulated alginate beads (Khan et al., 2014). On the other hand, almost most of the studies dealing with Co sorption on soils are based on the competitive sorption of Co, Cu, and Ni ions by a calcium-saturated soil (Harter, 1992), competitive sorption of Co, Cd, Ni, and Zn of solutes at low equilibrium concentrations of Co and with

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only one Co addition for each soil (Anderson and Christensen, 1988). This means that little information is available (McLaren et al., 1986) on the sorption and desorption process and the relation between sorption rate and soil composition, especially in calcareous soils. Thus, the purpose of this investigation was to study sorption and desorption reactions of Co on calcareous soils. Soil samples were selected based on a range of clay contents in order to represent the greatest possible range of sorption and desorption.

## 2. Materials and methods

### 2.1. Soil characteristics

The 10 soils used in this study were taken from different agricultural areas in Hamedan, western Iran and were sampled from 0–30 cm depth (Jalali and Sajadi Tabar, 2011). The data presented here for the cation exchange capacity (CEC), clay, silt and sand contents, organic matter (OM), calcium carbonate equivalent, electrical conductivity (EC) and pH (H<sub>2</sub>O) were taken from this reference, and were based on standard soil chemical analytical techniques (Rowell, 1994). Total Co was extracted by 4 M HNO<sub>3</sub> for 12 h (Sposito et al., 1983), and then measured by the atomic adsorption spectrometry (SpectrAA-220-Varian). Oxalate-extractable Fe (Fe<sub>0</sub>) and Al (Al<sub>0</sub>) were extracted with 0.175 M NH<sub>4</sub>-oxalate + 0.1 M oxalic acid adjusted to pH 3.0 (McKeague and Day, 1966). Iron and Al were determined in the extract using Varian, SpectrAA-400, and spectrophotometric method (Pansu and Gautheyrou, 2006), respectively.

### 2.2. Sorption isotherms

Cobalt sorption and desorption were determined using ten soil samples. Cobalt sorption curves were obtained by shaking 3 g of soils in a 50 ml centrifuge polyethylene tube with screw cap to which an equilibrating solution of CaCl<sub>2</sub> containing 0, 5, 10, 20, 40, 60, 100, and 200 mg Co l<sup>-1</sup> was added. The initial high Co concentrations used in the sorption experiments reflected the high concentration of water-soluble Co occurring in soils after exposing to the industry discharge which has high concentration of metals such Co.

The equilibrating solution included 0.01 M CaCl<sub>2</sub> and the soil/solution ratio was 1:10. 0.01 M CaCl<sub>2</sub> has an ionic strength comparable to natural soil solutions (Li and Shuman, 1997). After 24 h of equilibration, the tubes were centrifuged at 4000 rpm. We conducted preliminary kinetic experiments and found 24 h to reach equilibrium. This time was used for sorption experiments. The set of initial high dissolved Co concentrations used in the sorption experiments allowed adsorption sites to reach saturation and the maximum adsorption capacity was then calculated. The Co concentration in the supernatant was determined by the atomic adsorption spectra (SpectrAA-220-Varian). The quality control data measures included use of standard methods, rigorous checking of reagent blanks and standards were done. The detection limit for Co was 0.01 mg l<sup>-1</sup>. The standard solution for calibration and spiking, obtained from Merck (Germany), were prepared by diluting stock solutions of 1000 mg Co l<sup>-1</sup>. In order to check the precision of the instrument, calibration checks were performed after analysis of 30 samples and samples with known concentration of Co run after the analysis of every set of 40 samples. A soil reference material with certified Co concentration was not available. Therefore, several already analyzed soil samples were spiked and homogenized with varied amounts of standard solutions of Co and were analyzed to ensure the accuracy of the applied analytical procedures. The

average recovery percentage was 96.4. The amount of Co sorbed by soils was calculated by the equation:

$$S = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where  $S$  is the quantity of Co sorbed (mg kg<sup>-1</sup>),  $C_0$  is the initial concentration of the Co in solution (mg l<sup>-1</sup>),  $C_e$  is the equilibrium concentration of the Co in solution (mg l<sup>-1</sup>),  $V$  is the solution volume (ml), and  $M$  is the weight of air-dried samples (kg).

### 2.3. Curve fitting

The best-fit equilibrium isotherms were determined by simple linear, Langmuir and Freundlich equations. Cobalt sorption parameters were obtained by fitting experimental data to the Langmuir and Freundlich equations using the nonlinear procedure with Sigmaplot statistical software package version 11.0:

$$S = \frac{QbC_0}{1 + bC_0} \quad (2)$$

where  $b$  (l mg<sup>-1</sup>) is a coefficient which reflects the rates of sorption and desorption at equilibrium and is thus the bonding energy coefficient, and  $Q$  (mg kg<sup>-1</sup>) is the maximum sorption.

$$S = K_F C^n \quad (3)$$

where  $K_F$  (l kg<sup>-1</sup>) represents the Freundlich distribution coefficient, related to the soil adsorption capacity and  $n$  is an empirical constant.

$$S = K_d C \quad (4)$$

where  $K_d$  is a linear distribution coefficient.

The maximum buffer capacity (MBC) of the soil was estimated from the product of the Langmuir constant  $b$  and  $Q$  (Holford, 1979; Litaor et al., 2005). Statistical analysis was performed using the SPSS (version 13.1, Minitab Inc.) program.

The hysteresis index (HC) parameter was used to quantify sorption–desorption hysteresis and it was calculated based on the Co distribution coefficient (Xiangke et al., 2000):

$$HC = \frac{K_{d(\text{des})} - K_{d(\text{ads})}}{K_{d(\text{des})}} \quad (5)$$

where,  $HC$  is a hysteresis index, and  $K_{d(\text{ads})}$  and  $K_{d(\text{des})}$  are distribution coefficient (l kg<sup>-1</sup>) for sorption and desorption experiment, respectively. The  $HC$  equals unity if the sorption is totally irreversible and zero if all the sorbed metal is released.

### 2.4. Cobalt desorption

The residual soils from the sorption studies were shaken with 20 ml of Co-free 0.01 M CaCl<sub>2</sub> solution and suspensions were shaken for 1 h and left for 24 h at 24–25 °C and then shaken for another 1 h. Then the tubes were centrifuged (4000 rpm). The Co concentration in the supernatant was measured by atomic absorption spectrometry. Cobalt retained by soil was determined by taking the difference between initial sorbed Co and Co in desorption equilibration solution. The data obtained on Co desorption were fitted to the linear equation.

### 2.5. Cobalt saturation indices

The computer program Visual MINTEQ version 2.30 (Allison et al., 1991) was used to predict saturation indices (SI) of Co in the equilibrium solution concentration when 5 and 200 mg Co l<sup>-1</sup> were applied in the sorption experiments. Input to the model consisted of the measured concentrations of Co<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, PO<sub>4</sub><sup>3-</sup>,

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