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Sorption Characteristics of Hexavalent Chromium in the Soil Based on Batch Experiment and Their Implications to the Environment

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Abstract

The objective of this experimental study was to determine the kinetics and equilibrium sorption of Cr(VI) in soils collected from Hengshui City of Hebei Province, China, based on batch experiments. The main concentration for this paper is on the effect of soil pH, solute concentration and ionic strength as the variable factors in the sorption of Cr(VI) in soils and the assessment of their implications to the environment. Atomic Absorption Spectrophotometer (AAS) was used for Cr(III) analysis; UV-VIS Spectrophotometer for quantification of Cr(VI) in soil samples and determination of electrical conductivity and temperature of the soil samples; and Automatic Laser Particle Size Analyzer LS230 for the determination of soil physical characteristics. Results from this study show that adsorption and reduction are major reactions accounting for removal of Cr(VI) from soil solution. It is concluded that chemical reactions such as reduction, strongly influence Cr(VI) mobility in soil. Adsorption kinetics experiments indicated that Cr(VI) removal from soil solution increases with increasing solute concentration, with decreasing pH and with decreasing ionic strength. Adsorption reactions reached equilibrium within 12 hours in batch reactors. Increasing background electrolyte concentration (KCl) decreases Cr(VI) adsorption on soil. The Cr(VI) adsorption isotherm for this soils conforms well to the Langmuir isotherm at constant pH. Two Cr(VI) adsorption parameters: the maximum sorption capacity (Q_o) and Langmuir adsorption constant (K_L), were determined as 1.0135×10^{-4} mol/g and 0.0622 mg/L, respectively. The reduction of Cr(VI) into less toxic Cr(III), means reduction of significant environmental problems. Finally, this study advises relevant environmental governing authorities to observeperiodic monitoring of the status of Cr(VI) in soils.

1. Introduction

Chromium (Cr) is the seventh most abundant element on earth [1]. It exists in oxidation states ranging from 0, II, III, IV, V to VI, in which only two of them; Cr(III) and Cr(VI) are stable enough to occur in the environment [1] [2]. Cr(II), Cr(IV), and Cr(V) are unstable forms, and very little information is available about their hydrolysis [1] [2] [3]. Chromium is a ubiquitous contaminant of soils and groundwater, and is derived from both natural and anthropogenic sources [3]. Chromium compounds have various industrial applications, including chromium plating, metallurgy, pigment manufacturing, tanning and wood preservation [4]-[10]. Often wastes from such industries (*i.e.* sludge, fly ash and slag) are used as fill materials at numerous locations to reclaim marshlands, for tank dikes, and for backfill at sites following demolition [7]. Chromium manufacturing industries produce a large quantity of solid and liquid wastes containing hexavalent chromium. At many such sites, leaching and seepage of Cr(VI) from the soils into the groundwater pose a considerable health hazard to both plants and animals (including humans) [5]-[10]. Although both Cr(III) and Cr(VI) are the stable oxidation states of chromium in the environment, Cr(VI) is of particular concern due to its extreme toxicity (100 - 1000 times higher than that of Cr(III) [8] [9]. Due to its high solubility and adverse health effects, Cr(VI) poses a significant environmental hazard [11]. The treatment of these wastes is essential before discharging them to the environment. Cr(VI) compounds are highly water soluble, toxic and carcinogenic in mammals [5] [11]. In contrast, trivalent chromium is considered to be non-toxic as it precipitates at pH higher than 5.5 with the formation of insoluble oxides and hydroxides in soil and water systems [10] [11] [12].

Chromium, in its trivalent form (Cr(III)), is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipids metabolism in humans and animals [5] [11] [14]. In contrast, Hexavalent Cr(VI) is highly toxic (carcinogenic) and may cause death to animals and humans if ingested in large doses [13] [14] [15]. Recently, concern about chromium as an environmental pollutant has been escalating due to its build-up to toxic levels in the environment as a result of various industrial and agricultural activities [13]. Most research has been done to investigate the impacts of chromium on crops/plants [14] [15]. According to Sharma *et al.* [14], the toxic effects of chromium on plant growth and development include alterations in the germination process as well as in the growth of roots, stems and leaves, which may affect total dry matter production and yield. For example, it was reported that chromium caused visible lesions of interveinal chlorosis in maize (*Zea mays*) while plant physiological processes such as photosynthesis, water relations

and mineral nutrition were reported to be adversely affected [15]. Metabolic alterations in plants following chromium exposure could either be due to a direct effect on various enzymes or other metabolites or because of its ability to generate reactive oxygen species (ROS), which may cause oxidative stress [16] [17] [18].

All over the world, soil is regarded as the key element to human survival and can be described by various definitions according to its main utility. Heavy metals are natural constituents of rocks and soils in concentrations that do not represent any risk to animal or plants [14] [15] [16] [17] [18]. Some anthropogenic activities like the spreading of sewage sludge or fertilizers, the discharge of domestic and industrial effluents in land as well as atmospheric disposal, promote augmentation of these metals' concentrations to toxic levels. For example, tanning industry is, especially, a large contributor of Cr pollution to water resources [4] [19]. Chandra *et al.* [19] estimated that in India alone about 2000 to 3200 tons of elemental Cr escape into the environment annually from tanning industries, with Cr concentrations ranging between 2000 and 5000 mg·L^{-1} in the effluent compared to the recommended permissible limit of 2 mg·L^{-1} [5] [11].

Being one of the fastest growing economy, China is also encountering problems of soil pollution from heavy metals (chromium inclusive) [20] [21]. This is mostly accelerated with rapid expansion and increase in industrial development [22]. It is therefore the main objective of this research to study sorption characteristics of hexavalent chromium in the soils of China (Hengshui City of Hebei Province) based on batch experiment and determination of the associated possible environmental impacts.

2. Materials and Methods

2.1. Materials and Reagents

The main type of materials used in this study was soil from Hengshui City of Hebei Province, China. Concentrated hydrochloric acid was used for the determination of Total Inorganic Carbon Content (TIC) of soil; concentrated sulfuric acid, potassium hydrogen phthalate and dichromate reagent for the determination of soil reduction capacity; and ammonium oxalate and dithionitecitratebicarbonate (DCB) for the determination of reduced Cr(VI) in soil.

2.2. Equipment

The following laboratory equipment were used in this study; constant-temperature shaker bath for mixing soil suspensions, Atomic Absorption Spectrophotometer (AAS) for Cr(III) analysis, UV-VIS Spectrophotometer for quantification of Cr(VI) in soil samples and determination of electrical conductivity and temperature of the soil samples, Automatic Laser Particle Size Analyzer LS230 for determination of soil physical characteristics.

2.3. The Batch Experiments

Batch experiments were conducted to determine adsorption kinetics of Cr(VI) in

the soil with the influence of pH, solute concentration and ionic strength. These experiments also involved development of equilibrium adsorption isotherms from which soil maximum adsorption capacity and adsorption coefficient were determined. Furthermore, data on the removal of hexavalent chromium from soils were obtained from this study's batch experiments

2.4. Experimental Setup

Batch experiments were conducted in completely mixed reactors in a temperature-controlled room (25°C ± 3°C). Adsorption and desorption experiments were run to determine kinetics and equilibrium sorption and desorption parameters of Cr(VI) on soil samples. All batch experiments were conducted under oxic conditions.

2.5. Adsorption Kinetics

Short-term and long-term kinetics experiments were used to determine the time required for Cr(VI) to approach equilibrium during sorption and desorption. For short-term and long-term adsorption kinetics, identical reactor tubes were left on the shaker bath at varying pH values and for various times, ranging from 1 to 24 hours and 1 to 120 hours, respectively. Adsorption experiments were conducted in 100 ml, screw-top plastic centrifuge tubes. The soil (2.5 grams) was reacted with 50 ml of a solution. Hexavalent chromium was added to yield concentrations ranging between 1×10^{-1} and 5×10^{-2} M. The pH was adjusted by adding various volumes of 1.0 M HCl and NaOH. Soil suspensions were mixed through continuous shaking in a 25°C constant-temperature shaker bath. After mixing for the desired reaction time, the suspensions were centrifuged at 4000 rpm for 10 minutes and the supernatant solutions were passed through 0.45 μm millipore filters. Chromium concentrations in the supernatant solutions were determined by EPA 7196 Method [23] and adsorbed chromium was determined by the differences between the initial and final solution concentrations. The pH of each sample was also determined.

2.6. Adsorption Isotherms

Adsorption isotherms were determined in completely-mixed batch reactors in a temperature-controlled chamber. The soil suspensions were then prepared with 2.5 grams of soil and 50 ml of 0.01 M of KCl background electrolyte solution. Cr(VI) was added to yield ten concentrations ranging from 5×10^{-5} M to 5×10^{-4} M, and equilibrated at 25°C, constant temperature. After 120 hours equilibration time, suspensions were centrifuged and the dissolved chromium and pH were determined as described in the adsorption kinetic experiments. The effects of varying pH values and supporting electrolyte concentrations was also determined on Cr(VI) equilibrium isotherms.

2.7. Soil Pre-Treatment and Analysis

Wet soil samples collected from the field were kept in an open space (inside the

laboratory facility) for about two weeks to allow them dry by normal atmospheric air. The air-dried samples were then grinded and mixed well, and later on passed through a 2 mm stainless steel sieve to obtain a homogeneous sample. These samples were finally kept in plastic bags, ready for further analysis. pH of the soil samples were determined using pH meter (1:1 soil/water suspension method) and the determination of hexavalent chromium in the soil was determined by Colorimetric Method [23]. UV-VIS Spectrophotometer [24] was used for quantification of Cr(VI) as well as the determination of electrical conductivity and temperature of the soil samples (Table 1). The other portion of untreated soil samples were used to determine soil physical characteristics (Table 2) by using Automatic Laser Particle Size Analyzer LS230 [25].

3. Results and Discussion

3.1. Cr(IV) Adsorption Kinetics

Figure 1 shows hexavalent chromium removal from solution at different solute concentrations as a function of time. Removal of hexavalent chromium from solution showed a rapid initial uptake followed by very slow uptake kinetics. At around 24 hours the process started to approach equilibrium and attained maximum within 48 hours, almost for all three concentrations (0.26, 0.52 and 1.04 mg/L). Similar results were found for all kinetics of ionic strength and pH values as it can be seen on Figure 2 and Figure 3. Results of Cr(Vl) adsorption kinetics

Table 1. Soil chemical characterization experiment.

Parameter	Values	Method
pH	8.67	Soil: Water Soil Titration
Electrical Conductivity	300.8 μS/cm	Soil: Water Soil Titration
Chromium VI	0.005 mg/L	EPA: 7196A
Total chromium	0.087 mg/L	Atomic Absorption (FAAS)
Moisture content	0.94%	Oven at 105°C
Soil Temperature	29°C	Thermometer
Organic Content (TOC)	2.32 (%)	Carbon Analyzer
Calcium	1473 (mg/kg)	Ammonium Acetate
Magnesium	102 (mg/kg)	Ammonium Acetate
Potassium	364 (mg/kg)	Ammonium Acetate
Phosphate	10.1 (mg/kg)	Ion Chromatography
Sulfate	15 (mg/kg)	Ion Chromatography
Nitrate	20.2 (mg/kg)	Ion Chromatography
Soluble Iron	483 (mg/L)	DTPA
Soluble Manganese	12.5 (mg/L)	DTPA

Table 2. Soil physical characterization.

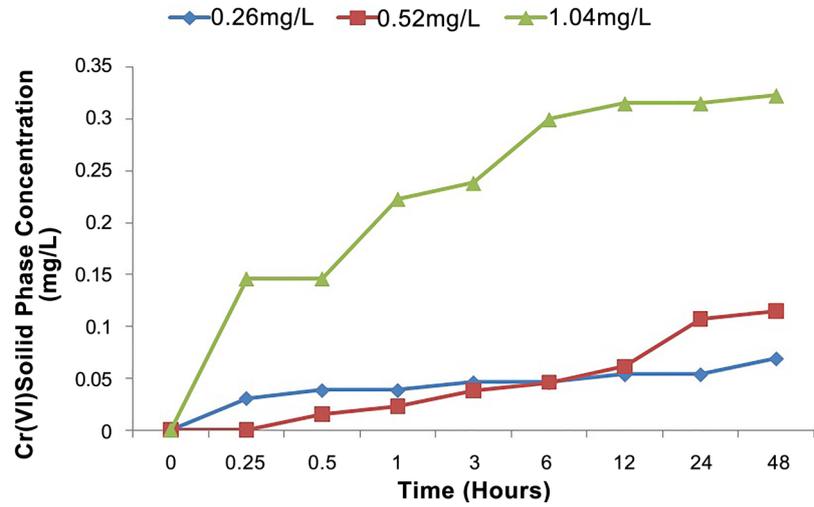| Physical	Percentage	Method
Silt	74	LS230
Clay	20	LS230
Sand	6	LS230

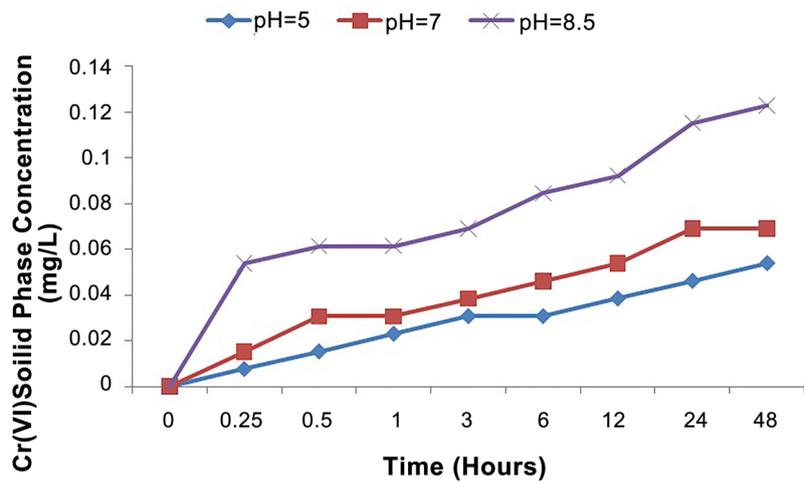**Figure 1.** The effect of solute concentration on Cr(VI) adsorption kinetics in the soil.

Figure 2. The effect of pH on Cr(VI) adsorption kinetics in the soil at constant solute concentration of 0.26 mg/L of Cr(VI).
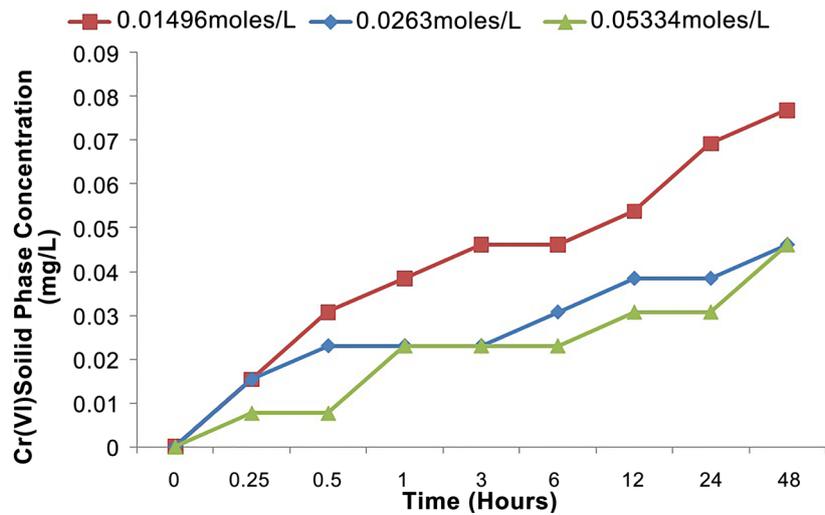

Figure 3. The effect of ionic strength (0.001 MKCl) on Cr(VI) adsorption kinetics at constant solute concentration of 0.26 mg/L Cr(VI).

showed that the equilibrium was approached within 48 hours reaction time. Adsorption kinetics of 0.26 mg/L Cr(Vl) as a function of time and at pH values of 5.20, 6.70 and 8.4 are demonstrated by plots of solid phase concentration against time (Figure 2). As Figure 2 shows, adsorption increases with increasing pH. Adsorption kinetics of 0.26 mg/L Cr(Vl) as a function of time are shown in Figure 3 showing the effect of ionic strength. Figure 3 shows the effect of Cr(VI) reduction on Cr(VI) adsorption kinetics experiment at concentration of 1.04 mg/L Cr(VI), 2.5 g of soil.

Chromium (VI) removal process is termed as a more time dependent removal. The kinetics of chromium removal in this study indicates that equilibrium was not achieved until after 48 hours reaction time (Figures 1-3). Cameron and Klute [26] explained such adsorption of solute to soils by a combination of equilibrium and kinetic models. These models incorporate a rapid reaction site which equilibrates instantaneously with adsorbate and a slow reaction site [27]. He described such a removal process as a physical non-equilibrium phenomenon. Our experiments showed that over the pH range considered, the Cr(VI) removal process exhibits a di-phasic behavior with time (Figure 2). An initial, rapid, short-term uptake (phase I) of chromium (Vl) is followed by a long-term, slower uptake (phase II). Reduction of Cr(VI) to Cr(III) was the suspected cause for slow Cr(VI) removal from solution and experimentally it was necessary to distinguish adsorption of Cr(VI) from Cr(VI) reduction to Cr(III).

Although studies [28] [29] [30] have found Phosphate (KH_2PO_4/K_2HPO_4) to be the best extracting agent for adsorbed Cr(VI) in soils, this study has shown that Cr(VI) reduction to Cr(III) is the major cause of Cr(VI) removal from the soils. Chromium extracted from the soil by 0.5 M phosphate solution at pH about 8 was defined as the adsorbed fraction. Thus, any chromium that was not extracted was assumed to be reduced to Cr(lll) which was immobile in the soil as a precipitate of $Cr(OH)_3$ (phase I) [31]. Cr(VI) adsorption was completed within 24 hours (Figure 1). Cr(VI) removal at longer reaction time (phase II) can be attributed to Cr(VI) reduction to Cr(III). It was concluded that phase I was largely due to diffusional transport and adsorption, as has been noted for the adsorption of Cr(Vl) on soil [32], while phase II was largely due to reduction of Cr(VI) to Cr(III).

3.1.1. Effect of Cr(VI) Concentration on Adsorption Kinetics

Chromium (VI) adsorption kinetics show that adsorption rate increased with increasing Cr(VI) concentration (Figure 1). Increased Cr(VI) uptake kinetics on the soil as Cr(VI) solution concentration increased is consistent with an adsorption removal mechanism because the rate of reaction is proportional to the concentration of the Cr(VI) solution [31].

3.1.2. Effect of pH on Cr(VI) Adsorption Kinetics

Chromium (VI) adsorption kinetics increased with decreasing solution pH (Figure 2). This is in agreement with the findings of Griffin *et al.* [33]. This can be explained by an increase in positive surface charges or electrostatic potential

on soil particles with decreasing pH, resulting in more adsorption sites available for Cr(VI). Increasing adsorption sites increase Cr(VI) adsorption rate because the rate of reaction between the solution and adsorbent is proportional to the concentration of the reactants. Similar results were obtained by James and Bartlett [34] for adsorption of Cr(VI) by various soils and $Fe(OH)_3$.

3.2. Chromium (VI) Adsorption Isotherms

Figure 4 shows an adsorption isotherm in which the effects of Cr(Vl) reduction are included. The dependence of the amount of Cr(Vl) adsorption at constant pH and different solution concentration of Cr(Vl) is illustrated by the curves in Figure 4. The adsorption isotherms for this soil conformed to the Langmuir equation [35]. Two Cr(Vl) sorption parameters; the maximum sorption capacity (Q_0) and Langmuir adsorption constant (K,) were determined in 48 hours isotherm experiments. Table 3 below reports the maximum adsorption capacity and Langmuir constant of Cr(Vl) equilibrium sorption at pH values from 7.5 to 8.00.

Adsorption isotherms were developed for Cr(VI) adsorption on the experimental soil after 100 hours reaction time by excluding reduced Cr(III) from total chromium removal. Figure 4 shows that the equilibrium adsorption of Cr(VI) on a natural soil conformed well to the Langmuir isotherm at constant pH. Similar results have been noted [32] [33] [36] for the adsorption of chromate on clay minerals, natural soils, and goethite, respectively. The maximum sorption capacity at pH of 8 was 1.527 mg/L soil solution. This value was lower than the maximum adsorption capacities reported by Zachara *et al.* [32], for the adsorption of

Table 3. Langmuir adsorption constant and maxima calculated from equilibrium isotherms.

Langmuir coefficient KL (mg/L)	Maximum adsorption capacity Qo (mol/g)
0.0622	1.0135×10^{-4}
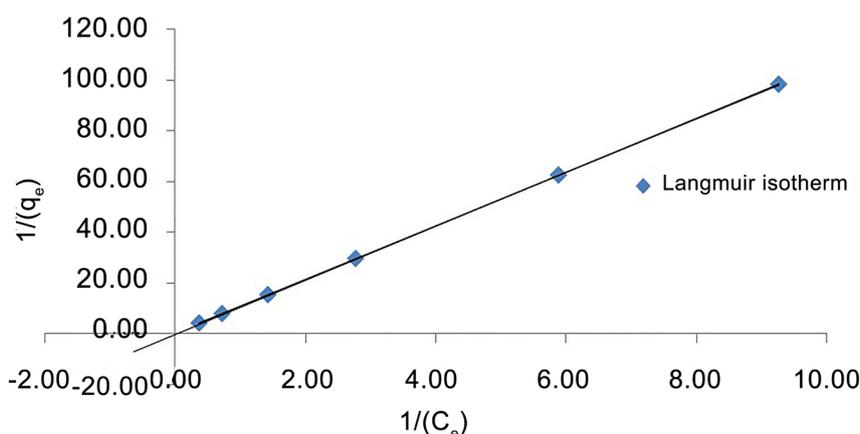
Figure 4. Linear Langmuir isotherm equation graph of 1/qe as a function of 1/Ce based on the results of adsorption isotherm experiment from which Langmuir coefficient (constant) and maximum adsorption capacity was obtained.

Cr(Vl) on two soils for which no inorganic carbon was detected. This compares with 2.32% of total Carbon contents including inorganic cabon (Table 1) for the experimental soil in this study, which might be explained due to their lower adsorption capacities. Inorganic carbon (CO_2 and HCO_3) decreases chromate adsorption by competing for non-specific adsorption sites [37] [38] [39].

3.2.1. Effect of Ionic Strength on Cr(VI) Adsorption Isotherms

Chromium (VI) adsorption edges in KCl electrolyte solutions indicated that higher ionic strength resulted in less Cr(VI) adsorption. Less Cr(VI) was adsorbed when electrolyte concentration was increased in soil. The effect of ionic strength is attributable to two effects: first, direct competition of Cl ion with Cr(VI) for oxyhydroxide surface sites [34] and second, decrease in the electrostatic potential near the surface sites [37]. Cr adsorption on the soil reduces site density, and consequently, reduces Cr(VI) adsorption. The electrostatic potential effect of C on Cr(VI) adsorption can be attributed to the effect of the surface potential on Cr(VI) surface complexation reactions [32].

3.3. Environmental Perspective

Results of this study can be extended to the assessment of the associated possible environmental challenges. The following aspects should be considered for the prevention of possible environmental impacts that might be caused by the presence of Cr(VI) in various environmental compartments;

3.3.1. Cr(VI) Reduction to Cr(III)

The study has shown that Cr(VI) is a major environmental concern amongst all Cr states, while Cr(III) is the most stable of all. Furthermore, it has been revealed that reduction of Cr(VI) to Cr(III) is the best method of dealing with environmental impacts of Cr(VI) in soils.

3.3.2. Cr(VI) Adsorption

It was also shown that adsorption of Cr(VI) is the second best method of reducing environmental consequences related with hexavalent chromium in soil. Although this process retains the species of toxic hexavalent chromium in the soil but it can be used as a temporary remedial towards minimizing the presence of chromium in the soil.

3.3.3. pH Effect

As it has been observed in this study, that an increase in pH favors oxidation of chromium (III) to toxic chromium (VI) and vice-versa, then the increase in soil pH has negative environmental impact to the soil while the decrease in soil pH is beneficial to our environment. So, our soils should be kept at low pH to avoid chromium related environmental impacts to both plants and animals.

3.3.4. Solute Concentration Effect

It has also been observed, the increase in solute concentrations favors adsorption of the solute in the soil, which promotes the availability of harmful chromium to

clean soils. This causes an increase in the amount of Cr(VI) in the environment resulting into possible negative environmental impacts. Therefore, release of Cr(VI) to the environment must be restricted.

3.3.5. Ionic Strength Effect

As it has been shown in this study, the presence of other metallic ions in the soil decreases the adsorption of Cr(VI) due to direct competition of the adsorption site on soil surface. This makes Cr(VI) species available on soil surface that may later be leached to contaminate groundwater systems or remain available for consumption by plants and animals. On the other hand, less ionic strength offers less competition and more Cr(VI) will be adsorbed in the soil, which is also unfriend to the environment. To control the effect of this factor there must be other soil minerals/materials such as organic matters that may force reduction of the available hexavalent chromium species in the soil.

4. Conclusion

Results from this study show that adsorption and reduction are major reactions accounting for removal of Cr(VI) from soil solution. While adsorption is low under the conditions present in this soil, reduction potential is high. The reduction process is highly time-dependent and continues until the reduction capacity of the soil is attained. In a nutshell, chemical reactions, such as reduction, strongly influence chromium mobility in soil. Adsorption kinetics experiments indicated that Cr(VI) removal from soil solution increases with increasing solute concentration, with decreasing pH and with decreasing ionic strength. Adsorption reactions reached equilibrium within 12 hours in batch reactors. Increasing background electrolyte concentration (KCl) decreased Cr(VI) adsorption on soil. The adsorption isotherm of Cr(VI) for this soil conforms well to the Langmuir isotherm at constant pH. Two Cr(VI) adsorption parameters: the maximum sorption capacity (Q_o) and Langmuir adsorption constant (K_L), were determined as 1.0135×10^{-4} mol/g and 0.0622 mg/L, respectively.

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