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Adsorption of hexavalent chromium in an industrial site contaminated with chromium in Mexico

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Abstract This work presents the problems left by a company that manufactured chrome-plated products for 20 years, without controlling its waste, until it was closed by the authorities in 1978. The raw material used was chromite (FeCr_2O_4). The presence of chromium in the groundwater has been observed in recent years. Hence, there is a need to understand the adsorption capacity of the soils and to explain the presence of chromium in the groundwater. The soils at the site are sandy silts with a minor presence of clay and fine sands, which would lead to an initial expectation of high adsorption. We analyzed the adsorption capacity of hexavalent chromium ($\text{Cr}^{\text{VI}+}$) in the soils based on adsorption isotherms, determined the charge of the soil particles, and evaluated Gibbs free energy. The adsorption capacity was evaluated for three soil samples (S1, S2, and S3), obtained from the core of a well drilled in 2009, at the site where the manufacturing plant was located and at two more sites within its radius of influence, in the direction of the underground water flow to ascertain that the chromium adsorption data obtained are representative for the aims of the study. Concentrations of total Cr and $\text{Cr}^{\text{VI}+}$ were analyzed throughout the core of the drilled wells, as well as the soil mass contained therein. The average concentration of

total Cr was 43.5 mg/kg, with a total mass of 21.1 g; whereas for $\text{Cr}^{\text{VI}+}$, the average concentration was 4.37 mg/kg with a mass of 2.12 g. A rough estimate with these values indicates that in the affected area (16,000 m^2) and at a depth of 65 m, where the current groundwater level starts, there will be 18.53 tons of total Cr and 1.86 tons of $\text{Cr}^{\text{VI}+}$. Adsorption isotherms were drawn and the linear, Freundlich, and Langmuir models applied; the Freundlich model was the best fit for two of the soils (S1 and S2), while for soil S3 it was the linear model. According to the values for the partition coefficient, K_d , obtained, the three soils showed low adsorption values. The net surface charge for each of the soils was determined, observing that for a broad pH range the charge was negative, which contributed to the low sorption of hexavalent chromium in the soils. The average $\text{Cr}^{\text{VI}+}$ adsorbed was 0.34 mL/g. Although this value represents a very low adsorption, it is sufficient to reveal the presence of chromium, even after more than 30 years, in the soil particles, particularly considering the reduction of groundwater level, which implies that the zone where the saturated zone had been is currently not saturated, and that chromium remained adsorbed. Lastly, the AG° thermodynamic parameter was calculated for each soil. In all cases, the value for the Gibbs free energy was positive, reflecting that the processes are not spontaneous, which concurs with the low adsorption results.

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Introduction

This work is important because we present evidences of soil and groundwater contamination that is affecting a

densely populated region of the State of Mexico, lying in the central region of the country, at coordinates N 19°41'20" and W 19°34'25". The adsorption capacity of many soils avoids migration of contaminants to the groundwater, as they are retained due to adsorption; hence, the present experiment was performed to prove this effect because of the concern generated by the high toxicity of hexavalent chromium ($\text{Cr}^{\text{VI}+}$).

The tremendous increase in the use of heavy metals due to rapid industrialization in the past decades has resulted in increased metallic substances in effluent streams. Heavy metal contamination in groundwater is an important environmental concern (Bajpai et al. 2012).

Chromium is one of the most hazardous metals that has been used widespread in diverse industries including electroplating, leather processing, mining industry, metal finishing, textile industry, and nuclear power plants (Abasi and Soni 1985).

We analyze herein the influence of chromium adsorption on the soil of a site previously occupied by a company that manufactured chrome-plated products for 20 years, without controlling its waste, until it was closed by the authorities in 1978. The raw material used was chromite (FeCr_2O_4). The industrial waste generated by the plant daily, over more than 10 years, was 12 tons of sodium chromate, 1 ton of potassium chromate, 8 tons of sodium sulfate, and 6 tons of aluminum hydroxide.

There was no control on the production of the different chrome-plated products in terms of the release of contaminants into the atmosphere, wastewater, or through waste disposal. The first manifestations of contamination appeared in 1975. In 1978, the company was closed following complaints from neighboring residents. Between 75,000 and 120,000 tons of waste was left at the site, mainly chromite, and approximately 3,600 tons of hexavalent chromium.

The presence of chromium in the groundwater has been observed in recent years. Concentrations of $\text{Cr}^{\text{VI}+}$ from 3.93 to 116 mg/L were found in wells near the source of the contamination (II-UNAM 2009). The aforementioned accounts for the need to understand the adsorption capacity of the soils and explain the presence of chromium in the groundwater. The soils at the site are sandy silts with a minor presence of clay and fine sands, which would lead to an initial expectation of high adsorption.

The most important toxic effects of hexavalent chromium are allergic contact dermatitis, skin and mucous membranes ulcerations, perforation of the nasal septum, asthmatic allergies, bronchial carcinomas, gastroenteritis, and hepatocellular deficiency (Baruthio 1992). In the particular case of the studied zone, the principal effects exerted on both company employees and residents of the area are perforation of the nasal

septum, kidney lesions, skin problems, numerous cases of cancer, and permanent damage or reduced sight (Cruz González 2009).

Chromium exists in two stable oxidation states, i.e., chromium (III) and chromium (VI). Effluents from industries contain both forms of chromium; however, $\text{Cr}^{\text{VI}+}$ is more toxic to plants, animals, and humans. Hexavalent chromium exists in different forms in aqueous solution, depending on the solution's pH, as acid chromates (HCrO_4^-), chromates (CrO_4^{2-}), and dichromates ($\text{Cr}_2\text{O}_7^{2-}$) (Tandon et al. 1984), always with a negative charge. Several studies present the current environmental challenges generated by chromium wastes at different sites worldwide.

The Sukinda Valley in India is producing around 8 % of chromite and has degraded nearby land for the last two decades. Due to large-scale opencast mining, around 7.6 million tons of rejected mineral and dump material has been lying in the area, which has been a constant source of hexavalent chromium. The concentration of $\text{Cr}^{\text{VI}+}$ exceeding permissible limits has been detected from samples of groundwater, surface water, mine water, and seepage water. Mine water quality shows that $\text{Cr}^{\text{VI}+}$ varies from 0.02 to 0.125 mg/L. In shallow-depth hand pumps, $\text{Cr}^{\text{VI}+}$ concentrations are found in considerable amounts and ranging between 0.03 and 0.8 mg/L. (Tiwary et al. 2005).

The Cr^{3+} in the soils is practically immobile as it adsorbs and forms complexes with organic and inorganic compounds. In addition, most hexavalent chromium compounds are highly soluble in water.

The reduction of chromates has been the subject of several works (Desjardin et al. 2002; Losi et al. 1994; Reynaud 2005).

The reduction of $\text{Cr}^{\text{VI}+}$ to Cr^{3+} by iron sulfide is favored by a low pH, a high initial $\text{Cr}^{\text{VI}+}$ concentration, and a high ratio of surface area to solution volume (Zouboulis et al. 1995; Patterson et al. 1997).

Other studies have focused on the treatment of $\text{Cr}^{\text{VI}+}$ in aquifers affected and those that supply water for human consumption. Campos et al. (2007) tested the use of a type of zeolite (mordenite) with mineralogical properties that favor cationic exchange and proved this as a $\text{Cr}^{\text{VI}+}$ adsorbent, in aqueous solution, with very good results.

A study was conducted in Algeria (Khérici-Bousnoubra et al. 2009) that revealed variations in the presence of chromate depending on the season. During the rainy season, the concentration allowed for drinking water (0.05 mg/L) was exceeded and when water levels were low, the concentrations were below the detectable limits. This evolution depends on the aquifer type (confined, unconfined) and on their mode of deposit (surface or deep aquifer). In the upper aquifer, chromate concentrations increase in rainy seasons.

The key mineral phases responsible for the fast release of $\text{Cr}^{\text{VI}+}$ are chromate salts, i.e., sodium chromate and sodium dichromate, whereas soluble chromatite (CaCrO_4) and hashemite (BaCrO_4) release $\text{Cr}^{\text{VI}+}$ very slowly. Thus, pH and mineral solubility have been identified as key factors in the retention and release of hexavalent CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ from Cromite Ore Processing Residue (COPR)-rich pond sediments (Shtiza et al. 2009).

The following activities and agreements were conducted over 30 years to address the problem presented in this work. Between 1976 and 1984, the *Secretaría de Recursos Hídricos* (Department of Agriculture and Water Resources) monitored continuously the quality of the groundwater (1978). In 1983, an industrial cemetery was built for chromium waste confinement. From 2002 to 2007, the CONAGUA (National Water Board) has followed up on the residual contamination in the local aquifer. Various studies have been conducted in the area due to the threat represented by this waste (SARH 1978; Gutiérrez et al. 1988).

In 2003, a multidisciplinary group was formed to conduct soil and aquifer studies and to remediate the area. CONAGUA signed a collaboration agreement with UNAM (*Instituto de Ingeniería*) in 2009 to analyze concentrations of total and hexavalent chromium in the soil and groundwater in the area. The work began with the perforation and construction of three 200-m wells. From one of the wells, 70 m of core was extracted and described for the petrographic analysis of different horizons; likewise, the lithological description of the formation and analyses for total and hexavalent chromium were performed (II-UNAM 2009).

The site is located at an alluvial-lacustrine plain (CONAGUA 2004). The geological configuration of the territory, expressed by its structures and petrology (mountains and rocks), was the result of two large events: first a tectonic compressive deformation that began at the end of the Paleozoic era and ended during the Mesozoic era, which raised the ground from the ocean floor to create tables, high plateaus, and folding mountains; and a second phase of distending deformation during the Cenozoic era, the Miocene period, which caused intense fracturing and faults, and the individualization of tectonic blocks. Most of the surface of the municipality presents extrusive igneous rocks from the Quaternary period of the Cenozoic era.

The municipality is situated within the Transmexican Volcanic Belt or Neovolcanic axis, characterized by the presence of a large amount of volcanoes, which, in their different phases of formation, gave rise to the Mexican basin, a closed basin that is also constituted by lacustrine deposits. These conditions determined the geology of the municipality. The material that predominates is made of lacustrine and alluvial soils.

The hydrogeological conditions indicate there is a shallow, unconfined aquifer that in its upper portion is limited by the groundwater level. The aquifer is found at a depth of between 25 and 35 m and comprises granular materials that are uncompressed or slightly compressed from consolidation.

The shallow aquifer material is from the quaternary geological age and is alluvial and fluvial, replenished vertically and horizontally; its water behavior is linked to variations in replenishment, high during the rainy season and very low during the dry season. The fluctuation of the groundwater level is important and presents scarce water yield.

Below this aquifer there is a stratum with very low permeability, formed by tuffite rocks, clay materials with intercalations of sands, gravels, and fractured volcanic rocks, such as andesites and basalts, probably from the later Tertiary age with a thickness of between 80 and 100 m.

This structure shows good consolidation and compression, from its high resistivity, and is practically impermeable and restricts water flow to a minimum both upwards and downwards, forming a confinement barrier for any underlying water saturated body. Clay is the dominant material in the first 70 m.

This stratum is characterized by the clay content and by the discontinuity of the subsoil. Below the previous body, the presence of a second aquifer has been identified, which is of the greatest importance in the basin; its upper level is at a depth of over 100 m approximately below the earth's surface. It is confined between two impermeable formations and is formed by semi-confined or fractured volcanoclastic materials from the Tertiary geological age, which are the oldest materials deposited in the Mexico Valley Basin (II-UNAM 2009) (Fig. 1).

The aquifer was used until the 1950s, through simple, shallow extraction, which provided small amounts as wells were built and exploited manually at a time of low water demand due to the small or scarce population in the area. These wells were found in the patios of some homes. As the population grew and industries built up in the area, wells were built for water supply and waterwheels started to disappear because of reduction of levels.

Today, the exploitation of this shallow aquifer is insufficient because of its constant reduction and may also constitute a risk factor, because, besides its very low water yield, it is highly likely that its waters present a significant content of contaminants from hexavalent chromium leaching, in addition to the discharges of wastewater from the industries established in the area.

According to the data obtained for the three wells built to a depth of 200 m, the aquifer currently provides a considerable flow of between 15 and 70 L/s per well, according to the characteristics of each. The water is of

Fig. 1 Scheme of the aquifers in the zone

good quality as it has remained free of the contamination that affects the shallow aquifer.

Most hexavalent chromium compounds are highly soluble in water. Depending on the pH, $\text{Cr}^{\text{VI}+}$ may be present in the water bodies and in household and industrial wastewaters as H_2CrO_4 , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, or CrO_4^{2-} . At a pH below 1, the predominant form is H_2CrO_4 , at the pH range from 2 to 6, the oxyanions HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ prevail, and at pH values above 8, only the oxyanion CrO_4^{2-} exists (Netzahuatl 2009).

Materials and methods

This work analyzes the adsorption capacity of the soils based on adsorption isotherms, and determines the charge of the soil particles and the Gibbs free energy.

Soils

The soils for the experiment are drawn from the core of one of the three 200-m wells drilled as part of the project (II-UNAM 2009). Seventy meters of core were extracted from the well. The core soils, in general, are sandy silts with a minor presence of clay and fine sands, with concentrations of chromium (Table 1). Porosity, volumetric density, retardation factor, electrical conductivity, redox potential, pH, and temperature were determined in the soils tested.

Adsorption tests

Adsorption is described as a process by which the liquid phase of an element or compound concentrates on the

Table 1 Classification and concentration of chromium on samples S1, S2 and S3

Sample	Depth range (m)	Classification	Total Cr (mg/kg)	$\text{Cr}^{\text{VI}+}$ (mg/kg)
S1	6.6–7.4	Coarse-grained sand followed by fine sands and sandy loams	11.08	0.6
S2	21.3–22.2	Fine-grained sand and sandy silt with small lenses of coarse sand	24.38	4.18
S3	38.2–38.5	Fine-grained sand and clayey silts	76.74	6.64

surface of another phase, usually a solid. One of the methods for obtaining the influence of the sorption of the compound on the soil is through adsorption isotherms.

Adsorbents are commonly characterized by their polarity. Polar or lyophilic adsorbents are those that have affinity with polar substances. The non-polar or lypophobes do not interact with water (Aranberri and Bismarck 2007). The degree of solubility of a dissolved substance is the most important factor for determining the intensity of the adsorption by the chemical compound. In terms of the sorbent, the organic matter and the surface area of the particles are the most influential factors in sorption.

The fundamental governing equation for chemical transport under saturated groundwater conditions is the advection, dispersion and sorption equation. This equation is derived from flux balance considerations about an elemental volume and for the one-dimensional flow case (Freeze and Cherry 1979).

$$\left[\frac{1 + \rho_b K_d}{n} \right] \frac{\partial C}{\partial t} = R \frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2}$$

where R , retardation factor, which relates the groundwater velocity with the sorbed compound. If $R = 1$, no sorption exists because both velocities are the same as that of the groundwater.

If the transfer of mass of the solute to the adsorption sites is rapid and the equilibrium corresponds to a linear model, the following occurs (Canter et al. 1987):

$$C_s = K_d C_e$$

The Freundlich model corresponds to a curve that relates the concentration of a solute on the surface of an adsorbent with the concentration of the solute in the liquid it is in contact with, but at a non-linear ratio, the equation for which is:

$$C_s = K_d C_e^n$$

C_s = sorbed mass of solute per unit of dry soil mass, C_e = solute concentration in aqueous phase, K_d = partition coefficient between soil and liquid phases, n = exponential coefficient of Freundlich.

The Langmuir model quantitatively describes the deposit of a large layer of molecules on an adsorbent surface as a function of the concentration of the material sorbed in the liquid with which it has contact. The graphic representation corresponds to a curve that rises until a constant value is reached, which represents the maximum adsorption capacity of the material.

The model selected is that which best fits the equation corresponding to one of the models. A 5,000-mg/L solution of chromium with potassium dichromate was prepared for the adsorption isotherms (NMX-AA-044-SCFI 2001).

The quantity of hexavalent chromium retained by the soil was calculated based on the equation:

$$C_s = \frac{(C_o - C_e)V}{m}$$

C_s = concentration of adsorbed chromium (mg/g), C_o = initial chromium concentration in solution (mg/L), C_e = final chromium concentration in solution (mg/L), V = volume of initial solution of chromium (mL), m = mass of soil (g).

For the isotherms, 10 g of the three types of soil (S1, S2, and S3) was placed in 250-mL flasks and 200 mL of the chromium solution was added at different concentrations (ASTM 2007). The flasks were shaken for 24 h in an orbital shaker.

The initial concentrations of chromium used were 50–500 mg/L for soils S1 and S2, for S3 the tests were performed reducing the initial concentrations to 10, 20, 30, 40, and 50 mg/L. After shaking, the solution was

centrifuged at 4,000 rpm following which the sample was filtered. The concentration of chromium in the supernatant liquid solution was determined with a Spectronic 21 D Milton Roy spectrophotometer, with a wavelength of 340–950 nm.

The properties and the behavior of any material can be affected by the charge of the soil. The zeta potential is an important indicator of the charge of soil and measuring this provides information on the phenomenon related to the charge. As the adsorption of any ion depends on its chemical structure, its concentration in dissolution, and the surface structure of the solid, the zeta potential measurements can be applied in this case to ascertain the arrangement of the soil charge on the surface of the solid (Aranberri and Bismarck 2007).

When two phases come into contact, a difference in potential between them usually develops. The region between the two phases is strongly marked by a separation of electrical charges. Therefore, there is an excess charge of a certain sign on the surface of the solid, which is neutralized by the charge with the opposite sign that is distributed throughout the dissolution.

If the surface of the solid phase in water has a positive charge, its electrostatic potential will be positive in terms of the dissolution; and if this contains dissolved ions, the potential will decrease further away from the solid surface and the further into the dissolution, more or less regularly until a value equal to zero infinitely far from the surface is achieved. The region where the liquid has a positive electrostatic potential will accumulate an excess of negative charges and will repel the electrolyte's positive ions. The arrangement of the positive charges on the surface of the solid and in the dissolution is commonly known as the double electrical layer in the interface.

The average charge of particles analyzed was measured with a ZETA-METER, model 3.0+, which consists of a microscope, a voltage generator, a zeta potential meter, and a GT2 CELL No 3378 electrophoretic cell, size: 0.0, K:68 with platinum electrodes.

The average charge for the three soils was measured. Each soil was ground with a mortar to produce colloids, thus the charges of all the particles are being measured. The size of the particles in a colloidal solution is from 10^{-4} to 10^{-7} cm. As the particles are so small, they present a large area per unit of volume. Thus, the surface effects stand out, which implies that the behavior of the colloidal dispersions is interpreted principally based on properties such as the zeta potential (Castellan 1976).

One hundred milligrams of each soil was weighed and placed in a 400-mL beaker with distilled water and shaken for 10 min. Then, 50 mL of solution was extracted. The natural pH was measured and HCl acid was added to lower

this and NaOH to raise it, obtaining a series that would cover a pH range from 2 to 10.

The pH levels were adjusted for various hours as the buffer capacity of the minerals was very high; the solutions were always drawn to their natural pH, once adjusted they were left for 24 h and the average surface load was measured.

The solutions at different pH were left in the shaker prior to measuring. The final pH for the sample was taken; then, the sample was removed from the shaker and placed in the electrophoretic cell. The electrodes were connected and different potentials were applied. Under the microscope, movement of particles was observed. In all cases, at extreme pH, near 2 and above 10, bubbling was observed; therefore, this reaction could affect the real value of the loads.

The Gibbs free energy means whether a process is spontaneous or not (De la Llata 2001). Negative ΔG° values imply a spontaneous process, whereas positive values mean it is not spontaneous; therefore, energy must be supplied to the system. This is calculated based on the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

On analyzing the adsorption process thermodynamically, to define its feasibility, it is observed that when the adsorbate meets the surface of the solid (adsorbent), its degrees of freedom are reduced; therefore, the entropy, ΔS , defined as the measure of a system's disorder, lowers. The negative values for the variation of the entropy progressively increase in order, as is the case for adsorption.

The Van't Hoff equation is used to obtain the ΔH° and ΔS° values in graphic form, based on the Gibbs free energy equation:

$$\Delta G^\circ = -RT\ln K_c$$

where R is the universal constant of the gasses, T the temperature in degrees Kelvin, and K_c is the equilibrium constant. K_c is determined as follows:

$$K_c = \frac{C_A}{C_e}$$

C_A = adsorbate concentration contained at sorbent surface, C_e = concentration in solution in equilibrium.

The present study only determined the adsorptions at 20 °C; therefore, neither the enthalpy nor the entropy was obtained.

Discussion of results

According to the definition of R , retardation factor, the contaminant's velocity is calculated with respect to the

velocity of the groundwater. When $R > 1$, it implies that there is a retardation with respect to the velocity of the groundwater due to adsorption, and hence, the contaminant will migrate R times slower than the water. Table 2 shows the results for temperature, weight, pH, redox potential, electrical conductivity, porosity, bulk density and retardation factor.

Results indicate that, for S1 and S2, R is of 1, that is, the velocity of the contaminant is practically the same as that of the water, migrating with it. For S3, due to the characteristics of the stratum, adsorption exists: although with a lower migration velocity of the hexavalent chromium than that of the water, which was not sufficient to avoid its reaching to the depths shown in Fig. 1 along all these years.

Results for the adsorption isotherms

For S1, the Freundlich model produced the best result ($R^2 = 0.96$) with a value of $K_d = 0.332$ mL/g and $n = 1.37$ (Fig. 2). For S2, the Freundlich model also presented the best fit ($R^2 = 0.99$) with $K_d = 0.0049$ mL/g and $n = 2.07$ (Fig. 3). Where, C_s is the sorbed mass of solute per unit of dry soil mass, C_e is the solute concentration in aqueous phase, K_d is the partition coefficient between soil and liquid phases and n is an exponential coefficient of Freundlich.

For S3, the linear model was the best ($R^2 = 0.92$) with $K_d = 0.7$ mL/g (Fig. 4). The values obtained for the adsorption of $\text{Cr}^{\text{VI}+}$, for the three soils, were very low despite the silt and clay content in some strata.

Charge of soil samples

Regarding the average surface charge of the soil particles analyzed, it was found that all presented a large buffer capacity as the adjusted pH did not hold its value, rather it was always drawn to the neutral pH (7.2) of the solution.

Figure 5 shows the values of the average surface charge for the three soils, and here it is observed that the same zeta potential trend continued at higher pH. The major difference in zeta potential among the three soils was only observed for the pH value of 2, when there is a positive charge. The three soils presented, for most pH values, a negative charge and this is one of the reasons why the adsorption was very low, considering that the $\text{Cr}^{\text{VI}+}$ has always a negative charge.

According to $\text{Cr}^{\text{VI}+}$ speciation studies (Sotelo Muñoz 2012), at pH values higher than 7, CrO_4^{2-} ions predominate, whereas at pH values between 1 and 6, HCrO_4^- predominates, which indicates that at normal pH values for natural waters, we can expect to find CrO_4^{2-} , HCrO_4^- , and $\text{Cr}_2\text{O}_7^{2-}$ ions, meaning ions with a negative charge. The

Table 2 Physicochemical results for soils

Sample	T (°C)	Mass (g)	pH	Redox (R mV)	Porosity (%)	Volumetric density g/cm ³	Retardation factor <i>R</i>	Electric conductivity (μS/cm)
S1	23.85	10.0	8.65	127.65	1.4	1.5	1	220.83
S2	23.85	10.0	8.07	91.03	1.4	1.5	1	99.1
S3	ND	10.0	ND	ND	1.3	0.9	1.48	ND

ND not data

Fig. 2 Freundlich model isotherm for S1, C_s = sorbed mass of solute per unit of dry soil mass, C_e = solute concentration in aqueous phase at equilibrium, K_d = partition coefficient between soil and liquid phases, n = exponential coefficient of Freundlich

Fig. 3 Freundlich model isotherm for S2

negative charge of both the ions and the soil particles makes the adsorption process very weak. The low adsorption concurs with the positive values of the Gibbs free energy, revealing that the processes were not spontaneous. The low adsorption is also explained by the high solubility of hexavalent chromium in water (Pawlisz et al. 1997).

Concentrations of total Cr and $\text{Cr}^{\text{VI+}}$ were analyzed throughout the core of one of the wells drilled (0–65 m), and the soil mass contained therein. Conducting a balance of mass, it was found that in a 1.185 m³ volume of the core,

Fig. 4 Linear model isotherm for S3

Fig. 5 Z potential vs. pH for soil samples

where both species are present, the average concentration of total Cr was 43.5 mg/kg, with a total mass of 21.1 g; whereas for $\text{Cr}^{\text{VI+}}$, the average concentration was 4.37 mg/kg with a mass of 2.12 g. A rough estimate with these values indicates that in the affected area (16,000 m²) and at a depth of 65 m, where the current ground water level starts, there will be 18.53 tons of total Cr and 1.86 tons of $\text{Cr}^{\text{VI+}}$.

The average $\text{Cr}^{\text{VI+}}$ absorbed was 0.34 mL/g. Although this value represents a very low adsorption, it is sufficient so that after more than 30 years there is chromium in the soil particles, particularly due to the reduction of the

Table 3 Data to obtain Gibbs free energy

Soil	Ce (mg/l)	Ca (mg/l)	K_c
S1	228.85	33.65	0.147
S2	268.9	43.61	0.16
S3	29.47	0.53	9.918

groundwater level, which implies that the zone where the saturated zone had been is currently not saturated, favoring chromium to remain adsorbed.

The low adsorption and the contaminant chromium load in the zone have resulted in leaching, and therefore, migration of the total and hexavalent chrome towards the aquifer.

Gibbs free energy

Table 3 shows the data to obtain the Gibbs energy.

Gibbs energy results:

ΔG for S1 = 5.167 kJ/mol

ΔG for S2 = 4.792 kJ/mol

ΔG for S3 = 10.404 kJ/mol

The results for the Gibbs free energy produced positive values in all cases, revealing that the processes were not spontaneous, which concurs with the low adsorption results.

Conclusions

The lowest adsorption level was obtained for S2 ($K_d = 0.0049$ mL/g), which was a fine-grained sand, sandy silts with little presence of thick sand. For S1, a value of $K_d = 0.332$ mL/g was obtained and for S3, which contains a higher percentage of clay (fine-grained sand and clay silts), the highest value was obtained ($K_d = 0.7$ mL/g).

There is a slight difference in the surface charge of the soils. Around pH 7, S2 depicted the highest negative charge, followed by S1, and finally, by S3. It should be recalled that a negative zeta potential implies the predominance of negative charges, but not the absence of positive charges.

Values obtained from the retardation factor, R , reveal that, given the characteristics of the soil and of hexavalent chromium, adsorption is insignificant probably due to the negative charge of both the soils and Cr^{VI} , and this is the reason for chromium migration to the indicated depth.

By analyzing the net surface charge of the particles of these soils, it is evidence of low affinity adsorption having chromate and solids to be both negative. This work focuses on highlighting the risk of groundwater contamination in

sites with this type of soil, due to its low adsorption capacity.

Despite such low adsorption levels, there are significant concentrations of total chromium and hexavalent chromium in the soil because the contaminant load was high and the long time elapsed. This is also due to the groundwater level having dropped, consequently increasing the unsaturated zone where the chromium has not had water as a dispersing agent. The positive values of the Gibbs free energy show that the processes are not spontaneous.

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