Sorption and Desorption Behaviour of Chromium in Soils of Punjab

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The present study was carried out to understand soil chromium (Cr) sorption/desorption phenomena, and hence Cr bioavailability in surface soils collected from Jalandhar, Ludhiana and Mandi Gobindgarh in Punjab. Chromium sorption isotherms were derived by sorption of Cr from solutions containing a range of concentrations equivalent to 50, 100, 300 600 and 900 µg Cr g^{-1} soil in the presence of a background electrolyte, 0.01 M Ca(NO$_3$)$_2$. Chromium desorption isotherms were derived from the Cr desorbed (µg g^{-1} soil) after each of five desorption periods, carried out by sequentially equilibrating same soil samples used for Cr sorption study in Cr-free 0.01 M Ca(NO$_3$)$_2$. It was observed that with the increase in rate of Cr application, amount of Cr sorbed by the soils also increased; however, the per cent Cr sorbed decreased. The Cr sorption data of the three selected soil samples were best described by Freundlich (R^2 = 0.986 to 0.994) followed by Langmuir (R^2 = 0.959 to 0.995), and Dubinin–Radushkevich (D-R) adsorption isotherms (R^2 = 0.926 to 0.973). The constants measuring adsorption capacity, derived from all the three adsorption isotherms, indicated that the soil from Mandi Gobindgarh has higher Cr sorption capacity than the other two soils. Desorption of Cr as well as per cent Cr desorbed from the selected soils increased with the increase in added Cr concentration. The Cr desorption data of the soils were very well described by Langmuir desorption isotherm (R^2 = 0.96 to 0.99). Desorption maxima derived was also observed to be higher in case of Mandi Gobingarh soil which implies that this soil has maximum desorption capacity. The differences in amounts of Cr sorbed and desorbed by experimental soils may be due to variation in soil parameters such as organic carbon and cation exchange capacity.

Key words: Chromium, sorption, desorption, soil, batch study, isotherms

Chromium (Cr) is known to be widespread chemical contaminant of soil and hence considered to be a threat to the environment. The two stable oxidation states of chromium are Cr(III) and Cr(VI), though it can exist in several oxidation states from 0 to VI. Among the two, Cr(VI) is the more toxic form of Cr due to its high mobility and water solubility. The Cr(VI) form is 100 times more toxic and more mobile than Cr(III) (Sang *et al.* 2002). The concentration of Cr in soil ranges between 5 and 1500 mg kg^{-1}. Untreated industrial waste, municipal sewage sludge *etc*. all contribute to Cr accumulation in soils. Elevated concentrations of this potentially harmful element in soils result mostly from industrial wastes or spills, particularly Cr-containing slag, ore refining, production of steel and alloys, pigment manufacture, leather tanning, wood preservation, and combustion of coal and oil are responsible for release of Cr to the environment. Lack of proper disposal facilities leads to serious groundwater and soil pollution (Huang *et al.* 2009). Farmers use sewage for irrigation as it contains essential nutrients but they are unaware that they are adding heavy metals into the soil which affects soil health and plant growth. Regular irrigation with sewage effluents has been found to increase heavy metals such as Cr in soil (Rattan *et al.* 2005; Aghabarati *et al.* 2008). High concentration of Cr in soils cause changes in the soil microbial population and negative impact on the cell metabolism of microorganisms (Shi *et al.* 2002).

The bioavailability of Cr in soil depends on its concentration in soil solution and the ability of the soil to release it from the solid surfaces. Chromium get sorbed on a wide range of soil constituents such as iron (Fe) and aluminium (Al) oxides, clay minerals and organic matter. A number of soil factors such as pH (Tzou *et al.* 2003), ionic strength, clay content (Stewart *et al.* 2003), competing effect of other cations (Monday and Michael 2004), inorganic and organic ligands influence the dynamic equilibrium between

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Cr in the soil solution and the sorbed phase. The information related to Cr sorption in soils with different soil physicochemical properties can be helpful to strengthen our present understanding of Cr sorption. In comparison to Cr sorption by soils, studies related to Cr desorption are limited.

In industrial cities of Punjab such as Ludhiana, Jalandhar and Mandi Gobindgarh, untreated waste from electroplating, dyeing, chemical and dairy industries is being released into sewage channels and farmers use this heavy metal contaminated water to irrigate the crops, making a entry pathway of Cr into the soil. Therefore, the present study was conducted to characterize the Cr behaviour in some soils of Punjab as described by the sorption/desorption isotherms.

Materials and Methods

Soil Sampling and Analysis

Three surface soil samples (0-15 cm depth) expected to differ in physicochemical properties, were collected from three different locations in Punjab *i.e.* Jalandhar, Ludhiana and Mandi Gobindgarh. The USDA system of soil classification was used for the determination of soil textural classes. Samples were air dried, crushed in wooden mortar and pestle, and then passed through a 2 mm sieve. The details of the measurements of the soil physicochemical processes are further explained in table 1.

Chromium Sorption-Desorption Studies

Batch equilibrium technique was adopted for the Cr sorption study. Sorption of Cr in soil was carried out by equilibrating the soil samples (3 g of soil samples in triplicate) with 30 mL of 0.01 *M* calcium nitrate $[Ca(NO_3)_2]$ solutions containing five different concentrations of Cr. The concentrations of Cr used in our study include 5, 10, 30, 60 and 90 µg mL^{-1} of Cr (equivalent to 50, 100, 300 600 and 900 µg Cr g^{-1} soil, respectively). We used potassium dichromate $(K_2Cr_2O_7)$ as a source of hexavalent Cr. Samples were allowed to equilibrate (in triplicate) for 24 h followed

by a 2 h shaking to attain the sorption equilibrium. We also performed an initial study prior to actual experiment to find out the time required to attain sorption equilibrium and observed that sorption did not increase after 2 h of shaking. Concentrations of Cr were measured in the decanted solutions using ICP-AES (Inductively coupled plasma atomic emission spectrophotometer). Difference in the mass of Cr in the solutions before and after equilibrium was considered as the amount of Cr sorbed per 3g of soil. Desorption was determined by measuring the Cr concentrations in the extracted solutions. Five extractions performed with (Cr free) 0.01 *M* $Ca(NO_3)_2$ solution for the same soil samples used for sorption studies. The data for amount of Cr sorption by per unit mass of soil under Cr concentrations was fitted to Frendlich, Langmuir and Dubinin Radushkevich (D-R) adsorption isotherms.

Analysis of Sorption and Desorption Data using Adsorption Isotherms

To further understand the sorption and desorption processes, we fitted our Cr sorption data to Langmuir and Freundlich adsorption isotherms. Further, to understand about the type of adsorption, the sorption data was fitted to Dubinin Radushkevich (D-R) adsorption isotherm. Desorption data was fitted to Langmuir desorption isotherm.

Langmuir adsorption isotherm: Langmuir adsorption equation was used to calculate the adsorption parameters, adsorption maxima 'b' and bonding energy coefficient 'K'. The linear equation can be written as:

$$C/(x/m) = 1/Kb + C/b \qquad \qquad …(1)$$

where, C is the equilibrium Cr concentration (µg mL^{-1}); x/m is the amount of Cr adsorbed by soil (µg g^{-1}); and

'b' and 'K' are Langmuir constants related to adsorption capacity and the bonding energy of the adsorbent for the Cr (mL µg^{-1}), respectively. The plot between C/(x/m) and C is a straight line.

Table 1. Physicochemical characteristics of the experimental surface soils

Sample No.	pH	EC (dS m^{-1})	Organic carbon (%)	CaCO$_3$ (%)	CEC [cmol(p$^+$)kg^{-1}]	Clay (%)	Total Cr (µg g^{-1})
Jalandhar	6.64	0.22	0.74	Absent	6.38	17.4	37.75
Ludhiana	7.18	0.32	1.12	0.77	11.74	13.1	2.70
Mandi Gobindgarh	7.12	0.21	1.94	Absent	32.98	13.5	35.40

Freundlich adsorption isotherm

Linearized Freundlich equation used is described below:

Log(x/m) = log K_f + n log c   …(2)

where, c denotes the equilibrium Cr concentration (µg mL^{-1} soil);

x/m is amount of Cr absorbed by the soil (µg g^{-1} soil); and

'K_f' and 'n' are empirical constants which measure the adsorption capacity and intensity, respectively.

A linear plot between log(x/m) and log c gives the value of 'K_f' (intercept) and 'n' (slope), respectively.

Dubinin Radushkevich (D-R) adsorption isotherm: It helps to distinguish between the chemical adsorption and physical adsorption. The D-R equation in linear form is written as:

$\ln Q_e = \ln Q_m - \beta \varepsilon^2$ …(3)

where,

Q_e = amount of Cr adsorbed per unit weight of soil (µg g^{-1});

Q_m = constant related to adsorption capacity;

β = constant related to mean free energy of adsorption (mol^2 KJ^{-2}); and

ε = Polanyi potential (KJ^2 mol^{-2})

ε can be obtained from following relation:

$\varepsilon = RT \ln(1 + 1/C_e)$ …(4)

where,

C_e = equilibrium concentration of Cr in solution after adsorption (mgL^{-1});

R (J/mol K) is the gas constants and T (K) is the absolute temperature.

The experimental data was evaluated by plotting $\ln Q_e$ against ε^2 to obtain value of Q_m and β from intercept and slope, respectively.

Results and Discussions

Physicochemical properties of the experimental soils

The physicochemical properties of the three

(Jalandhar, Ludhiana and Mandi Gobindgarh) experimental soils have been described in table 1. The pH of soils selected for this study ranged from 6.64 to 7.18, electrical conductivity (EC) from 0.21 to 0.32 dS m^{-1}, cation exchange capacity (CEC) from 6.38 to 32.98 cmol(p$^+$)kg^{-1} soil, clay content 13.1 to 17.4% and organic carbon (OC) from 7.4 to 19.4 g kg^{-1}. Total Cr content of soils ranged from 2.70 to 37.75 µg g^{-1} soil. The experimental soils varied in their physical and chemical characteristics, therefore, expected to show variation in amounts of Cr sorbed and desorbed.

Variation of Cr sorption with Cr application rate

The amounts of Cr sorbed with varying application rates (50, 100, 300, 600 and 900 µg g^{-1} soil) have been reported in table 2. It was observed that with increased Cr concentrations ranged from 50 to 900 µg g^{-1} soil, the amount of Cr sorbed also increased in all the three soils. This was expected because more Cr was available for sorption onto soil with the increase in application rate. Although we observed increase in Cr sorption with increase in application rates for all the three experimental soils, there were variations in the sorption amount among the experimental soils. The trend of maximum amount of Cr sorbed was in order of Mandi Gobindgarh > Jalandhar > Ludhiana at all levels of initially added concentrations. Among the polluted Jalandhar and Mandi Gobindgarh soils, the later has high sorption capacity though the pH of Jalandhar soil (6.64) is less than Mandi Gobindgarh soil (7.12). It implies that sorption of Cr also depends on physicochemical factors other than pH. Mandi Gobindgarh soils have high OC content which may have reduced the added hexavalent Cr(VI) to its trivalent form and this trivalent form get adsorbed onto soil colloids. Bolan and Duraisamy (2003) examined the fate of Cr(III) and Cr(VI) with and without organic matter and observed that adsorption of Cr(VI) was found to be negligible in absence of organic matter but in the

Table 2. Chromium sorbed (µg g^{-1}) at different levels of its addition by experimental soil

Location	Chromium sorbed (µg g^{-1}) after initial application				
	50	100	300	600	900
Jalandhar	6.92	12.06	29.12	46.10	53.52
	(13.8)	(12.1)	(9.7)	(7.7)	(5.9)
Ludhiana	6.31	11.81	29.86	46.53	52.51
	(12.6)	(11.8)	(9.9)	(7.8)	(5.8)
Mandi Gobindgarh	12.44	19.17	47.08	81.25	95.35
	(24.9)	(19.2)	(15.7)	(13.5)	(10.6)

*Figures in parentheses denotes "(Cr sorbed / Cr applied) × 100"

Table 3. Langmuir equations and Langmuir parameters for experimental soils

| Location	Linear equation	R^2	Adsorption maxima, b_{max} ($\mu g\ g^{-1}$)	Bonding energy coefficient, K ($mL\ \mu g^{-1}$)
Jalandhar	y = 0.011x + 0.601	0.994	90.909	0.018
Ludhiana	y = 0.011x + 0.626	0.989	90.909	0.017
Mandi Gobindgarh	y = 0.006x + 0.334	0.959	166.66	0.017

presence of added organic matter, adsorption of Cr(VI) increased inferring that Cr(VI) was reduced to Cr(III) by the organic matter and then get adsorbed in trivalent form. Jardine *et al.* (2013) also observed increased Cr(VI) sorption with the increased soil total organic carbon (TOC) content and decrease in pH by multiple linear regression analysis.

Chromium Adsorption Isotherms

The Cr sorption data significantly fitted to both Langmuir and Freundlich adsorption isotherms for all three experimental soils. The sorption data was well described by Langmuir adsorption isotherm with high values of R^2 (0.95 to 0.99) derived from data pairs of

$C/(x/m)$ and C_e of three soils (Table 3; Fig. 1a-c). Kwikima and Lema (2017) found that the sorption of Cr(VI) for the experimental soil confirms well to the Langmuir isotherm at constant pH. Two adsorption parameters: the maximum sorption capacity (Q_o) and Langmuir adsorption constant (K_l), for Cr(VI) were determined as 1.013×10^{-4} mol g^{-1} and 0.062 mg L^{-1}. Among three experimental soils, Mandi Gobindgarh soil had maximum sorption capacity (166.6 $\mu g\ g^{-1}$) as compared to other two soils, probably due to higher OC content which enhanced reduction of added hexavalent Cr to its trivalent form. Freundlich adsorption isotherm also very well described the Cr sorption as indicated by high R^2 values (0.98 to 0.99)
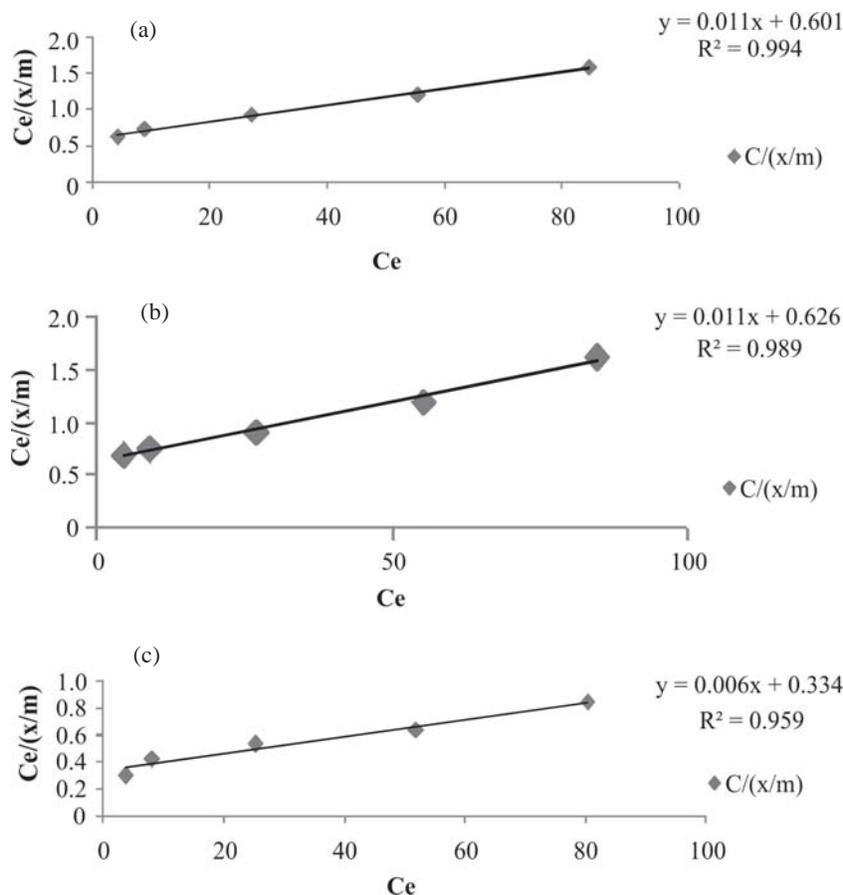
Fig. 1. Langmuir adsorption isotherm for (a) Jalandhar, (b) Ludhiana and (c) Mandi Gobindgarh soil

(Table 4, Fig. 2a-c). The value of adsorption capacity 'K$_f$' (relative affinity of adsorbent for adsorbate) of Mandi Gobindgarh soil was highest among three soils. As discussed earlier also, higher OC content could be responsible for its higher retention than other two soils. The higher OC may have enhanced the rate of reduction of Cr(VI) to Cr(III) in soils and the extent of Cr(VI) reduction has been observed to be positively correlated with the amount of dissolved organic carbon in the soil (Han *et al.* 2004). The transformed trivalent form get adsorbed on soils that enhances the adsorption. Jardine *et al.* (2013) also observed an increase in Cr(VI) sorption with the increase in soil TOC.

To find out the type of sorption *i.e.* whether physi-sorption or chemi-sorption based on the energy of activation, the Cr sorption data was fitted to Dubinin Radushkevich (D-R) adsorption isotherm. The sorption data well fitted to D-R adsorption isotherm. If the energy of activation is < 8 KJ mol^{-1}, the adsorption is physi-sorption and if the energy of activation is 8-16 KJ mol^{-1}, the adsorption is chemi-sorption in nature.

Since the energy of activation calculated using E$= 1/\sqrt{(-2B)}$ of all the three experimental soils is less than 8 KJ mol^{-1} (Table 5, Fig. 3a-c) which implies that sorption of chromium is physi-sorption *i.e.* Cr anions are held by Van der Waal forces on the soil colloids. Fonseca *et al.* (2009) studied Cr sorption in loamy sand soil (at pH 2 and 5) and observed that Cr sorption was well described by Dubinin–Radushkevich model and the value obtained for the

Table 4. Freundlich equations and Freundlich parameters for experimental soils

Location	Linear equation	R^2	Adsorption affinity (K$_f$)	n
Jalandhar	y = 0.705x + 0.412	0.992	2.6	0.705
Ludhiana	y = 0.732x + 0.366	0.985	2.3	0.732
Mandi Gobindgarh	y = 0.696x + 0.681	0.994	4.8	0.696
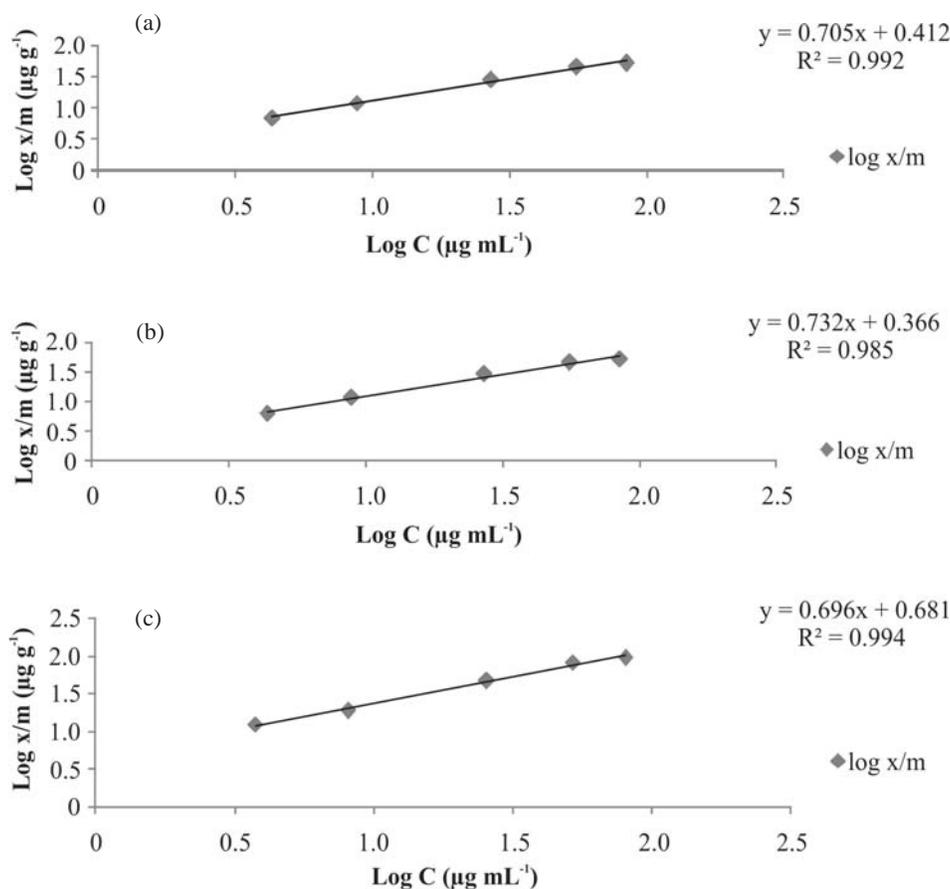
Fig. 2. Linearized Freundlich adsorption isotherm for (a) Jalandhar, (b) Ludhiana, and (c) Mandi Gobindgarh soil

Table 5. Dubinin Radushkevich equations and Dubinin Radushkevich parameters for experimental soils

Sample site	Linear equation	R^2	Q_m (mmol kg^{-1} soil)	β (mol^2 KJ^{-2})
Jalandhar	y = -0.052x - 0.057	0.960	0.94	3.10
Ludhiana	y = -0.055x - 0.038	0.973	0.96	3.02
Mandi Gobindgarh	y = -0.047x + 0.467	0.926	1.59	3.26
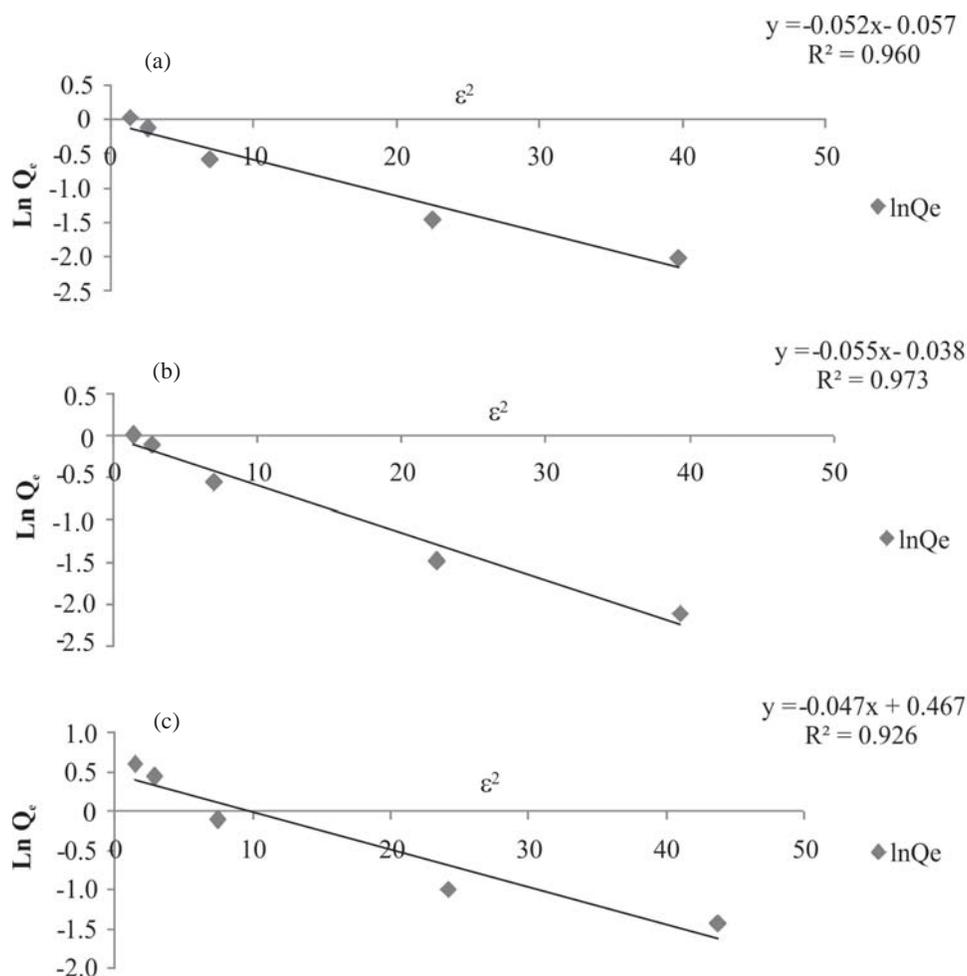
Fig. 3. Dubinin–Radushkevich adsorption isotherm for (a) Jalandhar, (b) Ludhiana and (c) Mandi Gobindgarh soil

mean energy of sorption was lower than 8 kJ moL^{-1}, indicating that Cr is retained mainly by physical forces.

Chromium desorption isotherms

The cumulative desorption of sorbed Cr over a period of five desorptions increased with the increase in the number of successive desorptions irrespective of the initial concentration of Cr added to each of these soils, however, the amount of Cr desorbed in every successive desorption decreased (Table 6). Also, within a soil, cumulative Cr desorbed increased with an increase in initially added chromium concentration from 50 µg g^{-1} to 900 µg g^{-1}. In case of Jalandhar soil, it increased from 1.08 to 39.71 µg Cr g^{-1}, while in Ludhiana soil it increased from 1.09 to 41.47 µg Cr g^{-1} and in Mandi Gobindgarh soil from 1.29 to 39.79 µg Cr g^{-1} (Table 6). With the increase in particular level of initially added Cr (50 to 900 µg Cr g^{-1}), the per cent Cr desorbed increased from previously sorbed Cr (Table 6). The per cent Cr desorbed increased from 15.7 to 74 for Jalandhar soil, 17.4 to 79 for Ludhiana soil and 10.4 to 41.7 for Mandi Gobindgarh soil (Table 6). Cumulative amount of Cr desorbed as well as per cent Cr desorbed were in the order Ludhiana soil > Jalandhar soil > Mandi Gobindgarh. This could

Table 6. Desorption of sorbed chromium initially added at different levels (µg g^{-1}) from experimental soils

Location	Levels of added chromium (µg g^{-1})				
	50	100	300	600	900
Jalandhar	1.08	3.52	11.34	28.17	39.71
	(15.7)*	(29.2)	(38.9)	(61.1)	(74.0)
Ludhiana	1.09	3.99	11.93	23.99	41.47
	(17.4)	(33.8)	(39.9)	(64.5)	(79.0)
Mandi Gobindgarh	1.29	1.98	8.92	22.60	39.79
	(10.4)	(10.3)	(18.9)	(27.8)	(41.7)

*Figures in parenthesis denotes "(Cr desorbed / Cr sorbed) × 100"

Table 7. Langmuir desorption equations and Langmuir parameters for experimental soils

Sample site	Linear equation	R^2	D_m (µg g^{-1})	K_d (mL µg^{-1})
Jalandhar	y = 0.014x + 0.202	0.970	71.42	0.069
Ludhiana	y = 0.013x + 0.222	0.967	76.92	0.058
Mandi Gobindgarh	y = 0.008x + 0.097	0.992	125	0.082

be due to relatively higher pH of Ludhiana soil among all three soils. Though the pH of Mandi Gobindgarh soil is similar to the Ludhiana soil but due to high content of organic carbon, Cr sorbed in its trivalent form onto soil after reduction and desorption of trivalent form decreases at higher pH. Also, the cation exchange capacity of soil is high which implies trivalent Cr is strongly sorbed onto soil. Due to this reason, desorption of Cr in this soil is relatively lesser. Azizian (1993) while studying Cr(Vl) desorption in soil columns observed a retarded Cr(Vl) desorption in a near neutral soil (pH 6.9). We fitted Cr desorption data to Langmuir desorption equations for the experimental soils and found that the Cr desorption data fitted well with the Langmuir desorption isotherm (Table 7). Among the soils, desorption maxima was highest in case of Mandi Gobingarh soil that implies that this soil has maximum desorption capacity. Lesser cumulative Cr desorbed by Jalandhar soil as compared to Ludhiana soil could be due to low pH of the former than later.

Conclusions

In the Cr sorption and desorption study performed in three different soils of Punjab, we observed an increase in Cr sorption in all of the soils with an increase in added Cr concentrations. The Cr sorption data of the three selected soil samples were significantly described by Langmuir (R^2 = 0.95 to 0.99), Freundlich (R^2 = 0.98 to 0.99) and Dubinin–Radushkevich (D-R) adsorption isotherms (R^2 = 0.92 to 0.97). It was observed that Cr adsorbed onto soil surface through physical forces by fitting the sorption data to D-R equation. Mandi Gobindgarh soil had maximum sorption capacity (166.66 µg g^{-1}) as well as desorption capacity compared to other two soils, probably due to higher organic carbon content which may have enhanced reduction of added hexavalent Cr to its trivalent form. The desorption of Cr as well as per cent Cr desorption from the selected soils increased with the increase in added Cr concentration. The Cr desorption data of the soils well fitted to Langmuir desorption isotherm (R^2 = 0.96 to 0.99). Results of present study will help in a better understanding of the chemical behavior of Cr in soils and, eventually, better design remediation method for Cr contaminated soils.

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