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Cr^{VI} adsorption on four typical soil colloids: equilibrium and kinetics

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Abstract: It is observed that the adsorption of chromium are greater on kaolinite minerals, red soil (R) and laterite (L) colloids than that on montmorillonite, indicotic black (IB) and yellow brown (YB) soil colloids. The adsorption process of Cr^{VI} on these media can be further described by Langmuir or Freundlich equation quite well. The adsorption reaction of Cr^{VI} is fast, and the adsorption equilibrium can be reached within the first two hours in moderate temperature. The adsorption quantity of Cr^{VI} to kaolinite mineral increased with the increasing pH in the range of 2.0 to 7.0, then decreased at higher pH. But it showed some consistence among the four soil colloids. The lower the pH, the stronger the adsorption. The possible mechanisms are further discussed here. Meanwhile the influence of temperature on Cr^{VI} adsorption on different soil colloid and clay minerals are also investigated.

Key words: Cr^{VI}; soil colloids; clay mineral; adsorption

Introduction

Chromium, which is toxic to man and other living organisms, presents potentially serious environmental problems throughout the world. Chromium mainly exists in two forms as Cr^{III} and Cr^{VI}. Cr^{III} is of less poisonousness, but Cr^{VI} exhibits a strong toxicity. When Cr^{VI} is discharged into water, soils or sediments, it would be distributed between soil (or sediment) and water (Chen, 1996). Specially, Cr^{VI}, in its high valence, is a relatively strong oxidant which can undergo redox reaction with soil constitutes, including minerals, aqueous inorganic ions, simple organic molecules and humic materials (Cifuentes, 1996; James, 1996). So, not only does the adsorption process of Cr^{VI} but also its chemical reaction occur simultaneously when Cr^{VI} enter soils and sediments, which result in the study very complex. Therefore, it is very interesting to study the adsorption behavior of Cr^{VI} on minerals and soils so that its migration and conversion processes on soils could be further interpreted.

The adsorption of Cr^{VI} to soil is strongly influenced by pH and coexisted negative ions. Anions, such as NO₃⁻, SO₄²⁻, Cl⁻, HPO₄²⁻ as well as higher pH usually decrease its adsorption to soil (James, 1983; 1996). Study on the conversion between Cr^{VI} and Cr^{III} in minerals and soils showed that Cr^{VI} could be reduced by organic matter and metal ions in soils (Chen, 1989; 1990; Zhu, 1982). Recently, catalytic reaction of Cr^{VI} and organic acid by MnO₂ and Al₂O₃ minerals was studied, and the reaction mechanism and model are successfully obtained (Deng, 1996). However only studying the reactions of chromium with minerals is very limited to extend to real system. It is important to understand the adsorption and conversion of Cr^{VI} on different absorbents in a complex system.

The aims of our study were to investigate (1) the adsorption equilibrium and kinetics of Cr^{VI} on four soil colloids and two clay minerals; (2) the effect of pH on Cr^{VI} adsorption; (3) the reaction of Cr^{VI} and humic substances of soil. The study on Cr^{VI} adsorption and reaction on soil colloids provides an important theoretical and practical information for our further works on the interaction of Cr^{VI} and organic pollutants on soil or minerals.

1 Experimental

1.1 Preparation of soil colloids

Air-dried soil samples, red soil (R, Udic Ferrisol), laterite (L, Udic Ferralisol), yellow

brown soil (YB, Uic Luvisol) and indicotic black soil (IB, Aquic Cambisol), are sieved through a 20 mesh screen, then, a portion of soil is weighed and soaked in deionized water and sonicated, followed washing by deionized water containing CaCl_2 for discharging chloride ion. The subsamples are dried under infrared lamp for further use. The total contents of Fe, Al and Si oxides in soil colloids are analyzed using DCP-AAS with fused $\text{Li}_2\text{CO}_3\text{-H}_3\text{BO}_3$ (Sheng, 1983). The active parts are obtained using $\text{H}_2\text{C}_2\text{O}_4\text{-(NH}_4\text{)C}_2\text{O}_4$, and CECs of colloids are performed with $\text{BaCl}_2\text{-H}_2\text{SO}_4$ method (Institute of Soil Science, 1978).

1.2 Experimental procedure

$0.100 \pm 0.002\text{g}$ soil colloid or mineral is weighed and placed into a plastic tube, then 10 ml solution with different Cr^{VI} concentration is added to perform the batch experiments. pH of soil colloids, determined with the equilibrated supernatant, is adjusted with 0.001 mol/L HCl or 0.001 mol/L NaOH to obtain the resulting solution with pH in the range of 2.5 to 8.0, and the ion strengths is 0.04 mol/L . In following, these samples are shaken 24h continuously for equilibrium experiments then centrifuged. The supernatant are used to analyze Cr^{VI} content. Cr^{VI} content is measured using a diphenylcarbazide solution colorimetric method by spectrometer with wavelength of 540 nm. Diphenyl carbazide solution is prepared as follows: 0.1g diphenylcarbazide is dissolved in 50 ml ethanol and 200 ml H_2SO_4 (1 volume H_2SO_4 + 9 volume water) is added, then stored in a brown bottle.

2 Results and discussion

2.1 Adsorption isotherms of Cr^{VI} on soil colloids

Table 1 The chemical properties of soil colloids

Colloid	OM, %	Fe_2O_3 , %	Al_2O_3 , %	SiO_2 , %	CEC, me/100g
IB	2.19	9.39* 2.23**	22.09* 3.00**	49.06*	76.35
YB	1.51	10.94* 5.27**	23.14* 4.00**	44.69*	52.96
R	1.26	11.18* 9.15**	29.08* 8.39**	40.86*	25.67
L	1.59	18.04* 6.55**	33.23* 15.7**	29.53*	18.31

* total content of Fe, Al and Si oxide; ** active part of Fe, Al oxide

Table 1 shows the chemical properties of four soil colloids. Red soil and laterite colloids have more metal oxides than yellow brown and indicotic black soil colloids. Among of

them, indicotic black and red soil colloids have highest and lowest organic matter content, respectively.

Cr^{VI} in aqueous solution exists mainly in the forms of HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ as negative charge ions. As shown in Table 2, the major form of Cr^{VI} in aqueous solution is HCrO_4^- in the range of 3.0 to 7.0. So, Cr^{VI} adsorption to soil was mainly contributed by HCrO_4^- , although $\text{Cr}_2\text{O}_7^{2-}$ have the stronger adsorption ability due to its larger aquatic radii. The ΔG_f° is -315.40 kcal/mol , -176.10 kcal/mol , -184.90 kcal/mol and -185.92 kcal/mol for $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , HCrO_4^- and H_2CrO_4 , respectively. Therefore, the quantity of $\text{Cr}_2\text{O}_7^{2-}$ will increase with increasing temperature.

Fig. 1 shows the adsorption isotherm of Cr^{VI} on four soil colloids, including yellow brown, indicotic black, red soil and laterite colloids. It is greater for Cr^{VI} adsorption to red soil and

Table 2 Change of species of Cr^{VI} with pH at aqueous solution ($C_0 = 10^{-4}\text{ mol/L}$)

	pH 3.0	pH 4.0	pH 5.0	pH 6.0	pH 7.0
$\text{H}_2\text{CrO}_4/\text{CrO}_4^{2-}$	1.6×10^1	1.6×10^{-1}	1.6×10^{-3}	1.6×10^{-5}	1.6×10^{-7}
$\text{HCrO}_4^-/\text{CrO}_4^{2-}$	2.8×10^3	2.8×10^2	2.8×10^1	2.8	2.8×10^{-1}
$\text{Cr}_2\text{O}_7^{2-}/\text{CrO}_4^{2-}$	4.0	4.0×10^{-1}	4.0×10^{-2}	4.0×10^{-3}	4.0×10^{-4}

laterite colloids than that to yellow brown and indicotic black colloids. Red soil and laterite colloids possess more Fe and Al oxide than yellow brow and indicotic black (Table 1), and Cr^{VI} adsorbed easily on such oxide surface (Xu, 1995). Therefore, it is reasonable that the adsorption quantities of Cr^{VI} on red soil and laterite colloids are larger than that on yellow brown and indicotic black ones.

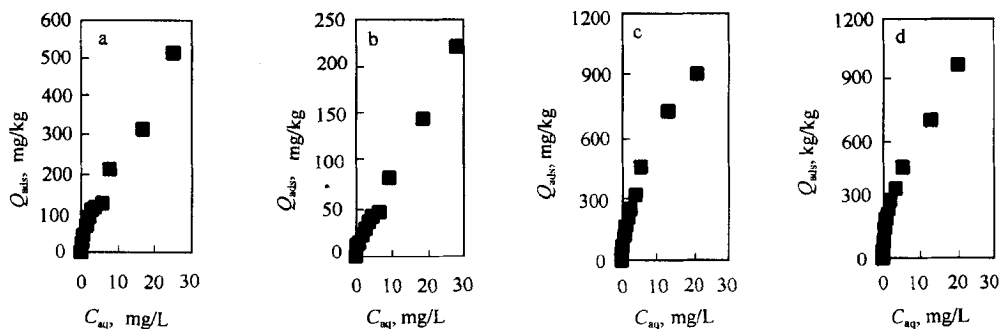


Fig. 1 Cr^{VI} adsorption isotherms on (A) YB; (B) IB; (C) R and (D) L colloid

Both of Langmuir and Freundlich equations can be used to describe the adsorption equilibrium of Cr^{VI} on soil colloids with a satisfying correlation coefficient (Table 3). However, C_0 from Langmuir equation for indicotic black and yellow brown soil colloids is somewhat larger than that for red soil and laterite ones, which is not agree with our experimental results. With Freundlich one, the simulated k values are conformation with the adsorption ability, also, $1/n$ decrease with the increasing adsorption capacity. So, Freundlich equation is more suitable for the simulation of Cr^{VI} adsorption on these soil colloids than langmuir one.

Table 3 Simulated results for Cr^{VI} adsorption on soil colloids ($T = 285K$) by Langmuir and Freundlich equations

Simulation equation	Simulation parameter	YB	IB	R	L
Langmuir	k	0.2132	0.005	0.125	0.09
	C_0	1394.0	1808.2	1247.9	1356.3
	R	0.9815	0.9965	0.9793	0.997
Freundlich	K	41.4	10.31	188.88	151.10
	$1/n$	0.765	0.917	0.531	0.5947
	R	0.9886	0.9972	0.9970	0.9978

Table 4 shows the equilibrium adsorption quantities of 5.0 mg/L Cr^{VI} on four soil colloids and two clay minerals.

Table 4 Adsorption quantity of Cr^{VI} on two minerals and four soil colloids ($C_0 = 5.0$ mg/L)

	Montmorillonite	IB	YB	Kaolinite	R	L
C_{eq} , mg/L	4.94	4.82	4.52	3.05	3.48	3.35
Q_{ad} , mg/kg	6.20	18.0	48.0	195.1	152.4	165.6

The adsorption quantity order is: kaolinite > L colloid \cong R colloid > YB colloid > IB colloid > montmorillonite. It suggests that Cr^{VI} is more mobile on indicotic black and yellow brown soil than on red and laterite soils.

2.2 Effect of pH on the adsorption of Cr^{VI} on soil colloids and minerals

Fig.2 shows the influence of pH on Cr^{VI} adsorption to kaolinite, IB, YB, R and L colloids. As for red and laterite colloids, the adsorption quantities increased with the decreasing pH, but for kaolinite, it is different. The adsorption of Cr^{VI} to kaolinite would decrease at higher acidity, which may be ascribed to the destructed -OH groups presented on kaolinite surface in acidic medium. Fe, Al oxide in red soil and laterite colloids can complex H⁺ to possess positive charges

which enhance its adsorption to negative charge of HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ (Xu, 1995). As shown in Fig. 2, red soil and laterite colloids have the same tendency on the change of Cr^{VI} adsorption with pH. The changes are small for montorillonite, indicotic black soil colloid. But yellow brown soil colloids showed the greatest change among these soil colloids.

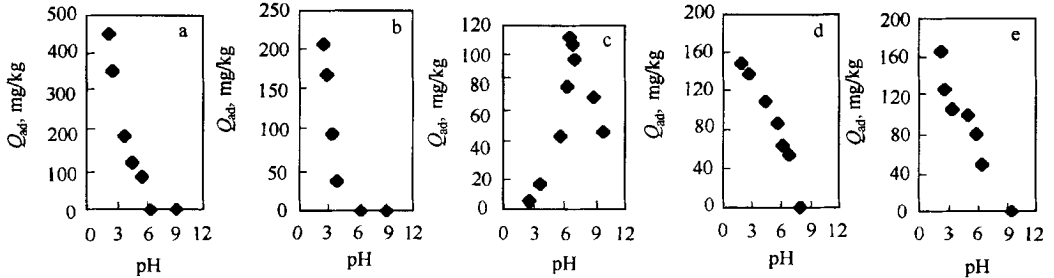


Fig. 2 Influence of pH on Cr^{VI} adsorption to (A) YB; (B) IB; (C) kaolinite; (D) L and (E) R soil colloid (the initial concentration of Cr^{VI} is 5.0 mg/L for A, B and 2.0 mg/L for C, D, E, respectively), $T = 295\text{K}$

Surface charge of minerals and soil colloids changes with equilibrium solution's pH, which resulted in the change of Cr^{VI} adsorption quantity on their surfaces. Metal oxides of soil colloid are the major load for the adsorption of negative charge ions. Such adsorption is divided into two types: non-specific adsorption and specific adsorption. The adsorption of Cr^{VI} on $\text{Fe}(\text{OH})_3$ colloid has been proved to be specific adsorption, moreover, the formation of HCrO_4^- in the aqueous phase corresponds with the formation of the Cr^{VI} surface complex, which suggests that release of H^+ during the adsorption process would possibly occur. But, such change was not observed due to the relatively small adsorption quantity.

2.3 Adsorption dynamic of Cr^{VI} on soil colloids

Experimental data as points in Fig. 3 showed the change of Cr^{VI} adsorption quantities with time. Cr^{VI} adsorption is very fast, and they can reach adsorption equilibrium within 2 hours. Compared with the reaction dynamic of Cr^{VI} with organic matter of soil (Wittbrodt, 1996), adsorption dynamic of Cr^{VI} is comparatively fast on these media, which can be used to differ adsorption and reaction portion of Cr^{VI} .

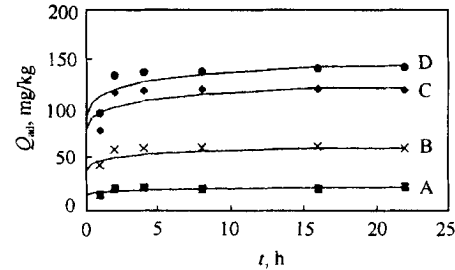


Fig. 3 Cr^{VI} in aqueous with equilibrium time (A) IB; (B) YB; (C) R and (D) L soil colloid, $T = 285\text{K}$, $C_0 = 2.0 \text{ mg/L}$ (points represent experimental data, and lines are the simulated results)

When first-order, second order, simple elovich and double-parameter rate equations ($Q_{\text{ad}} = kC_0 t^n$) are used to simulate the adsorption dynamics of Cr^{VI} on soil colloids, a good correlation is obtained for the double-parameter simulation equation as Table 4 ($p < 0.001$). Here, k represents the adsorption rate parameter. Table 5 indicates the order of k is red > laterite > yellow brown > indicotic black soil colloids, thus, Cr^{VI} adsorption on red and laterite soil colloids is faster than that on yellow brown and indicotic black ones. The resulting n is similar to Table 5 for all selected soil colloids.

Table 5 Results for double-parameter rate equation on Cr^{VI} adsorption

Parameters	IB	YB	R	L
k	8.93	24.31	56.74	48.52
n	0.088	0.09	0.084	0.083
R	0.9774	0.9792	0.9806	0.9716

From above observations, no obvious difference for reaching Cr^{VI} adsorption equilibrium time is observed among these four

