Adsorption Behavior of Hexavalent Chromium in Vadose Zone

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Abstract: Adsorption behavior of Cr (VI) in vadose zone, which is silty clay and clayey soil, was studied through kinetics experiments, isothermal adsorption experiments under various conditions, including different ph, temperature and organic contents. The results from kinetics experiments showed that the sorption progress of Cr (VI) has clear features in different stages, and adsorption equilibrium showed at 30 min, the adsorption rate of silty clay and clayey soil were 60%. The isothermal adsorption curve of Cr (VI) fitted closely with Freundlich equation model. When pH is 3-5 a plateau were seen, thereafter with increase in pH the adsorption rate of Cr (VI) dropped sharply and the minimum achieved at pH 10, the adsorption rate were only 35%. Adsorption rate of Cr (VI) increased gradually with the increase of temperature, the temperature of vadose zone is 14.7 ℃, according to the experimental results, the adsorption rate of Cr (VI) is about 40%. The use of organics represents an important contribution to the sorption of Cr (VI), sorption rate up to 100% when 30% of organic content. These studies will provide basis for manager to minimize the impacts, and provide basic data for pollution prevention and remediation of vadose zone.

Keywords: Cr (VI), Adsorption, Behavior, Vadose zone

Introduction

Chromium is an important resource in tanning, electroplating, dyeing, organic synthesis, etc., and widely used in industrial, agricultural production and laboratory. Rapid development of chromium production owing to the increasing demand of chromium and its compounds, but chromium production brought serious environmental pollution problems. China has produced more than six hundred and ten thousand tons of chromium slag since 1958, and the untreated was up to four hundred and ten thousand tons (Chai, 2010). And chromium will be introduced into natural waters by variety of industrial wastewaters including those from leather tanning, electroplating and metal finishing industries (Schneider, 2007). Chromium which is in natural water will gather in human body eventually. International Agency for Research on Cancer has confirmed that Cr (VI) and its compounds are carcinogenic, they enter bodies through skin, respiratory tract, enteron, mucosa, and are accumulated mainly in lung, pancreas and endocrine glands (Costa, 1997). When chromium concentration is accumulated to high levels, it will generate serious problems, when reaching 0.1 mg/g body weight, it can ultimately become lethal (Richard, 1991).

With increasing chromium manufacture and toxic of chromium, the pollution by chromium has received wide attention in recent years. In order to study the adsorption behavior of hexavalent chromium in vadose zone, design adsorption experiments of Cr (VI) through kinetics experiments, isothermal adsorption experiments and under various conditions, including different pH values, temperature and organic contents. Results of this study will provide the basis for vadose zone

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and groundwater pollution prevention has extremely significant.

Theoretical Basis

Adsorption Isotherm

Isothermal experiment is to examine the relationship between S (mg/g) and C (mg/L), which are pollutants amount adsorbed onto unit soil and concentration of contaminated liquid when reached equilibrium respectively. The Linear, Langmuir and Freundlich isothermal equations are most widely used for fitting the data.

Linear Isothermal Equation

Premise conditions of the equation are: the adsorbent soil single, and soil is porous media to absorption, the interaction between the solute and soil is greater than it between aqueous solution and solute. The equation is: $S = K_d C + b$

Distribution coefficient K_d means the distribution ratio of solute in solid phase and liquid. It is an important parameter of solute migration ability. The bigger the distribution coefficient is, the easier to adsorb, and not easier to migrate.

Langmuir Isothermal Equation

The Langmuir isothermal model assumes that, adsorption of each molecule is monolayer coverage, and each molecule to the surface has equal activation of adsorption energy (Chen, 2008). The Langmuir model takes the form:

$$\frac{C}{S} = \frac{1}{K_l S_m} + \frac{1}{S_m} C$$

Where K_l is the Langmuir equilibrium constant which is related to the affinity of binding sites, S_m is parameter of adsorption capacity.

Freundlich Isothermal Equation

Freundlich isothermal equation is based on adsorption on a heterogeneous surface(Ho, 2002). The equation can be written as:

$$\lg S = \lg K_f + n \lg C$$

Where K_f is the empirical constants.

The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of Cr by soil over the entire concentration range studied (Dubey, 2007).

Effect Conditions

Chromium exists in more than one redox state, and its behavior in vadose zone depends on different state (Guha, 2004), parameters such as pH, temperature, and organic content are quite important. These factors will be responsible for differences in adsorption mechanism. Chromium speciation is pH dependent (Richard, 1991), and pH of environment is the prominent factor in sorption of Cr (VI) (Youssef, 2004). Temperature affects the vibrational energies of the adsorbed molecule, facilitates the diffusion in micropore system, that chromium undergoes dehydration with increasing temperature (Weckhuysen, 1994). Organic matter can change the combination state of chromium; will affect its ability to adsorption on soil in vadose zone (James, 1983).

Material and Methods

Main mediums of vadose zone in study area, in gongyi, luoyang, are silty clay and clayey soil. Collected soil samples near the heap of chromium slag, and make sure the soil is not polluted by chromium, then air is dried at room temperature, remove surface plant debris and coarse materials, then passed through stainless steel sieves with 0.150 mm for experiments. Characteristics of soil are summarized in Table1.

Table1 Basic Characteristics of Soil Used in the Experiments

		Silty Clay	Clayey Soil
Moisture Content（%）		16.8	14.8
Dry Density（g/cm^3）		1.46	1.43
pH		7.5	7.8
Cr (VI)（ug/g）		13.86	14.02
Particle Classification (mm)	2.0-0.5	0	0.4
	0.5-0.25	0.3	0.2
	0.25-0.075	0.8	0.6
	0.075-0.05	9.7	7.3
	0.05-0.01	59.5	61.2
	0.01-0.005	11.5	12.5
	＜0.005	18.2	17.8

Experiments

Kinetics Experiments

Experiments of silty clay and clayey soil were carried out in conical flasks of 250 mL with suspensions of: (a) 20 g soil, which passed through stainless steel sievesof 0.150 mm, (b) 200 ml Cr (VI), or 200 ml distilled water as blank sample to eliminate the influence of Cr (VI) by soils, (c)a drop of 200 mg/L $HgCl_2$ as a bio-inhibitor. Then it was placed in oscillation box of 25℃ (±1℃), and shaken at 200 r/min to ensure equilibrium was reached. To the time stipulated, which is 10 min, 20 min, 40 min, 60 min, 90 min, 120 min, 140 min conical flasks were taken out, and be centrifuged at 4,000 r/min for 2 min, then test Cr(VI) concentration of suspension using spectrophoto metric method. Cr (VI) concentration after experiments $C=C_{sample}-C_{blank}$.

Isothermal Adsorption Experiments

Isothermal adsorption experiments of silty clay and clayey soil were operated with suspensions of: (a) 20 g soils, (b) 200 ml distilled water, or Cr (VI), the concentrations were 0.1 mg/L, 0.5 mg/L, 1 mg/L, 2 mg/L, 5 mg/L, 10 mg/L, (c) a drop of 200 mg/L $HgCl_2$. Then it was shaken to adsorption equilibrium time, which determined in kinetics experiments. Steps and computing methods like kinetics experiments above.

Effect Experiments

The effect experiments were mentioned above; only the specific conditions were described. The present studies were carried out at (a) soils with different pH, which were 2.13, 3.01, 4.07, 5.00, 6.04, 6.98, 8.02, (b) different temperature, 0℃, 5℃, 10℃, 15℃, 20℃, 25℃, 30℃, (c) different content of organic, 5%, 10%, 15%, 20%, 25%, 30%.

Results and Discussion

Kinetics Experiments

The sorption process has been described as a complex process, in which the properties of the sorbate and the solvent often play a critical role (Valderrama, 2008). The adsorption rate of soils for Cr (VI) increases with the increase of contact time then becomes constant after the equilibrium time reached. Fig.1 shows curve of Cr (VI) adsorption rate by silty clay, and clayey soil, and the curve can be divided into two stages: fast adsorption period and slow adsorption period.

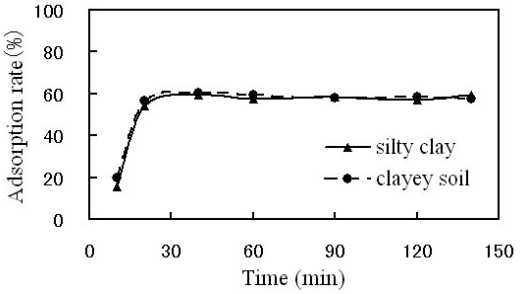

Fig.1 Curve of Adsorption Rate by Silty Clay and Clayey Soil

During 0-30 min of silty clay and clayey soil, it's the process showing fast kinetics and linear isothermal shapes, which may be due to the large amount of adsorption sites available at the beginning and no desorption takes place, adsorption rate can reach 60%.

During 30-140 min, there is not obvious change of adsorption rate. That is the adsorption rate equals to desorption rate, so the adsorption equilibrium stage has been reached.

It is clearly known that, the equilibrium was reached at 30 min, and the adsorption rate can reach 60%.

Isothermal Experiments

The equilibrium data were fitted to Linear, Freundlich and Langmuir isotherm models, the results of these models applied to the Cr (VI) on soils are shown in Fig.2, and the correlation coefficients (R^2), isotherm constants are presented in Table 2.

Table 2 Fitting Parameters for Cr (VI) Adsorption

		Silty Clay	Clayey Soil
Linear	K_d	0.0053	0.0053
	b	-0.0006	0.0025
	R^2	0.9061	0.9882
Langmuir	S_m	0.0667	0.045
	K_L	0.2467	0.3727
	R^2	0.7374	0.7748
Freundlich	K_f	0.011	0.099
	n	0.7654	0.6576
	R^2	0.9956	0.9941

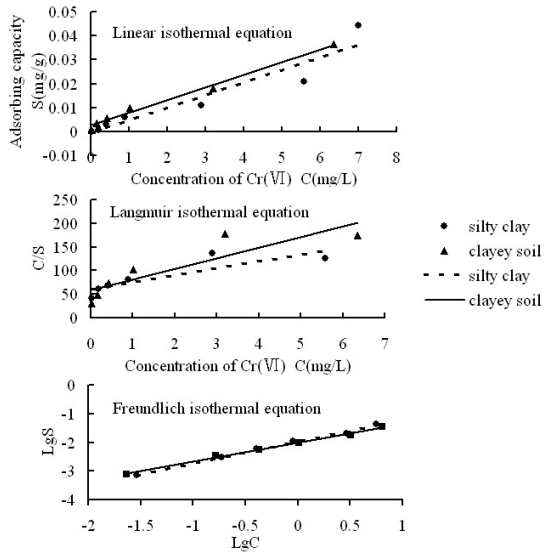

Fig.2 Adsorption Equilibrium Curves of Cr(Ⅵ) Adsorption on Soils

The high correlation coefficients between 0.900 and 0.999 indicate the data can be accurately described by these models. By comparing the data of correlation coefficients, a little difference among these models for Cr (VI) adsorption can be discovered. The Freundlich isotherm model is fitter than other isotherm models, due to the highest R^2 value, which consistent with previous research (Abat, 2012). K_f can reflect the adsorption strength and the adsorption capacity. According to the results, K_f of silty clay is 0.011, and clayey soil is 0.099, for more sticky material contained in clayey soil, more pollutants will be adsorbed, which is identical with experiment results.

PH Effect

The adsorption rate of different pH showed in Fig.3.

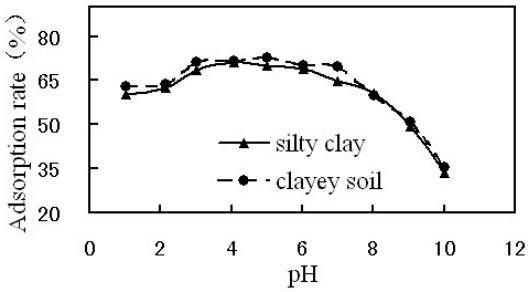

Fig.3 The Adsorption Rate of Different pH

PH value of solution is an important factor which controls the adsorption of Cr (VI). The figure shows that, when pH is 3-5 a plateau was seen, thereafter with increase in pH the adsorption rate of Cr (VI) dropped sharply and the minimum achieved at pH 10, the adsorption rate was only 35%.

One of the reason for the better adsorption rate observed at pH 5 may be attributed to that, Cr (VI) presents different form under the condition of different pH. Above pH 8, only CrO_4^{2-} is stable, and as the pH decreases into the region 3-5, the dominant species is $Cr_2O_7^{2-}$ (Dubey, 2007), and $Cr_2O_7^{2-}$ results the highest adsorption efficiency. The other is that, chromium of water soluble state and switching state increasing, precipitation and debris states lower when reduce pH value(Xue Liu, 2010), leading migration ability of chromium enhancement in soil, that is high adsorption rate.

Temperature Effect

The adsorption rate of different temperature is showed in Fig 4.

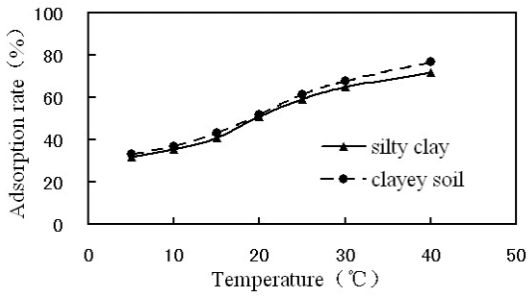

Fig.4 Adsorption Rate of Different Temperature

It is observed that the adsorption rate increased with increase of temperature. In fact, changing the system temperature will modify the adsorption rate of vadose zone soils (Khezami, 2005).

Adsorption rate of silty clay and clayey soil for Cr (VI) increased gradually with the increase of temperature. It is visible that the adsorption of Cr (VI) was influenced by the environment temperature obvious. The environment temperature affected the adsorption capacity, response speed and adsorption mechanism during adsorption.

The temperature of vadose zone in gongyi approximation to the annual average temperature, which is 14.7 ℃. According to the experimental results, the vadose zone soils adsorption rate of Cr (VI) is about 40%.

Organic Matter Effect

Adsorption rate of different organic matter is showed in Fig 5.

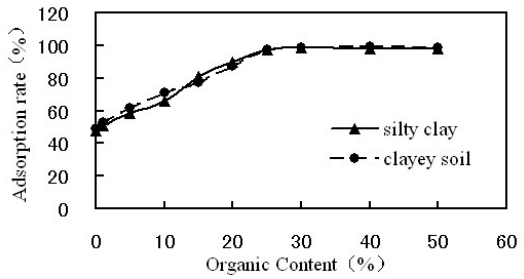

Fig.5 Adsorption Rate of Different Organic Matter

It is observed that organic content has a huge impact to the adsorption rate.

When the organic content reached 30%, adsorption rate of silty clay and clayey soil for Cr (VI) has reached 97.4% and 98.00%, increased 49.6% and 49.6% respectively than that without organic matter.

Carbon dioxide, variety of organic acids and heat generate in the process of organic decomposition, which have effects on pH and temperature of reaction environment, and effect on the adsorption rate of Cr (VI) (Bing Yang, 2006). On the other hand, organic matter increases activation of iron manganese oxide, which enhances the combination ability of chromium (Huggins, 2000), which all helps to increase the adsorption rate of Cr (VI).

According to the results of this experiment, improving the organic content of vadose zone as far as possible will improve the anti-pollute ability of Cr (VI).

Conclusion

(1) Kinetics experiments showed that the sorption progress of Cr (VI) has clear features of different stages, and adsorption equilibrium showed at 30 min, adsorption rate was 60%.

(2) The isothermal adsorption curve of Cr (VI) fit closely with Freundlich equation model.

(3) When pH is 3-5 a plateau was seen, thereafter with increase in pH the adsorption rate of Cr (VI) dropped sharply and the minimum achieved at pH 10, the adsorption rate was only 35%.

(4) Adsorption rate of Cr (VI) increased gradually with the increase of temperature, the temperature of vadose zone is 14.7 ℃, according to the experimental results, the adsorption rate of Cr (VI) is about 40%.

(5) The use of organics represents an important contribution to the sorption of Cr (VI), sorption rate is up to 100% when 30% of organic content.

The studies will provide basis for manager to minimize the impacts, and provide basic data for pollution prevention and remediation of vadose zone.

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