

UDC 544.723.23: 661.642.5,661.875.27

DOI: 10.15372/CSD20180115

## Adsorption of Arsenite and Dichromate Ions by Soils of Udmurtia

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(Received May 25, 2017; revised January 22, 2018)

### Abstract

By the example of four types of soils of Udmurtia, sorption process by them of arsenic and chromium ions in extremely toxic forms is considered. Langmuir and Freundlich isotherms are constructed based on acquired experimental data and constants pointing to weak adsorption power of soils of the Non-Black Earth Zone in relation to these anions are determined. The high solubility of arsenic and chromium species against weak sorption capacity of soils determines environmental risks of active migration of As(III) and Cr(VI) anions along soil profile. Their mobility should be taken into account during environmental monitoring.

**Keywords:** arsenite ion, dichromate ion, adsorption, Langmuir isotherm, Freundlich isotherm, adsorption constants

### INTRODUCTION

Chemical pollution of the environment is one of the most significant factors in biosphere destruction; in particular, heavy metals pose a special threat among xenobiotics. It is known that chromium and arsenic anions are dangerous toxicants. Probable pollution of the environment of Udmurtia by arsenic-containing substances is related to the destruction of chemical weapons, in particular, lewisite; on the other hand, in the territory of the Republic, there is a large number of enterprises in the metallurgical industry that are potential sources of entering chromium compounds into natural objects. In Russia, arsenic belongs to Hazard Class I and chromium – to 2; the toxicity of both elements depends on their degree of oxidation: chromium is most toxic in the highest degree of oxidation (VI), and arsenic – in the lowest (III). The maximum permissible concentration (MPC) for the most toxic forms of the studied elements

is 2.0 mg/kg of soil for arsenic and 0.05 mg/kg of soil for chromium(VI), with both elements are present as ready soluble compounds [1, 2]. The high solubilities of compounds contribute to their migration along the soil profile, which may lead to contamination of groundwater and open water bodies. Reliable environmental risk assessments can be obtained only on the basis of an exact representation of processes occurring with pollutants in the environment. The study of adsorption processes of arsenic and chromium anions by soils of common types of Udmurtia is relevant to the development of measures to prevent the spread of pollutants in natural media.

### EXPERIMENTAL

Sorption processes of arsenic(III) and chromium(VI) anions were studied under laboratory conditions for  $A_0$  levels of the most

common soils of Udmurtia: sod-highly podzolic, slightly washed; sod-carbonate leached soft-washed; grey forest podzolized. Table 1 gives the agrochemical characteristics of soils. Selection, transportation, and storage of soil samples were performed in accordance with standards [3, 4]. Soil sample preparation and determination of such agrochemical indicators, as hygroscopic moisture content, pH of water and salt extracts, and humus content, were carried out according to standard methods [5]. The pH value of the soil extract was determined by the potentiometric method using I-160 MI ionomer.

To study sorption processes, initial solutions of arsenite and dichromate ions with metal contents of  $60.0 \text{ mg/dm}^3$  and  $0.7 \text{ mg/dm}^3$ , correspondingly, were prepared by dissolution of samples of appropriate analytically pure  $\text{NaAsO}_2$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  salts; the precise concentration was determined spectroscopically. Adsorption isotherms were acquired by variation of initial concentrations in suspensions of arsenite and dichromate ions from 2.95 to 58.99 and 0.036 to  $0.720 \text{ mg/dm}^3$ , respectively. To air-dry soil samples, a solution of the corresponding metal salt of different concentrations in the ratio of 1 to 9 was poured, then the phases were stirred by a homogenizer for several days until equilibrium was achieved. The amount of metal absorbed per soil unit was determined according to the ion concentration in the initial solution and filtrate. The concentration of anions in the filtrates was determined by electrothermal atomization atomic absorption spectrophotometry using Shimadzu-AA7000 instrument (Japan) according to the standard procedure M-02-902-125-2005 [6]. All experiments were carried out in triplicate; there were determined average values with a boundary

of the relative error of  $\pm 11 \%$  (at  $P = 0.95$ ). Ultra-pure reagents were used for spectral analysis.

## RESULTS AND DISCUSSION

Chemical absorbability is the ability of a soil to absorb and exchange species present in the surface of colloidal particles (in the diffusion layer) for soil solution ions. Sorption plays an important part in fastening of polyvalent anions by soils. Anion nature, colloid composition, and medium reaction have a significant effect on the degree of chemical absorption: the more amphotoids are present in a soil, the more acidic is expressed the medium reaction, and the stronger the chemical absorption of anions is signified; humic substances reduce the rate of uptake of anions.

Sorption determines matter distribution between soil phases depending on xenobiotic content in the system. The most important sorption characteristic is an adsorption isotherm.

To study the adsorption process, the findings were computed for compliance with Langmuir or Freundlich isotherms. The Langmuir model assumes that adsorption occurs over certain homogeneous sections located in the adsorbent surface. The model equation has the following form:

$$C_{\text{sorb}} = Q_{\text{max}} \frac{K_L C}{1 + K_L C} \quad (1)$$

or in the linearized form:

$$1/C_{\text{sorb}} = 1/Q_{\text{max}} + 1/Q_{\text{max}} K_L C \quad (2)$$

where  $C_{\text{sorb}}$  is amount of the component adsorbed by the solid phase related to its mass;  $C$  is equilibrium concentration of the component in the solution;  $K_L$  is empirical adsorption coefficient, or Langmuir coefficient characterizing bond strength

TABLE 1

Main agrochemical parameters of soil samples

Soil type	Granulometric composition	Hygroscopic moisture	Humus, %	pH		$\Delta\text{pH}$
				H <sub>2</sub> O	KCl	
Sod-strong-podzolic sandy loam	Sandy	2.65	7.69	6.22	5.58	-0.64
Sod-highly podzolic slightly washed	Heavy clayloam	2.68	1.58	6.23	5.22	-1.01
Sod-carbonate slightly washed	Same	2.51	3.28	6.63	5.57	-1.06
Gray forest podzolic	«	2.49	4.74	6.41	5.37	-1.04

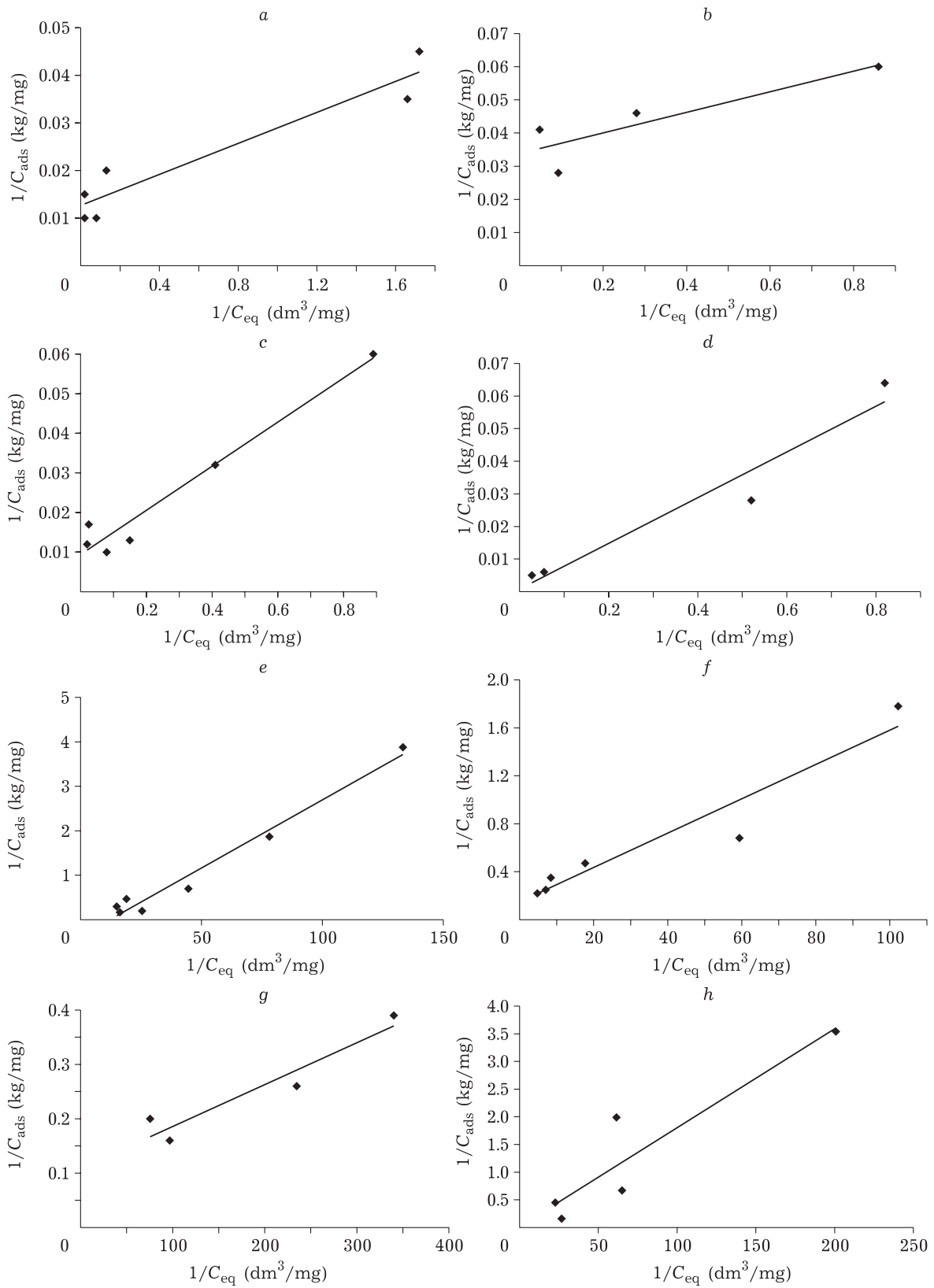


Fig. 1. Langmuir isotherms of sorption of arsenite (a-d) and dichromate ions (e-h) with  $A_0$  levels of sod-highly podzolic sandy loam (a, e), sod-highly podzolic slightly washed (b, f), sod-carbonate leached slightly washed (c, g), and gray forest podzolic soils (d, h).

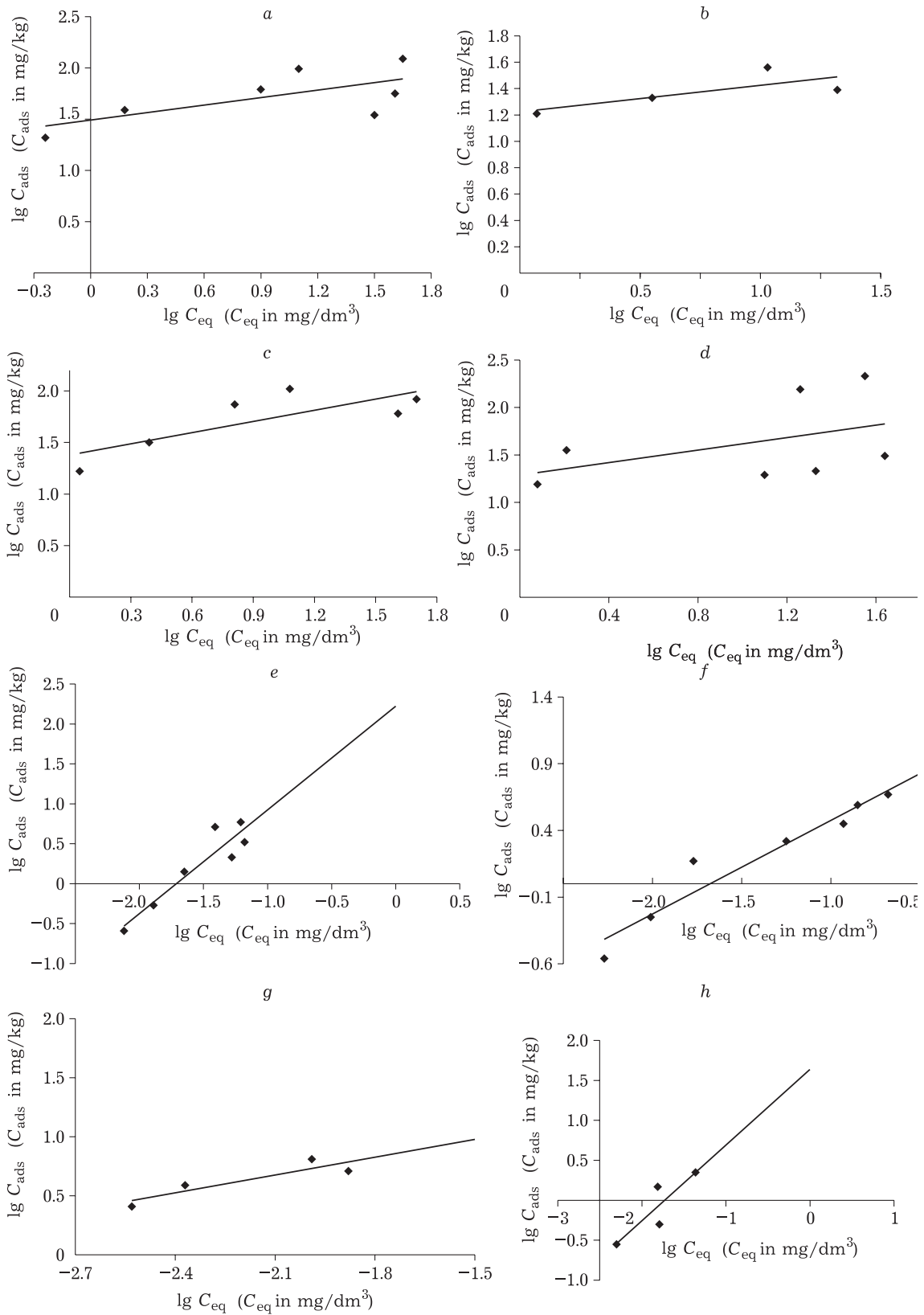


Fig. 2. Freundlich isotherms of sorption of arsenite (a-d) and dichromate ions (e-h) with  $A_0$  levels of sod-highly podzolic sandy loam (a, e), sod-highly podzolic slightly washed (b, f), sod-carbonate leached slightly washed (c, g), and gray forest podzolic soils (d, h).

between the element and the sorption sections and the energy of their interaction;  $Q_{\max}$  is maximum adsorption, or Langmuir monolayer capacity.

When a Langmuir isotherm does not correspond to the available experimental data, the Freundlich adsorption model is often used. It better describes the behavior of weakly crystallized or amorphous adsorbents with an almost continuous distribution of surface sections over the adsorption energy (inhomogeneous surface). Adsorption isotherm equation in a heterogeneous surface in several layers has the form:

$$C_{\text{sorb}} = K_F C^{1/n} \tag{3}$$

or in the linearized form:

$$\lg C_{\text{sorb}} = \lg K_F + 1/n \lg C \tag{4}$$

where  $C_{\text{sorb}}$  is the amount of the component adsorbed by the solid phase related to its mass;  $C$  is equilibrium concentration of the component in the solution;  $K_F$  is Freundlich adsorption coefficient characterizing the total sorption capacity of the solid phase;  $1/n$  is empirical exponent in the Freundlich equation, usually  $n > 1$ .

To describe sorption of As(III) and Cr(VI) by soils of four types of the Udmurt Republic, the linearization of the Langmuir and Freundlich equations is used. It was found that depending on a number of factors, adsorption isotherms of each element might vary (Fig. 1, 2). For example, adsorption of arsenic by soils almost corresponds to the linearized Langmuir equation (see Fig. 1, a-d), herewith, in the option with sod-highly podzolic slightly washed soils (see Fig. 1, b), there is a satisfactory correspondence of the model only in the region of low pollutant concentrations; with increasing As(III) content

(>25 mg/dm<sup>3</sup>), this equation is not applicable. Low values of the concentration constant of adsorption equilibrium ( $K_L$ ) (Table 2), which characterizes the intensity of the process and, in fact, is the ratio of the ion distribution between the solid phase and the solution, indicate that the studied soil types are not able to retain arsenite ions. In the laboratory, the highest affinity to arsenite is recorded for sod- highly podzolic sandy loam soil; further, according to a decrease in bond strength of between metal ion and sorption sections, there are gray forest podzolic and sod-carbonate leached soft soils. Computed maximum monolayer capacity of Langmuire monolayer of the soil absorption complex (SAC) (see Table 2) is observed for sod-carbonate leached slightly washed soil that is used very slightly.

The findings for soil absorbency with respect to Cr(VI) are in satisfactory agreement with the linearized form of the Langmuir isotherm (see Fig. 1, e-g). The determined absorption coefficient for dichromate ion (see Table 2) is significantly less than a similar indicator for arsenite and indicates the almost total absence of interaction between chromium anion and sorption sections of the soil. The impossibility of generating a strong bond between SAC and anions can be explained by a negative charge of soil colloids [7]:  $\text{pH}_{\text{KCl}} - \text{pH}_{\text{H}_2\text{O}} \approx -1.0$  (see Table 1), which prevents sorption of similarly charged arsenic and chromium ions; herewith, due to a more negative charge of dichromate ion, its fixation in the soil is almost impossible. Thus, the weak energy of the interaction between arsenite and dichromate ions and soil colloids

TABLE 2

Langmuir and Freundlich parameters for adsorption of arsenite and dichromate ions by soils of Udmurtia

Arsenite-ion				Dichromate-ion			
$Q_{\max}$ , mg/kg	$K_L$ , dm <sup>3</sup> /mg	$K_F$	$1/n$	$Q_{\max}$ , mg/kg	$K_L$ , dm <sup>3</sup> /mg	$K_F$	$1/n$
<b>Sod-strong-podzolic sandy loam</b>							
58.82	0.95	26.92	0.29	4.03	-6.7	1.57	1.36
<b>Sod-strong-podzolic slightly washed</b>							
0.13	-0.69	14.79	0.25	11.76	-0.1	1.90	0.88
<b>Sod-carbonate leached slightly washed</b>							
125.00	0.15	17.78	0.54	1.09	-0.5	-5.08	1.19
<b>Gray forest podzolic</b>							
71.43	0.19	18.62	0.44	208.33	-0.31	-3.29	1.48

causes quite easy washing of anions from the soil.

Not all experimental data for sorption of Cr(VI) were consistent with the Langmuir isotherm (see Fig. 1, *h*), therefore, to describe sorption of soils by As(III) and Cr(VI), the linearized form of the Freundlich equation was also used (see Fig. 2, *a-h*). Experimental points are located near the straight line with high arsenite content ( $>3.0 \text{ mg/dm}^3$ ) in the studied soil samples (see Fig. 2, *a-c*), therefore, this model is suitable for describing the adsorption of arsenic soils;  $K_F$  values vary in the 14.79–26.92 range (see Table 2). As with Langmuir constants, Freundlich constants confirmed a higher affinity to arsenite ion in sod-strongly podzolic sandy soil, afterwards, in descending order of the total sorption capacity of the solid phase with respect to the sod-carbonate leached weak-mashed and sod-strong-soiled soils in relation to arsenite ion. Compared to other investigated samples, sod-highly podzolic sandy loam soil is characterized (see Table 1) by the minimum (absolute value) negative charge of adsorbent surface (almost in two times compared to others) and the maximum humus content. According to the granulometric composition, it is characterized by the smallest particle size and, accordingly, the largest specific surface area, and, therefore, greater absorbency. Similar regularities of the effect of physical and chemical properties of three Californian soils on adsorption of arsenite ion were found by the authors of [8], who also stated the weak retention capacity of soils in relation to this anion.

Adsorption isotherms of Cr(VI) by the studied soils demonstrated different Freundlich behaviour of the ion (see Fig. 2, *e-h*). Experimental data were tested for the compliance to the linearized form of the Freundlich model that, as a whole, describes well sorption processes by the samples under study in relation to dichromate ion (see Fig. 2, *e-g*). This allowed computing appropriate constants (see Table 2). A portion of points calculated for grey forest soils, both in relation to chromium (see Fig. 2, *h*) and arsenic (see Fig. 2, *d*) to a greater or lesser extent are removed from the isotherm line, which indicates the incomplete correspondence to the Freundlich equation.  $K_F$  values for dichromate ion vary in the limits from  $-5.08$  to  $1.90$  for soil level A. Negative parameters of sorption of anions are interpreted by Gedtroits [9] as negative absorption of substances. Negative sorption is due to a decrease in the concentration

of anions in the inside portion of the sorption film. As a consequence, their concentration in diffusion and hence, more mobile layers of the aqueous film increases, which reinforces processes of washing out of anions from the soil and migration into water bodies. Low values of the constants for the sod-highly podzolic soils (see Table 2) also indicate their weak retention capacity with respect to Cr(VI), much lower compared to adsorption of arsenite ion. Thus, the sorption capacity of the soil also depends on anion charge value: with increasing its absolute value, adsorption decreases. According to experimental data (see Table 1, 2), the amount of humus in the soil does not affect the degree of adsorption of chromate, in particular, gray forest soil has quite a weak sorption capacity in relation to both anions.

The computed Freundlich constants are in complete agreement with the data obtained earlier by us for the effective half-lives for anions. For example, they are 1.01 [10] and 3.01 years [11] for sod-highly podzolic slightly washed soil and arsenite ion in the soil of this type, respectively, and correspond to the maximum value of  $K_F$  of 1.90. On the other hand, pollutants as heavy metal cations have the effective half-life in several dozens and hundreds of years, for instance, for  $\text{Cr}^{3+}$  cation, it is 51 years [12].

## CONCLUSION

The sorption intensity of pollutants by soil determines pollutant arrival volumes into groundwater during chemical pollution. The results acquired by us attest to the weak sorption capacity of soils in relation to arsenic and chromium anions. Herewith, the absorptive capacity of the adsorber dramatically decreases and metal washout rate increases with a rise in pollutant ( $\text{AsO}_2^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ ) anion charge value. Failure of soils typical for Udmurtia towards durable fixation of pollutants in the anion form should be considered in event planning to prevent their distribution in natural environments.

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