

## Composite sorbent based on $\text{Fe}_3\text{O}_4$ with $\text{Fe}(\text{N}_2\text{H}_4)_x\text{Cl}_y$ for the removal of Chromium(VI) from wastewater

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**ABSTRACT** The paper presents a methodology for the synthesis of iron complex with hydrazine hydrate  $\text{Fe}(\text{N}_2\text{H}_4)_x\text{Cl}_y$ . The  $\text{Fe}(\text{N}_2\text{H}_4)_x\text{Cl}_y$  complex was investigated by X-ray phase analysis and scanning electron microscopy. Upon hydrolysis, the  $\text{Fe}(\text{N}_2\text{H}_4)_x\text{Cl}_y$  complex forms a composite sorbent, which is  $\text{Fe}_3\text{O}_4$  in a shell of  $\text{Fe}(\text{N}_2\text{H}_4)_x\text{Cl}_y$  complex. The composite sorbent can be used to treat wastewater from Cr(VI) ions and is effective in the pH range of 2 to 12. Based on the adsorption and electrokinetic potential data, a conclusion about the nature of the terminal groups of the adsorbent was made, a scheme of the structure of its electrical double layer and the adsorption mechanism were proposed. Depending on the conditions, Cr(VI) can be adsorbed on the composite sorbent or reduced to Cr(III). The efficiency of the composite sorbent in the removal of Cr(VI) ions was tested on a sample of real wastewater.

**KEYWORDS** Iron complex with hydrazine, magnetite sol, chromium adsorption, heavy metals, adsorption isotherms.

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### 1. Introduction

The deterioration of drinking water quality is a global world problem that research groups around the world are working on [1–3]. There are many tasks to purify water from ecotoxicants of artificial and natural origin [4–6]. Technologies such as adsorption purification [7–9], membrane purification [10–12] and reagent purification [13–15] are widely used.

Among the ecotoxicants of artificial origin, Cr(VI) compounds occupy a special place. Cr(VI) has a low maximum permissible concentration (MPC) value in drinking water of  $0.05 \text{ mg}\cdot\text{L}^{-1}$  [16], so a high degree of wastewater is required. The topic of extraction of chromium compounds from wastewater is wide presented, many adsorbents have been developed [5, 17–19]. Reagent technologies [20, 21] are most often used for treatment of electroplating effluents from the main amount of chromium. The main approach is to reduce Cr(VI) to less hazardous Cr(III) compounds (MPC in drinking water –  $0.5 \text{ mg}\cdot\text{L}^{-1}$  [16]) and its further precipitation in the form of sludge. For Cr(VI) reduction, Fe(II) salts are mainly used, for example, rather cheap divalent iron sulfate [20].

Adsorption methods are one of the most promising for additional treatment, removal of residual concentrations of Cr(VI) from wastewater [22]. Adsorptive water treatment can be regenerative (i.e., with extraction of the substance from the adsorbent and its utilization) and destructive, in which the substances extracted from wastewater are stored in landfills or destroyed together with the adsorbent. The efficiency of adsorptive treatment reaches 80 – 95 % and depends on the chemical nature of the adsorbent [23].

Active carbons [24, 25], synthetic [26] and magnetic sorbents [27] are used as sorbents. Mineral sorbents include: clays, gels [26, 28], oxide hydrates [29], nanoactivated complexes of natural zeolite and diatomite [30]. Composite sorbents are a rather new type of adsorption materials. Modified montmorillonites are examples of composite sorbents [31, 32]. Modified and stabilized null-valent iron sols have been widely investigated [33]. This type of adsorbents can be categorized as destructive because after adsorption, the adsorbent binds firmly to the adsorbate, forming interaction products and, as a rule, is not regenerated. Due to this interaction, a high degree of water purification from ecotoxicants

can be achieved. Surface-modified sols of highly dispersed particles can also be referred to composite sorbents [34–36]. Also composite sorbents based on magnetite [37] or nanoparticles of magnetite are often used for Cr(VI) adsorption [38].

Methods for the preparation of magnetite nanoparticles are fairly well studied [39–41], however, methods for the preparation of composite sorbents using magnetite particles are constantly evolving, and each new composite usually requires a new synthesis method.

The present work describes a method for the extraction of chromium (VI) compounds using hydrazine and iron complexes. This type of compound was first described in 1908 by Franz and von Mayer [42] and the formula  $Fe[N_2H_4]_2Cl_2$  was determined. In further studies of these compounds [43], it was found that the amount of hydrazine and chlorine can be different and described compounds  $Fe[N_2H_4]_2Cl_4$  in which hydrazine is in the protonated form. The present work describes a simplified version of the synthesis of a compound of hydrazine with iron with the approximate formula  $Fe(N_2H_4)_xCl_y$ , which is a precursor for the synthesis of a composite sorbent. The presented composite sorbent is effective for Cr(VI) removal from wastewater and allows to obtain chromium-iron concentrate of regular composition.

The aim of the work is to synthesize  $Fe(N_2H_4)_xCl_y$  complex, to synthesize a sol of  $Fe_3O_4$  particles in the shell from  $Fe(N_2H_4)_xCl_y$  complex, to apply the obtained sol for the extraction of Cr(VI) compounds from aqueous solutions.

## 2. Experimental part

### 2.1. Synthesis of composite sorbent

The first step of the synthesis was to obtain the compound  $Fe_x(N_2H_4)_yCl_z$ . For this purpose, 6.19 g of iron (II) chloride (p.a., “LenReaktiv”) was first stirred with 25 mL of distilled water on a top-drive stirrer IKA RW 20 digital (IKA-Werke, Germany) at a speed of 600 rpm until complete dissolution. Then 25 mL of ethyl alcohol (95 wt%, “Khimproduktsiya”) and 2 mL of 10 % hydrochloric acid solution (puriss. spec., “Vekton”). In a separate beaker a hydrazine hydrate solution was prepared by taking 50 mL of distilled water and adding 3.62 g of hydrazine hydrate (puriss. spec., imp. “Vekton”). Then at 600 rpm stirring was dosed hydrazine hydrate solution into ferric chloride solution for 45 minutes, after completion of dosing was stirred for another 15 minutes. The reaction produced a light green precipitate, which turned light orange in air with time. The precipitate was filtered off, washed with three portions of ethyl alcohol and dried at 75 °C for 1 hour in air atmosphere.

To obtain the composite sorbent, hydrolysis was carried out. For this purpose, 1 g of  $Fe[N_2H_4]_2Cl_2$  compound was mixed with 14 mL of distilled water, stirred for 5 minutes until the formation of a dark gray precipitate. The mixture was kept for 48 hours at a temperature of 15 – 25 °C. A composite sorbent sol with an iron concentration of 2 wt% was obtained. If necessary, it is possible to centrifuge or magnetically separate the solution and precipitate and obtain the composite sorbent in powder form, but as a sol the sorbent is more convenient to dispense in adsorption studies.

### 2.2. Characterization of the material

The morphology and chemical composition of the  $Fe[N_2H_4]_2Cl_2$  precipitate surface were investigated by scanning electron microscopy (SEM) using a Carl Zeiss EVO 40 microscope (Carl Zeiss AG, Germany) with an accelerating voltage of 20 kV on a V-shaped tungsten cathode. Tablets were prepared by pressing, after which the investigated surface was ground using abrasive materials. The final surface treatment was performed using silicon carbide-based sanding paper with a grain size of ~2 microns. The elemental composition of the surface was determined by energy dispersive X-ray spectroscopy (EDS) using an INCA X-Act energy dispersive X-ray analyzer with an active detector area of 10 mm<sup>2</sup> (Oxford Instruments plc, UK). Statistics were typed for one minute (lifetime 85 – 90 %) for each of five different points in different compositional contrast areas.

The phase composition of the sample was determined by powder X-ray diffraction. The images were taken at room temperature (298 K) on a D8 ADVANCE diffractometer (Bruker, Germany) (Cu-K $\alpha$  radiation, 30 kV, 40 mA, position-sensitive detector VENTEC-1,  $\beta$ -filter). The data were recorded over an angle range of 10 – 80 °C with a step of 0.021 °C in  $2\theta$  and a point exposure equal to 1135 s. The phase composition and crystal structure of the sample were determined from X-ray diffraction data using the DIFFRAC.EVA V5.1 software package (Bruker AXS (2019), Bruker AXS GmbH, Germany) and the International Center for Diffraction Data ICDD PDF4 Release (2020) database [44]. Structure refinement was carried out by full-profile analysis using the TOPAS program [45]. The structure of  $Mn(N_2H_4)Cl_2$  [sp. gr. 12,  $a = 9.08(1)$  Å;  $b = 8.01(1)$  Å;  $c = 4.29(1)$  Å,  $\beta = 105.5(1)$ ,  $Z = 2$ ; PDF 04-016-1449] was taken as an initial model.

The electrokinetic potential of the composite sorbent was determined by a DelsaNanoC analyzer (Beckman Coulter, USA) in the range of pH values from 2 to 12. The determination is based on the measurement of electrophoretic mobility of particles using the Doppler effect. Depending on the nature of the particles and the dispersion medium, the zeta potential ( $\zeta$ ) is calculated from the electrophoretic mobility ( $\mu$ ) using either the Smoluchowski or Hückel equation. In order to choose the right equation, the Henry function  $f(k\alpha)$  is calculated independently and values between 1 and 1.5 are obtained [39]. The Smoluchowski equation (1) was chosen to calculate the electrokinetic potential because the value of  $f(k\alpha)$  is 1.43, which is closer to 1.5.

$$\zeta = \frac{\eta U_0}{E \varepsilon \varepsilon_0}, \quad (1)$$

where  $\eta$  is the viscosity of the medium, cSt;  $U_0$  is the linear velocity of the dispersed phase particles  $\text{cm}\cdot\text{s}^{-1}$ ;  $\varepsilon$  is the relative dielectric permittivity of the medium;  $\varepsilon_0$  is the electric constant;  $E$  is the electric field strength.

X-ray diffraction analysis of the precipitate formed during chromium extraction at optimum pH was performed on a XRD 7000 diffractometer (Shimadzu, Japan) with Cu- $K_\alpha$  radiation in continuous scanning mode at a speed of  $1^\circ/\text{min}$  in the range of angles  $2\theta = 20 - 100^\circ$ . The phase analysis was performed using the international ICDD PDF-2 file system with built-in modules of automatic phase search and semi-quantitative analysis by the corundum number method.

The particle size of the composite sorbent was determined by dynamic light scattering on a Zetasizer Nano S90 (Malvern, UK), laser radiation source with a maximum of 632.8 nm. The sol was diluted 100 times with glycerol, measurements were performed at  $20^\circ\text{C}$  taking into account the solvent properties (viscosity 1412 mPa·s, refractive index 1.474), and the number of replicates was 3.

### 2.3. Adsorption study

To obtain the dependence of Cr(VI) adsorption on pH, model solutions containing  $50\text{ mg}\cdot\text{L}^{-1}$  of chromium were prepared by diluting the initial solution of potassium dichromate  $1\text{ mg}\cdot\text{L}^{-1}$  (1.4145 g (p.a., "Reakhim") per 500 mL of distilled water):

- (1) pH 1.0 – 2.5 with sulfuric acid solution (puriss., "UfaKhimProekt");
- (2) pH 3.5 – 6.3 by acetate buffer solution (1 M of NaOH (p.a., "UfaKhimProekt") and 1 M of  $\text{CH}_3\text{COOH}$  (puriss., "Nevinnomyssky Azot"));
- (3) pH 7.0 by NaOH solution with addition of 1 M of  $\text{NaNO}_3$  (puriss., "UfaKhimProekt");
- (4) pH 8.0 – 10.0 by ammonia buffer solution (1 M of  $\text{NH}_4\text{OH}$  (p.a., "Sigma Tec") and 1 M of  $\text{NH}_4\text{Cl}$  (puriss., "Vekton"));
- (5) pH 12.0 with 1 M of NaOH solution.

The pH was monitored using an I-160 MI ionometer (Izmeritel'naya Tekhnika, Russia).

In adsorption study, 2.5 mL of composite sorbent was added to 20 mL of Cr(VI) solution with a certain pH value, stirred for 2 hours on a rotary mixer RM-1L (SIA "ELMI", Latvia). Then the solution and sorbent were separated by filtration using a paper filter "Blue Ribbon" ("Melior XXI").

The residual chromium concentration in the filtrate was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) on a SpectroBlue spectrometer (Spectro Analytical Instruments, Germany). The degree of chromium sorption ( $R$ , %) was calculated as the ratio of the difference between the initial ( $C_0$ ,  $\text{mg}\cdot\text{dm}^{-3}$ ) and equilibrium ( $C_e$ ,  $\text{mg}\cdot\text{dm}^{-3}$ ) concentrations of chromium in solution to the initial concentration:

$$R = \frac{C_0 - C_e}{C_0} \cdot 100\% \quad (2)$$

The amount of adsorbed chromium per 1 g of sorbent (equilibrium sorption capacity) –  $q$  ( $\text{mg}\cdot\text{g}^{-1}$ ), was calculated by the formula:

$$q = \frac{(C_0 - C_e) \cdot V}{m} \cdot 1000, \quad (3)$$

where  $V$  is the volume of solution,  $\text{dm}^3$ ;  $m$  is the mass of sorbent, g.

To study the influence of temperature on the adsorption process, adsorption isotherms (dependences  $q = f(C_e)$ ) were obtained at temperatures of 293 K, 313 K and 333 K.

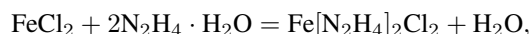
### 2.4. Removal of chromium from a real wastewater sample

As a real chromium-containing sample of wastewater, a water sample of JSC "Russian Chromium 1915" was taken before the stage of reagent treatment – a solution with chromium concentration of  $350\text{ mg}\cdot\text{L}^{-1}$  and  $\text{pH} = 11.5$ . Wastewater was filtered. 1 mL of 5 % sol of composite sorbent was added to 20 mL of filtrate, and stirred for 15 minutes. Sorbent was separated by centrifuge OPn-8 ("TNK"Dastan", Kyrgyz Republic) for 20 min at a speed of 7000 rpm. In the filtrate, the content of total chromium was determined by ICP-AES method. In addition, we performed an experiment comparing the efficiency of chromium removal by composite sorbent with chromium removal by treatment with iron (II) sulfate. For this purpose, wastewater was filtered, 0.0993 g  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$  (p.a., "JSC Reakhim") was added to 20 mL of filtrate, and stirred for 15 minutes. The solution and precipitate were separated by centrifugation. Chromium content was determined in the filtrate. Similarly, the experiment was performed for  $\text{pH} = 5.4$ , adding a few drops of concentrated sulfuric acid to the wastewater. The experimental conditions were similar to those described above. The only difference was that 2 mL of sol or 0.1986 g  $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$  was added. The content of hexavalent chromium in the wastewater after adsorption was determined by spectrophotometric test with 1,5-diphenylcarbazide (p.a., sole proprietor S.A. Smirnova doing business as "InterKhim") [46].

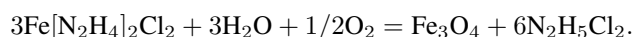
### 3. Results and discussion

#### 3.1. Synthesis of iron complex with hydrazine hydrate

During the interaction between iron (II) chloride and hydrazine hydrate, the following chemical reaction took place:



and as a result  $Fe[N_2H_4]_2Cl_2$  complex was formed, which was then filtered and washed with several portions of ethyl alcohol. The X-ray diffraction of the complex (Fig. 1a) confirms that there is a single phase. When the solid/water ratio is increased up to 1:14, the dissolution of  $Fe[N_2H_4]_2Cl_2$  complex increases, and its hydrolysis occurs, which in the presence of air oxygen leads to the formation of magnetite phase, the surface of which is completed by particles of  $Fe[N_2H_4]_2Cl_2$  complex:



Thus, particles of composite sorbent with the ratio of magnetite/iron complex phases 1:3 are formed, which is confirmed by X-ray studies (Fig. 1b). The system comes to a state of equilibrium and there is no further transformation of phases with increasing exposure time, and this means that there are factors preventing hydrolysis, the main of which is the formation of an electrical double layer (EDL). The synthesis scheme (Fig. 1c) shows the sequence of interactions prior to the formation of EDL.

It is worth noting that in this variant of synthesis, the main stabilization of the sol occurs due to the high value of the electrokinetic potential. A rather atypical picture is observed for the dependence of the electrokinetic potential on the pH of the medium (Fig. 2a). The high positive charge of the surface is maintained up to pH 9, and after that the surface sharply changes the sign of the charge and becomes negative, which indicates the rearrangement of the structure and the formation of a new type of sol. The value of the electrokinetic potential indicates high mobility of sol particles, and in this case the electrostatic stability factor plays a key role. The sign of the electrokinetic potential up to pH 9 suggest the structure of two-phase particles: the outer layer consists of hydrazine complex, and the inner layer contains magnetite. The high positive electrokinetic potential of the surface is due to complex iron ions or protonated hydrazine ions.

Protonating in acidic medium, hydrazine acquires a positive charge, which is compensated by chloride ion. Thus, it can be considered that the composite sorbent is a sol of  $Fe_3O_4@Fe(N_2H_4)_xCl_y$  particles. An important characteristic of the composite sorbent is the particle size, because it is the particle size that is associated with the stability of the sol, the specific surface area of the particles and the sorption characteristics. A rather narrow particle size distribution with a maximum of 30.7 nm (Fig. 2b), obtained by dynamic light scattering, indirectly indicates the formation of particles with a "core/shell" structure and that the process comes to equilibrium and no further particle enlargement occurs.

The absence of larger sized agglomerates is also noteworthy, although the particles have their own magnetic moment, and no additional dispersion by ultrasound or high speed agitation was performed prior to particle size measurement.

#### 3.2. Microscopic studies

The results of scanning electron microscopy examination of the sample of iron complex with hydrazine hydrate (Fig. 3) show that the sample is homogeneous and crystalline. The surface of the sample appears inhomogeneous under magnification, primarily due to topological contrast caused by grinding.

Light inclusions on the gray background should be attributed to compositional contrast. Its appearance is due to the fact that the chemical composition locally deviates from the ideal  $Fe:Cl:N=1:2:4$  ratio (Fig. 3a). The elemental maps show that the distribution of iron and chlorine in the sample surface is generally homogeneous, but there are regions with fluctuations in chemical composition. Using X-ray energy dispersive point analysis, it is shown that the iron content varies between 11.47 – 16.29 at%, chlorine 24.63 – 35.00 at% and nitrogen 48.71 – 63.89 at% in different regions. Thus, iron excess and deficiency regions of  $Fe(N_2H_4)_{1.7}Cl_{1.8}$  and  $Fe(N_2H_4)_{2.8}Cl_{2.1}$  are observed, respectively. That is, the exact formula of the compound has not yet been established, so in general we use the record of the compound –  $Fe(N_2H_4)_xCl_y$ .

#### 3.3. Investigation of chromium adsorption by the composite sorbent sol

Studies of chromium adsorption from Cr(VI) solution depending on pH of the medium (Fig. 4) showed the efficiency of the composite sorbent in the pH range from 2 to 12. The dependence of the degree of chromium adsorption on the pH of the medium shows that in a wide range of pH almost all chromium (about 99.9 %) is adsorbed, which proves the efficiency of the sorbent.

Decrease in adsorption at  $pH < 2$  is most likely due to the decrease in the electrokinetic potential of the composite sorbent and its dissolution.

To reveal the nature of the interaction of the composite sorbent with Cr(VI) ions, the dependence of adsorption on temperature was investigated (Fig. 5a).

At 293 K, the isotherm comes to saturation and probably monolayer adsorption occurs. The maximum capacity of the sorbent according to the graph is  $385 \text{ mg} \cdot \text{g}^{-1}$ . At temperatures above 313 K, the isotherm acquires an S-shaped form, which indicates either multilayer adsorption or the occurrence of chemical interactions in parallel with adsorption

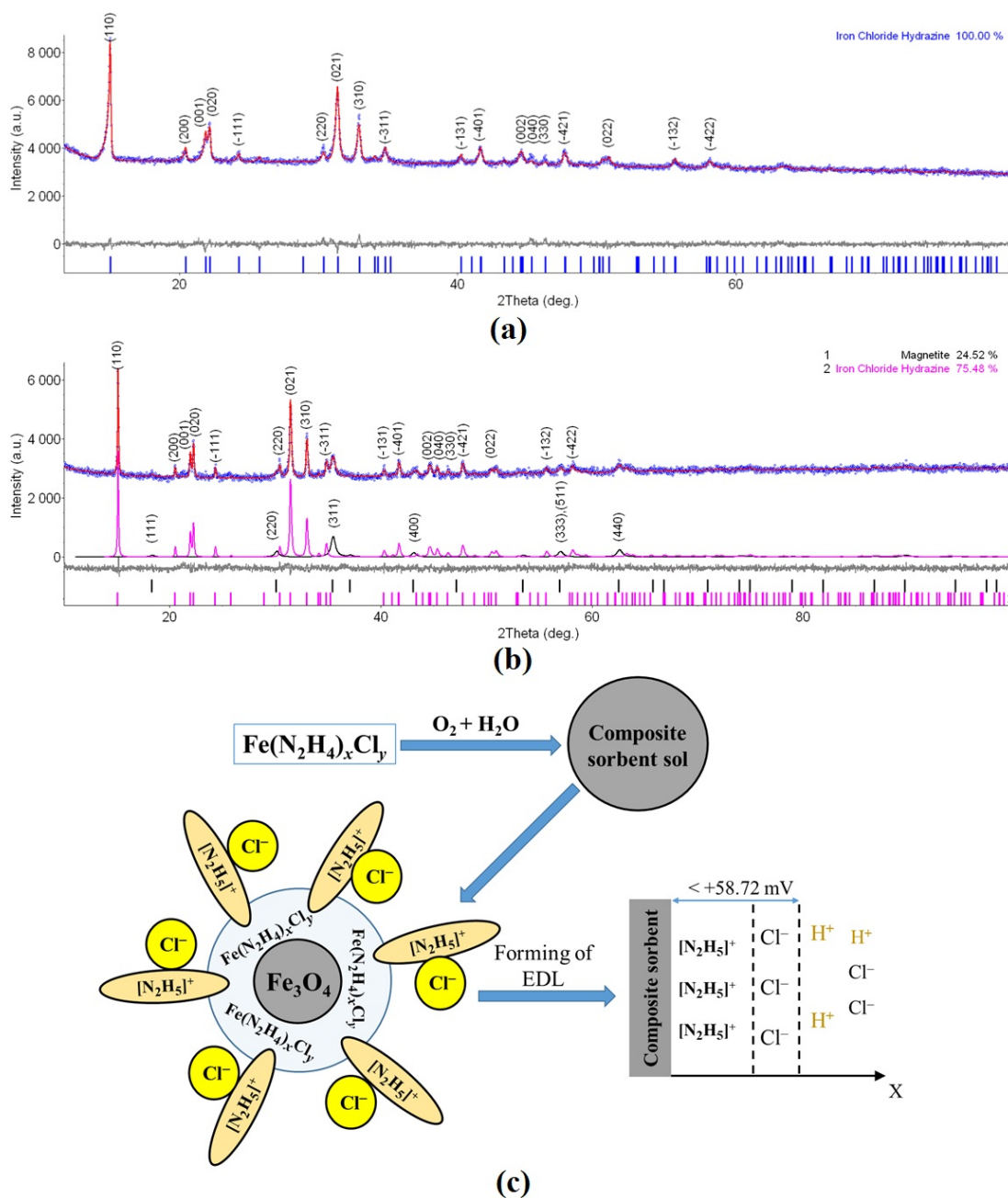


FIG. 1. Validation of the composite sorbent and synthesis scheme. XRD patterns of (a) Fe[N<sub>2</sub>H<sub>4</sub>]<sub>2</sub>Cl<sub>2</sub> complex and (b) Fe<sub>3</sub>O<sub>4</sub>@Fe(N<sub>2</sub>H<sub>4</sub>)<sub>x</sub>Cl<sub>z</sub> sample (@ is designation of the particle “core/shell”, to the left of the symbol phase – core, to the right – shell). Experimental (blue dots) and calculated (red curve) diffractograms, and difference curve (gray) of the sample. Vertical dashes correspond to Bragg reflections of the compounds. Scheme of formation and structure of EDL of the sol at pH values < 9 (c)

interactions. The ultimate capacity of the composite sorbent in this case cannot be calculated from the linear dependence (Fig. 5a), but it can be assumed that it will exceed 500 mg·g<sup>-1</sup>.

By plotting the linear dependence in Langmuir coordinates (Fig. 5b), it can be seen that at 293 K, the dependence has a linear form, but as the temperature increases, the dependence deviates from linear (the correlation coefficient decreases), which indicates multilayer adsorption or chemical interaction. That is, it is possible to assume the occurrence of at least three variants of reactions:

- (1)  $\text{HCrO}_4^- + \text{N}_2\text{H}_4 + 3\text{H}^+ = \text{Cr}^{3+} + \text{N}_2 + 4\text{H}_2\text{O}$  (redox reaction with N<sub>2</sub>H<sub>4</sub> as the reducing agent);
- (2)  $\text{HCrO}_4^- + \text{composite sorbent} + 7\text{H}^+ = \text{Cr}^{3+} + \text{Fe}^{3+} + 4\text{H}_2\text{O}$  (redox reaction with Fe<sup>2+</sup>);
- (3)  $\text{N}_2\text{H}_5^{5+} + \text{HCrO}_4^- = \text{N}_2\text{H}_5\text{HCrO}_4$  (ion exchange interaction).

Adsorption at 293 K is satisfactorily described by the Langmuir model, which means that monolayer adsorption occurs at this temperature, and this corresponds to the ion-exchange interaction (variant 3). At temperatures 313 and

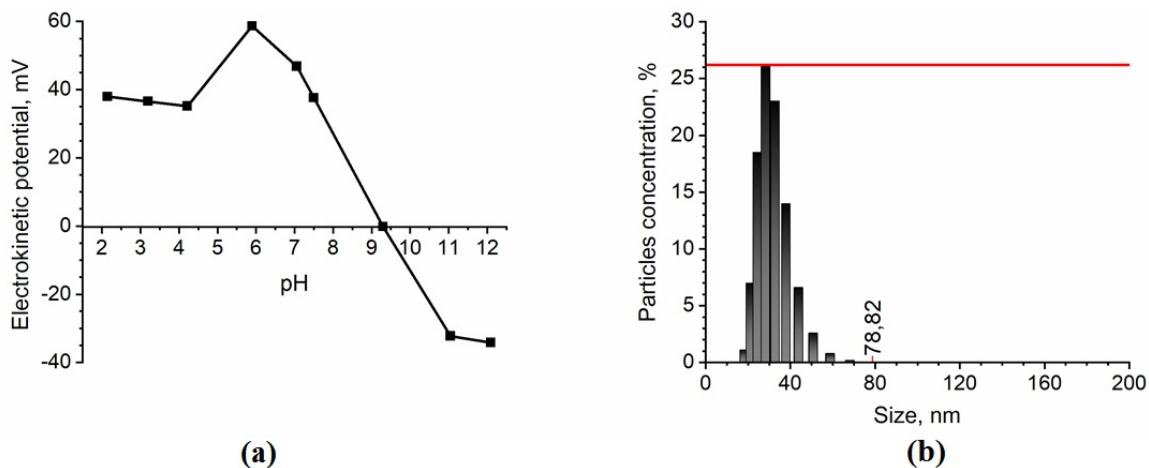


FIG. 2. Characteristics of the composite sorbent sol: dependence of the electrokinetic potential on the pH of the medium for the sol  $Fe_3O_4@Fe(N_2H_4)_xCl_y$  (a), dependence of the size (diameter) of the composite sorbent particles on the concentration by dynamic light scattering (b)

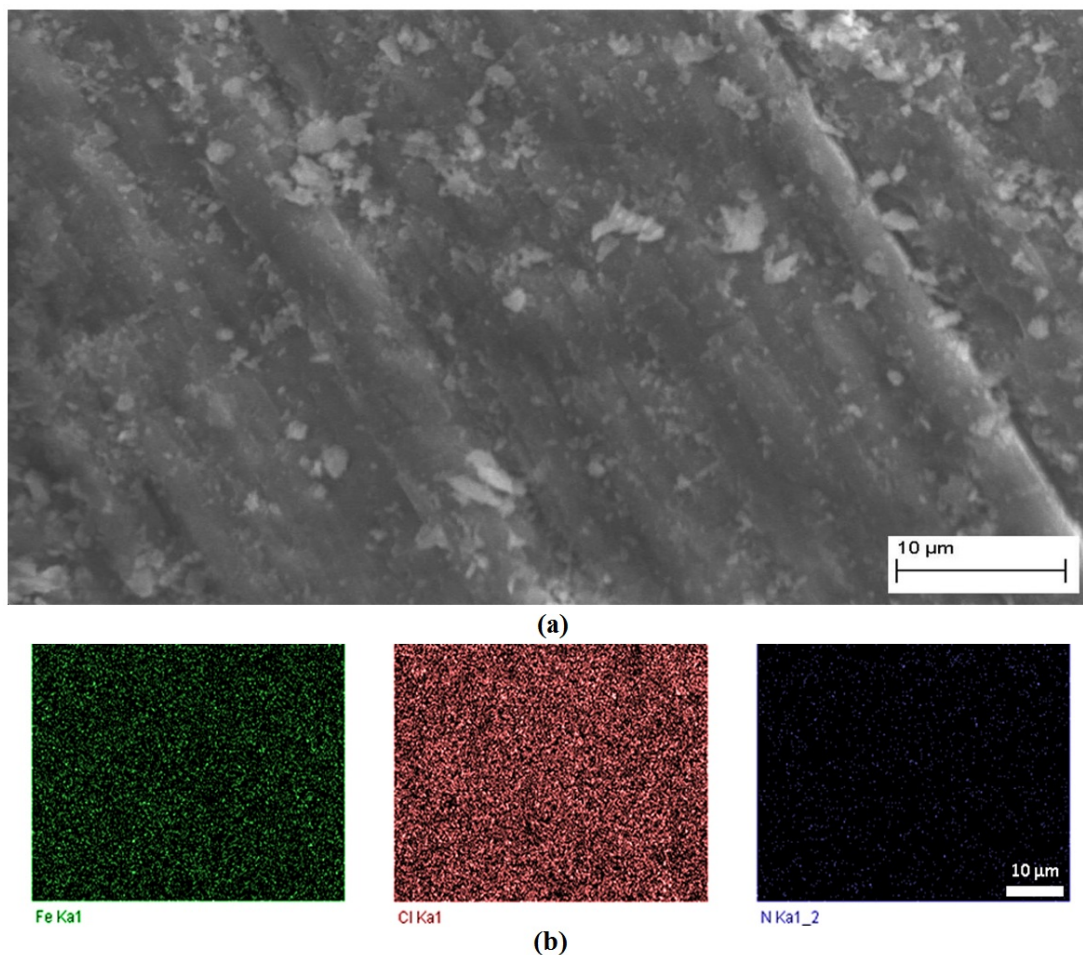


FIG. 3. Image of the  $Fe(N_2H_4)_xCl_y$  tablet surface in secondary electrons (a) and element distribution maps (b)

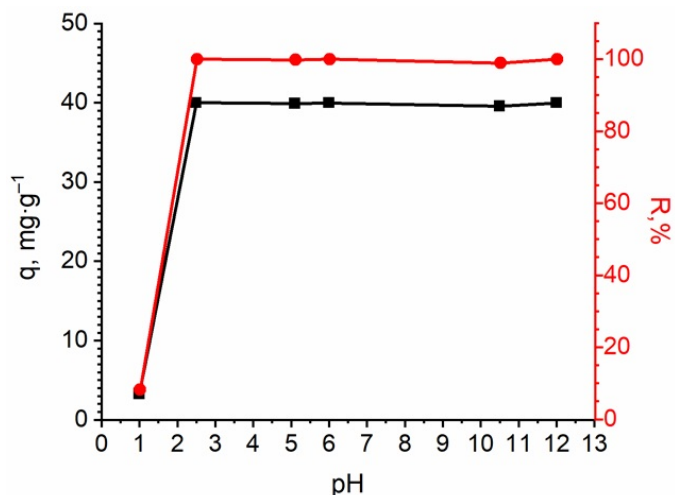


FIG. 4. Dependence of chromium adsorption on pH on Fe-sol (left axis, black color), of chromium adsorption degree on composite sorbent, % on pH (right axis, red color). Initial concentration of Cr(VI)  $50 \text{ mg}\cdot\text{L}^{-1}$ , adsorption time 2 h, temperature 293 K

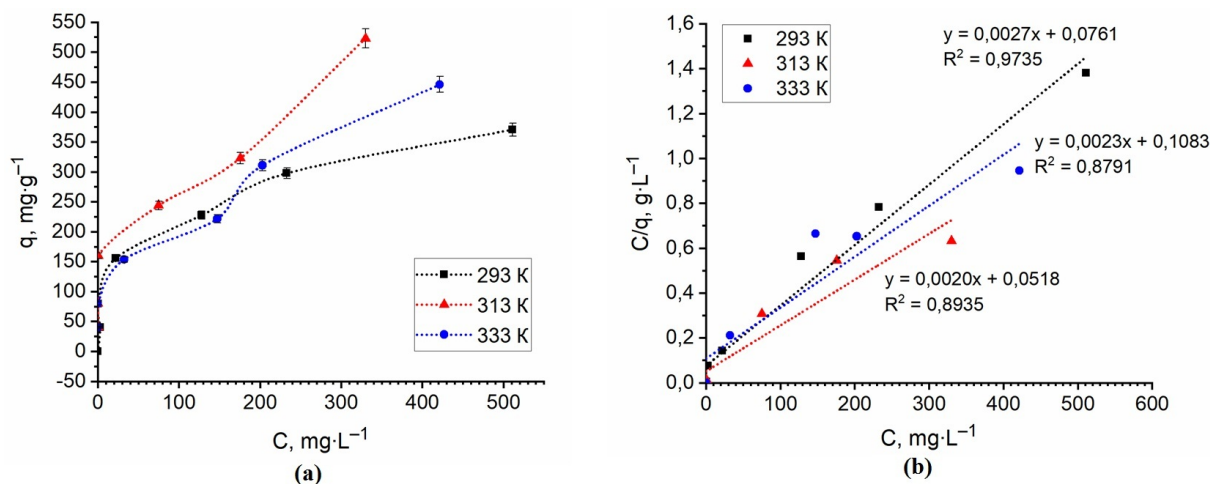


FIG. 5. Adsorption isotherms of Cr(VI) on composite sorbent (a); linear dependence of  $C - C_e/q$  for composite sorbent (b); pH = 5.0, acetate buffer, stirring 2 hours

333 K (Fig. 5a) we observe S-shaped adsorption isotherms, which is characteristic of polymolecular adsorption on non-porous sorbents, which may indirectly indicate the occurrence of chemisorption, i.e., in this case, variants 1 and 2 take place.

### 3.4. Purification of a real water sample from chromium (VI)

Adsorption of chromium (VI) from waste water of JSC “Russian Chromium 1915” before the stage of reagent treatment was carried out at temperature 290 K and pH = 5.4. The initial concentration of chromium in this water was  $350 \text{ mg}\cdot\text{L}^{-1}$ . After treatment with composite sorbent sol according to the procedure described in the experimental part, we determined the content of total chromium by ICP-AES method in supernatant, it amounted to  $0.087 \text{ mg}\cdot\text{L}^{-1}$ , which is less than MPC for trivalent chromium in drinking water. Hexavalent chromium was not detected in the solution after sorption (according to the test with 1,5-diphenylcarbazide).

X-ray phase analysis of the sorbent after adsorption of chromium showed the presence of FeO(OH) phases with tetragonal and orthorhombic structure and  $\text{Fe}_{1.8}\text{Cr}_{1.2}\text{O}_4$  (Fig. 6).

When the composite sorbent interacts with Cr(VI), iron passes into iron metahydroxide, and Cr(VI) – into Cr(III), while forming a solid solution of substitution – in the compound  $\text{Fe}_{1.8}\text{Cr}_{1.2}\text{O}_4$  chromium replaces iron in its positions in the spinel structure.

For comparison, tests were carried out with the currently used reagent for water purification from chromium (VI) compounds – iron (II) sulfate [47], with the same molar concentration of iron as when using the composite sorbent sol.

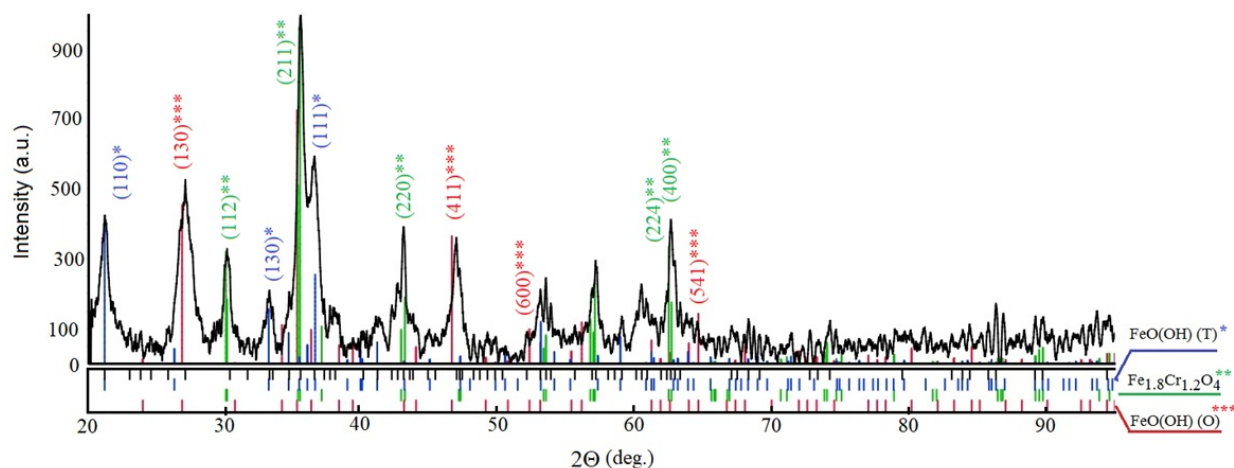


FIG. 6. XRD of the composite sorbent after Cr(VI) adsorption and results of X-ray phase analysis: the upper set of dashes is the dashed diagram of the sol after adsorption; the dashed diagrams below are in order from top to bottom: tetragonal FeO(OH),  $Fe_{1.8}Cr_{1.2}O_4$ , orthorhombic FeO(OH)

TABLE 1. Results of chromium removal from wastewater of JSC “Russian Chromium 1915” by two methods

Treatment	pH	$C_{Cr}$ after treatment, $mg \cdot L^{-1}$	R, %
$FeSO_4 \cdot 7H_2O$	5.4	225.6	35.5
	11	5.3	98.5
Composite sorbent	5.4	0.084	99.98
	11	26.4	92.5

According to the experimental data (Table 1), the composite sorbent sol is significantly superior to iron (II) sulfate in acidic medium and less effective in strongly alkaline medium.

In addition, in the acidic environment, it is possible to reach the MPC value for trivalent chromium. Also an important factor is that the product of chromium precipitation with composite sorbent is not contaminated with sulfur compounds, and all chromium passes into the trivalent state, forming a compound of regular composition  $Fe_{1.8}Cr_{1.2}O_4$ .

Thus, using the composite sorbent sol obtained by the proposed method it is possible to effectively remove Cr(VI) from the wastewater of metallurgical companies. Also we have to remember that hydrazine is toxic substance (MPC is  $0.01 \text{ mg} \cdot \text{L}^{-1}$ ) [16] and some quantity of hydrazine can penetrate to the aqua solution during working of sorbent. However, this is not a problem if we treat the effluent, as hydrazine readily decomposes into nitrogen and water when it interacts with oxygen [48], active chlorine or by the catalytic reaction in the presence of transition metals.

The proposed technological approach makes it possible to treat wastewater containing Cr(VI) to a residual concentration of  $0.084 \text{ mg} \cdot \text{L}^{-1}$  (with chromium remaining only in the form of Cr(III)), and to obtain a material of sufficiently regular composition, predominantly containing compounds of Cr(III) and iron. This material can be used for production of ferrochrome, chrome cast iron, metal flux or as a component in the production of ceramic products.

#### 4. Conclusions

The paper presents a method of synthesis of  $Fe(N_2H_4)_xCl_y$  complex where  $x = 1.7 - 2.8$ ,  $y = 1.8 - 2.1$  and subsequent formation of composite sorbent particles with a “core-shell” structure, in which the core is magnetite particles, and the shell is represented by  $Fe(N_2H_4)_xCl_y$  complex, which forms the positive charge of the surface. Such a composite sorbent allows the effective removal of Cr(VI) compounds from solutions in the pH range from 2 to 12. The  $Fe(N_2H_4)_xCl_y$  complex was certified by XRD, SEM and EDS methods. Based on the specificity of the interaction between the sorbent and Cr(VI) compounds, a scheme of the structure of its electrical double layer and adsorption mechanism is presented. Depending on the conditions, Cr(VI) can either adsorb on the surface of the highly dispersed sorbent or be reduced to Cr(III) by it. Purification of a sample of real wastewater by the obtained composite sorbent sol at room temperature in adsorption mode was carried out, it was shown that it allows to completely purify wastewater from Cr(VI) and from Cr(III) to concentrations below the MPC values in drinking water. At the same time, a high adsorption capacity of  $385 \text{ mg} \cdot \text{g}^{-1}$  and an adsorption degree of 99.9 % are achieved. The sludge after sorption can be used to obtain commercial products used in metallurgy as a substitute for ferrochrome. Comparison of wastewater treatment from chromium by composite



sorbent sol with the classical method of treatment using ferrous sulfate at different pH values of the medium showed that the sorbent  $\text{Fe}_3\text{O}_4 @ \text{Fe}(\text{N}_2\text{H}_4)_x \text{Cl}_y$  is effective in acidic environment, and allows to reach the MPC value, and ferrous sulfate is effective at pH = 11, but its use does not reach the MPC and sludge is obtained, not suitable for further use, because it is heavily contaminated with sulfur compounds.

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