

Mechanism of Sorption of Cr(VI) by Nanoparticles of Synthetic Magnetite

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Abstract

The results of investigation of kinetics and mechanism of sorption of chrome(VI) by nanoparticles of synthetic magnetite in a model solution are presented. The model solution contained 400 mg/l of Na_2SO_4 and 50 mg/l of Cr(VI) (in the form of potassium chromate). Investigations were carried out at different temperatures and pH of the model solution. Particles of magnetite had the average diameter 32 nm and the specific surface area 36.3 m^2/g evaluated by BET method. It was found that at sorption of chrome(VI) by magnetite two processes simultaneously proceed: (1) Simple physical adsorption and (2) Chemical reaction of interaction of Cr(VI) with magnetite (the chemisorption). The parameters of these processes at different temperatures and initial pH of the model solution were defined. The chemical reaction of interaction of chrome(VI) with magnetite was described by equation of reaction of the first order related to concentration of Cr(VI) in solution. Established relations allow evaluating the amount of magnetite for removal of chrome(VI) from polluted natural waters and sewage. For verification of the established relations additional experiments for cleaning sewage of some enterprise of Sverdlovsk region (Russia) from Cr(VI) by magnetite were carried out. As a result satisfactory coincidence of experimental and theoretical data was found.

Keywords: Sorption; Nanoparticles; Magnetite; Cr(VI); Equation of reaction; Sewage

Introduction

Purification of natural waters and wastewaters from Cr(VI) is an important ecological task and it is consequence of toxicity of chrome(VI). One of the perspective methods for the removal of Cr(VI) from solution is sorption. This method does not increase mineralization of solutions and this allows to use it for removal of Cr(VI) from polluted natural waters and wastewaters (for the purposes of their subsequent use in municipal services).

Recently we investigated sorption of chrome(VI) by the nanopowder of synthetic magnetite (Fe_3O_4) from the model aqueous solution that imitated polluted waters [1]. The choice of magnetite was caused by several reasons. First, magnetite is ferromagnetic material and after sorption of pollutants it may be separated from solution with the help of magnetic field. Second, nanopowder of magnetite can be easy produced from sewage of etching branches [2], and it reduces a price of its production. Third, particles of magnetite produced by this method have small size and great specific surface area [1].

The study showed that magnetite is highly effective sorbent for removal of Cr(VI) from polluted waters, and the process of sorption of chrome(VI) by magnetite is irreversible and has chemisorption character [1]. Then it was found that separation of nanopowder of magnetite from solution after sorption can be sharply accelerated under action of magnetic field [3,4]. The nanoparticles of magnetite (16-53 nm in diameter) form large aggregates of micron sizes (2-30 microns) in water solutions. However, it does not influence on process of sorption and all surfaces of the nanoparticles in the aggregates are accessible for sorption [1]. It simplifies fitting of amount of magnetite for purification of polluted solutions. In particular, one can use directly the specific surface area of the powders of magnetite in the technological calculations.

The obtained results coordinate well with the data of other researchers. So in work [5] it is shown that sorption of Cr(VI) by magnetite is described by isotherm of Langmuir for simple physical adsorption. But at the same time the presence of the chemisorption and possible formation of a chemical composition of chrome with iron was indicated there. In our work we also marked it and suggested that at interaction of chrome(VI) with magnetite some oxidation-reduction reaction takes place in which Cr(VI) is recovered to Cr(III), and Fe(II) in magnetite is oxidized to Fe(III) [1]. Later we confirmed this supposition by voltammetric and X-ray photoelectron spectroscopy studies of surface of nanopowders of magnetite before and after sorption of chrome(VI) [6,7]. The last result coincides with data of Yua et al. [8] where it was also established that at sorption of Cr(VI) by magnetite the chrome(VI) is recovered to Cr(III) and perhaps replaces Fe(III) in the lattice of magnetite.

According to Yua et al. [8] and Yuan et al. [9], the sorption of chrome(VI) by magnetite is described by isotherm of Langmuir and this coordinates with results of Lesnikovich et al. [5], but it is in contradiction with physic chemistry of the process. In fact, isotherm of Langmuir supposes the presence of dynamic balance between adsorbent and adsorbate, and it is correctly only for physical adsorption, but in the present case, authors like Lesnikovich et al. [5], Yua et al. [8] and Yuan et al. [9] recognized, the chemisorption, i.e. irreversible process, takes place.

From the data of Chowdhury and Yanful [10], it follows that sorption of Cr(VI) by magnetite-maghemite nanoparticles proceeds slowly (during about 200 min) and is described by Freundlich isotherm. In analogous study of Chowdhury et al. [11] it was also found that removal of chrome(VI) by mixture of magnetite and maghemite demands about 150-200 min, and the sorption process is described by Langmuir isotherm. The chemical analysis of the sorbent after the sorption showed that concentration of maghemite increased in it from 70 to 89%, and oxidation of Fe(II) to Fe(III), and recovery of Cr(VI) to Cr(III) occurred [11].

Thus, the following contradiction takes place: on the one hand the sorption of chrome(VI) by magnetite is described by equations of simple physical adsorption (Langmuir, Freundlich), but on the other hand all researchers recognize that in the present case some chemisorption process proceed, and it is practically established that some oxidation-reduction reaction between Fe(II) and Cr(VI) occurs. In the present work we try to solve this contradiction. For this purpose we have made more detailed investigation of mechanism and kinetics of sorption of hexavalent chrome by nanosized synthetic magnetite.

Experimental

Like and earlier Linnikov et al. [1], experiments were carried out using a model solution, which imitates polluted natural waters and wastewaters. The model solution contained 400 mg/l of Na_2SO_4 and 50 mg/l of Cr(VI) (in the form of potassium chromate). After preparation the solution had $\text{pH}=7.4-7.8$. The nanopowder of magnetite was produced by method of thermo-chemical precipitation from water solutions of FeSO_4 [1,2]. The method consisted of precipitation of $\text{Fe}(\text{OH})_2$ from solution of FeSO_4 at $\text{pH}=10-12$ with following aeration of the obtained suspension by air and heating it to $60-90^\circ\text{C}$ [2].

The structure and size of the produced nanopowder of magnetite were analyzed by X-ray and TEM, and it was detailed described earlier [12]. The specific surface area was evaluated by BET method (from desorption of Ar).

The produced nanopowder of magnetite (FIG.1) had following characteristics: Fe_3O_4 – 100%, structure – cubic, the specific surface area of particles – $36.3 \text{ m}^2/\text{g}$, the average diameter of particles according to BET (the magnetite density used at this calculation was taken as $5180 \text{ kg}/\text{m}^3$ [13]) – 32 nm and the same according to X-ray – 47.4 nm.

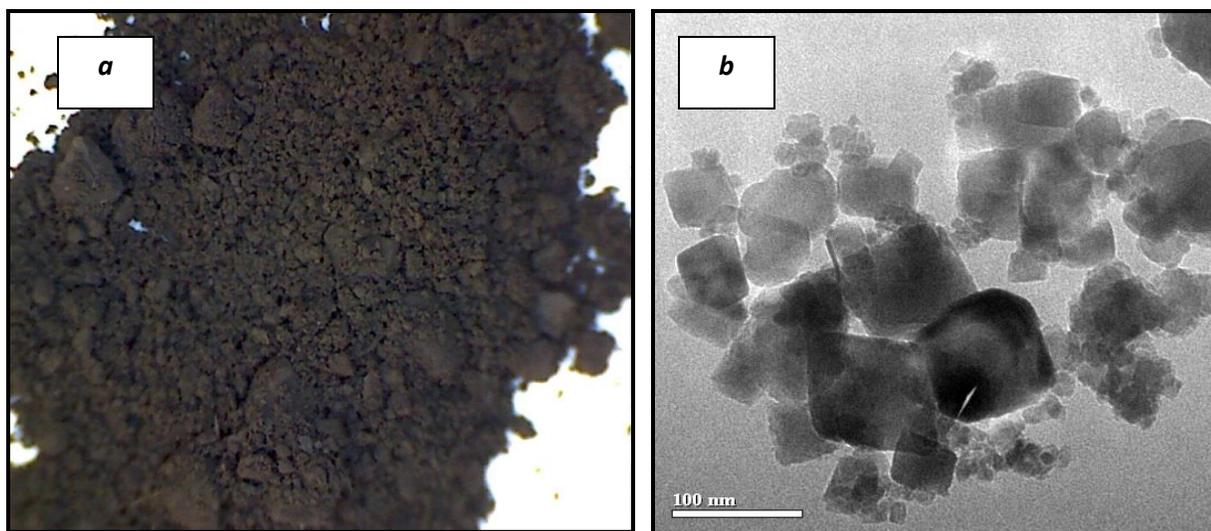


FIG.1. Typical visual and TEM images of produced magnetite powder.

Two series of experiments were done. The first one was carried out at a room temperature $25 \pm 2^\circ\text{C}$ and at periodic mechanical agitation of solutions (static experiments, static conditions). The volume of the model solution in the every run was 50 ml. The total time of exposition of solutions with the powder of magnetite varied from several hours to seven and more days. During this time samples of solution for analysis were taken periodically from the model solution with magnetite.

In the second series experiments were carried out in thermostatic Teflon cell at continuous agitation of solution by magnetic stirrer (dynamic experiments). At the beginning of the every run 150 ml of the model solution was put into the cell. Then the solution in the cell was heated to required temperature ($60-98^\circ\text{C}$) at continuous agitation by magnetic stirrer. After that the powder of magnetite was quickly put into the cell, and the model solution with the powder of magnetite was kept in

the cell at constant temperature ($\pm 0.1^\circ\text{C}$) for 5-10 h. During every run samples of solution were also taken for analysis from the cell.

After completion of the each run the powder of magnetite was separated from the model solution with fine paper filter and washed by distilled water and then air-dried up at temperature 80°C . The obtained powders of magnetite after sorption were investigated using different methods. Results of these investigations of the powders of magnetite before and after sorption of Cr(VI) were published earlier [1,3,4,6,7,12].

Some part of experiments was carried out at various pH of the model solution. Correction of pH was performed using 0.1 N solutions of NaOH and H_2SO_4 . In these runs the powder of magnetite was added into the model solution only after correction of its pH to the required value, and heating of it to the required temperature. At the end of the experiment the powder of magnetite was separated from the solution and again pH of the solution was measured.

Concentration of Cr(VI) in solutions was determined by colorimetric analysis with diphenylcarbazide at 540 nm using spectrophotometer KFK-2 (Russia) [14].

Results and Discussion

Some results of the first series of experiments (at static conditions) are presented in FIG. 2. As is seen from FIG. 2a, the sorption of Cr(VI) at room temperature proceeded very slowly and in some cases after 302 days from the beginning of the process it does not reach equilibrium. So, after 302 days of exposition the residual concentration of Cr(VI) in the solution at $S=18.15 \text{ m}^2$ was 0.23 mg/l, and at $S=36.3 \text{ m}^2$ – 0.1 mg/l. This coordinates well with our previous results and again points out that in the present case some chemisorption process takes place (since, simple physical adsorption finishes very quickly) [1].

From FIG. 2b one can see rapid decreasing of concentration of Cr(VI) at the beginning of the sorption process (right away after introduction of the powder of magnetite into the solution). After that a long period of its slow reduction follows. It allows to suppose that at sorption of Cr(VI) by magnetite two processes proceed simultaneously: (1) the simple physical adsorption and (2) the chemical reaction of interaction of Cr(VI) with magnetite (the chemisorption). In addition, at the beginning of the sorption the first process predominates.

For verification of this assumption the experimental data presented in FIG. 2a were recalculated using equation of Langmuir [15]:

$$A = A_\infty \frac{K \cdot C}{1 + K \cdot C} \quad (1)$$

where A is the value of adsorption, mg/m^2 ; A_∞ is the capacity of adsorption monolayer, mg/m^2 ; K is the constant of adsorption equilibrium, $1/\text{mg}$.

Results of these calculations in the coordinates of linear form of Eq. (1) are shown in FIG. 3. It is seen that the experimental data on sorption of Cr(VI) at the duration of the sorption process of 240 min and 28 h are well approximated by straight lines. This confirms that equation of Langmuir correctly describes these experimental data, and this is evidence that during this time period simple physical adsorption takes place. At more long duration of the sorption process (7 days and more) the dependences transform into the curvilinear form (FIG. 3, line 7 days). This point out predominance of the chemisorption in this period of the sorption process (the dependences for duration above 7 days are not presented in FIG. 3 in order to not overload it).

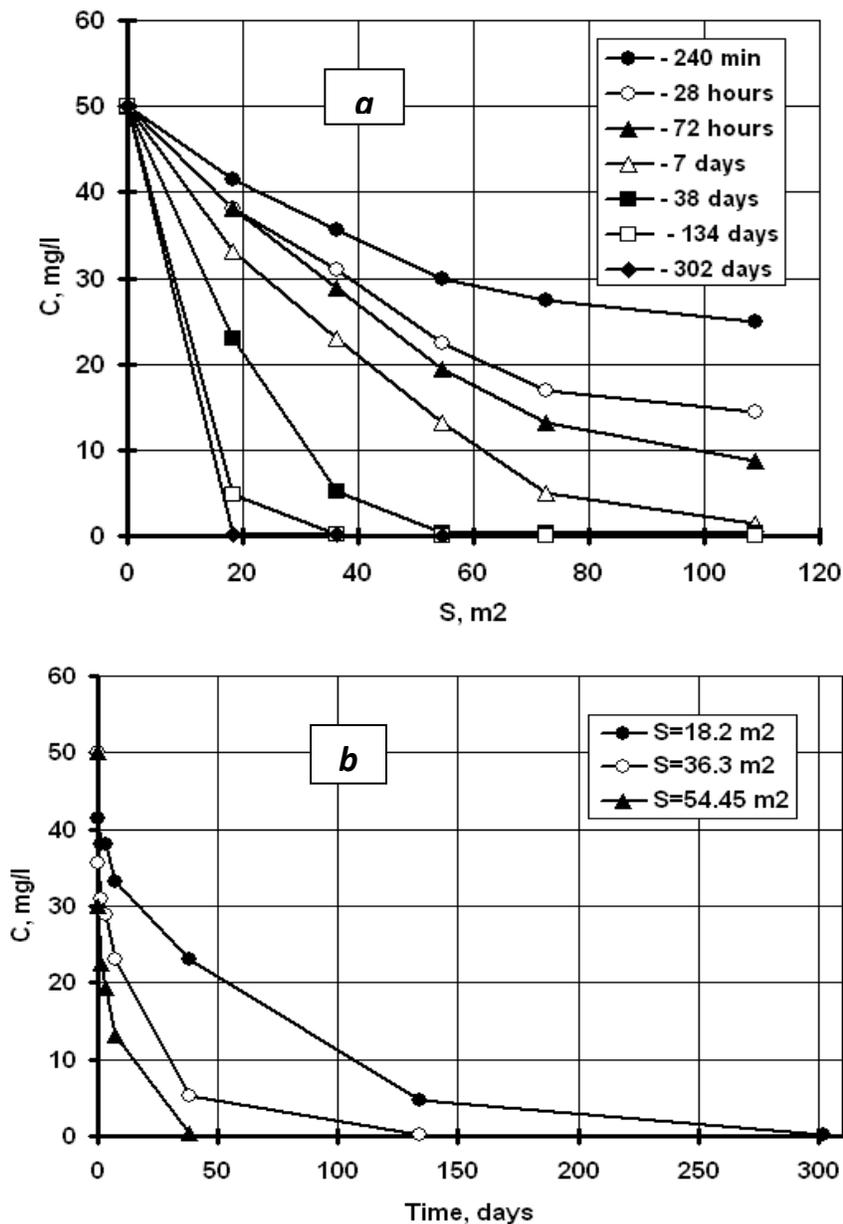


FIG.2. Relation of the residual concentration (C) of Cr(VI) in the model solution to the total surface area (S) of the powder of magnetite in the solution and duration of the sorption process (temperature $25 \pm 2^\circ\text{C}$).

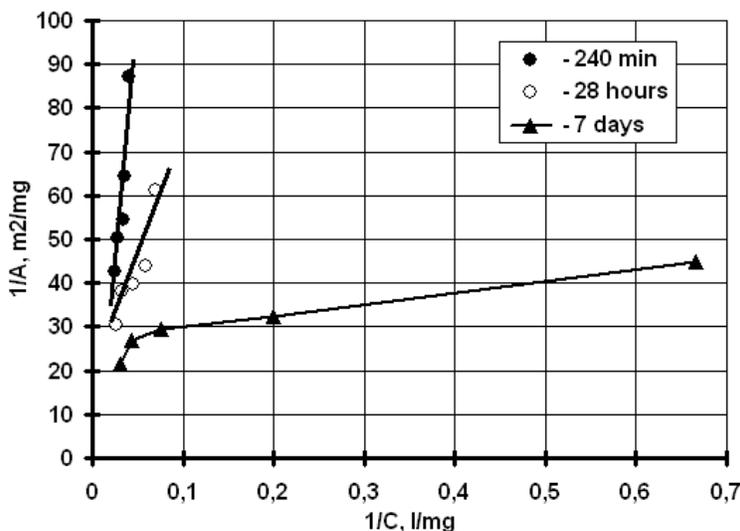
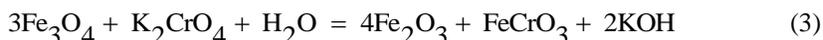


FIG. 3. Data on sorption of Cr(VI) by magnetite in the coordinates of Eq. (1).

As seen, the obtained result coincides with data of works [5,8,9,11] where duration of the sorption process also did not exceed 200-250 min. And now contradictions in experimental data and conclusions of a number of investigators become clear [5,8-11].

Like it was mentioned above, during of the sorption of chrome(VI) by magnetite the oxidation of Fe(II) to Fe(III) and recovery of Cr(VI) to Cr(III) occur. This allows to suppose that the chemisorption process is determined probably by one of the next reactions:



According to the above equations the process of sorption of Cr(VI) by magnetite must be accompanied by increase of pH of solution. Really, the last was detected in the experiments (FIG. 4). From FIG. 4 one can see that pH of the solution shifted into alkaline zone (the initial solution had $\text{pH} \approx 7.5$) during the long-duration sorption experiments. However, after aging for 7-38 days the further change of alkalinity occurred non-uniformly. So, at $S=20-40 \text{ m}^2$, as before, pH of the solution increased to $\text{pH}=9.2-9.4$, but at $S>40 \text{ m}^2$, on the contrary, it decreased to $\text{pH}=8-9.2$. Then after 134 days of the sorption the decrease of pH of the solution at different S was observed. And after 302 days the solution had $\text{pH}=8.2$ at $S \approx 20 \text{ m}^2$ and $\text{pH} \approx 7.3$ at $S > 20 \text{ m}^2$ (FIG. 4).

The found effect was probably caused not only by the chemisorption of Cr(VI) by magnetite but also interaction of magnetite with water at long aging in the solution, and it demands further investigation.

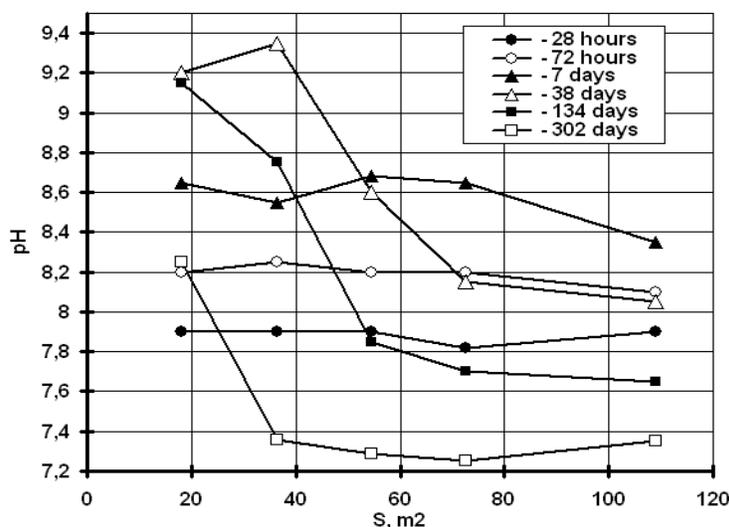


FIG. 4. Changing of pH of the solution depending on the total surface area of the powder of magnetite in the solution and duration of the sorption process (temperature $25 \pm 2^\circ\text{C}$).

If the chemisorption process proceeds according to Eq.(2) then particles of chrome oxide(III) must appear in deposit. However, the careful microscopy analysis of magnetite after the end of the sorption process did not find this phase in it [1,12]. In addition, the voltammetric and X-ray photoelectron spectroscopy studies also did not detect particles Cr_2O_3 in the deposit [6,7]. In works of other researchers there is no information on detection of particles of new phase in deposits of magnetite after finish of sorption process, too [8-11]. Therefore, one may suppose that the chemisorption proceeds according to Eq.(3). Moreover, the formation of mixed compound of chrome with iron takes place not in volume of the solution or on surface of magnetite but in the thin surface layer of the last.

For comparison of the found change of alkalinity of the solution with the theoretical one (according to Eq.(3)) and determination of other parameters of the chemisorption process several dynamic experiments were carried out. In these runs different amounts of magnetite were added into 150 ml of the model solution. These experiments showed that the theoretical value of pH of the solution after finish of the sorption not always coincides with the experimental one. So, at sorption at 98°C with the mass of magnetite of 0.3 g the final (equilibrium) concentration of chrome(VI) in the solution was 31 mg/l and the solution had pH=10.1. Appropriate calculation with Eq.(3), without accounting of hydrolysis of sulphate and chromate ions that are in the solution, gives pH=10.3. This, in our opinion, coincides satisfactorily with the experimental value. However, in other experiment with the mass of magnetite of 1 g the final concentration of chrome(VI) in the solution was 0.12 mg/l and pH=9.75. The theoretical calculation for this experiment gives pH=10.71. As is seen, in the last case there is significant difference between experimental and theoretical values. This difference may be explained, if one supposes that some part of ions OH^- , which form during reaction (3), is adsorbed by the surface of magnetite. For verification of this supposition two additional runs were carried out. In the first one the powder of magnetite was added into the model solution (2 g of Fe_3O_4 into 50 ml of the solution), without introduction into the solution of potassium chromate and at continuous agitation of it by magnetic mixer. Then 0.1 N solution of NaOH was slowly added into this suspension and during this procedure the equilibrium pH of the suspension was measured. In the second run was the same but without introduction of the powder of magnetite into the solution. The obtained titration curves are shown in FIG. 5.

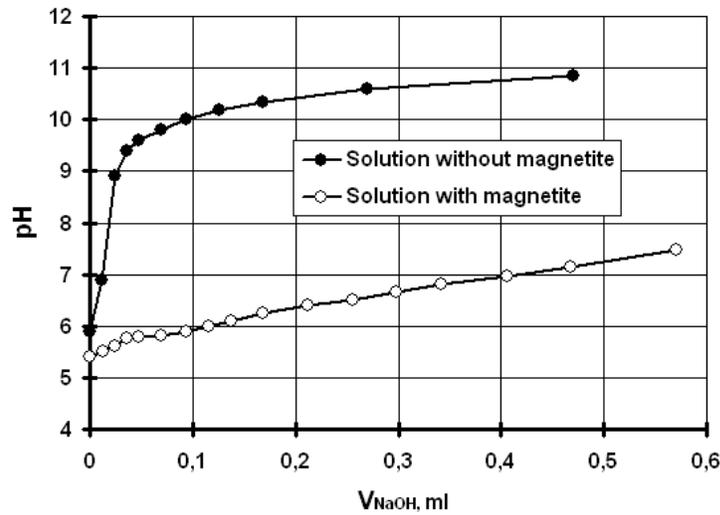


FIG. 5. Influence of magnetite on the change of pH of the solution of Na_2SO_4 (400 mg/l, 50 ml) during titration of it with 0.1 N solution of NaOH; V_{NaOH} is the volume of added 0.1 N solution of NaOH.

From FIG. 5 is seen, the suspension of magnetite, in contrast to the solution of Na_2SO_4 , behaves like a buffer solution, preventing increase of pH of the solution at adding of alkali into it. This confirms the assumption on adsorption of ions OH^- by magnetite.

Further one may suppose that if the chemisorption of Cr(VI) by magnetite proceeds according to Eqs.(2) or (3) then in the kinetic mode of the process the total speed of it may be described by following equation:

$$-\frac{dC}{d\tau} = k \frac{S}{v} \exp\left(-\frac{E}{RT}\right) \cdot C^z \quad (4)$$

where v is the volume of solution, m^3 ; k is the kinetic coefficient of the reaction; E is the activation energy of the chemisorption process, J/mol ; R is the universal gas constant, $\text{J/(K}\cdot\text{mol)}$; T is the temperature, K ; τ is the time, s ; z is the order of the equation. If the chemisorption proceeds according to Eq.(2) then the experimental data must be described by Eq.(4) with $z=2$, otherwise we have to find $z=1$.

For verification of Eq.(4) and determination of its parameters several dynamic experiments on the sorption of Cr(VI) by magnetite at high temperatures and different initial values of pH of the solution were carried out. In these runs the increased concentration of magnetite in the solution was used. Hence, decreasing of the surface area of magnetite, which was available for the sorption of Cr(VI), was negligible. Some of the obtained results are presented in FIG. 6-8.

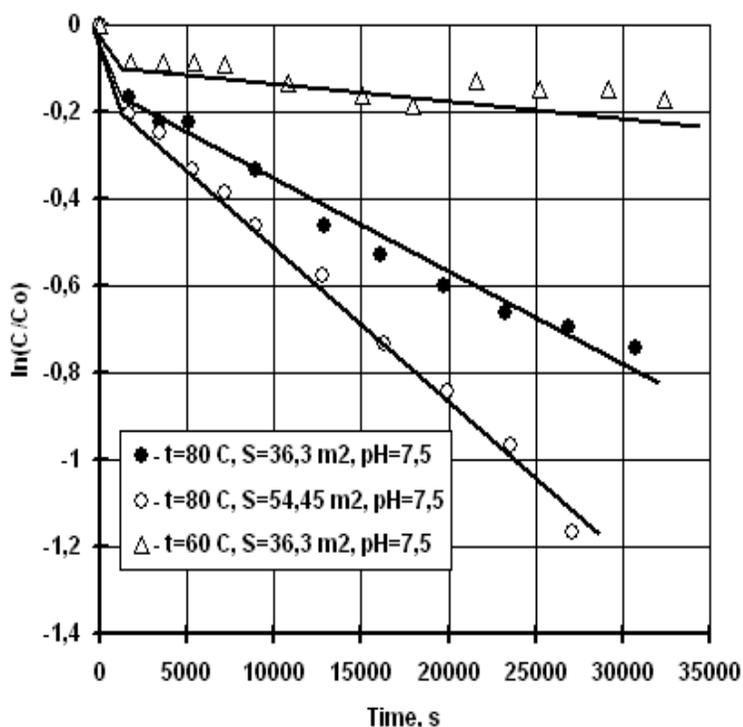


FIG. 6. Kinetics of the sorption of chrome(VI) by magnetite at temperatures 60 and 80°C in the coordinates of Eq.(4) after integration with $z=1$, where C_0 is the initial concentration of chrome(VI) in solution.

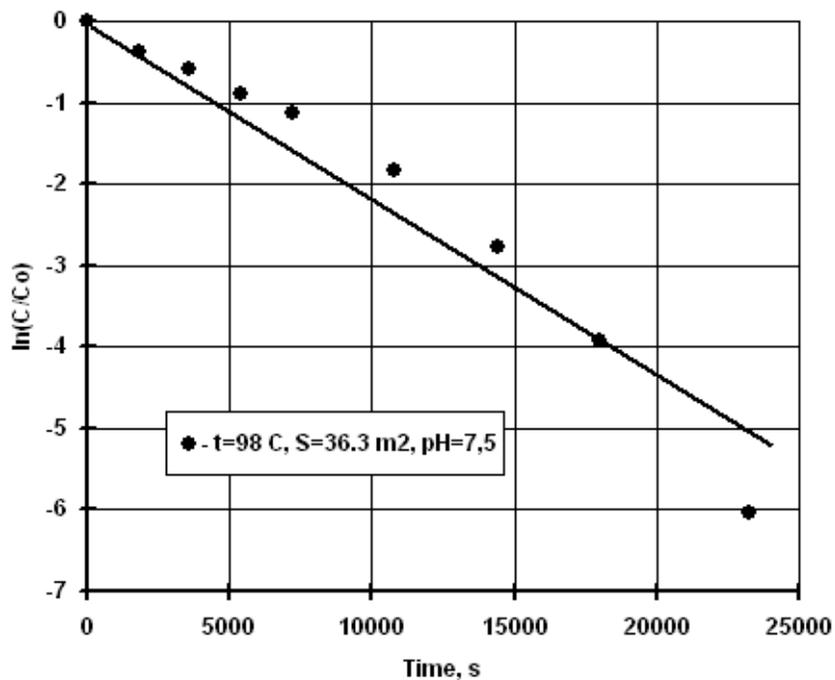


FIG. 7. Kinetics of the sorption of chrome(VI) by magnetite at temperature 98°C in the coordinates of Eq.(4) after integration with $z=1$.

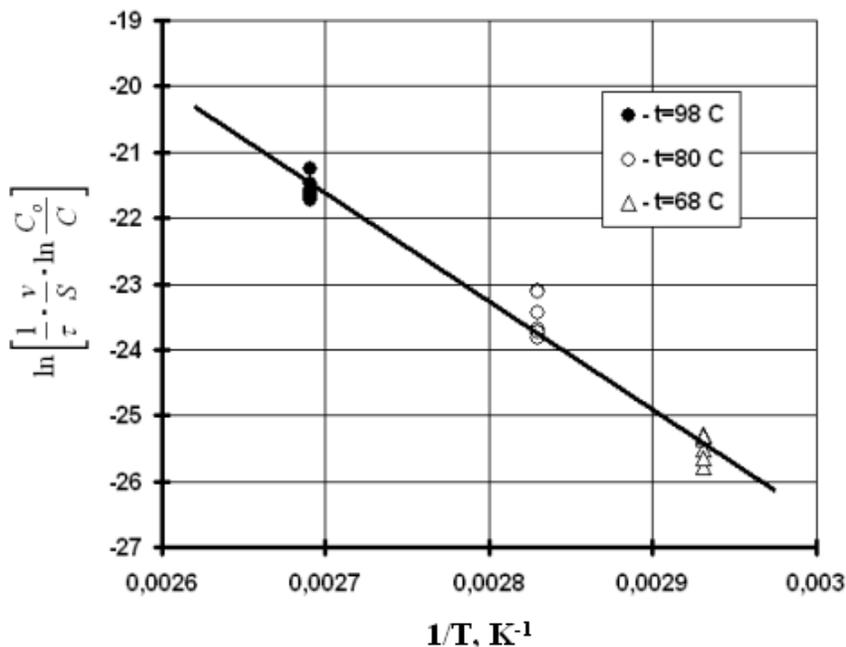


FIG. 8. Experimental data on the kinetics of the sorption of chrome(VI) by magnetite at pH=10.5, S=54.4 m² and temperatures 68, 80 and 98°C in the coordinates of transformed Eq.(4) after integration with z=1.

Relations presented in FIG. 6-8 confirm that Eq.(4) correctly describes obtained experimental data only with z=1 (substitution of the experimental data into Eq.(4) after its integration with z=2 gives curvilinear relations). This points out that interaction of Cr(VI) with magnetite may proceed according to reaction (3).

From FIG. 6 is seen that at temperatures 60 and 80°C the first experimental points deviate from the theoretical linear relation. This is evidence that simple physical adsorption predominates at the initial period of the sorption process. However, when the temperature increases up to 98°C the all experimental points may be approximated by the theoretical straight line that corresponds to Eq.(4) (FIG. 7). It is obviously, that in the last case (at temperature 98°C) the rate of the chemisorption exceeds the rate of simple physical adsorption. It should be noted that in all experiments simple physical adsorption proceeded very quickly (within first 5-10 min from the beginning of the sorption process). And so we could not study its kinetics and find the equation of the process.

The conducted experiments showed that parameters of the chemisorption process depend on the initial value of pH of the solution (TABLE 1).

TABLE 1. Dependence of parameters of Eq.(4) with z=1 on the initial value of pH of the solution (S_n is the standard deviation of E; n is the number of measurements of E; R_c is the coefficient of correlation; F is the Fisher test).

pH	k, m/s	E, kJ/mol	S _n , kJ/mol	n	R _c	F
3.3	5953.89	89.9	4.5	34	0.962	401.3
4.8	10855.69	113.7	7.3	40	0.929	240.8

7.5	$230.436 \cdot 10^5$	117.2	6.4	34	0.956	338.8
9.15	$2829.84 \cdot 10^5$	126.7	5.5	23	0.980	523.7
10.5	$25990.2 \cdot 10^5$	133.4	4.3	26	0.988	982.3

According to data of TABLE 1 the reaction of interaction of chrome(VI) with magnetite has high activation energy. Therefore, taking into account nanosize of particles of the magnetite, one may draw conclusion that even without agitation of solution the chemisorption process will proceed in the kinetic mode.

From TABLE 1 is seen, that with increase of the initial value of pH of the solution the growth of pre-exponential factor in Eq.(4) and also of the activation energy of the chemisorption process is observed. High values of the coefficient of correlation and Fisher test confirm that formula (4) correctly describes the obtained experimental data at $z=1$.

The experiments showed that the final value of pH of the solution was different from the initial one in the every run, i.e. pH of the solution changed during the sorption process. Obviously, this was caused by reaction (3) and by partial adsorption of ions OH^- on the surface of magnetite. However, this did not transform substantially the linear relations in FIG. 6-8, but, apparently, slightly reduce accuracy of determination of the parameters of Eq.(4). Besides, it was found that there were additional factors decreasing precision of determination of the parameters of Eq.(4). So, according to the last a linear relation between product $(k/v) \cdot S$ and S must be observed. But the calculation using obtained experimental data gives a curvilinear relation (FIG. 9 and 10).

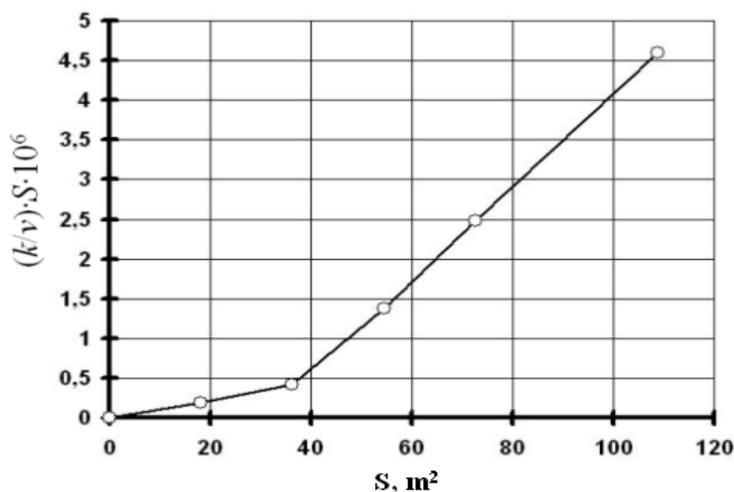


FIG. 9. Relation of product $(k/v) \cdot S$ versus the surface area of magnetite in the solution, $t=25 \pm 2^\circ\text{C}$, $\text{pH}=7.5$.

From FIG. 9 and 10 one can see decrease of factor $(k/v) \cdot S$ at small values of S (in the range of 10-40 m^2). This, probably, is caused by the reducing of active (free of Cr(VI)) surface area of magnetite in the solution. This effect, seemingly, is a result of physical sorption of chrome(VI) on the surface of magnetite right away after introduction of it into the solution (above was mentioned that this process proceeds very quickly). Farther, with increasing of S the fraction of the active surface area of magnetite also increases (chrome(VI) is not enough already for covering sufficient part of the surface of magnetite), and the factor $(k/v) \cdot S$ reaches its true value. In addition, the fraction of chrome(VI), which was adsorbed by magnetite by means of physical adsorption, decreases with increase of temperature of the sorption process (please compare FIG. 6 and 7), and corresponding “flexure” in relation $(k/v) \cdot S$ versus S also reduces (FIG. 10).

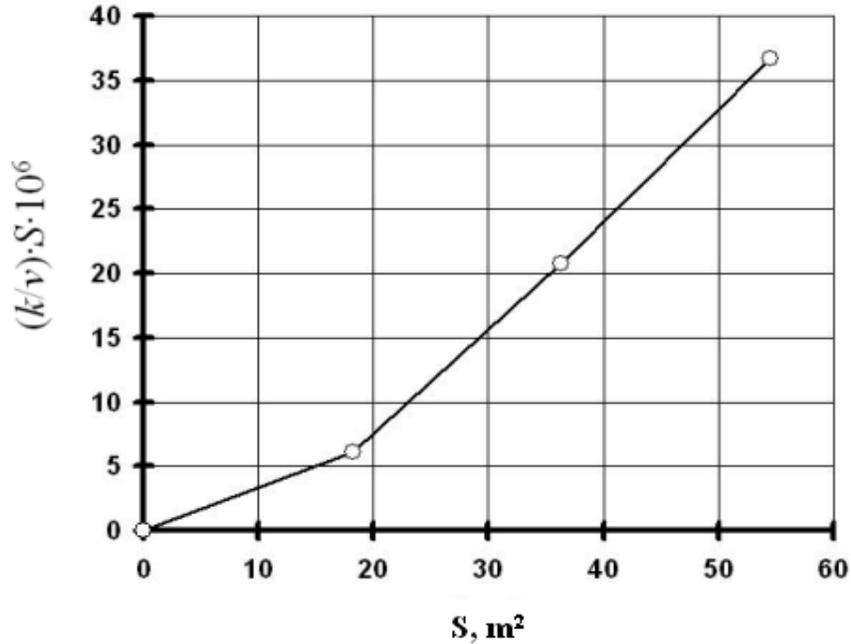


FIG. 10. Relation of product $(k/v) \cdot S$ versus the surface area of magnetite in the solution, $t=80^\circ\text{C}$, $\text{pH}=7.5$.

The aim of another part of dynamic experiments was determination of the adsorption capacity and full sorption capacity of magnetite (in the relation of Cr(VI)) depending on initial value of pH of the solution. Here under adsorption capacity we mean the amount of chrome(VI), which is adsorbed by the magnetite during first minutes of the sorption process (these points “fall out” from the relation described by Eq.(4), (FIG. 6). Under the full sorption capacity we mean the maximum amount of chrome(VI), which may be removed by magnetite during its long exposition in the solution containing Cr(VI). It is clear that growth of temperature of solution allows considerably reducing this exposition time.

The runs for determination of the adsorptive and full sorption capacities of magnetite in the relation of Cr(VI) were carried out at small concentration of the magnetite in the solution. Some results of these experiments are shown in FIG. 11. As is seen, the adsorption equilibrium in the solution at 25°C reaches out very quickly, during a few minutes. At 98°C the sorption process is longer and it finishes in about 5.5 h.

The adsorption capacity was estimated from runs at temperature $25\text{-}27^\circ\text{C}$ (since at such low temperature the contribution of the chemisorption into the total sorption is very small, it begins substantially appearing only in several hours from the beginning of the sorption process, (FIG. 3), hence it may be easily excepted) and was calculated with formula:

$$A_\infty = \frac{(C_o - C_a) \cdot v \cdot 10^3}{S} \quad (5)$$

where C_a is the concentration of chrome(VI) in the solution at reaching of adsorption equilibrium, mg/l. It should be noted that, of course, this method of determination of the adsorption capacity is not fully correct and for more precise determination of it one should use equation of Langmuir. However, for engineering designs, in our opinion, this estimation of value of the adsorption capacity have satisfactory accuracy.

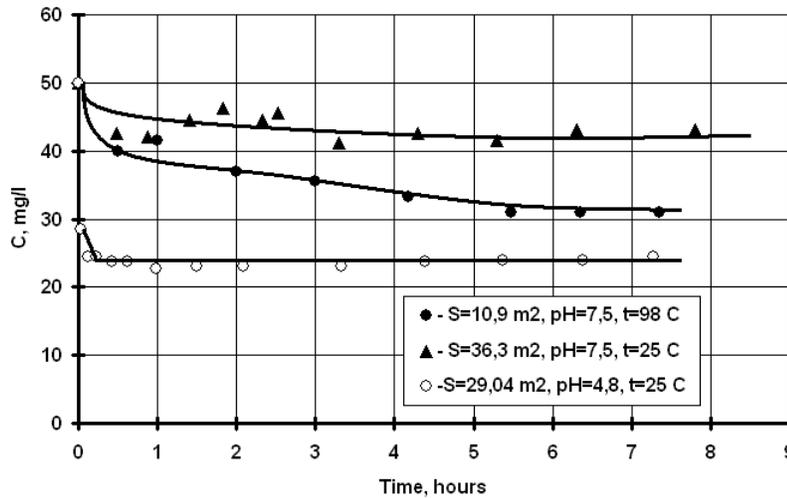


FIG. 11. Kinetics of the sorption of chrome(VI) at different temperatures and initial values of pH of the solution.

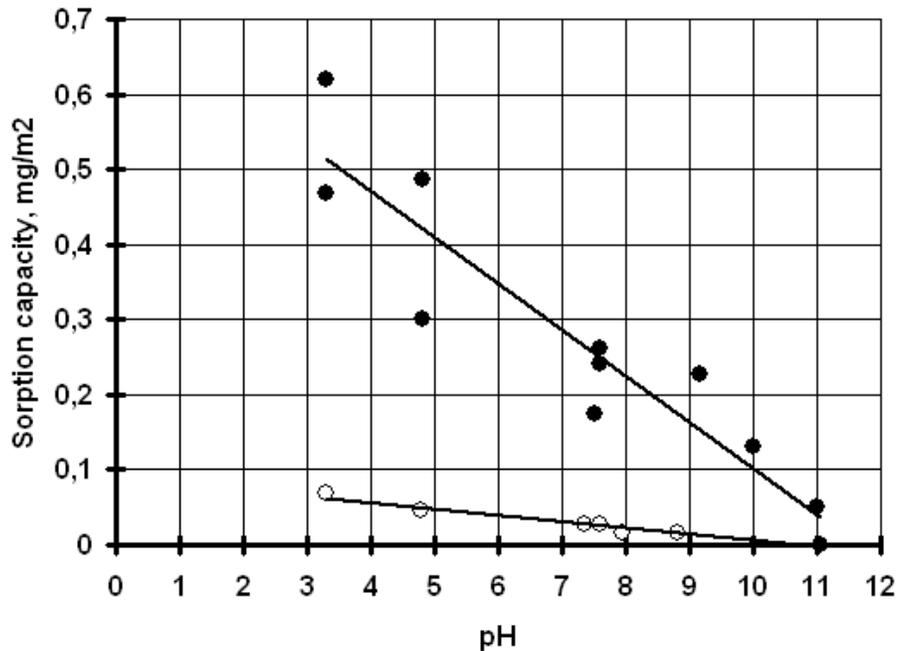


FIG. 12. Relation of the adsorptive (○) and full sorption (●) capacities of magnetite to initial value of pH of the solution.

The full sorption capacity of magnetite was determined at temperature 60-98°C and calculated with similar formula:

$$A_f = \frac{(C_o - C_f) \cdot v \cdot 10^3}{S} \quad (6)$$

where A_f is the full sorption capacity of magnetite, mg/m^2 ; C_f is the concentration of chrome(VI) in the solution after the end of the sorption, mg/l .

Obtained summary results are presented in FIG. 12, where relations of the adsorptive and full sorption capacities of magnetite to initial values of pH of the solution are shown. It is seen, that experimental points in both cases are well approximated by straight lines. The adsorptive and full sorption capacities of magnetite in the respect of Cr(VI) fall with increase of pH of solution, and at $\text{pH}=11$ they practically equal to zero. At $\text{pH}=3.3$ the full sorption capacity of magnetite is on order of magnitude more than adsorption capacity. The obtained results qualitatively coordinate with data of works [8-10]. However, the found there analogous relations have a curvilinear form. It should be noted that in above works the total value of effectiveness of the adsorption and the chemisorption processes was determined. From FIG. 12 one can see that with increase of pH of solution these processes change differently and it gave, apparently, observed the curvilinear relations [8-10].

The found relation of the adsorptive and full sorption capacities of magnetite in the respect of Cr(VI) to initial value of pH of solution may be explained by the following way. It is known, in the wide range of pH the chrome(VI) is in solution mainly in the form of negative ions HCrO_4^- and CrO_4^{2-} [8,10,16]. However, like corresponding measurements showed, the particles of magnetite in the field of low pH have positive charge but at high pH – negative. Isoelectric point (pzc) for the particles of magnetite, in dependence on composition of solution, its temperature and age of magnetite, is in the range of $\text{pH}=6-8$ [4,10,17,18]. Thus, at low pH of solution the adsorption of Cr(VI) by magnetite is caused, probably, by electrostatic interaction between positive particles of magnetite and negative ions of chrome(VI). The positive charge of particles of magnetite changes on negative one at high pH of solution. Correspondingly, at high pH of solution the adsorption of Cr(VI) by magnetite sharply fall (the particles with the same charge push away each other).

Thus, the obtained results testify that at sorption of chrome(VI) by magnetite two processes proceed simultaneously: (1) simple physical adsorption and (2) chemical interaction of Cr(VI) with magnetite (the chemisorption). At sorption at low temperatures of solutions the process of physical adsorption prevails during the initial period of time, but at sorption at temperatures near 100°C the removal of chrome(VI) from solutions is proceeded mainly owing to the chemisorption. The obtained results may be used for optimization of processes of purification of natural waters and wastewaters from Cr(VI) by magnetite. So, the relations in FIG. 12 allow to estimate the required amount of magnetite for removal of chrome(VI) from polluted solutions owing to the sorption process. The relations are described by equations:

$$A_\infty = -0.0086\text{pH} + 0.0913 \quad (7)$$

$$A_f = -0.0615\text{pH} + 0.7168 \quad (8)$$

Note, at a long contact of magnetite with solution that contains Cr(VI) it is necessary also to take into account kinetics of the chemisorption process, which is described by Eq.(4) at $z=1$. The parameters of the chemisorption process were given above in TABLE 1.

In order to estimate an accuracy of predictable depth of purification of polluted solutions from chrome(VI) with the obtained relations the special experiments were conducted. For these runs the sewage of one of the enterprises of Sverdlovsk region (Russia) was used. The sewage had following chemical composition on main components (mg/l): Ca^{2+} -115, Cr(VI) – 195, Mg^{2+} -38, Na^+ -570, SO_4^{2-} -900, HCO_3^- -288, mineralization – 2245; pH–7,66. The experiments were carried out at static conditions and the obtained results are presented in FIG. 13 and 14.

So, the change of the residual concentration of chrome(VI) in sewage during the first two hours from the beginning of the sorption process is shown in FIG. 13. Above was found that in this period of the sorption process simple physical sorption of Cr(VI) on magnetite prevails. Therefore, the value of residual concentration of chrome(VI) in the solution may be calculated with formula (7).

At more duration of the sorption process the residual concentration of chrome(VI) in the solution must be calculated using Eq.(4) at $z=1$ and the corresponding parameters of this equation (TABLE 1).

From FIG. 13 and 14 it is seen, that some discrepancy between experimental data and theoretical relations takes place. However, taking into account significant differences between chemical compositions of the model solution and sewage, the obtained results, in our opinion, may be recognized as satisfactory ones.

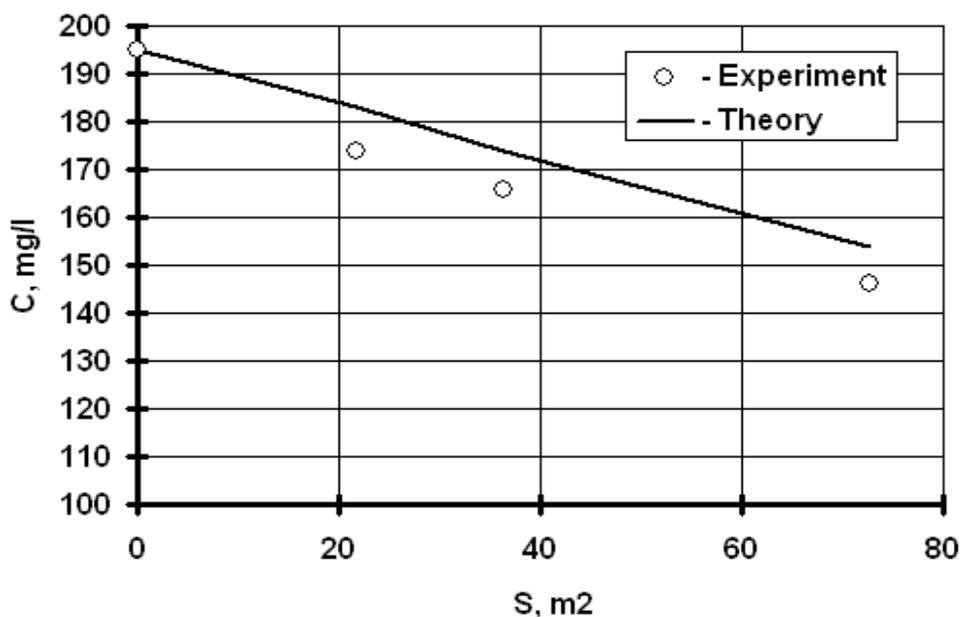


FIG. 13. Change of residual concentration of chrome(VI) in sewage depending on the total surface area of the powder of magnetite in the solution (the duration of the sorption process was 2 h, temperature $25 \pm 2^\circ\text{C}$).

Conclusion

The sorption of chrome(VI) by nanopowder of synthetic magnetite (Fe_3O_4) from the model water solution, which imitated polluted natural waters and sewage, has been investigated. It was found that at sorption of chrome(VI) by magnetite two processes proceed simultaneously: (1) simple physical adsorption and (2) chemical reaction of interaction of Cr(VI) with magnetite (the chemisorption). It was shown that adsorption of Cr(VI) by magnetite is described by Langmuir isotherm. The chemisorption process (the chemical reaction of interaction of chrome(VI) with magnetite) is described by equation of reaction of the first order related to concentration of Cr(VI) in solution. The parameters of these processes at different temperatures and initial pH of the model solution were defined. Established relations allow evaluating the amount of magnetite for removal of chrome(VI) from polluted natural waters and sewage.

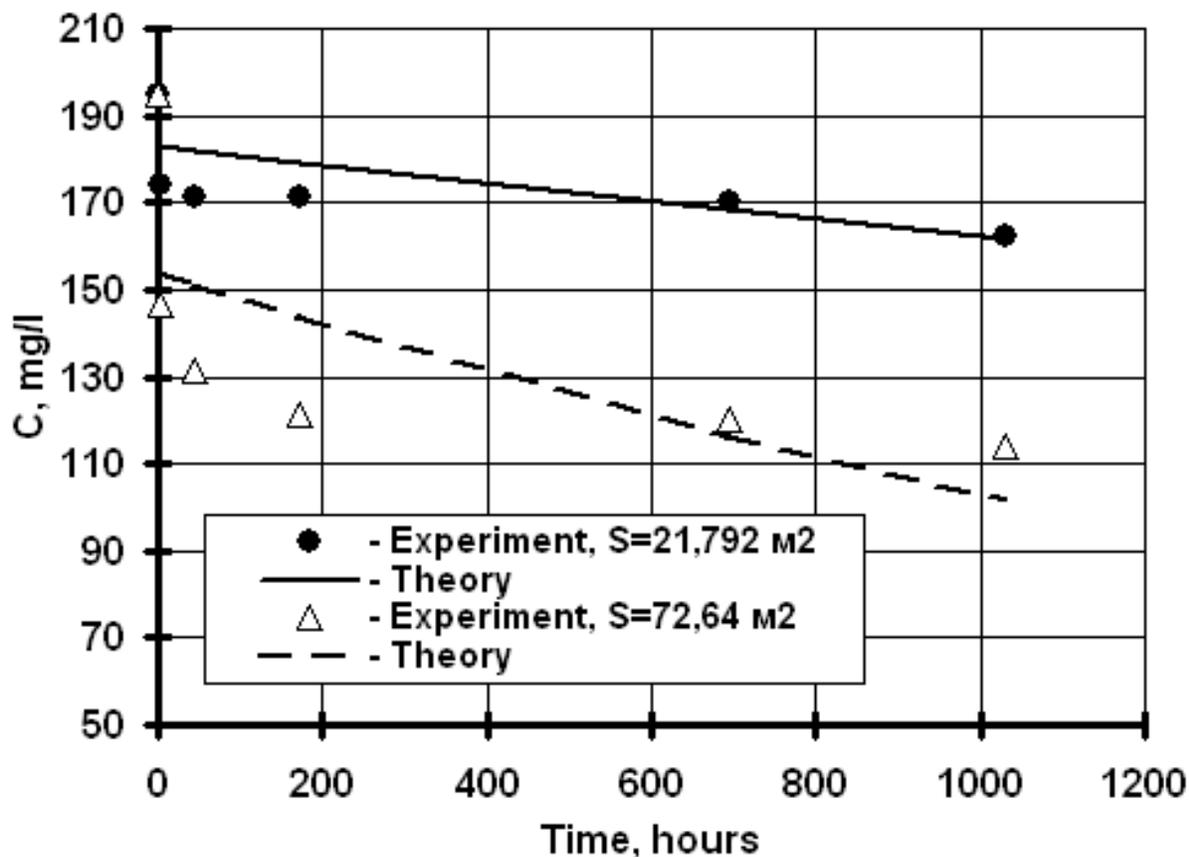


FIG. 14. Change of residual concentration of chrome(VI) in sewage depending on the total surface area of the powder of magnetite in the solution and the duration of the sorption process (temperature $25 \pm 2^\circ\text{C}$).

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