Composite method of sewage treatment for chromium ion (VI)

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Abstract. The sewage, containing hexavalent chromium, appears at the different productions, where the main component of technological process is chromic acid. The influence curve has been constructed showing the dependence of the value of the sorption of chromium ions (III) on native bentonite clay. Maximum degree of the treatment is 96.25 % (original concentration is 0.024 mg/ml, minimum degree is 37.63 % (original concentration is 0.481 mg/ml). All the values of residual concentration exceed maximum permissible concentration according to chromium ions. A composite method of sewage treatment of galvanic production for chromium ion (VI) by means of pre-transforming it to chromium ion (III) and adding of bentonite clay and ferric chloride (III) in model solutions has been studied. Ferrum ions after the treatment are not detected in the solution. Optimal mass ratio of metal coagulant to clay in both cases is 1:4000.

1. Introduction
Galvanic production is one of the basic sources of environment pollution with heavy metal ions, which are hazardous for biosphere including natural water. In this connection, natural water treatment for their contents has become quite a serious problem [1].

The main source of heavy metal ions is sewage water. The volume of sewage is quite great due to non-perfect method of workpiece washing and it requires large water consumption (2–3.3 m³ per 1 m² of workpiece surface). This leads to the decrease of efficiency of treatment facility work and as a result the transfer of toxic ions of heavy metals into the environment in the above norm quantity.

One of the composite components of pollution is the compositions of hexavalent chromium, which are considered to be the strongest oxidation agents and can cause serious disease even under short-term influence. The sewage, containing hexavalent chromium, appears at machine-building and metal-processing industries during etching operation, passivation and electropolishing of steel articles, where the main component of technological process is chromic acid. The whole stock of galvanic shops of most industrial enterprises comprises from 10 to 500 mg/l of chromates [2–4]. In separate cases during volley of sewage chromium content may rise to 1000 mg/l, while the maximum permissible concentration of hexavalent chromium comprises 0.05 mg/l.

One of the most widespread methods of sewage treatment for chromium ions (VI) is based on the reconstruction of hexavalent chromium (at the first stage) to trivalent chrome with the following deposition of chromium ions (III) in the form of hydroxide (reagent method). However, as the practice shows, this method does not always bring satisfactory results [5]. According to the data of different researches bentonite clays are effective adsorbents of ions of various metals and are widely used in this connection. On this basis we have conducted the research for the elaboration of composite method of treatment of galvanic production sewage for chromium ions with the use of bentonite clay.
2. Experimental part

The bentonite clay of Zyryanskoe deposit has been used as a sorbent. Native and activated clay has been produced at the enterprise PTC “Bentonite” (Kurgan). The clay activation has been performed with the using of solid sodium carbonate as an activator. Before that the clay has been grinded and dried at the temperature of 105 ± 5°C in the desiccator for 4 hours. Then it has been pounded to a finely-dispersed state. For the analysis 0.5000 g of the clay sample has been taken per 50 ml of the studied model solution. The samples have been weighed on the analytic balance GR–200 (A&D Japan).

The initial solution of chromic sulphate (III) in the concentration 0.1 mg/ml has been prepared in the flask for 500 ml from 0.24049 g Cr₂(SO₄)₃·6H₂O dissolved in a small quantity of distilled water. Then water has been added into the flask to the mark. The precise concentration of chromium ions (III) in the solution has been determined by titration method according to the reaction of substitution with potassium iodide. The released iodine has been titrated by the solution of sodium thiosulphate. The solutions with a lesser concentration of chromium ions (III) have been prepared by the method of successive dilution.

The determination of trivalent chrome content in the model solution before and after the treatment has been performed photometrically according to the reaction with diphenylcarbazide after it has been oxidized to ions Cr (VI) [6]. The method is based on the diphenylcarbazide oxidation by chromium (VI) in sulfuric medium to the red violet compound, in which chromium is in a deoxidized state of Cr³⁺ and diphenylcarbazide has been oxidized to diphenylcarbazone. The optical density of the received solution has been estimated on the spectrophotometer SPEKOL 1300 (Analytik Jena AG Germany). The influence of the bentonite clay on the concentration of chromium ions (III) in the model solution has been studied for the initial concentrations of metal ions: 0.025 mg/ml; 0.050 mg/ml; 0.100 mg/ml; 0.150 mg/ml; 0.200 mg/ml; 0.250 mg/ml; 0.500 mg/ml. The clay mass of 0.5000 g and 50 ml of the model solution have been put into the conical flask. Then the vessels have been locked with corks and shaken in the shaker during 3 hours. After clay separation by centrifugation, residue (equilibrium) concentration of chromium ions (III) has been determined in the model solution.

Exact pH value for determination sorption capacity of clay at various pH values of the model solution has been set with the help of 1M of the solution of sulphuric acid and 2M of the solution of sodium hydroxide. The concentration of chromium ions has been 0.1 mg/ml. The solution has been in contact with the clay for 3 hours.

Aluminium sulphate Al₂(SO₄)₃ and ferric chloride FeCl₃ have been used as coagulants to treat the solutions. In order to keep acidity of the original solutions within the operating range of coagulant activity, pH values have been brought to 5.56. Afterwards the coagulant has been introduced. pH value has been controlled with the apparatus «Expert-001».

To choose the optimal quantity of coagulant, the sample weight of 0.5000 g has been put into conical vessels, containing clay and coagulant in the quantity of 1 mg, 0.5 mg, 0.25 mg, 0.125 mg (calculated as aluminium or ferrum quantity) so that a ratio of coagulant mass by the mass of water comprised 1:500; 1:1000; 1:2000; 1:4000. Then 50 ml of the model solution has been introduced and shaken for 3 hours. After that the residual content of chromium ions (III), ferrum (III) and aluminium have been determined in the model solution.

The method of aluminium determination is based on the quantitative extraction of hydroxiquinolate aluminium by chloroform in weak acid medium (pH 4.35 – 4.5). Chloroform layer turn into yellow and green colour. Ferrum ions (III) determined photometrically according to the reaction with sulfosalicylic acid.

The dependences of settling time of bentonite clay suspension on the quantity of the added coagulant have been studied according to standard technique [7]. Equivalent researches have been carried out on the model solutions of chromates with their preliminary reducing to the trivalent chromium.

3. Results and discussion

The sorption values of the chromium ions (III) on the bentonite clay with concentration of metal ions within the range 0.024–0.481 mg/ml presented on the figure 1.
The cutoff rating decreased from 96% to 38% with the increasing of concentration of chromium ions (III) (table 1).

However, with the original concentration of chromium ions in the solution being 0.258 mg/ml, the degree of treatment rises which is expressed in the influence curve of the value of the sorption of the original concentration of chromium ions in the form of a bend (figure 1).

The residual concentration of chromium ions (III) in the solution after the treatment in all the cases exceeds maximum permissible concentration (MPC). Maximum permissible concentration on chromium ions for water bodies of drinking, household / cultural and social water use comprises 0.5 mg/l.

Clay activation has allowed improving its sorption capacity a little due by the substitution of calcium and magnesium ions by sodium ions in the clay exchange complex. Sodium ions incline better to ion exchange [8, 9]. As a result the concentration of chromium ions in the solution after the treatment has not decreased significantly (table 2).

While studying the influence of pH model solution within the range from 1 to 9 on the value of sorption of chromium ions (III) by bentonite clay it has been stated that in the system «solution of metal salts – clay» pH values change in the range of 8.2 – 9.8.

| Concentration of chromium ions (III) before treatment, mg/ml | Residual concentration of chromium ions (III) after treatment, mg/ml | Sorption, mg/g | Degree of treatment, % |
|---------------------------------------------------------------|------------------------------------------------------------------|----------------|------------------------|
| 0.024                                                         | 0.0009 ± 0.0001                                                  | 2.31 ± 0.02    | 96                     |
| 0.048                                                         | 0.011 ± 0.002                                                   | 3.6 ± 0.2      | 77                     |
| 0.103                                                         | 0.040 ± 0.001                                                  | 6.2 ± 0.1      | 61                     |
| 0.146                                                         | 0.080 ± 0.006                                                  | 6.6 ± 0.4      | 45                     |
| 0.211                                                         | 0.12 ± 0.01                                                   | 9.0 ± 0.1      | 43                     |
| 0.258                                                         | 0.099 ± 0.005                                                  | 15.8 ± 0.5     | 62                     |
| 0.481                                                         | 0.30 ± 0.02                                                   | 18.5 ± 0.7     | 38                     |

**Figure 1.** Dependence of sorption value on original concentration of Cr (III) in model solution.

**Table 1.** Results of treatment of model solution for chromium ions (III) by non-activated (native) bentonite clay of Zyryanskoe deposit.
Table 2. Results of treatment of model solution for chromium ions by activated bentonite clay of Zyryanskoe deposit.

| Concentration of chromium ions (III) before treatment, mg/ml | Residual concentration of chromium ions (III) after treatment, mg/ml | Sorption, mg/g | Degree of treatment, % |
|---------------------------------------------------------------|------------------------------------------------------------------|-----------------|------------------------|
| 0.103                                                         | 0.032 ± 0.002                                                   | 6.53           | 69                     |
| 0.211                                                         | 0.112 ± 0.007                                                   | 9.90           | 47                     |

Table 3. Results of treatment of model solution for chromium ions (III) by composition of coagulant (Al$_2$(SO$_4$)$_3$) and clay.

| Mass ratio of ions Al to clay | Content of chromium ions (III) in solution, mg/ml | Content of aluminium ions in solution, mg/ml | pH of solution | Sorption of chromium ions (III), mg/g | Degree of treatment for chromium ions (III), % |
|------------------------------|-----------------------------------------------|---------------------------------------------|----------------|---------------------------------------|-----------------------------------------------|
|                              | before treatment                              | after treatment                             | before treatment | after treatment                       |                                               |
| 1:500                        | 0.12                                          | 0.103                                       | 0.018 ± 0.001   | 200                                   | 5.0 ± 0.1                                    | 4.0                                           | 8.45                                         | 82                                           |
| 1:1000                       | 0.10                                          | 0.13                                        | 0.013 ± 0.001   | 100                                   | 0.8 ± 0.1                                    | 4.2                                           | 8.98                                         | 88                                           |
| 1:2000                       | 0.08                                          | 0.11                                        | 0.011 ± 0.001   | 50                                    | 0.46 ± 0.07                                  | 4.4                                           | 9.11                                         | 89                                           |
| 1:4000                       | 0.06                                          | 0.08                                        | 0.008 ± 0.001   | 20                                    | 0.26 ± 0.07                                  | 4.6                                           | 9.43                                         | 92                                           |

While increasing pH, the value of sorption has risen from 0.8 mg/g (pH=1) to 16 mg/g (pH=10) in case of the original concentration of chromium ions being 0.258 mg/ml. Experimental data about sorption isotherms (pH 8.2 – 9.8) indicate that the main limitative process is the formation of hydroxocomplexes of metal ions Me(OH)$^+$ on the surface of the bentonite clay.

Figure 2. Influence of sorbent composite on degree of treatment of model solution for chromium ions (III): initial concentration of Cr (III) (hatched column), concentration of Cr (III) after treatment (unshaded column).
At the same time, when pH values are more than 9, the formation of slow-soluble complexes $\text{Me(OH)}_2$ starts, which is also proved in the research [8]. It is also known that adsorption capacity of montmorillonite in relation to positively charged hydroxocomplexes of heavy metals is higher than in relation to ions [9, 10].

As a possible coagulant we considered aluminium sulphate. Mass ratio of aluminium ions to clay has been changed from 1:500 to 1:4000. In the solution pH has been controlled. The received data are presented in table 3 and figure 2.

The degree of the treatment increases from 82 to 92% while decreasing the quantity of aluminium sulphate, introduced into the solutions. This may be connected with coagulant dilution and salt hydrolysis intensification on cation which means that most part of aluminium salt may take part in the treatment process. For the first two systems maximum permissible concentration is in excess (maximum permissible concentration of aluminium for water bodies of drinking, household / cultural and social water use comprises 0.2 mg/l), at mass ratio of aluminium to clay equal to 1:2000 and 1:4000 maximum permissible concentration is not in excess. Thus, the conditions of chromium solution treatment by coagulants had been chosen.

The advantage of using aluminium sulphate is in the fact that sewage treatment plants already use aluminium salts as a coagulant and the introduction of the additional quantity of clay to the available reagent will make the task of the treatment easier.

While using ferrous chloride as a coagulant, the treatment of the solutions by coagulant and bentonite clay has been carried out at different ratio of ferrum ions (III) and clay. The results of the experiment of using combined method are presented in table 4 and in figure 3. While introducing ferrous chloride (III) in different mass ratio the degree of the treatment increases from 83 % (ratio 1:500) to 94 % (1:4000). If to use less quantity of coagulant, hydrolysis of ferrous chloride (III) intensifies and as a result the degree of solution treatment increases. It is necessary to emphasize that ferrum has not been detected by photometric method, (maximum permissible concentration of Fe) for household and drinking water use is equal to 0.3 mg/l.

**Table 4.** Results of treatment of model solution for chromium ions (III) by composition of coagulant $(\text{FeCl}_3)$ and clay.

| Mass ratio of ions Fe(III) to clay | Content of ions Cr(III) in solution, mg/ml | Content of ions Fe(III) in solution, mg/ml | pH of solution | Sorption of ions Cr(III) mg/g | Degree of treatment for ions Cr(III) % |
|-----------------------------------|-------------------------------------------|------------------------------------------|---------------|------------------------------|--------------------------------------|
|                                   | before treatment                          | after treatment                          | before treatment | after treatment | before treatment | after treatment | before treatment | after treatment | before treatment | after treatment |
| 1:500                             | 0.018 ± 0.002                             | 200                                      | 0              | 3.5             | 8.5               | 83            |
| 1:1000                            | 0.01 ± 0.001                              | 100                                      | 0              | 4.2             | 9.2               | 90            |
| 1:2000                            | 0.009 ± 0.002                             | 50                                       | 0              | 4.7             | 9.4               | 92            |
| 1:4000                            | 0.007 ± 0.001                             | 20                                       | 0              | 4.9             | 9.6               | 94            |

The carried out research has demonstrated that the application of the combined method with the use of ferrum salts (III) and aluminium may be recommended in the complex with the reagent method of treatment for chromium ions (III), as well as an independent method of treatment at comparatively low concentrations of chromium ions (III) in sewage. It is known that after the use of reagent method of treatment and settling of Cr(OH)$_3$, sewage having pH 8–10, must be neutralized. While using two-step treatment there is no need for neutralization as the introduction of the compound of the clay and metal salt leads to the decrease of pH value to desired index. So, maximum treatment for chromium ions (III) is achieved with the use of bentonite clays and ferrous chloride (III) as a coagulant in the mass ratio of...
it to the clay being 1:4000 (degree of treatment is 94%). The least degree of treatment has been fixed while using the combination of aluminium sulphate and clay.

![Figure 3](image_url)

**Figure 3.** Influence of sorbent composite on degree of treatment of model solution for chromium ions (III): initial concentration of Cr(III) (*hatched column*), concentration of Cr (III) after treatment (*unshaded column*).

### 4. Conclusions

The influence curve has been constructed showing the dependence of the value of the sorption of chromium ions (III) on native bentonite clay on the original concentration of ions in the model solution. Maximum degree of the treatment is 96.25% (original concentration is 0.024 mg/ml); minimum degree is 37.63% (original concentration is 0.481 mg/ml). All the values of residual concentration exceed maximum permissible concentration according to chromium ions. Clay activation has slightly influenced the degree of solution treatment for chromium ions (III).

The use of the combined method with the use of bentonite clay as a sorbent and ferrous chloride (III) or aluminium sulphate as coagulants ensures the degree of model solution treatment for trivalent chromium to 92% and 94% (for aluminium and ferrum salts). For the same concentrations of the original solution of the salt (0.103 mg/ml) the clay gives results that are worse by 1.5 times.

Ferrum ions after the treatment are not detected in the solution, while introducing aluminium salt in the solution after the treatment by studied methods the residual concentrations from 5 to 0.26 mg/ml of this ion are fixed, in some cases they exceed maximum permissible concentration Al.

Optimal mass ratio of metal coagulant to clay in both cases is 1:4000.

The most effective method of solution treatment for chromium ions (III) is a combined one with the use of bentonite clay and ferrous chloride (III) (mass ratio of ferrum ions (III) to clay is 1:4000).

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