Study of the adsorption of heavy metal ions from binary and multicomponent solutions by ceramic chips

I V Zykova and V A Isakov
Yaroslav-the-Wise Novgorod State University, 41, ul. B. St. Petersburgskaya, Veliky Novgorod, Russian Federation
E-mail: Irina.Zikova@novsu.ru

Abstract. The adsorption of heavy metal ions from binary solutions was studied using Co (II) as an example in the concentration range from 1 to 50 mg/dm3 and the adsorption of heavy metal ions from multicomponent solutions using Co (II), Ni (II) and Cu (II) by fractions of ceramic chips of 0.5-1.0 mm and 1.0-2.0 mm. It was established that the value of the ultimate saturation of Co (II) ions with ceramic chips depends on the pH value. The maximum value of the ultimate saturation for Co (II) ions is reached at pH = 9, the smallest – at pH = 3. An increase in temperature from 273 to 353 K leads to an increase in the ultimate saturation for Co (II) ions. Experimental data on the sorption of metal ions from multicomponent solutions show that the rate of achievement of the ultimate saturation of the sorbent in a metal depends on the value of the ionic radius. The ultimate saturation limit for a metal at the same concentration of metals and the presence of other metals is greatest for Cu (II), the smallest for Co (II). The results of the study indicate the high efficiency of ceramic chips as a sorbent of heavy metal ions from wastewater of various industries, which indicates the possibility of practical use of ceramic chips for wastewater treatment from heavy metals, especially taking into account the availability and the possibility of using it without regeneration with recycling in production pigments.

1. Introduction
Waste water treatment of various industries from impurities of heavy metals still remains relevant. Among the possible adsorbent materials, the battle of ceramic production is of interest – an inexpensive and affordable material that is resistant to temperature, does not require regeneration, since it has the ability to alloy with metals at a temperature of 1100-2000 °C and can be used in the manufacture of ceramics.

Ceramic chips are aluminosilicate containing a mixture of oxides of aluminum, silicon, calcium, potassium, etc. To date, there is no consensus on the specific adsorption of hydrolyzable cations on isomorphic oxides. Only a single approach has been taken in describing adsorption as a concentration of metal in the surface layer due to the implementation of non-Coulomb forces. We can distinguish the following ideas about adsorption on “oxide” adsorbents [1]:

1. adsorption-hydrolysis models and the concept of ion-solvate interactions, taking into account the role of solvation shells of ions as a barrier in the interaction of ions with active centers of the surface;
2. coordination theories that treat adsorption as a chemical process of ligand replacement in the coordination sphere of a “bulk complex” in a solution to a surface ligand.

The close relationship between the adsorption on the surface of oxides and the hydrolysis of metal salts in the liquid phase was established experimentally, the adsorption proceeds all the more, the higher the degree of hydrolysis, and only hydrolyzed forms of ions can change the charge on the surface of the
sorbent. When considering the adsorption of cations, it is necessary to take into account the possibility of not only surface complexation, but also “surface” precipitation, which is possible at pH values of solutions corresponding to the precipitation of hydroxides into the solid phase. In this case, a new hydroxide surface forms on the adsorbent – the formation of the so-called new surface phase, the composition of which can continuously change due to the adsorption of new layers of hydroxide precipitate.

To date, a large number of studies devoted to the problem of the specific adsorption of metal cations on oxides have been carried out, a number of patterns have been identified that make it possible to predict the behavior of oxide systems – hydrolyzable cation in a wide range of conditions [2-5]. Based on the analyzed data, it was suggested that ceramic chips are capable of absorbing ions of metals such as cobalt, copper, chromium, etc. from wastewaters.

2. Materials and methods
The adsorption of Co (II) ions was studied on 0.5-1.0 mm and 1.0-2.0 mm fractions of ceramic chips at temperatures of 279-353 K, pH of solutions in the range from 3 to 9, and Co (II) ion concentrations of 1-50 mg/dm$^3$. The ratio of the solution of Co (II) ions to ceramic chips was 100:1. The degree of achievement of the ultimate saturation of the adsorbent was judged by the change in the concentration of metal in the aqueous phase in time. The analysis of Co (II) ion concentrations was carried out by atomic absorption spectroscopy. To achieve the ultimate saturation of the adsorbent in the absorbed component, the system was kept for up to 96 hours with constant stirring.

3. Results and discussion
According to the experimental data, 24 hours are generally sufficient to establish a constant concentration of metal in the aqueous phase. The basic amount of metal sorbed in 1-4 hours. The error of determination was ≈ 5% rel.

The degree of achievement of the ultimate saturation of the sorbent for cobalt ions under the studied conditions most rapidly occurred at pH = 3 (figure 1), however, the value of the ultimate saturation at this pH was the lowest, ceteris paribus (figure 2). On the surface of aluminosilicate there are two types of hydroxyl groups – isolated and bound in pairs by hydrogen bonds. Isolated groups interact first. As adsorption and partial compensation of the charge on the surface, hydrogen bonds break and new centers appear that contribute to an increase of the ultimate saturation.

In aqueous solutions, depending on the pH value, Co (II) ions are in different forms (table 1).

According to the experimental data, the highest value of the ultimate saturation is characteristic for pH = 9, the smallest for pH = 3. The data obtained confirm the mechanism of interaction of the complex ion: first, with the surface groups of OH aluminosilicates, as a positive charge accumulates on the surface, hydrogen bonds break and new centers form, new complex ions are adsorbed and H$^+$ ions are released into the solution (the pH of the solution decreases with time from 9 to 8.7-8.4).

![Figure 1](image1.jpg)  
**Figure 1.** Change in the degree of achievement of the ultimate saturation of the sorbent from the 

![Figure 2](image2.jpg)  
**Figure 2.** The dependence of the ultimate saturation of the sorbent on the concentration of
duration of phase contact. The concentration of cobalt ions in the initial solution is 50 mg/dm³, T = 293 K. The sorbent fraction is 0.5-1.0 mm. pH of the aqueous phase: 1 – 9.2; 2 – 6.1; 3 – 3.0.

Table 1. The molar fractions of the complex ions of Co (II) in solution at various pH values.

| pH value | Cation shape | Complex share |
|----------|--------------|---------------|
| 3.0      | [Co(H₂O)₆]²⁺ | 0.932         |
|          | [CoOH(H₂O)₃]⁺ | 3.7·10⁻²      |
|          | [Co(OH)₂(H₂O)₄]⁻ | 5.8·10⁻⁴     |
|          | [Co(OH)₃(H₂O)₃]⁻ | 2.9·10⁻²     |
| 6.0      | [Co(H₂O)₆]²⁺ | 1.5·10⁻¹⁵     |
|          | [CoOH(H₂O)₃]⁺ | 7.9·10⁻⁷      |
|          | [Co(OH)₂(H₂O)₄]⁻ | 1.5·10⁻⁵     |
|          | [Co(OH)₃(H₂O)₃]⁻ | 0.999      |
| 9.0      | [Co(NH₃)₆]²⁺ | 1.000         |
|          | [Co(NH₃)₅(H₂O)]²⁺ | 1.6·10⁻¹⁰   |

In an acidic environment, Co (II) ions are in the form of an aquacomplex. In a slightly acidic environment, Co (II) ions are in the form of an anionic complex.

An increase in temperature leads to the displacement of water molecules from the surface of the sorbent and, accordingly, the access of various forms of metal is facilitated. In addition, an increase in temperature increases the degree of hydrolysis and, thereby, the value of the ultimate saturation of the sorbent increases (figure 3). It is also impossible to exclude the mechanism of chemisorption of metals by ceramic chips. The measured values of the electrical conductivity of the solutions of Co (II) ions, which are at the level of 10⁻¹ cm/m, indicate the presence in the solutions of hydrolyzed forms of the studied metal. The values of redox potentials (160–300 mV) do not change during sorption.

The experimental data confirm that at pH = 9.0 and T = 353 K the highest value of the ultimate saturation is observed, and in some cases the degree of achievement of the ultimate saturation of the sorbent approaches 100%.

Figure 3. The effect of temperature on the value of the ultimate saturation of the sorbent at pH = 9. The particle size is 0.5-1.0 mm. Co (II) ion concentration in the initial solution, mg/dm³: 1 – 10; 2 – 20; 3 – 50.
Experimental data on the sorption of metal ions from multicomponent solutions show that the rate of reaching the ultimate saturation of the sorbent in a metal depends on the ion radius in the first hours of contact (figure 4), and after 16-24 hours it becomes almost the same for all metals. Probably, the ionic radius (Table 2) is important because, at the initial stage, external diffusion is the limiting factor of sorption.

For nickel ions (the smallest values of ionic radii) after 4 hours, the degree of achievement of the ultimate saturation exceeds 70%, and for larger copper ions only 35%.

![Figure 4. Dependence of the degree of achievement of the ultimate saturation of the sorbent for metals on the duration of phase contact at 353 K, pH = 6, grain diameter 0.5-1 mm; metal concentration in the initial solution, mg/dm³: Co (II) – 10, Ni (II) – 20, Cu (II) – 50. 1 – Ni (II); 2 – Co (II); 3 – Cu (II).](image)

Table 2. The values of the radii of the studied ions [6].

| Ion     | Ionic radius, A without hydration shell | Radius of hydrated aqua complex, A |
|---------|----------------------------------------|----------------------------------|
| Co (II) | 0.72                                   | 8.0                              |
| Ni (II) | 0.69                                   | 7.4                              |
| Cu (II) | 0.73                                   | 8.3                              |

The ultimate saturation value for metal at the same concentration of metals and the presence of other metals is greatest for Cu (II) ions, the smallest for Co (II) ions (table 3). It is known that specific adsorption proceeds the better, the higher the degree of hydrolysis [pK(Cu(OH)₂)=13.2; pK(Ni(OH)₂)=8.55 and pK(Co(OH)₂)=9.2] [7].

Table 3. The values of the ultimate saturation of ceramic chips for metals upon adsorption from multicomponent systems at 353 K and pH = 6.

| Grain diameter, mm | The concentration of metals in the initial solution, C₀, mg/dm³ | and the value of the ultimate saturation, a, mg / g |
|-------------------|---------------------------------------------------------------|-----------------------------------------------|
|                   | Cobalt            | Nickel           | Copper          |
|                   | C₀    | a    | C₀    | a    | C₀    | a    |
| 0.5-1.0            |       |      |       |      |       |      |
| 5                  | 0.21  | 0.47 | 25    | 2.40 |
| 10                 | 0.43  | 1.45 | 50    | 3.50 |
| 15                 | 0.47  | 2.36 | 75    | 3.97 |
| 20                 | 0.70  | 3.60 | 100   | 4.16 |
| 1-2                | 0.32  | 0.47 | 25    | 2.43 |
| Concentration (mg/dm³) | Saturation (mg/g) | Concentration (mg/dm³) | Saturation (mg/g) |
|------------------------|------------------|------------------------|-------------------|
| 10                     | 0.36             | 40                     | 2.21              |
| 15                     | 0.46             | 50                     | 3.49              |
| 20                     | 0.60             | 80                     | 4.09              |
|                        |                  | 100                    | 4.16              |

The total value of the ultimate saturation of the sorbent for metals depends on their concentration in the initial solution and on the grain diameter (figure 5).

![Figure 5](image_url)

**Figure 5.** The effect of the concentration of metals in the initial solution on the ultimate saturation of the sorbent at 353 K, pH = 6, grain diameter 0.5-1 mm: 1 – Co (II); 2 – Ni (II); 3 – Cu (II).

### 4. Conclusion

The results of the study indicate the high efficiency of ceramic chips as a sorbent of heavy metal ions from wastewater of various industries, which indicates the possibility of practical use of ceramic chips for wastewater treatment from heavy metals, especially taking into account the availability and the possibility of using it without regeneration with recycling in production pigments.

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