INTRODUCTION

The level of heavy metal pollution has risen sharply over the past 50 years as a result of the exponential increase in the use of heavy metals in industrial processes. They formed in the process of human life and have become one of the most dangerous hydrosphere pollutants [Mushtaq et al. 2020; Jaiswal et al. 2018]. The metals that infiltrate into water bodies can concentrate in organisms and form toxic compounds while migrating in the ecosystem along food chains [Pawan 2012; Li et al. 2020; Zhou et al. 2020].

Heavy metals in the periodic table of elements are one of the large groups with an atomic mass of more than 50 atomic units. This group includes more than 40 metals, such as copper, zinc, cadmium, lead, chromium, nickel, cobalt, iron and others [Chen 2012; Mance 1987].

The sources of metals entering the aquatic environment are non-ferrous metallurgy, paint and varnish industry, machine-building industry, galvanic production, production of batteries [Sonone et al. 2020; Dolina 2008]. The chemical composition and concentration of effluents of these industries are pretty diverse in quantitative and qualitative characteristics, including, for example, such areas as chromium plating, copper plating, galvanizing etc. Urban wastewater treatment plants are sometimes insufficient to treat such wastewater, so they should be treated directly at enterprises, introducing technologies into production processes. Physicochemical, chemical and biological methods can carry out wastewater treatment from heavy metal ions. One of the promising methods is ion exchange. Its advantages are: cleaning to the water quality criteria, reusing water after purification, treating mixed effluents, selective releasing substances from water, reusing ion exchange resins after their regeneration.

In order to predict the efficiency of wastewater treatment from metal ions on an industrial scale, mathematical models, such as Langmuir, Henry isotherms, Thomas, Freundlich models, etc., are used increasingly often.

For the mathematical description of the initial sorption curves under dynamic conditions (dependence between the concentration of ions in the eluate and the sorption time (or the missed volume of the solution)) at a given constant filtration rate of the solution through a column with cation exchange resin, the Thomas model [Thomas 1944; Hanbali et
al. 2014; Xu et al. 2013; Nwabanne et al. 2012] is used most often. It is one of the most reliable models, characterized by simplicity, ease of use and it well describes the physico-chemical processes.

**MATERIAL AND METHODS**

Model solutions of metal sulfates: copper, zinc, cadmium and nickel were used to study the sorption processes. The metal concentrations were 10 meq/dm³, 20 meq/dm³ and 50 meq/dm³. The ion exchanger with a volume of 20 cm³ was placed in a glass column with a diameter of 2 cm [Koliehova et al. 2019]. The solution consumption of the sorption process ranged from 10 cm³/min to 15 cm³/min. In the sorption process, the samples with a volume of 100 cm³ to 500 cm³ were taken. The model solution with metal was passed through the ion exchange column filled with a cation exchange resin KU-2-8. The concentration of heavy metal ions, acidity, alkalinity and pH were monitored in the selected samples.

TEDC (the total exchange dynamic capacitance) of the metals sorbed on the cation exchange resin was determined by the formula, meq/dm³:

\[
TEDC = \sum_{i=1}^{n} \left( \frac{C_{init} - C_i}{V_i} \right) \cdot V_i
\]  

(1)

where: \(C_{init}\) is the initial metal ions concentration in the solution, meq/dm³; \(V_i\) is the volume of the sorbent mass, g (for this case 7.4 g); \(C_i\) is the metal ions concentration in the \(i\)-th sample, meq/dm³; \(V_s\) is the volume of sample, cm³; \(n\) is the number of samples taken.

The Thomas model was used for mathematical modeling of sorption processes. Thomas model is described by the dependence:

\[
\frac{C}{C_0} = \frac{1}{1 + \exp \left( K \left( \frac{Q M}{v} - C_0 t \right) \right)}
\]  

(2)

where: \(K\) is the constant of the Thomas model, dm³/mg·h; \(Q\) is the maximum metal concentration in the solid phase, mg/g; \(v\) is the volumetric rate of solution filtration through the column (the solution consumption through the column), dm³/h; \(M\) is the sorbent mass, g; \(t\) is time, h; \(C\) is the metal concentration in the solution, meq/dm³; \(C_0\) is the initial metal concentration, meq/dm³.

The filtration time was calculated when measuring the volumes of filtered solutions and a constant filtration rate by the formula:

\[
t = \frac{V_p}{v}
\]  

(3)

where: \(V_p\) is the volume of the filtered solution.

The application of the Thomas model, which describes the dynamic sorption curves, is reduced to determining the constant of the Thomas model (Table 1) by experimental results. The kinetic coefficient and the sorption column capacity can be determined by the linear dependence of \(ln(C/C_0 - 1)\) on \(1/(V_p/v)\). The dependence can be represented as:

\[
ln \left( \frac{C}{C_0} - 1 \right) = K \left[ \frac{Q M}{v} - C_0 \left( \frac{V_p}{v} \right) \right]
\]  

(4)

\[
K = \frac{ln \left( \frac{C_0}{C} - 1 \right)}{\left[ \frac{Q M}{v} - C_0 \left( \frac{V_p}{v} \right) \right]}
\]  

(5)

The mass was calculated for 20 cm³ of the cation exchange resin KU-2-8 based on the specific volume of 2.7 cm³/g: \(M = 7.4\) g. In the case of the sorption of copper ions under dynamic conditions, the kinetic coefficient (the constant of the Thomas model) was equal to 0.00976 dm³/mg·h (Table 1). The maximum concentration of the metal at the selected concentrations of \(C_0\) was determined by TEDC:

\[
Q = E_t \frac{V_i N}{1000 \cdot M}
\]  

(6)

where: \(E_t\) is TEDC, meq/dm³; \(N\) is the equivalent metal weight, for Cu²⁺ 31.77 mg; \(M\) is the resin mass, g (for this case 7.4 g); \(V_i\) is the resin volume, cm³.

For example, based on equation (2) for copper ions, the Thomas model can be written as:

\[
C = \frac{C_0}{1 + \exp \left( 0.00976 \left( \frac{Q M}{v} - C_0 \left( \frac{V_p}{v} \right) \right) \right)}
\]  

(7)

**RESULTS AND DISCUSSION**

Figures 1–3 show the initial sorption curves of copper, zinc, nickel and cadmium ions on the KU-2-8 cation exchange resin at initial metal concentrations of 10 meq/dm³, 20 meq/dm³ and
The choice of these concentrations was due to the fact that with a cation exchange resin capacity of approximately 2000 meq/dm³, even with the cation exchange resin volume of 20 cm³, the volume of solutions filtered through the cation exchange resin reaches 1–6 dm³. The time to construct each curve will be quite significant at the solution consumption of 0.9 dm³ per hour at selected concentrations. If the heavy metal concentrations are 1–2 orders of magnitude lower, the research time will stretch for months and years. On the other hand, the mathematical processing of the results will allow predicting the efficiency of the resin and the extraction of heavy metal ions at much lower concentrations.

As shown in Figure 1, the total exchange dynamic capacity (TEDC) of the cation exchange resin in the H⁺-form on the metal cations reached approximately 2000 meq/dm³. The capacity to breakdown reached approximately 1000 meq/dm³. The solution’s initial concentration of copper, zinc, nickel, and cadmium reached 10 meq/dm³.

The TEDC of cation exchange resin reached approximately 2100 meq/dm³ and the dynamic exchange capacity before breakdown was 1100 meq/dm³ at the metal concentration of 20 meq/dm³ (Figure 2). The TEDC of cation exchange resin amounted to 2090 meq/dm³ and the dynamic exchange capacity before breakdown – 1050 meq/dm³ at the initial concentration of metals 50 meq/dm³ (Figure 3).

In this case, the ion exchange processes took place in equivalent quantities and the extraction efficiency of heavy metal ions in the selected ranges of initial concentrations varied little. The main indicators – the TEDC of the cation exchange resin and the exchange dynamic capacity before breakdown (EDCₙ) that does not depend on the initial concentration. The breakdown concentration, in this case, was taken as the concentration of metals 1 mg/dm³.

The ion exchange equivalence was also indicated by the data on the change in the acidity of solutions during the sorption of metal ions (Figs. 1–3). In general, the initial solution acidity when passing through the cation exchange resin in the acid form is proportional to the amount of sorbed metals, regardless of the initial concentration of metal ions. The higher the initial concentration of the solution of copper, zinc, nickel and cadmium ions, the higher the acidity of the filtered solution, the lower the pH of these solutions. At the concentration of heavy metal sulfate of 10 meq/dm³ (Fig. 1), the acidity varied in the range of 10–0.1 meq/dm³, and the pH increased from 2.22 to 4.08. At the concentration of metal solutions of 20 meq/dm³ (Fig. 2), the acidity varied from 20 meq/dm³ to 0.01 meq/dm³, and the pH increased from 1.60 to 4.55; at 50 meq/dm³ (Fig. 3), the acidity

![Figure 1](image.png)

**Figure 1.** The average values of the concentration of copper, zinc, nickel and cadmium (1), acidity (3), pH (4) from the volume of 0.01 n solutions of metal sulfates passed through the cation exchange resin KU-2-8 in the H⁺ - form (Vᵢ = 20 cm³). Curve (2) was calculated according to the Thomas model.

| Form of cation exchange resin | Metal | Cu  | Zn  | Cd  | Ni  |
|------------------------------|-------|-----|-----|-----|-----|
| H⁺                           |       | 0.00976 | 0.0130 | 0.0050 | 0.01218 |

| Form of cation exchange resin | Metal | Cu  | Zn  | Cd  | Ni  |
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| H⁺                           |       | 0.00976 | 0.0130 | 0.0050 | 0.01218 |

Table 1. The value of the constant K for the Thomas model of the initial curves of sorption of copper, zinc, cadmium and nickel on the cation exchange resin KU-2-8.
decreased from 50 meq/dm$^3$ to 0.05 meq/dm$^3$, the pH increased from 1.57 to 4.5.

The theoretically obtained curves of the Thomas model (Fig. 1–3) coincide with the experimental curves of the sorption of heavy metals.

**CONCLUSIONS**

The sorption processes of copper, zinc, cadmium and nickel ions on the KU-2-8 cation exchange resin in the acid form at different concentrations of heavy metals were studied.

The mathematical Thomas model for the initial sorption curves of metals on the cation exchange resin KU-2–8 in the H$^+$-form under dynamic conditions at the constant filtration rate of the solution through the column was calculated. The theoretically calculated curves coincide with the curves obtained experimentally in approximately 95%. This mathematical model can be used to predict the efficiency of wastewater treatment from heavy metal ions.

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