Mathematical Description of the Process of Adsorption of Metal Ions by Modified Zeolites in Adsorbers with a Fixed Adsorbent Layer

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Abstract. The solution of the problem of mathematical description of the processes occurring directly in the adsorber apparatus with a fixed layer of the solid phase and comparisons of the results with known classical representations is presented. The following characteristics were calculated: equivalent particle diameter of the sorbent, permissible fictitious velocity of wastewater, adsorber diameter, hydraulic resistance, Reynolds criterion, Prandtl test, Nusselt mass transfer criterion, external and internal mass transfer coefficients, mass transfer coefficients (including taking into account longitudinal mixing), general number of transfer units. The calculation was made taking into account that in the adsorber under consideration the fixed layers of adsorbent are located on cassettes, the distance between which is 0.01 m, which affects some characteristics of the adsorber apparatus with a fixed layer of a solid phase (modified zeolite).

1. Introduction

In practice, the treatment of industrial wastewater from metallurgy, engineering, railway transport from heavy metal compounds, periodic adsorption units with a fixed adsorbent layer are used [1-3]. The qualitative characteristics of wastewater discharged from various industries vary significantly. Therefore, it is necessary in each case to solve the technological problem of choosing the most effective sorption materials that are selective with respect to the extraction of toxic components (Ni²⁺, Zn²⁺, Cu²⁺) from wastewater. Substantiation of the choice of one or another sorption material is possible only on the basis of investigations to create new sorbents and a comparative analysis of their characteristics with known sorbents tested in wastewater treatment processes [4-8].

As a raw material for creating new sorbents effective in the recovery of heavy metals (Ni²⁺, Zn²⁺, Cu²⁺) from industrial wastewater, we investigated zeolite-containing tuffs of the Holinsky deposit in East Transbaikalia [9,10]. Modifiers of natural minerals were high organosilicon compounds (hexamethyldisilazane [(CH₃)₃Si-]₂NH and tetraethoxysilane (C₂H₅O)₄Si) [11], as well as a sulfur polymer obtained from epichlorohydrin wastes, the main component of which is 1,2,3-trichloropropane [12].
The results of investigations confirmed by patents [13, 14] showed that when using these modifiers, the degree of extraction of heavy metal ions Ni\textsuperscript{2+}, Zn\textsuperscript{2+}, Cu\textsuperscript{2+} from industrial wastewater increases significantly. When setting up and conducting complex experimental investigations with the participation of new sorbents, it seemed appropriate to solve the problem of mathematical description of processes occurring directly in adsorbers with a fixed layer of a solid phase and to compare the results with known classical ideas in the works of Yu. I. Dytnersky. and N.I. Gelperin [15,16].

2. Experimental investigations. Results and discussion

In this case, in the technological chain of the scheme for treating industrial wastewater from heavy metal ions, there are two adsorbers with a fixed layer of a solid phase. In the first of them, the adsorption stage occurs, and in the second, the sorbent is regenerated. Calculation of the adsorber was carried out for a wastewater flow rate of 300 m\textsuperscript{3}/day. This value is accepted as the maximum possible load on the local treatment facilities of railway transport enterprises [17].

If transverse non-uniformity is not taken into account, then the concentrations inside the adsorber will depend on two variables: time \( \tau \) and longitudinal coordinate \( z \), which originates from the entrance of the separated mixture into the adsorbent layer. The differential equation of material balance, which characterizes this dependence, taking into account the absence of longitudinal mixing, has the following form:

\[
\frac{\partial c}{\partial \tau} + \rho_{bulk} \frac{\partial X}{\partial \tau} + \omega \cdot \frac{\partial c}{\partial z} = 0 ;
\]

where \( \varepsilon \) is the porosity of the layer; \( \rho_{bulk} \) is the bulk density of the adsorbent; \( \omega \) is the fictitious speed of a media moving through a layer; \( c \) - concentration of adsorbed substance in it, kg / m\textsuperscript{3}; \( X \) is the concentration of the extracted component in the adsorbent (kg/kg of pure adsorbent).

The total material balance of the adsorption process for the entire time period of adsorption-desorption is determined from the following expression:

\[
\omega \cdot c_u \cdot \theta - \omega \cdot \int_{0}^{\mu} c_{eq} d\tau = \rho_{bulk} \cdot \int_{0}^{\mu} (X_{\tau=0} - X_{H})dz + \varepsilon \cdot \int_{0}^{\mu} (c_{eq} - c_{eq0})dz ;
\]

where \( C_u \) is the initial concentration of metal ions in the media passing through the layer; \( X_{H} \) is the initial concentration of metal ions in the adsorbent; \( \theta \) is the time interval of the stages of adsorption-desorption; \( H \) is the height of the adsorbent layer.

The first part of equation (2) characterizes the difference between the amounts of adsorbed substance that entered into adsorber with incoming wastewater and adsorbed substance that left the adsorber together with this media during the given technological process. This difference is considered per unit cross-sectional area. The left integral of the second part determines the increase in the amount of adsorptive in the adsorbent (for desorption, it has a negative value). The second integral is for the liquid phase inside the layer (per unit of cross section) [15]. In some cases, equation (2) can be simplified taking into account the fact that only the first terms of the right and left sides of the equation are of essential importance for adsorption, and in the case of desorption, the second term is of the left side; from the right side is the first term of the equation. In order to calculate the operation characteristics of the adsorber as a mass transfer apparatus, it is necessary to determine the concentration profiles (dependences of \( c \) on \( z \) and \( X \) on \( z \) for a given \( \tau \)) and output curves (dependences of \( c \) on time for a given \( \tau \)).

If the adsorption process is described by a convex equilibrium line, then the equation of material balance takes the following form:

\[
c = c^e(X_H), X = X_H \quad \text{if} \quad z > z_1 ;
\]

\[
c = c^e_H, X = X^e(c^e_H) \quad \text{if} \quad z < z_1 ;
\]

where \( z_1 \) is the minimum height of the adsorbent layer:

\[
z_1 = \frac{w \cdot \tau \cdot [c^e_H - c^e(X_H)]}{\varepsilon \cdot [c^e_H - c^e(X_H) + \rho_{bulk} \cdot (X^e(c^e_H) - X_H)]} ;
\]

2
Since \( c(X_n) = 0 \), then
\[
z_i = \frac{w \cdot \tau \cdot C_H}{\varepsilon \cdot C_H + \rho_{bulk} \cdot X^* (c_H)} ;
\]
(5)

In the field of \( z_1 < z \) the phase concentrations are determined by the relations:
\[
z \cdot (\varepsilon + \rho_{bulk} \cdot \frac{dX^*}{dc}) = w \cdot \tau ; \quad X = X^* (c) ;
\]
(6)

Based on the work of [15] adsorption isotherm is described by the equation:
\[
X^* (c) = \frac{0.375 \cdot C_H}{1 + 8 \cdot C_H} ;
\]
(7)

At a number of railway transport enterprises in the scheme of wastewater treatment from various pollutants, including heavy metal ions, BAU brand activated carbon is used as adsorbent. Therefore, in the present investigations, the task was to compare the main indicators of adsorption processes using BAU and the modified zeolites obtained by us [18]. To obtain reliable and comparable results, the following calculations were performed below. The equivalent particle diameter of the sorbent is determined by the formula:
\[
d = \frac{6}{\rho_{bulk} \cdot a} ;
\]
(8)

where \( a \) is specific surface of the sorbent, in our case, activated carbon and zeolite, respectively.

Permissible fictitious speed of wastewater is calculated by the formula:
\[
w = \frac{0.0167 \cdot \rho_{bulk} \cdot d \cdot g}{\rho_f} ;
\]
(9)

where \( \rho_{bulk} \) is bulk density of sorbent (activated carbon and zeolite, respectively), kg / m³; \( d \) is an equivalent granule diameter of activated carbon and zeolite, respectively, m; \( \rho_f \) is the density of the liquid containing metal ions, kg / m³.

Considering the fact that in the under consideration adsorber the fixed layers of the modified zeolite are located on cassettes, the distance between which is 0.01 m, it is necessary to consider the velocity of the liquid in this space, since it changes, due to the fact that there are no zeolite grains there. The permissible fictitious velocity of wastewater in the inter-cassette space is calculated by the formula:
\[
w_{air} = \sqrt{\frac{0.0167 \cdot \rho_{air} \cdot d \cdot g}{\rho_f}} ;
\]
(10)

where \( \rho_{air} \) is air density. We accept a working speed of 75% of the permissible value:
\[
w_c = 0.75 \cdot w ;
\]
(11)

The diameter of the adsorber is determined by the following formula:
\[
D_a = \frac{4V}{\pi \cdot w_a} ;
\]
(12)

where \( D_a \) is the diameter of the absorber with adsorbents from activated carbon and natural zeolite, respectively m; \( V \) is the flow rate of the mixture, m³ / s.

Next, the diameter of the adsorber is reduced to the values of the standard series and recalculated the actual fictitious speed of wastewater according to the formula:
\[
w_c = \frac{4 \cdot V}{\pi \cdot D_a^2} ;
\]
(13)

where \( w_c \) is velocity of wastewater in adsorber with loading from coal or zeolite, m/s;

The height of the loading layer in the adsorber is assumed to be \( H = 1.6 \) m. The minimum loading height \( z_1 \) is calculated using the formula:
\[
z_1 = \frac{w_c \cdot \tau \cdot C_H}{\varepsilon \cdot C_H + \rho_{bulk} \cdot X^* (C_P)} ;
\]
(14)

where \( z_1 \) is minimum height of the loading layer of coal and zeolite, respectively.
To calculate the hydraulic resistance, which is affected by the properties of the granular loading layer, it is necessary to determine the porosity of spherical particles as follows:

$$\varepsilon = 0.375 + 0.34 \cdot \frac{d}{D}$$  \hspace{1cm} (15)

where $\varepsilon$ is the porosity of the particles of activated carbon and zeolite, respectively, $\text{m}^3/\text{m}^3$. Thus, the hydraulic resistance of the layer will be:

$$dp = \left[ \frac{150 \cdot (1 - \varepsilon)^2 \cdot \mu_y \cdot w_r}{\varepsilon^3 \cdot d^2} + 1.75 \cdot \frac{(1 - \varepsilon)}{\varepsilon^3} \cdot \rho_y \cdot \frac{w_r^2}{d} \right] H;$$  \hspace{1cm} (16)

where $dp$ is hydraulic resistance of the loading layer of coal and zeolite, respectively; $\mu_y$ is the dynamic viscosity of wastewater. In the inter-cassette space of 0.01 m, the hydraulic resistance will change, since there are no spherical adsorbent particles, a different density of the media and, accordingly, a different velocity of the fluid. Thus, the final hydraulic resistance of the layer will be:

$$dp = \left[ \frac{150 \cdot (1 - \varepsilon)^2 \cdot \mu_y \cdot w_r}{\varepsilon^3 \cdot d^2} + 1.75 \cdot \frac{(1 - \varepsilon)}{\varepsilon^3} \cdot \rho_y \cdot \frac{w_r^2}{d} \right] H_{1-3} + 0.02 \cdot \left[ 150 \cdot \mu_y \cdot w_{0.01} + 1.75 \cdot \rho_y \cdot w_{0.01}^2 \right];$$  \hspace{1cm} (17)

To calculate the mass transfer coefficients, it is necessary to know the values of the Reynolds, Prandtl criteria and the Nusselt mass transfer criterion.

1. The Reynolds criterion is calculated by the formula:

$$Re = \frac{w_r \cdot d \cdot \rho_r}{\mu_y};$$  \hspace{1cm} (18)

where $Re$ is Reynolds criterion for an apparatus with loading layers from coal and zeolite, respectively.

The Prandtl criterion is calculated using the following formula:

$$Pr = \frac{\mu_y}{\rho_y \cdot D_y};$$  \hspace{1cm} (19)

where $D_y$ is the diffusion coefficient in the liquid phase under adsorber conditions.

The Nusselt mass transfer criterion is found from the expressions:

$$Nu = \frac{0.355 \cdot Re^{0.641} \cdot Pr^{0.333}}{d};$$  \hspace{1cm} (20)

where $Nu$ is Nusselt mass transfer criterion for adsorber with loading from coal and zeolite, respectively.

2. The coefficient of external mass transfer is calculated using the following formula:

$$\beta_e = \frac{Nu \cdot D_y}{d};$$  \hspace{1cm} (21)

where $\beta_e$ is external mass output coefficient for an adsorber with a loading layer of coal and zeolite, respectively. The coefficient of internal mass output is found by the equation:

$$\beta_i = \frac{10 \cdot D_y \cdot \rho_{sol} \cdot X_{eq}}{d \cdot (1 - \varepsilon) \cdot C_H};$$  \hspace{1cm} (22)

where $\beta_i$ is internal mass output coefficient for an adsorber with a loading layer of coal and zeolite, respectively; $D_y$ is diffusion coefficient in the solid phase (activated carbon and zeolite, respectively); $X_{eq}$ is the equilibrium concentration of metal ions in activated carbon and zeolite, respectively.

3. The calculation of mass transfer coefficient is made according to the formula:

$$Ky = \frac{1}{\left( \frac{1}{\beta_e} + \frac{1}{\beta_i} \right)};$$  \hspace{1cm} (23)

where $Ky$ is mass transfer coefficients for an adsorber with a loading layer of coal and zeolite, respectively. We introduce an additional diffusion resistance of longitudinal mixing in order to take into account the decrease in the driving force of mass transfer due to the deviation of the movement of wastewater from the ideal displacement mode [19].
The coefficient taking into account longitudinal mixing is determined by the following formulas:

$$\beta_{pr} = \frac{0.0567 \cdot w_{r} \cdot d}{(1 - \varepsilon) \mu_{r}}^{0.22};$$

where $\beta_{pr}$ is coefficient taking into account longitudinal mixing for an adsorber with loading from coal and zeolite, respectively.

Volumetric mass transfer coefficients are determined by the following equations:

$$K_{y_{V}} = a \cdot K_{y};$$

where $K_{y_{V}}$ is volumetric mass transfer coefficient for an adsorber with a loading layer of coal and zeolite, respectively.

4. The total number of transfer units for layers of height $H_{1-3}$, taking into account the inter-cassette space of 0.01 m between the three layers, is calculated by the formulas:

$$n_{o} = K_{y_{V}} \cdot \left(\frac{H_{1-3}}{w_{r}} + \frac{0.02}{w_{0,01}}\right);$$

Table 1. Adsorber calculation results.

| Characteristic                          | Adsorbed heavy metal ions by activated carbon brand BAU / modified zeolite |
|----------------------------------------|--------------------------------------------------------------------------|
|                                        | Ni$^{2+}$       | Zn$^{2+}$       | Cu$^{2+}$       |
| Bulk density, kg / m$^3$               | 550 / 770       | 550 / 770       | 550 / 770       |
| Equivalent diameter of a granule, mm  | 0.5 / 2.0       | 0.5 / 2.0       | 0.5 / 2.0       |
| Specific surface, m$^2$ / g            | 750 / 800       | 750 / 800       | 750 / 800       |
| Equivalent particle diameter, nm      | 14.5 / 9.7      | 14.5 / 9.7      | 14.5 / 9.7      |
| Working velocity, 10-2 m / s           | 0.54 / 1.23     | 0.54 / 1.23     | 0.54 / 1.23     |
| Adsorber diameter, m                  | 0.9 / 0.6       | 0.9 / 0.6       | 0.9 / 0.6       |
| Porosity of spherical particles, m$^3$/m$^3$ | 0.375/0.376   | 0.375/0.376   | 0.375/0.376   |
| Hydraulic resistance, Pa              | 16173 / 4456    | 16173 / 4456    | 16173 / 4456    |
| The height of the adsorbent layer, m  | 1.6 / 1.6       | 1.6 / 1.6       | 1.6 / 1.6       |
| Reynolds criterion                    | 2.68 / 24.45    | 2.68 / 24.45    | 2.68 / 24.45    |
| Prandtl criterion                     | 0.097 / 0.097   | 0.121 / 0.121   | 0.097 / 0.097   |
| Nusselt Mass Transfer criterion       | 0.82 / 3.37     | 0.88 / 3.63     | 0.82 / 3.36     |
| The coefficients of external mass output, cm/s | 0.17 / 1.75 | 0.146 / 1.51 | 0.17 / 1.75 |
| Coefficients of internal mass output, cm/s | 0.026 / 0.009 | 0.021 / 0.007 | 0.026 / 0.015 |
| Mass transfer coefficients, cm / s    | 0.17 / 1.75     | 0.416 / 1.51    | 0.17 / 1.75     |
| Coefficients taking into account longitudinal mixing of mass output, cm / s | 0.101 / 0.375 | 0.101 / 0.375 | 0.101 / 0.375 |
| Mass transfer coefficients taking into account longitudinal mixing, cm / s | 0.146 / 0.309 | 0.171 / 0.3 | 0.063 / 0.308 |
| Volumetric mass transfer coefficients, s$^{-1}$ | 1.1 / 2.47 | 1.28 / 2.4 | 0.473 / 2.48 |
| Total number of transfer units         | 324 / 322       | 377 / 313       | 139 / 323       |
where $n_o$ is the total number of transfer units for an adsorber with loading from coal and zeolite, respectively.

3. Conclusion
The presented calculation results allow us to draw the following conclusions: the use of modified zeolites in devices - adsorbers with a fixed adsorbent layer in the process chain for wastewater treatment from heavy metals makes it possible to increase the efficiency of the extraction of toxic components. It is known that an important component of the adsorption process is the overcoming of the hydraulic resistance of the loading layer [20], which is 4 times less for modified zeolite than for activated carbon, which increases the adsorption capacity of the layer and allows reaching the set value for wastewater treatment updated standards for the quality of purified streams by the content of heavy metal ions.

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