Investigation of Thermodynamics of Adsorption of Cadmium Ions Cd (II) from Model Solutions by Glass Fiber Materials

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Abstract. Thermodynamic regularities of the adsorption of cadmium ions Cd (II) using BSTV basalt fiber and M20-STV-2.0 and M20-UTV-0.6 glass fibers are investigated. The adsorption capacity of the investigated fibers with respect to the cadmium ion Cd (II) was determined. The degree of adsorption, values of the distribution coefficient, and adsorption equilibrium constants for the Langmuir and Freundlich models were determined. The adsorption equilibrium for the cadmium ion Cd (II) is well described by the Langmuir model. Thermodynamic characteristics of the process were determined: the change in the Gibbs energy, the change in the enthalpy and entropy of the adsorption process at three temperatures. The change in the Gibbs energy corresponds to the spontaneous occurrence of the adsorption process. A decrease in the change in the Gibbs energy of adsorption in a series of fibrous materials (BSBV basalt fiber – M20-STV-2.0 glass fiber – M20-UTV-0.6 glass fiber) is due to the entropy effect. The adsorption of cadmium ions Cd (II) on glass fiber materials is exothermic. The values of the thermal effects, found by the graphical method in accordance with the isobar equation of the chemical reaction, do not exceed 25 kJ / mol and indicate the physical nature of the process.

1. Introduction

Heavy metal ions (ITM) are contained in the wastewater of many industrial enterprises. Heavy metals such as lead, cadmium, mercury are superecotoxicants, since they have a wide range of toxic effects, exhibit toxicity in relatively low concentrations, and are capable of accumulation in living organisms.

The most dangerous are compounds of cadmium, lead and mercury. Like other heavy metals, cadmium reacts with sulphhydryl groups of protein macromolecules, thereby reducing the activity of enzymes. Soluble cadmium compounds negatively affect the synthesis of glycogen in the liver, accumulate in the kidneys, disrupt phosphorus-calcium metabolism, which can lead to osteoporotic phenomena [1].

Cadmium is a byproduct of zinc and lead melting and anode material in nickel-cadmium batteries. Cadmium sulfide pigments are found in many polymers. Cadmium salts are used in the electroplating industry to apply anticorrosive coatings to metal products and can get into the environment with wastewater.

In wastewater treatment sorption methods are used at the final stage to remove heavy metal ions (ITM). Activated carbons, silica gels, ion-exchange resins – cation exchangers, natural aluminosilicates (zeolites, clay minerals), peat, sapropel are traditionally used as sorbents. Some industrial waste has an adsorption capacity, they are foam concrete, ceramic chips, metallurgical slags, carbonate-containing waste, plant waste (sawdust, tree bark, cake and meal, beet pulp, etc.) [2–3]. When using such sorbents, two tasks are solved: waste disposal and water purification.
There are cases when sorption properties are found in materials traditionally used for other purposes, for example, glass fiber materials intended for heat and sound insulation and the manufacture of aerosol filters [4]. Basalt fibers are referred to as fiberglass materials. Unmodified basalt fiber has shown the ability to adsorb iron (bi- and trivalent) from water [5]. The adsorption capacity of porous basaltic rocks is known and more studied [6–8].

In this work, the thermodynamic characteristics of the adsorption process of ITM are determined using glass fiber materials. Samples of three types of oxide fibers were used as sorbents:

- basalt super-thin staple fiber of the BSTV brand;
- super-thin staple fiberglass of the M20-STV-2.0 brand;
- ultra-thin staple fiberglass of the M20-UTV-0.6 brand.

Average fiber diameters do not exceed 3.0 μm, 2.0 μm, 0.6 μm, respectively. Fibers of the M20-UTV-0.6 and M20-STV-2.0 brands are made from glass balls of the ShSSch-20 brand. All materials are formed by layers of randomly interwoven fibers, interlocked by forces of weak mechanical interaction.

Basalt fiber chemical composition (wt %) is as follows: SiO₂ (43-51), Al₂O₃ (10-17), Fe₂O₃ (10-15), CaO (8-13), MgO (4-15) etc. [11]. Chemical composition of ShSSch-20 glass (wt %) is as follows: SiO₂ (61.5±0.7), Na₂O (12.7±0.5), Al₂O₃ (7.2±0.5), CaO (8.0±0.7), ZrO₂ (4.8±0.5), B₂O₃ (3.0±0.5), K₂O(1.6±0.5), Fe₂O₃ (1.2±0.3) etc. [11].

2. Objects and methods of research

The ionometric method for determining the concentration of Cd (II) ions in a solution is based on measuring the potential difference arising in an electrochemical circuit composed of an indicator, selective with respect to Cd (II) ions, an ELIS-131Cd electrode and a silver chloride reference electrode.

The research methodology is described in detail in the article [10]. In the course of the study, the kinetic curves of adsorption were constructed, the time for establishing the adsorption equilibrium was determined, the degrees of extraction of the Cd (II) ion by three fibers and the distribution coefficients of the ion on three fibers were calculated. With increasing concentration, a decrease in the degree of adsorption of the cadmium ion Cd (II) is observed, which is due to the final adsorption capacity of the fiber. This indicator has a higher value when the M20-STV-0.6 brand glass fiber is used as an adsorbent and reaches 78% at an ion concentration of 5 mg / dm³.

The distribution coefficient Kᵩ equal to the ratio of the specific adsorption to the equilibrium concentration of the adsorbate in the volume of the solution, characterizes the degree of ion affinity to the adsorbent surface. At a Cd (II) ion concentration equal to 5 mg / dm³, the Kᵩ values are (cm³ / g) as follows: 912; 756 and 1732 for adsorption on BSTV, M20-STV-2.0 and M20-UTV-0.6 fibers, respectively. A higher Kᵩ value for the M20-UTV-0.6 brand glass fiber may be due to its larger specific surface area.

The idea of the nature of the adsorption process of heavy metal ions on any sorbent basalt fiber can be obtained using adsorption isotherms. In order to determine the adsorption equilibrium constants, the equations of adsorption isotherms by I. Langmuir and G. Freundlich were used. I. Langmuir’s model describes monomolecular adsorption on active sites with the same adsorbent – adsorbate interaction energy. The empirical equation of G. Freundlich describes well the cases of adsorption, when the dependence of the interaction energy of the adsorbent – adsorbate on the fraction of occupied active centers is exponential. The adsorption equilibrium constants are presented in table 1.

The adsorption equilibrium of Cd (II) ions is better described by the Langmuir model, as follows from the data in table 1. The adsorption of cadmium ions on the M20-STV-0.6 brand glass fiber is stronger, since it is characterized by a larger value of the constant of adsorption equilibrium.
active regions of the adsorbent. In cases with glass fibers of the M20:

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Table 1. Adsorption equilibrium constants at T = 298 K.

| Fiber       | A∞·10^3, mol / g | K_L·10^3, dm^3/mol | Determination coefficient R² | K_F·10^3, mol/g | 1/n | Determination coefficient R² |
|-------------|------------------|--------------------|------------------------------|-----------------|-----|------------------------------|
| BSTV        | 0.5455           | 2.457              | 0.9983                       | 170.41          | 0.822 | 0.9807                      |
| M20-STV-2.0 | 0.5329           | 1.551              | 0.9970                       | 164.28          | 0.841 | 0.9848                      |
| M20-UTV-0.6 | 0.6534           | 4.182              | 0.9975                       | 69.53           | 0.707 | 0.9855                      |

An analysis of the data in table 2 shows that with an increase in temperature, the constant of adsorption equilibrium and the value of the limiting specific adsorption decrease. The adsorption equilibrium is shifted towards desorption, which is characteristic of physical adsorption due to weak adsorbent-adsorptive interactions. A decrease in the constant of adsorption equilibrium is natural, since adsorption is an exothermic process.

Table 2. Thermodynamic characteristics of adsorption process at different temperatures.

| Fiber       | T, K | lnK  | ΔH, kJ / mol | ΔG_T, kJ / mol | ΔS_T, J/mol-K |
|-------------|------|------|--------------|----------------|---------------|
| BSTV        | 298  | 7.807| -19.342      | -18.198        |
|             | 308  | 7.638| -24.77       | -19.558        | -16.906       |
|             | 318  | 7.175| -18.969      | -18.226        |               |
|             | 298  | 7.346| -18.200      | 17.174         |
| M20-STV-2.0 | 308  | 7.254| -13.08       | -18.575        | 17.834        |
|             | 318  | 7.020| -18.560      | 17.226         |
|             | 298  | 8.338| -20.658      | 47.876         |
| M20-UTV-0.6 | 308  | 8.194| -6.39        | -20.982        | 47.373        |
|             | 318  | 8.183| -21.635      | 47.937         |

For the adsorption process, the change in the Gibbs energy, the change in enthalpy and the change in entropy, the most important thermodynamic functions of state, were determined. The change in the Gibbs energy was calculated using the Van't Hoff isotherm equation \( \Delta G_T = -RT\ln K \). To determine the thermal effect of adsorption, a graphical method based on the application of the isobar equation was used. In integral form, the equation is as follows: \( \ln K = \text{Const} - \Delta H / (RT) \). The tangent of the angle of inclination of a straight line in coordinates \( \ln K = f(1 / T) \) is \( -\Delta H / R \). And the change in enthalpy is, respectively, equal to \( \Delta H = -R\cdot\tan\theta \). The entropy change was calculated using the Gibbs-Helmholtz equation \( \Delta S_T = (\Delta H - \Delta G_T) / T \). The results of calculations and constructions are presented in table 2.

The adsorption process proceeds spontaneously; therefore, the change in the Gibbs energy is negative; in addition, \( \Delta G_T \) is practically independent of temperature. The change in the Gibbs energy corresponds to the adsorption constants of the Cd (II) ion: the greater the value of the constant of adsorption equilibrium, the more negative the change in the Gibbs energy, i.e., the greater the chemical affinity of the adsorbent (the M20-UTV-0.6 fiber) and adsorptive. The values of the enthalpy of adsorption depend on the nature of the glass fiber material. The greatest thermal effect was determined for the adsorption of the Cd (II) ion on the BSTV basalt fiber. In general, the values of the heat of adsorption do not exceed 10–30 kJ / mol, which indicates the physical nature of the adsorption process.

As a rule, during adsorption on solid sorbents, the entropy of the system decreases, which is due to the ordering of adsorptive ions on the surface of the adsorbent. In cases with glass fibers of the M20-STV-2.0 and M20-UTV-0.6 brands, there is not a decrease, but an increase in entropy, which can be explained by the disordering of water dipoles during the interaction of Cd (II) ions with active regions of the glass fiber surface [11]. A decrease in the change in the Gibbs energy of the adsorption process in a series of fibrous materials, BSBV basalt fiber – M20-STV-2.0 glass fiber – M20-UTV-0.6 glass fiber, is due to the entropy effect.
3. Conclusion
The investigated glass fiber materials exhibit adsorption capacity for the cadmium ion Cd (II). The obtained experimental data on the adsorption of Cd (II) ions are better described by the Langmuir model. The adsorption of Cd (II) ions on M20-STV-0.6 glass fiber is stronger, since it is characterized by a larger value of the adsorption equilibrium constant. The limiting specific adsorption of Cd (II) ions on M20-STV-0.6 glass fiber is also of greater value. The thermal effects of adsorption do not exceed 10–30 kJ / mol, which is typical for physical adsorption. An increase in entropy during adsorption is possible due to the disordering of water dipoles in the adsorption layer.

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