Thermodynamic estimation of adsorption ability of modified zeolites

M V Obuzdina¹, E A Rush¹

¹ Federal Agency of Railway Transport, Irkutsk State Transport University (ISTU), 15, Chernishevskogo str., Irkutsk, 664074, Russia

E-mail: obuzdina_mv@mail.ru, lrush@mail.ru

Abstract. The article presents the results of original investigations of the thermodynamic laws of sorption extraction of Ni²⁺, Zn²⁺, Cu²⁺ from wastewater. As an adsorbent, a natural zeolite from the Holinsky deposit of the klinoptilolite type, modified with a sulphur polymer, obtained from waste in the production of epichlorohydrin was proposed. The limiting parameters of the adsorption process are described by the Langmuir equation. The graphical method the limiting value of adsorption, the adsorption equilibrium constant, the differential heat of adsorption, the adsorption rate constant, the activation energy, the Gibbs energy was founded. It is proved that the investigated processes obey the laws of physical adsorption and are spontaneous.

1. Introduction

The energy of adsorption processes is one of the most important components in their investigations. The investigations of structure of natural and modified zeolites, the identification of adsorption process mechanism, the direct investigation of energy heterogeneity and other problems require the use of modern precision physicochemical methods. Heats of adsorption can be determined either directly by measurement using a calorimeter or by calculation based on various experimental data [1].

In microporous systems, during adsorbent – adsorbate interactions, bulk filling of the adsorption space takes place. Therefore, the volume of micropores becomes the main geometric parameter, and the specific surface loses its physical meaning for microporous adsorbents [2]. Representatives of microporous adsorbents with an extremely narrow pore distribution are dehydrated zeolites. A remarkable feature of zeolites is the presence of exchangeable cations in their adsorption cavities, which create high gradients of electrostatic fields [3]. The adsorption of molecules on the adsorbent limits, inhibits their mobility; the interaction between the adsorbate and the adsorbent reduces the mobility of the molecules [4]. A decrease in the degree of mobility of molecules as a result of adsorption leads to a decrease in entropy [5].

2. Results and discussion

In previous investigations, conducted by us, we investigated the thermodynamic laws of sorption extraction of oil products and heavy metal ions from industrial wastewaters by zeolites from the Holinsky deposit, modified by high organosilicon compounds HMDS – hexamethyldisilazane [(CH₃)₃Si-]₂NH and TEOS - tetraethoxysilane (C₂H₅O)₄Si [6,7,8].

The actual direction of modern development of physical chemistry is to increase the reactivity of solids by chemical modification to obtain new sorbents from them [9, 10]. Therefore, the goal of our
further research was defined as a directional change in the physicochemical properties of the natural zeolitive rocks of klinoptilolite type of Holinsky deposit [11] by means of modification with sulfur polymere, obtained from epichlorohydrin production wastes. The main component of the waste is 1,2,3-trichloropropane [12].

The obtained kinetic characteristics of the extraction of Ni$^{2+}$, Zn$^{2+}$, Cu$^{2+}$ from industrial wastewater of railway transport enterprises are presented in detail in our previous works [13]. Let us consider the adsorption capacity of klinoptilolites, modified by sulfur polymer from the point of view of thermodynamic estimation.

The limiting parameters of the adsorption process can be qualitatively obtained by describing the isotherm by the Langmuir equation:

$$ A = A_\infty \frac{K_p \cdot C}{1 + K_p \cdot C}, $$

where $A$ – current value of adsorption, mg/g; $A_\infty$ – maximum value of adsorption, mg/g; $K_p$ – adsorption equilibrium constant; $C$ - concentration of solution, mg/l.

The isotherm in the coordinates of the Langmuir equation is linearized. Dividing the unit on the left and right sides of the equation, we obtain the equation of a straight line in coordinates $1/A=f(1/C)$:

$$ \frac{1}{A} = \frac{1}{A_\infty} + \frac{1}{A_\infty \cdot K_p \cdot C}. $$

Equation (2) allows graphically finding the constants $A_\infty$ and $K_p$ in the Langmuir equation. Figure 1 shows the adsorption isotherm of heavy metal ions by a zeolite, modified by a sulphur polymer, for example Ni$^{2+}$ and Cu$^{2+}$. The line cut off by the straight line on the y-axis is $1/A_\infty$. According to the tangent of the angle of a straight line, the adsorption equilibrium constant $K$ can be found by the formula:

$$ K_p = \frac{1}{A_\infty \cdot \tan \alpha}. $$

**Figure 1** Adsorption isotherms of Ni$^{2+}$ (a) and Cu$^{2+}$ (b) with zeolite, modified by sulfur polymer in Langmuir coordinates at various temperatures

Table 1 presents the constants $A_\infty$ and $K$ of the Langmuir equation for the sorption of Ni$^{2+}$, Zn$^{2+}$, Cu$^{2+}$ ions on a zeolite, modified with a sulfur polymer at different temperatures. The data in Table 1 indicate that with increasing temperature, the value of $A_\infty$ increases, and the equilibrium constant $K_p$ decreases.
Table 1. Constants of the Langmuir equation for the adsorption of Ni$^{2+}$, Zn$^{2+}$, Cu$^{2+}$ of zeolite, modified by sulphur polymer

| Temperature, K | Ni$^{2+}$ | Zn$^{2+}$ | Cu$^{2+}$ |
|---------------|-----------|-----------|-----------|
|               | $K_p$ A$_p$*10$^{-3}$, mg/g | $K_p$ A$_p$*10$^{-3}$, mg/g | $K_p$ A$_p$*10$^{-3}$, mg/g |
| 1             | 2         | 3         | 4         | 0,67      | 4,92      | 0,12      | 293 | 975 | 72,67 | 972 | 2,17 |
| 313           | 515       | 0,91      | 3,98      | 0,26      | 601       | 2,57     |
| 333           | 245       | 6,15      | 2,77      | 0,55      | 345       | 2,96     |

Adsorption is a spontaneous process. The thermal effect in the range of changes in the degree of filling of the adsorption space is characterized by the differential heat of adsorption [14]. To calculate the isosteric heat of adsorption, the Klaiperon – Clausius equation is applied at $A = \text{const}$:

$$
\frac{\Delta \ln C}{\Delta (1/T)} = -\frac{Q}{R}
$$

(4)

$$
Q = -R \cdot \frac{\Delta \ln C}{\Delta (1/T)}
$$

(5)

where $A$ – the sorbent capacity, mg/g; $T$ - temperature, K; $R$ – the gas constant: $R = 8.31$ J/mol·K; $C$ – the equilibrium concentration of heavy metal ions in solution, mg/l.

Isostere of adsorption is an important function that carries direct information about the heat of adsorption. When $A = \text{const}$:

$$
\ln C = f\left(\frac{1}{T}\right).
$$

(6)

The differential heat of the sorption of metal ions (see Figure 2) can be calculated from the angles of inclination of the isoster, converting equation (5) into the following form:

$$
Q = -R \cdot \tan \alpha \quad \text{when} \quad A = \text{const}
$$

(7)

**Figure 2** Isoster adsorption Ni$^{2+}$ (a) and Cu$^{2+}$ (b) of zeolite, modified by sulphur polymer, at different temperatures

The results of the calculation are presented in table 2. The adsorption rate constant $K$ was calculated using the first-order adsorption rate equation. The equation of the rate of adsorption of the first order in differential form is:
\[
\frac{dc}{dt} = K \cdot C .
\] (8)

The equation for the rate of adsorption in integral form:

\[
K = \frac{2.303}{t} \cdot \lg \frac{C_0}{C}
\] (9)

where \(C_0\) – the initial concentration of metal ions in solution, mg/l, \(C\) – the equilibrium concentration of metal ions in solution, mg/l, \(t\) - time. From equation (9) it is easy to get:

\[
tg \alpha = 0.434 \cdot K
\] (10)

where \(\alpha\) – the angle of inclination of the tangent to the kinetic curve to the positive direction of the x-axis. The results of the calculation of the adsorption rate constant are presented in Table 2.

**Table 2.** The results of calculation of the rate constants, Gibbs Energy, the heat of adsorption of Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\) of zeolite, modified by sulfur polymer

| Temperature, \(T\), K | Ni\(^{2+}\) | Zn\(^{2+}\) | Cu\(^{2+}\) |
|-----------------------|-----------|-----------|-----------|
|                       | \(K\), sek\(^{-1}\) | \(\Delta G\), kJ/mol | \(Q\), kJ/mol | \(K\), sek\(^{-1}\) | \(\Delta G\), kJ/mol | \(Q\), kJ/mol | \(K\), sek\(^{-1}\) | \(\Delta G\), kJ/mol | \(Q\), kJ/mol |
| 1                     | 2         | 3         | 4         | 5         | 6         | 7         | 8         | 9         |
| 293                   | 0.69      | -16.76    | -5.39     | 0.44      | -3.88     | -4.64     | 0.57      | -16.75    | -3.11     |
| 313                   | 1.29      | -16.24    | -7.37     | 0.74      | -3.59     | -6.01     | 1.21      | -16.64    | -4.1      |
| 333                   | 1.82      | -15.22    | -8.42     | 1.18      | -2.82     | -6.65     | 1.63      | -16.17    | -5.49     |

To find the adsorption rate constant \(K\), it was necessary to construct the kinetic sorption curves of Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\). The results of the calculation are presented in Table 2. An analysis of the data in Table 3 shows that an increase in the adsorption rate \(K\) is observed as the temperature increases. This can be explained by the fact that with increasing temperature the movement of molecules becomes more intense, and they more quickly interact with the surface of the adsorbent.

The appearance of the kinetic curves of dependence of the adsorption of metal ions by a zeolite, modified by sulfur polymer, indicates an increase in the rate of adsorption with increasing temperature. The curves obtained at higher temperatures lie above the curves obtained at low temperatures. Thus, the process is activated [15].

Only active molecules with activation energy, i.e. excess energy, in accordance with the Arrhenius equation can penetrate into the pores and adsorb [16]. The reaction rate constant is associated with the activation energy by the following relationship:

\[
K = A \cdot e^{-E_a/RT}
\] (11)

where \(K\) – reaction rate constant, s\(^{-1}\); \(A\) – constant; \(E_a\) – activation energy, kJ/mol; \(R\) – the universal gas constant; \(T\) – temperature, K.

From formula (11), we obtain the following expression for calculating the activation energy:

\[
E_a = -2.303 \cdot R \cdot \frac{\Delta \ln K}{\Delta (1/T)} = -2.303 \cdot R \cdot tg \alpha
\] (12)

where \(tg \alpha\) – the slope angle of graphical dependence \(\lg K = f (1/T)\).
If the adsorption obeys the Langmuir equation, i.e. the equilibrium constant \( K_p \) does not depend on the degree of filling of the sorbent surface, then the Gibbs energy (see table 2) of adsorption can be calculated using the Vant-Hoff isotherm equation:

\[
\Delta G = -R \cdot T \cdot \ln K
\]  

(13)

where \( K_p \) – the constant of adsorption equilibrium in the Langmuir equation; \( R \) – the universal gas constant; \( T \) - temperature, K; \( \Delta G \) – Gibbs energy, kJ/mol.

The activation energy of sorption of \( \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+} \) of zeolite, modified by sulfur polymer, is 10.24 kJ/mol; 5.75 kJ/mol and 14.03 kJ/mol, respectively. The temperature dependence and the values of the sorption activation energy indicate that investigating processes obey the laws of physical adsorption. An analysis of the Gibbs energy calculation results indicates its negative value. This confirms the fact that adsorption is a spontaneous process.

3. Conclusion

In the course of the experimental investigations, a thermodynamic estimate was made of the adsorption capacity of the modified klinoptilolites of the Holinsky deposit in Eastern Transbaikalia with respect to heavy metal ions. A sulfur polymer obtained from waste in the production of epichlorohydrin was used as a modifier. The degree of sorption purification with respect to heavy metal ions is close to 100%.

Adsorption isotherms are presented in the coordinates of Langmuir, which allowed us to find the maximum value of adsorption and the constant of adsorption equilibrium. For the solution of further thermodynamic problems, the isosteric method was chosen. The differential heat of adsorption of \( \text{Ni}^{2+}, \text{Zn}^{2+}, \text{Cu}^{2+} \) was determined depending on the angle of inclination of the isoster.

As a result of the analysis of the constructed kinetic curves of adsorption of heavy metal ions, the adsorption rate constants were calculated. The results of the calculation of the activation energy and Gibbs energy, determined by the graphical method, are presented. It is proved that the investigated processes obey the laws of physical adsorption and are spontaneous.

References

[1] Devdariani O G 1980 Aut. dis. ... cand. technical sciences (Tbilisi: Tbilisi Order of the Red Banner of Labor State University) p 24.
[2] Dubinin M M 1987 Adsorption and porosity (Moscow: VACH) p 172
[3] Chelishchev N F, Berenshtein B G, Volodin V F 1987 Zeolites is a new type of mineral raw materials (Moscow: Nedra) p 176
[4] Brek D 1976 Zeolitic molecular sieves (Moscow: World) p 781
[5] Vernov A V and Lopatkin A A 1979 Zh. physical chemistry 53 12 3161-3166
[6] Obuzdina M V 2011 Modern technologies. System analysis. Modeling 31 3 209 213
[7] Rush. E A and Obuzdina M V 2013 Izvestia Transsib (Omsk: Omsk State Transport University) 13 1 27-34
[8] Patent of the Russian Federation Patent No. 2524111 (07.27.2014)
[9] Dabija O N 2012 Sorption and chromatographic processes 6 12 860-866
[10] Solovyova Y V, Krasnova T A, Yustratov V P 2010 Ecology and Industry of Russia. 4 54-58.
[11] Kotov P A 1995 Fields of Transbaikalia (Moscow: Geoinformmark) 280
[12] Patent of the Russian Federation Patent No. 2624319 (07.03.2017)
[13] Obuzdina, M V, Rush E A, Korchevin N A, Shaluch L V 2017 Bulletin of the Technological University. 20 7 149-155
[14] Timofeev D P 1962 Adsorption kinetics (Moscow: Publishing House of the Academy of Sciences of the USSR) p 252
[15] Greg S and Singh K 1984 Adsorption, specific surface area, porosity (Moscow: Mir) p 306
[16] Prigochin I and Condepudi D 2002 Modern thermodynamics (Moscow: Mir) p 464