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MECHANISM AND MATHEMATICAL MODEL OF H_2S CHEMISORPTION ON MODIFIED BENTONITE

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Abstract. New H_2S adsorbent was synthesized on the basis of bentonite. It was analyzed using elemental and BET surface area analysis. Models and mathematical representations of mechanisms that govern the chemisorption of hydrogen sulfide on the chemically treated bentonite were presented. The models adequacy was assessed by means of statistic *t*-criterion.

Keywords: hydrogen sulfide, chemisorption, modified bentonite, copper.

1. Introduction

Hydrogen sulfide (H_2S) is the major air pollutant when it is emitted to atmosphere by industrial enterprises. It is one of the most common by-products of chemical plants, textile and leather manufactures *etc.*

There are a lot of commercial treatment techniques that can be used for H_2S removal [1-3] depending on gas volumes and purification rate requirements. Existing methods differ by physicochemical, technical and economic indices, technological and equipment implementation, though the highest purification rate can be reached by chemical adsorption. The main drawbacks of this method are bulky equipment and the high prices of adsorbents. For this reason the creation of new effective, environmentally safe and wide applicable sorbents on the basis of cheap raw products is the matter of high concern.

Natural minerals are the most available, cheap, harmless and highly efficient sorbents; though in the native state they do not possess high sorption efficiency. Sorption properties of natural minerals can be improved by means of acid or alkaline activation [4-8] and chemical modifying [9-18].

In this paper we present the results of hydrogen sulfide chemisorption investigation by chemically modified bentonite. The aim of this paper is to develop a mathematical model of chemisorption kinetics for prediction the sorption properties of a synthesized sorbent.

2. Experimental

2.1. Materials

2.1.1. Carbonate-rich bentonite (Bentonite)

The bentonite was collected from Yaziv sulfur deposit, Lviv region, Ukraine. It contains 45–50 % montmorillonite and 15–20 % calcium and magnesium carbonates [19]. The chemical composition of this bentonite was presented by Datsenko [20]. The bentonite was dispersed in water with bentonite:water ratio equals to 1:20. Unwanted materials such as impurities, leaves and tree roots were removed by vibrosieving. After that the samples were centrifugated and left in the desiccator for storage with the bentonite-water content $40\pm 3\%$.

2.1.2. Cu- modified bentonite (Cu-bentonite)

Fifty grams of original bentonite were dispersed into two liters of water. As the reaction between carbonate-rich bentonite and copper (II) chloride is too slow at room temperature, the reaction was carried out on a water bath at 333–343 K. Then 28 ml of $200\text{ g}\cdot\text{l}^{-1}$ copper (II) chloride solution was added dropwise. After decomposition of the carbonates the samples contained a high amount of copper hydroxide. The presence of Cu^{2+} ions in the solution was tested by the reaction with potassium ferrocyanide. The modified bentonite was washed, centrifugated and dried to a constant mass at $373\pm 5\text{ K}$.

2.2. Methods

2.2.1. BET

The surface area was measured with a Micromeritics ASAP 2010 instrument by adsorption of nitrogen at 77 K. Prior to adsorption measurements, the samples were degassed under vacuum of 20.8 Pa at 398 K for 30 min. The results of BET surface area analysis are shown in Table 1.

Table 1
BET surface area of bentonite, fresh and sulfided samples

Adsorbent	BET surface area, $\text{m}^2 \cdot \text{g}^{-1}$	Loss rate, %
Bentonite	26	-
Cu-bentonite fresh	38	52.7
Cu-bentonite sulfided	18	

2.2.2. Elemental analysis

Atomic absorption spectrophotometer Hitachi Z-5300 was used for determination of Ca^{2+} (limit of detection 2.4 ppm), Mg^{2+} (limit of detection 0.1 ppm), Fe^{3+} (limit of detection 0.3 ppm), Cu^{2+} (limit of detection 0.7 ppm) content. The results of elemental analysis are shown in Table 2.

Table 2
The results of atomic absorption spectroscopy analysis

	Ca^{2+}	Mg^{2+}	Cu^{2+}
Bentonite	3.99 %	0.33 %	0.01 %
Cu-bentonite	1.23 %	0.20 %	4.28 %

2.2.3. Sorption kinetics

The sorption of hydrogen sulfide was carried out at room temperature under atmospheric pressure. Approximately 1 g of the sample (1–2 mm granule size) was packed into a syringe (50 ml). After gas (90 % H_2S) has been pumped into the syringe, needle orifice was blocked. Then the load was set on the pistol. Gas volume-time relation was noted. Time was fixed by a stop watch. Pressure in the system was kept up at the atmospheric level.

3. Results and Discussion

In order to obtain the set of data for development of chemisorption mathematical model the series of observations of H_2S adsorption rate variation under constant concentration, pressure and temperature in the system were carried out. On the basis of obtained data the graph of H_2S molar flow and time relationship was plotted (Fig. 1).

In Fig. 1 two distinct areas of adsorption rate change can be identified. This is caused by availability of external and internal surface of adsorption. We propose the chemisorption mechanism that consists of the following stages: diffusion of adsorbate molecules from the gas flow to the surface of adsorbent grain (external diffusion), chemical reaction on the grains surface,

adsorbate invasion through the pore area of the adsorbents grain to the active centers (internal diffusion) and chemical reaction in the pores of the grain.

For kinetics investigation a few assumptions have been made: i) a solid sorbent is the particle of a spherical shape; ii) concentration of H_2S is equal and constant along the surface of the particle, thus the factor of external diffusion can be neglected.

The first stage is characterized by a high H_2S adsorption rate, and the process is limited only by the rate of the reaction between hydrogen sulfide and copper hydroxide deposited on the surface of the grain. With the lapse of time the quantity of the active centers on the adsorbent surface decreases and chemical interaction shifts into the pore area.

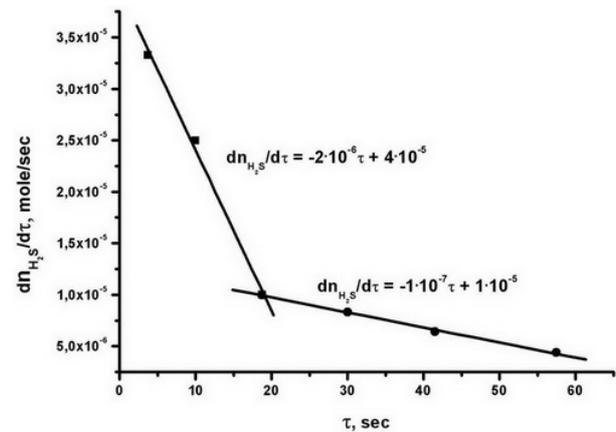


Fig. 1. Dependence of H_2S molar flow $\frac{dn_{\text{H}_2\text{S}}}{dt}$ of Cu-bentonite on time

The first stage of adsorption is carried out within a kinetic region and it can be described by the rate equation:

$$\left(\frac{dn_{\text{H}_2\text{S}}}{dt} \right)_{\text{max}} = k \cdot F_{0\text{ext}} \cdot C_{\text{H}_2\text{S}}^m \quad (1)$$

where $\left(\frac{dn_{\text{H}_2\text{S}}}{dt} \right)_{\text{max}}$ is H_2S adsorption rate at the initial time

of sorption, mol/s; k is coefficient in the rate equation, m/s; $F_{0\text{ext}}$ is conventionally external surface area of fresh adsorbent, that consists of the external surface area and easy-to-reach surface macroporosity, m^2 ; $C_{\text{H}_2\text{S}}$ is concentration of hydrogen sulfide in the gas flow, mol/m^3 ;

m is order of reaction. Linear behavior of $\left(\frac{dn_{\text{H}_2\text{S}}}{dt} \right)$ proves that on the first stage of adsorption exponent $m = 1$.

Conversion of H_2S weigh fraction into a molar concentration was performed according to the following relation [21]:

$$C_{H_2S} = \frac{r_{st.} \cdot X_{H_2S}}{M_{mix.}} \quad (2)$$

where $r_{st.}$ is density of the gas mixture at standard conditions, g/l; X_{H_2S} is weigh fraction of hydrogen sulfide in a gas mixture, that is equal to 0.9; $M_{mix.}$ - molar weight of the gas mixture, that is equal to 33.5 g/mol.

According to the Eq. (2), molar concentration of hydrogen sulfide in the gas mixture equals to:

$$C_{H_2S} = \frac{1.495 \cdot 0.9}{33.5} = 0.040 \text{ mol/l} = 40 \text{ mol/m}^3$$

The conventionally external surface area of the grain $F_{0ext.}$ corresponds to the quantity of active centers, so it is proportional to the mass of deposited copper:

$$\frac{F_{0ext.}}{F_{\Sigma}} = \frac{m(Cu)_{0ext.}}{m(Cu)_{\Sigma}} \quad (3)$$

where F_{Σ} is total surface area of the adsorbent, m^2 ; $m(Cu)_{0ext.}$ is mass of copper deposited on the external surface of the adsorbent, g; $m(Cu)_{\Sigma}$ is total mass of deposited copper, g.

Total surface area of the adsorbent is known from Table 1 and is equal to 38 m^2/g . Total mass of deposited copper in 1 g of adsorbent was defined by elemental analysis (Table 2). It is equal to $42.8 \cdot 10^{-6}$ kg.

Mass of copper deposited on the external surface of the adsorbent was calculated from the reaction:



Since the maximum volume of the gas that can be adsorbed on the first stage is approximately $12 \cdot 10^{-3}$ l, so $m(Cu)_{0ext.} = 30.8 \cdot 10^{-3}$ g. According to the relation (3) $F_{0ext.} = 27.35 \text{ m}^2$.

From the straight-line equation (see Fig. 1) it arises

that if $t \rightarrow 0$, $\left(\frac{dn_{H_2S}}{dt}\right)_{\max} \approx 4 \cdot 10^{-5} \text{ m}^3/\text{s}$. Thus the rate

coefficient in the Eq. (1) can be calculated as follows:

$$k = \left(\frac{dn_{H_2S}}{dt}\right)_{\max} / F_{0ext.} \cdot C_{H_2S}^m =$$

$$= 4 \cdot 10^{-8} / 27.35 \cdot 40 = 3.7 \cdot 10^{-8} \text{ m/s} \quad (5)$$

Adequacy of the model was assessed by means of statistic t . Estimated value of t comes to 1.89 and the critical value for 2 degrees of freedom and confidence interval 95 % is $t = 4.30$ [22]. Since the estimated value of t is less than a critical value, the model is adequate and it can be used for determination of H_2S adsorption rate of the Cu-modified bentonite clay depending on the available surface area of adsorbent.

The second stage of adsorption is carried out within the internal diffusion region, where the internal diffusion rate is significantly lower than the reaction rate. Taking into account the high chemical activity of the copper-containing material, the layer-by-layer chemisorption of H_2S is expected. Mathematically it can be described by Fick's second law in a spherical coordinate system with the boundary conditions:

$$\begin{cases} \frac{\partial C}{\partial t} = D^* \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r} \right) & 0 \leq r \leq R \\ C(r = R, t) = C_{H_2S} \\ C(r, t = 0) = 0 \end{cases} \quad (6)$$

where C is concentration of H_2S in the pore area at any point of time at any distance from the external surface of the particle, mol/m^3 ; t is time, s; D^* is coefficient of internal diffusion, m^2/s ; r is moving radius, m; R is particle radius, in our case $R = 0.75 \cdot 10^{-3}$ m.

The system (6) has the following solution [23]:

$$\frac{\bar{C}}{C_{sat.}} = 1 - \sum_{n=1}^{\infty} \frac{6}{p^2 n^2} \cdot e^{-p^2 n^2 \frac{D^* t}{R^2}} \quad (7)$$

where \bar{C} is average H_2S concentration in the pore area, mol/m^3 ; $C_{sat.}$ is adsorbent saturation concentration, mol/m^3 .

At high values of τ components $n \geq 2$ may be neglected. Having taken the logarithm of the ratio (7) at $n = 1$ (steady regime zone) we get:

$$\ln \left(1 - \frac{\bar{C}}{C_{sat.}} \right) = \ln \frac{6}{p^2} - p^2 \frac{D^* t}{R^2} \quad (8)$$

In order to define the coefficient of internal diffusion D^* the experimental data were presented as the linear

dependence $\ln \left(1 - \frac{\bar{C}}{C_{sat.}} \right) = f(t)$ (Fig. 2).

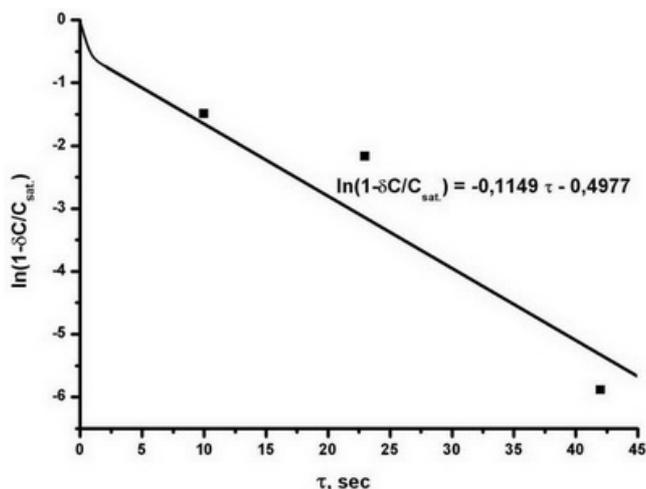


Fig. 2. Dependence of $\ln(1 - \bar{C}/C_{sat.}) = f(t)$

Coefficient of internal diffusion was determined by the tangent of line inclination to the X-axis.

$$D^* = 6.6 \cdot 10^{-9} \text{ m}^2/\text{s}$$

Adequacy of the model was assessed by means of statistic t . Estimated value of t comes to 1.77 and the critical value for 2 degrees of freedom and confidence interval 95 % is $t = 4.30$ [22]. Since the estimated value of t is less than the critical value, the model is adequate and it can be used for determination of H_2S adsorption rate of the Cu-modified bentonite clay depending on time.

4. Conclusions

Mathematical model presented in this paper gives an opportunity to choose the optimal conditions for the process of exhaust gases purification from hydrogen sulfide by means of synthesized sorbent. It is based on the amount of the substance passing through the adsorbent layer. It also allows calculating the time of adsorbents saturation.

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МЕХАНІЗМ ТА МАТЕМАТИЧНА МОДЕЛЬ ХЕМОСОРБЦІЇ H_2S НА МОДИФІКОВАНОМУ БЕНТОНІТІ

Анотація. Синтезовано новий адсорбент сірководню на основі бентоніту. Його склад визначали за допомогою елементного аналізу. Площу питомої поверхні розраховували за методом BET. У статті наведено моделі та математичний опис механізму хемосорбції сірководню на хімічно модифікованому бентоніті. Адекватність моделей оцінювали за допомогою t -критерію.

Ключові слова: сірководень, хемосорбція, модифікований бентоніт, мідь.