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DYNAMIC CHARACTERISTICS AND EFFICIENCY ASSESSMENT OF THE ADSORPTION METHOD FOR WATER PURIFICATION BASED ON THE LANGMUIR ISOTHERM

Abstract. This study provides an analysis of the mass transfer kinetic characteristics relevant to the treatment of mining industry wastewater using a porous adsorbent, based on filtration equations and the Langmuir adsorption isotherm. The findings reveal that the coefficient defining the adsorption rate has a considerable impact on the behavior of kinetic curves. The calculations show that an increase in this coefficient leads to a steeper concentration curve, which progresses along the apparatus's axis over time, resulting in a more frontal process. The initial concentration of the substance being removed is critically important: as this initial concentration diminishes, the operational lifespan of the apparatus is significantly prolonged. Within the developed mathematical model, an estimate is derived for the time-averaged concentration of the pollutant in the treated water volume, which is a key indicator of the absorber efficiency. This estimate reveals that the concentration of the pollutant in the treated water volume, denoted as c_R , depends on the initial concentration and the characteristics of the adsorption isotherm. As the adsorption rate coefficient β increases, the purification efficiency improves, meaning the ratio of the pollutant concentration c_R to the initial concentration decreases. Conversely, if the initial concentration decreases (while β remains unchanged), the purification efficiency slightly declines (i.e., the aforementioned ratio increases); therefore, the coefficient β is crucial to the overall process and, consequently, to the final outcome. The estimates of calculation accuracy presented at the end of the article demonstrate a remarkably satisfactory correlation with calculations derived from the mass balance of purified water alongside the water retained in the porous adsorbent. Thus, the study demonstrates that when a formal mathematical representation of the adsorption process is established (specifically, the Langmuir isotherm) the suggested mathematical model is applicable for assessing the operational lifespan and effectiveness of a particular adsorbent, in addition for monitoring the dynamic characteristics of filtration flow and the kinetics involved in the water purification process.

Keywords: water purification, adsorption, concentration, Langmuir isotherm.

1. Introduction

At present, waters discharged by the mining industry are under intense scrutiny from the public and environmentalists, as their polluting impact on the environment is becoming hazardous [1, 2]. A diverse range of techniques and technologies is available for the treatment of mining waters, allowing for the effective management of this issue in numerous cases. The substantial global knowledge amassed in this domain suggests that this intricate problem should be tackled through the application of a wide variety of treatment methods [1, 3, 4]. Among currently known purification techniques, adsorption-based water treatment occupies a prominent position and is widely employed for the removal of aromatic compounds, dyes, heavy metals, valuable constituents, and other substances. Typically, it constitutes an integral component of a broader, comprehensive treatment process, which may also incorporate filtration, reverse osmosis, evaporation, membrane technologies, and similar methods. While a vast arsenal of adsorbents is already available for this purpose, new materials continue to be developed – primarily based on natural carbon and plant-derived materials [5–8].



Various mathematical models are employed to describe the adsorption process, one of which is the Langmuir model. The Langmuir adsorption formula for a specific component of a solution takes the following form [9, 10]:

$$a = \frac{A\beta c}{(1 + \beta c)}, \quad (1)$$

where a is the adsorption capacity (kg/m^3), c is the mass concentration of the component being removed from the solution; A is the adsorbent capacity for this substance (kg/m^3), and β is a parameter characterizing the adsorption rate.

It should be noted that, strictly speaking, Formula (1) is valid for a substance that forms a monolayer over the adsorbent surface. In all other scenarios, as noted in [9], the mechanism of adsorption may vary significantly. Nevertheless, this relationship often remains valid for both gas mixtures and solutions. This is clearly demonstrated in studies [5, 6]. Furthermore, [6] highlights that the adsorption capacity of activated carbons in solutions is based on two distinct physical mechanisms: the influence of surface forces and the existence of functional groups. However, in both cases, the Langmuir model frequently demonstrates superiority in various situations, thus enabling this relationship to act as a fundamental framework for characterizing the adsorption process. Of course, should the situation demand it, an alternative functional form can be utilized to derive the necessary parameter.

The objective of this study is to conduct a numerical assessment of the efficiency of an adsorption-based method for purifying a flowing fluid stream, and to elucidate the kinetic aspects of this process based on equations of fluid filtration flow and a known adsorption isotherm (specifically, the Langmuir isotherm).

2. Methods

The mathematical representation of filtration flow issues of this nature relies on the mass conservation equation along with Darcy's equation [11]. Let us write out the one-dimensional equation of mass conservation for the component under consideration:

$$\frac{\partial(\varepsilon\rho c)}{\partial t} + \frac{\partial(\varepsilon\rho uc)}{\partial x} + \frac{\partial}{\partial x} \left(\rho D_{EF} \frac{\partial c}{\partial x} \right) + g, \quad (2)$$

where t is time (s); x is the spatial coordinate (m); u is velocity (m/s); ρ is the density of the fluid mixture, (kg/m^3); c is the mass concentration of the component; ε is the adsorbent porosity; D_{EF} is the effective diffusion coefficient (m^2/s); and $g = -\partial a/\partial t$ represents the mass gain or loss of the component under consideration associated with the adsorption process ($\text{kg}/(\text{m}^3 \cdot \text{s})$).

Let us assume that the adsorbent layer is uniform and that its porosity remains unchanged. Additionally, we assume that equilibrium in the adsorption process is reached almost instantaneously concerning the filtration parameters—that is, the time

needed for molecular equilibrium to be established at the surface is significantly less than the characteristic time scales of the diffusion and filtration processes. This limiting model of the process is of particular interest because it provides an upper bound for the efficiency of the purification process. Given that the fluid is incompressible (meaning its density can be considered constant throughout the entire domain) and that the concentration c is a relatively small quantity, we assume that the flow velocity within the porous medium is constant—specifically, $u = 0.001$ m/s. The selection of this specific value is dictated by general principles of filtration, and, in particular, by the applicability of Darcy's law. The boundary conditions for c are defined by the following relations:

$$\text{at } \zeta = 0 \quad c = c_0; \quad \text{at } \zeta = 1 \quad \partial c / \partial \zeta = 0, \quad (3)$$

where $\zeta = x/L$, L is the length of the porous body (m), and c_0 is the concentration of the pollutant at the inlet.

The effective diffusion coefficient D_{EF} in equation (2) according to [12] is expressed through the diffusion coefficient D as $D_{EF} = \varepsilon D / \gamma$. The tortuosity coefficient γ in this equation serves as a fitting parameter that is associated with the internal structure of the pore space. In [12], a series of formulas are presented that may vary significantly from one another, yet are well-suited for each specific case. Selecting the appropriate formula for tortuosity may present a distinct challenge for certain materials utilized as adsorbents. For our modeling task, we will employ the formula that has been established for coal seams [13]

$$\gamma = \varepsilon + 1.5(1 - \varepsilon). \quad (4)$$

The solution to equation (2), taking into account (4) and the boundary conditions (3), was conducted numerically using an explicit finite difference scheme.

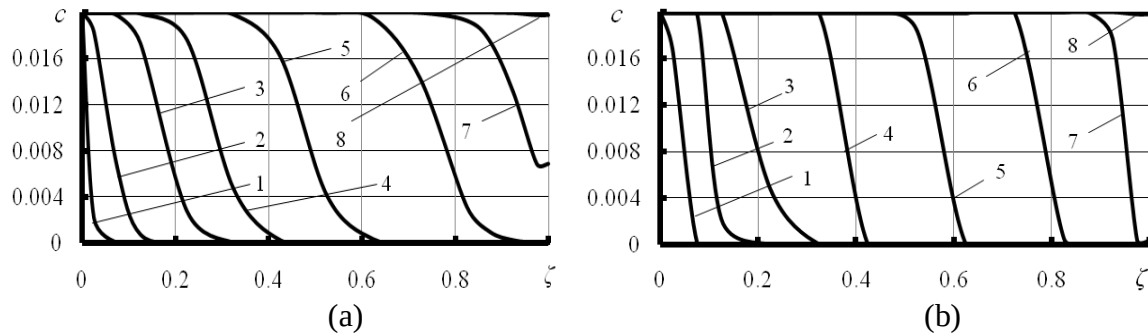
3. Results and discussion

In the calculations, it was accepted: $D = 2 \cdot 10^{-9}$ m²/s; $\varepsilon = 0.3$ (porosity was considered constant both over time and in space); $\rho = 1000$ kg/m³; $L = 1$ m; time scale $T = L/u = 1000$ s. In formula (1), the quantities A and β are experimental. For our calculations, we will assume the value of A to be 200 kg/m³ (which is quite high, yet a realistic figure for activated carbons). Furthermore, considering that the value of β is determined experimentally in practice and can vary significantly, we will vary it in our calculations from 10 to 1000.

Two primary scenarios for the calculation were conducted: $c_0 = 0.02$ and $c_0 = 0.004$, with the coefficient β set to values of 10, 20, 50, 100, 200, 500, and 1000. Figures 1 (a) and (b) illustrate the curves of concentration changes along the porous medium as a function of the dimensionless time ($\tau = t/T$).

Figure 1 illustrates that the absorption of the component by the adsorbent leads to an almost frontal alteration along the length of the working body. The curves for

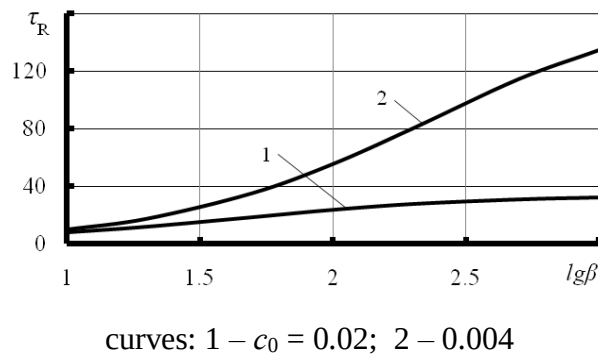
$\beta = 100$ are noticeably steeper than those for $\beta = 10$. At the end of the channel, the concentration c , which is nearly zero, remains for a certain duration until a wave of concentration rise approaches this point. With its arrival, the concentration here sharply increases, and the purification process concludes, as the concentration at the end becomes equal to that at the beginning of the apparatus. The curves provided indicate a dynamic adsorption process in the context of [14]. Similar curves have also been obtained for gas in the work [15].



(a) – $\beta = 20$, curves: 1 – $\tau = 0.04$; 2 – 0.6; 3 – 1.8; 4 – 3.0; 5 – 5.0; 6 – 8.0; 7 – 10; 8 – 12.1.

(b) – $\beta = 200$, curves: 1 – $\tau = 1.0$; 2 – 3.0; 3 – 6.0; 4 – 10; 5 – 15.0; 6 – 22.0; 7 – 26; 8 – 27.6.

Figure 1 – Variation in the concentration of the adsorbed substance within the flow along the porous body as a function of the dimensionless time for $c_0 = 0.02$



curves: 1 – $c_0 = 0.02$; 2 – 0.004

Figure 2 – Dimensionless operating time of the apparatus as a function of the coefficient β and c_0

Figure 2 illustrates the dimensionless operating times of the apparatus (τ_R) as a function of the coefficient β . The operating time of the apparatus is conventionally defined as the dimensionless time interval during which the outlet concentration changes from zero to c_0 . It is evident from the figure that as the value of β increases, the operating time also increases, and it appears that further increases will asymptotically approach a certain value. Additionally, this figure clearly demonstrates that the initial value of c_0 significantly impacts the operating time curve. This is understandable, as a lower concentration of the adsorbed substance in water necessitates a longer time for it to saturate the adsorbent capacity. Consequently, it follows that the effective duration of the adsorbent's operation is directly related to the initial concentration of the pollutant and, naturally, to the degree of purification. The degree of purification can be assessed by the subsequent Figure 3.

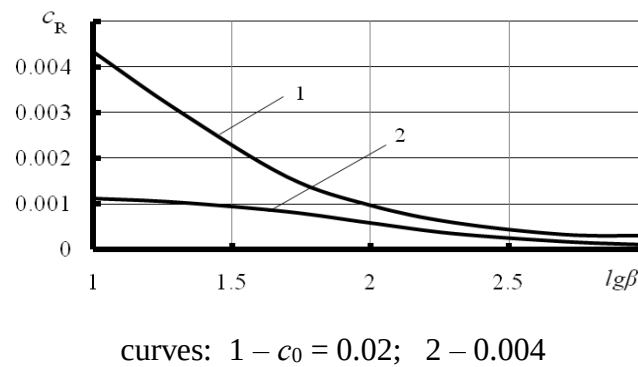


Figure 3 – The relationship of the averaged concentration of the pollutant in the mass of water discharged from the apparatus over its operational period

Figure 3 illustrates the curves representing the average concentration of the substance in the water that has flowed out of the apparatus during its operation. This is a significant indicator of the adsorber's efficiency. From Figures 2 and 3, important parameters emerge that characterize the adsorbent—namely, its operational time and the degree of purification in relation to the initial value c_0 .

Now we will demonstrate the accuracy of the calculations performed (Table 1).

Table 1 – Values of adsorbed masses of the substance for two scenarios at different values of β

β	m – formula (1)	m - calculation	error, %	m - formula (1)	m - calculation	error, %
10	33.333	32.33	3.01	7.692	7.46	3.02
20	57.143	55.3	3.225	14.815	14.404	2.773
50	100	97.09	2.91	33.333	32.454	2.638
100	133.333	129.6	2.8	57.143	55.666	2.585
200	160	155.84	2.6	88.889	86.62	2.553
500	181.818	176.64	2.848	133.333	130.007	2.495
1000	190.476	184.96	2.896	160	155.937	2.54

Table 1 presents the values of adsorbed mass per unit area $m = a \cdot L$ (kg/m²) of the substance for two scenarios at various β values. The second column ($c_0 = 0.02$) and the fifth column ($c_0 = 0.004$) display the mass values calculated using formula (1) at the point when the process is complete and the adsorbed mass is in equilibrium. The third and sixth columns show the mass values of the substance that was adsorbed during the operation of the apparatus, derived from numerical calculations.

The provided error values in percentage indicate that the compared quantities are closely aligned, meaning the calculation was conducted satisfactorily. From the last row of the table at $\beta = 1000$, it is evident that the adsorption value, particularly in the first variant, is already quite close to its maximum value ($m = A \cdot L$) at a relatively low equilibrium concentration c_0 .

4. Conclusion

The calculations conducted have demonstrated the frontal nature of the cleaning process under the selected parameters, as well as the impact of adsorption parameters

and the initial concentration of the contaminating component on its efficiency. The values obtained for the operating time of the adsorber and the concentrations of the residual mass of the adsorbed component can provide insights into the effectiveness of using a particular adsorbent.

Thus, through a formal description of the adsorption process using a mathematical model, one can trace the dynamic aspect of the filtration flow and assess the operating time and efficiency of a specific adsorbent.

Conflict of interest

Authors state no conflict of interest.

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ДИНАМІЧНІ ОСОБЛИВОСТІ І ОЦІНКА ЕФЕКТИВНОСТІ АДСОРБЦІЙНОГО МЕТОДУ ОЧИЩЕННЯ ВОДИ НА ОСНОВІ ІЗОТЕРМИ ЛЕНГМЮРА

Єлісєєв В.І., Луценко В.І., Беркут В.Д.

Анотація. У цій роботі на основі фільтраційних рівнянь та ізотерми адсорбції Ленгмюра проведено розрахунки кінетичних характеристик масообміну при доочищенні забруднених вод гірничодобувної промисловості у пористому адсорбері. Результати розрахунків показують значний вплив коефіцієнта, що характеризує швидкість адсорбції, на характер кінетичних кривих. Розрахунки показали, що зі збільшенням цього

коефіцієнта зростає крутість кривої концентрації, що згодом переміщається вздовж осі апарату, і процес набуває фронтального характеру. Важливе значення при цьому мають величини початкових концентрацій речовини, що видаляється. Зі зменшенням значень початкових концентрацій час працездатності апарату значно збільшується. У даній математичній моделі отримано оцінку середньої за часом концентрації забруднюючої речовини в обсязі очищеної води, яка є ще однією важливою величиною, що характеризує роботу адсорбера. З неї випливає, що величина концентрації забруднюючої речовини в обсязі очищеної води c_R залежить від початкової концентрації та параметрів ізотерми адсорбції. Зі збільшенням коефіцієнта, що характеризує швидкість адсорбції, ступінь очищення підвищується, тобто, відношення концентрації забруднюючої речовини c_R до початкової концентрації зменшується. Зі зменшенням початкової концентрації при тих же коефіцієнтах β ступінь очищення дещо знижується (ставлення зазначених величин підростає), внаслідок чого величина коефіцієнта β відіграє важливу роль у процесі і, відповідно, в кінцевому результаті. Наведені наприкінці статті оцінки точності розрахунків показують цілком задовільний збіг з розрахунком за балансом мас очищеної води та води, що залишається в пористому адсорбенті. Таким чином, показано, що при формальному математичному описі процесу адсорбції (в даному випадку ізотерми Ленгмюра) за допомогою запропонованої математичної моделі можна оцінити час роботи та ефективність того чи іншого адсорбенту, а також простежити динамічну складову фільтраційної течії та кінетику процесу очищення води.

Ключові слова: очищення води, адсорбція, концентрація, ізотерма Ленгмюра.