Modeling and Optimization of the Process of Separation of Heavy Metal Ions from Wastewater Aimed at Protecting the Ecosystem in Non-Stationary Conditions

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Abstract. Pollution of wastewater from the fuel and energy complex, petrochemical and metallurgical industries with heavy metals is one of the urgent environmental problems of modern industry. Arsenic, copper zinc, etc. its ions are highly toxic, accumulate in bottom sediments and disrupt biosphere processes. Developing effective wastewater treatment technologies is a priority within the framework of sustainable development. Heavy metals (As, Pb, Cu, Zn) with water pollution pose a serious threat to ecosystems and human health. The adsorption process is one of the widely applied engineering methods for the efficient and environmentally safe removal of these pollutants. The effective sorption conditions of heavy metal ions were determined using natural and modified adsorbents, following that continuous optimization of the process was carried out. The effect of initial metal concentration, pH, adsorbent dose and contact time on adsorption efficiency has been studied. The optimal conditions of the technological process have been determined by means of mathematical modeling. The results showed that under optimal conditions (pH = 6.7, dose = 1.8 g/L, contact time = 120 min), the adsorption efficiency was higher than 96%. The process obeys the pseudo-secondary kinetic model and aligns well with the Langmuir isotherm, indicating monomolecular absorption. The results of the study allow preventing the pollution of the ecosystem with the heavy metals, as well as formulating sustainable engineering approaches for environmentally safe treatment of industrial wastewater. The developed model can be applied in designing environmentally friendly adsorber systems.

Keywords: Ecosystem, Heavy Metals, Adsorption, Mathematical Modeling, Wastewater Treatment, Optimization, Sustainable Development.

1. Introduction

Modern industrial development, especially the fuel and energy complex, metallurgy and petrochemical sectors, has led to an increase in environmental impact. One of the most dangerous consequences of this effect is the ingress of industrial wastewater contaminated with heavy metal ions into ecosystems. Heavy metals such as arsenic

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(As), lead (Pb), copper (Cu), zinc (Zn) are non-biodegradable, toxic and accumulating (accumulative) components migrate into the bottom sediments of water bodies, disrupting the long-term ecological balance, passing through the biological chain to the human body, causing serious harm to health [1,2]. Neutralizing this type of pollutants generated in industrial production and separating them from wastewater is of strategic importance in terms of sustainable development and ecosystem protection. For the separation of heavy metals, various technologies are applied – chemical sedimentation, membrane filtration, ion exchange, biosorption and adsorption methods. But among them, the adsorption process stands out for its simplicity, effectiveness and economic efficiency [3-5]. Studies in recent years have shown that natural and modified adsorbents (for example, activated charcoal, natural zeolites, materials enriched with bentonite or iron oxides) can significantly reduce the concentration of heavy metal ions in water. At the same time, modeling and optimizing the behavior of these processes in non-stationary modes (under conditions of variable flow rate, concentration and pH) simulating real industrial conditions is of particular importance [6-10]. The purpose of this work is to develop scientific foundations aimed at preserving the ecosystem by modeling and optimizing the process of separation of heavy metal ions from wastewater. Kinetic and isothermal patterns of adsorption on the basis of various natural and modified adsorbents were investigated, the main factors affecting the effectiveness of the process (pH, initial concentration, amount of adsorbent, contact time) were determined and optimal conditions were selected [6-10].

2. Materials and methods

The aim of the study was to model and optimize the process of separation of heavy metal ions (As^{3+}, Pb^{2}+, Cd^{2}+ and Zn^{2}+) from wastewater. The studies were carried out in laboratory conditions adapted to the technological waters of Azerbaijan industrial enterprises.

2.1. Selection and preparation of adsorbents

Two main types of adsorbents were used in the study: modified zeolite and activated charcoal-chemical modification with HCl (0.1 M) and $FeCl_3$.Solutions were prepared to increase the adsorption capacity of the surface. The prepared samples were dried at a temperature of 105 °C for 24 hours, ground to a particle size of 0.5–1 mm and stored in a dry state.

2.2. Adsorption conditions

The experiments were carried out in non-stationary (dynamic) and stationary (static) modes. Concentration of primary metal ions: 50-150mg/ L, pH range: 2-12, adsorbent dosage: 0.5-2.0 g/L, contact time: 20-180 min, temperature: (21 ± 1) °C. The pH values were adjusted with NaOH or HCl solutions. Mixing was carried out using a magnetic stirrer at 200 rpm. Figure 1 shows a graph of the normal probability (output concentration, mg/l). Figure 2 shows a graph of the main effects for the output concentration. As can be seen from figure 2, the initial concentration, adsorbent dose, and adsorption process temperature significantly affect the adsorption capacity of the adsorbent. In figure 3 the interaction graph for the output concentration is illustrated. The results indicate that the interaction effects of temperature, adsorbent dose, and initial concentration have a significant impact on the process output concentration. In figure 4 a graph of the dependence of the Pareto output concentration on the dose is shown. adsorbent. It can be seen that the output concentration varies with the dose adsorbent and temperature.

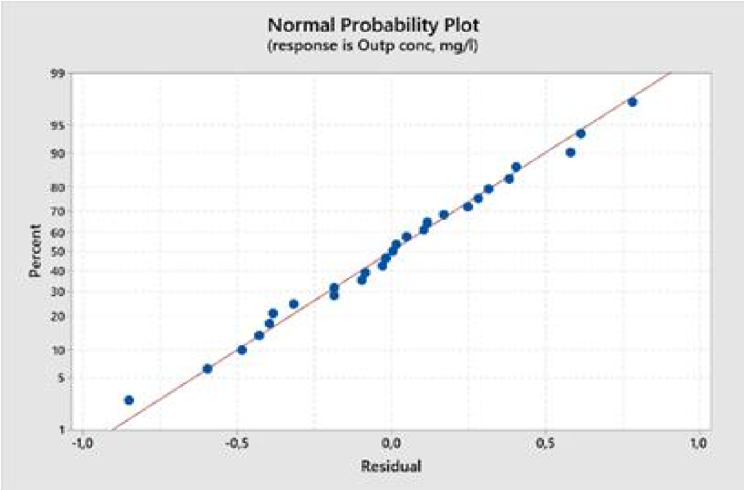

Fig.1. Normal Probability Plot (response is Output concentration, mg/l)

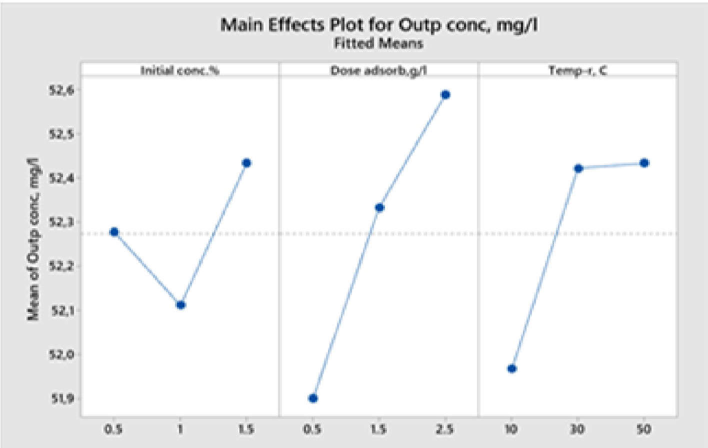

Fig.2. Main effects Plot for Output concentration, mg/l

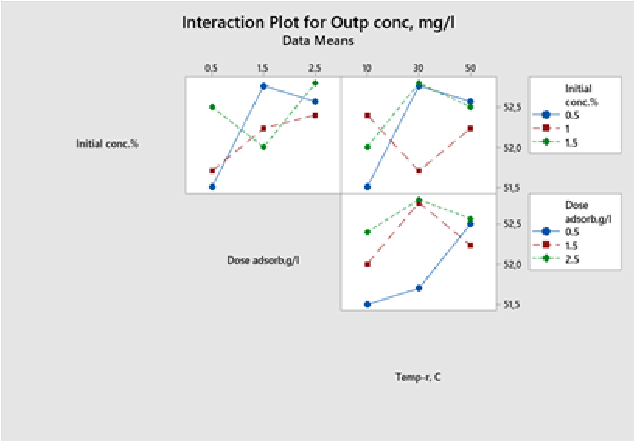

Fig.3. Interaction Plot for Output concentration mg/l

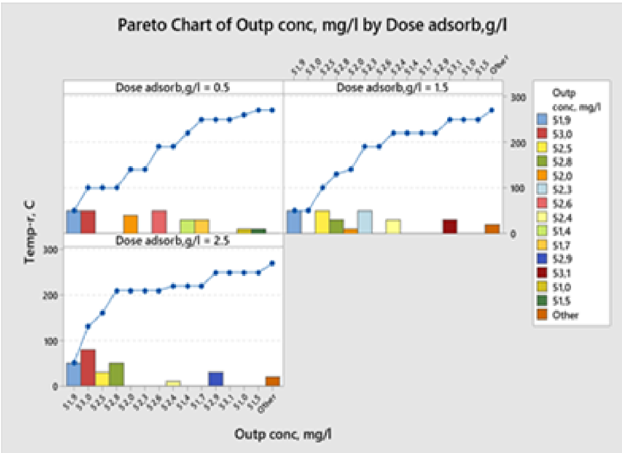

Fig.4. Pareto Chart of Output concentration, mg/l by Dose adsorbent, g/l

Experiments and calculations were carried out for all heavy metal ions As, Pb, Cu and Zn. It was found that the greatest number of As ions are released among all heavy metal ions. Since the characteristics of the curves of heavy metal ions Pb, Cu, and Zn are the same, graphs are described only for the heavy metal ion As. It has been established hat the adsorption capacities(mg/g) of heavy metal ions from waste water in clinoptilolite are as follows. As -52,3; Pb-43,6; Cu-36,7; Zn-22,8

Characteristics of unsteady conditions in the experiments carried out, the adsorption process was studied under conditions of time-varying flow rates and con centrat ions. This made it possible to bring the simulation closer to real industrial conditions. Nonstationary conditions are under stood to mean time-varying gradients of concentration and mass transfer in a system, as well as the nonlinear behavior of diffusion in pores. When designing and optimizing adsorption processes, it is very important to correctly evaluate the values of kinetic, diffusion and adsorption coefficients. For this purpose, we used a previously developed mathematical model of adsorption [11]. The mathematical model of the adsorption of heavy metal ions Pb^{2+}, As^{3+}, Zn^{2+} and Ni2+ from industrial wastewater consists of the equations of the adsorbed substance in a continuous phase and the kinetic equations in the form:

$$m\frac{\partial c(x,t)}{\partial t} + \vartheta\frac{\partial c(x,t)}{\partial x} + (1-m)\frac{\partial a(x,t)}{\partial t} = D_e\frac{\partial^2 c}{\partial x^2} \quad (1)$$

$$\frac{\partial a(x,t)}{\partial t} = \beta_{об}\cdot(c - c_0) \quad (2)$$

$$a(x,t) = \Gamma\cdot c(x,t) \text{t=0}, \ c(x,0) = 0, \text{ x=0 } c(0,t) = C_0 \quad (3)$$

Here c(x,t), a(x,t)-accordingly, the concentrations of the adsorbent and adsorbate; x,t are the coordinates for the height of the layer and time; ϑ-is the flowrate of raw materials, m is the porosity of the layer; De is the effective diffusion coefficient, consists of the sum of the coefficients of molecular and longitudinal diffusion between granules;$\beta_{ob}$is the total mass transfer coefficient; c_p is the equilibrium on centration of the adsorbent;$\Gamma$is the Henry coefficient. Laplace-Carson transformation was applied:

$$c(t) = \frac{1}{V}\int c(A,t)dV \quad (4)$$

From formula (1) tode termine the effective diffusion coefficient D_e, we obtain the following formula:

$$D_e = \frac{\vartheta^2}{4[m+(1-m)\Gamma]} \quad (5)$$

Here $k_T$is the inverse of the Kramp function. Formula (5) is identical to the one given in for finding D_e. The results of experimental studies: the dependence of the ratio of the adsorbent c/c_o on the adsorption time t is given in the table.1.

Table1. Dependence of the ratio of the adsorbent C/C_O on the time of adsorption time t

Time t, min	C/C_0		
	ϑ_1=0,05 m /s	ϑ_2=0,03 m/s	ϑ_3=0,01m/s
0	0	0	0
10	0,15	0,04	0,02
20	0,82	0,71	0,57
40	0,96	0,84	0,75
60	0,98	0,91	0,83
80	0,99	0,95	0,88
100	0,99	0,96	0,91
120	1	0,98	0,94

To find the total mass transfer coefficient β_{ob} from equation (2), we use the Zhukhovitsky-Tikhonov-Zabezhinsky formula:

$$\sqrt{t} = \sqrt{\frac{\Gamma}{\vartheta}\sqrt{x} - K_T\sqrt{\frac{\Gamma}{\beta_{об}}}}, \tag{6}$$

$$K_T = \text{arcф}\left(1 - \frac{c}{0{,}54 \cdot C_0}\right) \tag{7}$$

where, $f(K_T)$ is the Kramp function. Tode termine the numerical values of the parameters D_e and β_{ob} using formulas (5), (6), calculations were performed on a computer based on the program. As a result, based on the conducted experimental studies, depending on the ratio of the adsorbent C/C_0, the numerical values of the parameters D_e and β_{ob} were determined. The dependencies were approximated by the equations:

$$\beta_{об} = 1{,}378 \cdot \left(\frac{C}{C_0}\right)^2 + 1{,}705 \cdot \frac{C}{C_0} + 0{,}002 \tag{8}$$

$$D_e = 7{,}997 \cdot \left(\frac{C}{C_0}\right)^2 - 12{,}763 \cdot \frac{C}{C_0} + 6{,}137 \tag{9}$$

The coefficients of the equations were found by calculations based on the Matlab system in the Optimization Toolbox environment. Thus, the system of equations (1)-(7), (8) and (9), which describes the dynamics of the adsorption of the components of the gas mixture in a fixed adsorbent layer, forms a complete mathematical model of the dynamics of the process under consideration under conditions of unsteadiness of the process [12-21].

3. Conclusion and Recommendations

In this research, the treatment of heavy-metal-contaminated wastewater by adsorption was investigated under non-stationary (dynamic) conditions, reflecting the variable nature of real industrial processes. The study demonstrated that time-dependent changes in flow rate, concentration, and temperature exert a significant influence on adsorption kinetics, and reliance solely on static or equilibrium models cannot adequately represent the complexity of the real process. The optimized technological regime (pH ≈ 6.7, adsorbent dose 1.8 g/L, contact time 120 min, initial concentration $C_0 \approx$ 0.5- 2,5 mg/L) ensured more than 96% removal efficiency in both laboratory experiments and dynamic simulations. The developed numerical model, based on non-stationary mass-transfer equations, accurately reproduced the experimental breakthrough curves (R^2 = 0.987–0.995), revealing the combined effect of flow dynamics and micropore diffusion as the dominant mechanism. These findings form a reliable basis for large-scale industrial implementation and environmentally responsible decision-making. The significance of this research extends beyond technological optimization. The application of dynamic adsorption models allows for a more accurate assessment of the impact of industrial discharges on aquatic ecosystems. In particular, it contributes to reducing acute toxicity risks to aquatic organisms (phytoplankton, benthic invertebrates, fish), preserving the self-purification capacity of freshwater ecosystems, minimizing bioaccumulation and bio magnification of heavy metals in food chains, strengthening the link between industrial operations and long-term ecosystem health. Thus, dynamic adsorption models serve not only as process-engineering tools but also as effective instruments for ecosystem protection and sustainable environmental management.

3.1 Recommendations for Industrial Application

For industrial application, it is recommended to implement real-time monitoring integrated with proportional–integral–derivative (PID) control to ensure stable system performance under variable operating conditions. Pilot-scale dynamic testing should be expanded to identify optimal operating regimes under fluctuating industrial loads, while dynamic optimization of sorbent regeneration and consumption is advised to reduce energy demand and associated environmental burdens. Adoption of this approach can substantially reduce heavy-metal emissions and ecological risk, support biodiversity preservation, and minimize waste generation through efficient adsorbent regeneration. Additionally, the use of non-stationary modeling frameworks is recommended to improve the treatment of pollution under non-steady industrial conditions.

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