Study of the efficiency of water treatment from ammonium ions by a calcined sorbent from ash-and-slag waste

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Experimental studies of sorption on water treatment from ammonium ions by a calcined sorbent based on ash-and-slag waste from thermal power engineering have been carried out. The calcined sorbent was obtained by calcining samples of ash-and-slag from coal combustion at the Novocherkassk State District Power Plant at a temperature of 600 °C for 30 min. The sorption capacity of a sorbent with a dose of 2.0 g per 50 mL of a model solution, a stirrer speed of 200 rpm, pH 7, and sorption time from 10 to 180 minutes was studied. The influence of the initial concentration of model solutions with the content of ammonium ions 5, 20, 50 and 100 mg/L on the amount of adsorption and treatment efficiency was studied. The highest treatment efficiency of 60% was obtained for an initial concentration of ammonium ions in a solution of 20 mg/L. Processing of experimental data was carried out according to the models of pseudo-first, pseudo-second-order and intra-particle diffusion kinetics. The best description of the experimental data was obtained using the pseudo-first-order model, which has the highest value of the coefficient of determination. The adsorption equilibrium in the system ammonium ions – calcined sorbent was studied for the initial concentration of ammonium ions in solution: 5, 20, 30, 50, 100, 200, 300 mg/L. Processing of experimental data on equilibrium was carried out on the basis of two-parameter adsorption isotherms: Langmuir, Freindlich and Temkin. The value of the coefficient of determination according to the Langmuir isotherm is the largest $R^2 = 0.9904$. Dependences between the cleaning efficiency at adsorption equilibrium and the initial concentration of ammonium ions in solution for the system ammonium ions – calcined sorbent are obtained. With an increase in the initial concentration of ammonium ions in the solution, the treatment efficiency at low initial concentrations increases, and decreases with increasing concentration.

Keywords: treatment efficiency, ammonium ion, sorbent, ash-and-slag waste.

Исследование эффективности очистки воды от ионов аммония прокалённым сорбентом из золошлаковых отходов

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Проведены экспериментальные исследования сорбции по очистке воды от ионов аммония прокалённым сорбентом на основе золошлаковых отходов теплоэнергетики. Прокалённый сорбент получен путём прокаливания образцов золошлака от сжигания угля Новочеркасской ГРЭС при температуре 600 °С в течение 30 мин. Исследована сорбционная способность сорбента с дозой массой 2,0 г на 50 см³ модельного раствора, частота вращения перемешивающего устройства 200 об./мин, pH 7, время сорбции от 10 до 180 мин. Изучено влияние исходной концентрации модельных растворов с содержанием ионов аммония 5, 20, 50 и 100 мг/дм³ на величину адсорбции и эффективность очистки. Наибольшая эффективность очистки 60% получена для исходной концентрации ионов аммония в растворе 20 мг/дм³. Обработка экспериментальных данных проведена по моделям кинетики псевдопервого, псевдовторого порядка и диффузионной. Лучшее описание экспериментальных данных получено по модели псевдопервого порядка, имеющей наибольшее значение коэффициента детерминации. Изучено адсорбционное равновесие в системе ионы аммония – прокалённый сорбент для исходной концентрации ионов аммония в растворе: 5, 20, 30, 50, 100, 200, 300 мг/дм³. Обработка экспериментальных данных по равновесию проведена на основе двухпараметрических изотерм адсорбции: Ленгмюра, Фрейндлиха и Темкина. Значение величины коэффициента детерминации по изотерме Ленгмюра является наибольшим $R^2 = 0,9904$. Получены зависимости между эффективностью очистки при

адсорбционном равновесии и исходной концентрацией ионов аммония в растворе для системы ионы аммония – прокалённый сорбент. С ростом исходной концентрации ионов аммония в растворе эффективность очистки при малых исходных концентрациях возрастает, а с увеличением концентрации падает.

Ключевые слова: эффективность очистки, ион аммония, сорбент, золошлаковые отходы.

The presence of ammonium ions in surface and wastewater (WW) indicates their bacterial contamination by pathogenic microorganisms. This is due either to the location of the water body near the disposal site for hazardous objects [1], or to insufficient treatment of household wastewater [2]. In work [3], various technologies for wastewater treatment are considered and the characteristics of sorbents and research conditions are given. A large number of works are devoted to the study of mineral natural zeolites for the treatment of wastewater from ammonium ions, such as clinoptilolite [4–6], calcium bentonite [7], halloysite [8], analcime [9], dispersed silica [10], etc.

Currently, the treatment of wastewater from ammonium ions using sorbents based on industrial waste has become widespread. Let's look at this issue in more detail.

In a study [11], the authors used activated carbon obtained from coconut shells as a sorbent to purify water from ammonium ions (India). The coconut shell was heated to 400 °C in increments of 10 °C/min in an inert atmosphere of nitrogen, and upon reaching 400 °C, it was kept for 4 hours. The resulting coal weighing 50 g was treated with 250 g of an aqueous 85% solution of orthophosphoric acid with permanent stirring and heating up to 85 °C for 4 hours. Then the sample was dried in vacuum at a temperature of 110 °C for 24 hours. Next, the sample was activated in a vertical cylindrical muffle at 800 °C in a nitrogen flow at a nitrogen flow rate of 100 mL/min. The samples were washed with water until the pH value was neutral and dried at 110 °C to obtain activated carbon. The resulting sorbent weighing 2 g was placed in a flask with 50 mL of a solution containing ammonium ions. In the test mixtures, we varied the pH values of solutions (5, 6, 7, 8, 9 and 10 pH units), solution temperatures (10, 20, 30, 40 and 50 °C), contact time (up to 120 min), and initial ion concentration ammonium (500, 1000, 1500 and 2000 mg/L), sorbent particle size (300 and 600 μm). Based on the data obtained, Langmuir and Freundlich isotherms were constructed and thermodynamic coefficients were determined. At a solution pH value of 9, temperature 10 °C, initial concentration of ammonium ions 500 mg/L, the maximum equilibrium value of sorption capacity was noted to be 2.48 and 2.28 mg/g for sorbents with particle sizes of 300 and 600 μm, respectively.

In [12], scientists from Nepal and South Korea used activated carbon obtained from waste tires by pyrolysis in various media as a sorbent to purify water from ammonium ions. The adsorption isotherm and kinetic curves were studied at the optimal pH value of 9. The adsorption isotherm was better fitted by the Freundlich model than by the Langmuir model. The equilibrium adsorption capacity of the monolayer, calculated by Langmuir, was 277.8 mg/g at room temperature. The adsorption reached equilibrium after 120 min, and the kinetic data fit well to a pseudo-second-order model with a constant rate of $5.3 \cdot 10^{-3}$ L·g/(mg·min). Adsorption of ammonium ions by activated carbon was carried out from real water samples collected from different places in the Kathmandu Valley (Nepal).

In [13], the authors studied zeolite waste from fluid catalytic cracking units, which are widely used in the oil refining industry, as the basis of a sorbent for treating water from ammonium ions.

In [14], the authors used fly ash from coal combustion, generated at a thermal power plant in Shanghai (China), as the basis of a sorbent for purifying water from ammonium ions. A sample of fly ash weighing 15 g was treated with 150 mL of 2.0 M sodium hydroxide solution at boiling for 48 hours. Afterwards, the mixture was centrifuged and the supernatant was removed. The precipitate was washed three times with double-distilled water, then twice with ethanol, and dried at a temperature of 45 °C. Next, the sample was treated with 0.01, 0.1, 0.9 and 1.8 M solutions of sulfuric acid for 6 hours, the precipitate was separated by centrifugation, washed with double-distilled water and alcohol and dried. Then samples weighing 0.4 g were placed in 40 mL of a solution containing 2.5 to 1200 mg/L of ammonium nitrogen and the mixture was stirred for 24 hours at room temperature. The highest degree of extraction, about 60%, was achieved when a sample treated with a 0.01 M sulfuric acid solution interacted with a solution containing 10 mg/L of ammonium nitrogen. The effect of solution pH on the degree of extraction of ammonium ions was studied.

The degree of extraction of ammonium ions is about 60% and is in the pH range of solutions from 5 to 10.

Chinese scientists in a study [15] used two types of fly ash from coal combustion generated at thermal power plants (Yunnan Province) to purify water from ammonium ions: high calcium oxide content 37.55% and low calcium oxide content 3.31%. A sample of fly ash was treated with sodium hydroxide solution, dried at a temperature of 100 ℃ for 12 hours and sifted through a sieve with a mesh size of 150 μm. To study the equilibrium, the resulting sorbents weighing 0.1 g were placed in a conical flask with a capacity of 100 mL, 50 mL of a solution with an ammonium ion concentration of 100 mg/L was added, and the mixture was stirred at a stirring speed of 180 rpm for 360 min on a thermostatic shaker at a temperature of 25 ℃. Equilibrium occurred within 60 minutes, so for further studies a contact time of 1.25 hours (75 minutes) was adopted. To study the kinetics of the adsorption process, the authors placed 0.1 g of sorbent in a conical flask with a capacity of 100 mL, added 25 mL of a solution with a concentration of ammonium ions from 10 to 300 mg/L, adjusted the pH of the solution to a value of 8 (optimal pH) and stirred the mixture at rotation speed of the mixing device is 180 rpm for 75 minutes on a thermostatic shaker at a temperature of 25 ℃. The value of the mass fraction of ammonium ions in the sorbent under experimental conditions reached about 2 and 16 mg/g for samples with high and low calcium content, respectively, and equilibrium occurred already at 60 min. The results are presented in the form of Langmuir and Freundlich isotherms. The calculated equivalent values of the mass fraction of ammonium ions in the sorbent were 3.17 and 23.8 mg/g for samples with high and low calcium content, respectively.

Indonesian scientists conducted studies of fly ash from coal combustion at five power plants to purify model WW solutions from ammonium ions. 300 mL of a model solution with an ammonium ion concentration of 780 mg/L was placed in glass containers with a volume of 500 mL. Then 4.5 and 7.0 g of fly ash were added as a sorbent and sorption was carried out for 150 minutes at a mixing device rotation speed of 180 rpm at pH 8. The maximum degree of ammonium ion extraction of 14% was achieved at a sorbent dose of 4.5 g, and 17% at a dose of 7.0 g. The adsorption value of ammonium ions in the saturated sorbent was 7.17 mg/g [16].

The treatment of wastewater samples from sewage treatment plants from ammonium ions (Zaragoza, Spain) before discharge into the Ebro River was carried out with zeolites of various properties and compositions obtained on the basis of alkaline hydrothermal treatment of fly ash samples [17]. Various doses of sorbent were placed into a 20 mL WW sample with permanent stirring for 30 min at room temperature. The efficiency of ammonium ions extraction from the WW sample by three different zeolites during static sorption ranged from 50 to 84%. With dynamic sorption by passing 50 mL of dry matter through a column filled with 100 g of sorbent, the efficiency of ammonium ion extraction reached 71%.

We have developed a calcined sorbent from ash-and-slag waste (ASW) of the Novocherkassk State District Power Plant [18], the physicochemical parameters of which were determined and presented in [19]. The calcined sorbent has been tested for the treatment of wastewater from petroleum products [20]. It has been experimentally established that the sorbent has adsorption capacity towards ammonium ions. The use of ash waste throughout Russia will reduce the alienation of territory and reduce the risk of illness for people living in residential buildings near ash dumps.

The purpose of the work is to experimentally study the sorption treatment of water from ammonium ions using a calcined sorbent.

Objects and methods of research

The object of research was a calcined sorbent based on the ashes of the Novocherkassk State District Power Plant, accumulated at the ash dump according to the hydraulic ash removal scheme; subject of research – sorption capacity, treatment efficiency, adsorption equilibrium, sorption kinetics; research methods – spectrophotometric analysis.

The air-dry ASW sample was placed in a laboratory muffle furnace LOIP LF-5/11-G1 with a TS87B control module (Russia) and kept for 30 minutes at a temperature of 600 ℃. Temperature control was carried out using a digital small-sized thermometer TCM 9410/M1 (Russia). At the end of the holding time, the resulting calcined sorbent was cooled in air at room temperature. To study the sorption properties of the calcined sorbent, a 2 g sample of it was placed in model aqueous mixtures with different initial contents of ammonium ions with a volume of 50 mL in conical flasks with a capacity of 100 mL. Magnetic cylindrical stirrers were placed in the flasks, installed on a magnetic stirrer MM 2A

(Czech Republic) and the mixture was stirred for a certain time at a rotation speed of the stirring device of 200 rpm. Then the solutions were removed from the stirrer and filtered through a "blue ribbon" ashless paper filter (Russia) installed in a glass funnel. In the resulting filtrate, the mass concentration of ammonium ions was determined by the spectrophotometric method by reaction with Nessler's reagent with the formation of a colored compound at a wavelength of radiation passing through the solution of 425 nm. The content of ammonium ions was calculated using a pre-established calibration dependence on the optical density of solutions. Optical density measurements were carried out using a PE-5300VI spectrophotometer (Russia).

The content of ammonium ions in solutions X, mg/L, was determined by the expression:

$$X = \frac{C \cdot 50}{V},\qquad(1)$$

where C is the content of ammonium ions, found from a previously constructed calibration characteristic, mg/L; V – volume of a solution aliquot taken for analysis, mL; 50 – volume of the analyzed solution, mL;

$$C = \frac{D + 0.00233}{0.64269},\qquad(2)$$

where D is the optical density according to the spectrophotometer.

The sorption capacity (adsorption value) of the calcined sorbent A, mg/g, with respect to ammonium ions was calculated using the equation taking into account the pore volume of the sorbent:

$$A = \frac{C_0V - [C(V - v_P m)]}{m} = \\ = \frac{(C_0 - C)V}{m} + Cv_P,\qquad(3)$$

where C_0 is the initial concentration of ammonium ions in solution, mg/L; C is the current concentration of ammonium ions in the solution after sorption for a certain period of time, mg/L; V – volume of the initial solution ($V = 0.05$ L); m – sorbent mass, g; v_p – specific pore volume of the calcined sorbent ($v_p = 0.506 \cdot 10^{-3}$ L/g).

The extraction efficiency of ammonium ions E, %, was determined by the ratio of the amount of ammonium ions absorbed by the sorbent to the amount of ammonium ions in the original solution, expressed as a percentage:

$$E = \frac{C_0V - (V - v_P m)C}{C_0V} \cdot 100 = \\ = \left(\frac{C_0 - C}{C_0} + \frac{v_P mC}{C_0V} \right) \cdot 100 .\qquad(4)$$

The phase equilibrium constant K_e, L/g, was calculated as the ratio of the equilibrium adsorption value A_e, mg/g, to the equilibrium concentration of ammonium ions C_e in the solution, mg/L:

$$K_e = \frac{A_e}{C_e}.\qquad(5)$$

Results and discussion

The influence of the initial concentration of ammonium ions in solution on the amount of adsorption and treatment efficiency. 7 model solutions each containing ammonium ions of 5, 20, 50 and 100 mg/L were prepared. The sorption capacity of the sorbent was studied with a dose of 2 g per 50 mL of model solution, the rotation speed of the mixing device was 200 rpm, pH = 7, and the sorption time was 10 to 180 min. The research results are shown in Table 1.

Figure 1 shows the dependences of the treatment efficiency E, %, of water from ammonium ions on the sorption duration τ, min, at various initial values of ammonium ion concentrations in the solution C_0, in mg/L: 5, 20, 50 and 100. The highest efficiency $E = 60\%$ was obtained for $C_0 = 20$ mg/L.

From Figure 1 it follows that the efficiency of water treatment from ammonium ions reaches its maximum value with a sorption duration of 180 minutes.

Kinetic models of adsorption. We have processed the experimental data on the basis of two-parameter kinetic models of adsorption, widely used in the study of sorption by modified sorbents [9, 21, 22]:

– pseudo-first-order (Lagergren):

$$A_\tau = A_e(1 - e^{-k_1\tau})\qquad(6)$$

– pseudo-second-order (Ho and Mackay):

$$A_\tau = \frac{A_e^2 k_2 \tau}{A_e k_2 \tau + 1}\qquad(7)$$

– diffusion (Morris-Weber):

$$A_\tau = k_p \tau^{1/2} + C\qquad(8)$$

where A_τ is the value of sorption capacity at time τ, mg/g; k_1, k_2 – adsorption rate constants of the pseudo-first and pseudo-second-order models; k_p – diffusion rate constant; C – parameter associated with the thickness of the boundary layer, mg/g.

Linearization of equations (6)–(7) has the form:

$$\ln(A_e - A_\tau) = \ln A_e - k_1\tau \qquad (9)$$

$$\frac{\tau}{A_\tau} = \frac{1}{k_2 A_e^2} + \frac{\tau}{A_e} \qquad (10)$$

Tables 2–4 show the values of the parameters of equations (6)–(8), obtained by processing data for initial concentrations of ammonium ions in solution of 5, 20, 50 and 100 mg/L. The parameter A_e in the pseudo-first-order model is determined by the selection method until the value $\ln A_e$ is reached, equal to that intercepted by a straight line on the ordinate plotted in coordinates $\ln(A_e - A_\tau)$ from τ. The relative error (discrepancy) is no more than 0.02%. A similar approach, called the trial and error method, is considered in [23].

The obtained coefficient of determination of the models $R^2 > 0.9$ (Tables 1–3) indicates the

Table 1

The effect of the initial concentration of ammonium ions in the solution
on the amount of adsorption and treatment efficiency

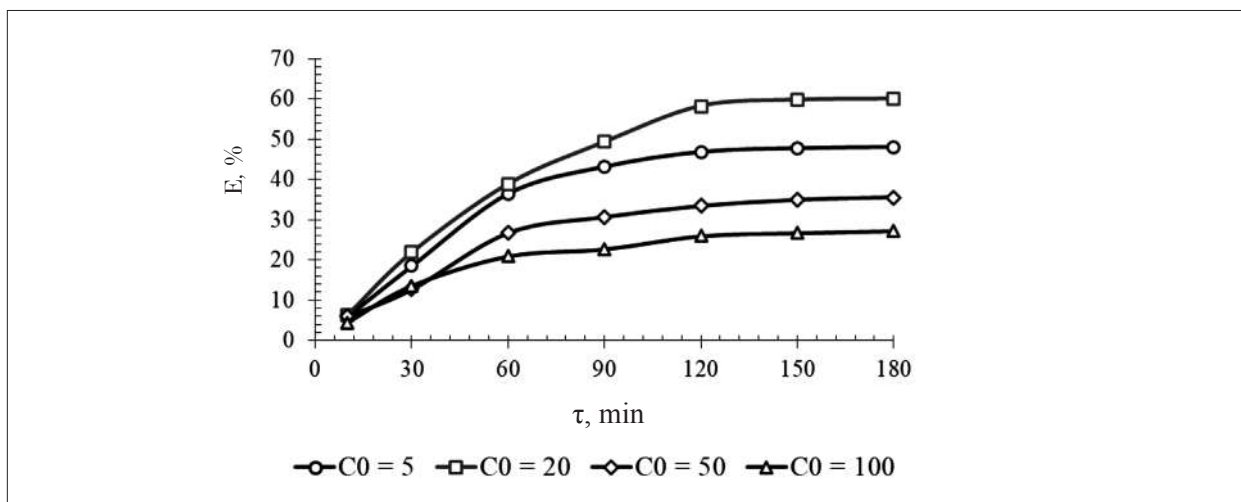| Contact time τ, min	Mass of sorbent m, g	Solution optical density D	Aliquot of solution taken for analysis V, mL	Concentration of ammonium ions in solution after sorption C, mg/L	Treatment efficiency E, %	Adsorption value A, mg/g
Initial concentration of ammonium ions in solution 5 mg/L						
10	1,9999	0,306		4,797	5,992	0,0075
30	1,9993	0,265		4,160	18,492	0,0231
60	2,0010	0,206		3,242	36,482	0,0456
90	1,9981	0,184	5	2,899	43,188	0,0540
120	2,0005	0,172		2,713	46,848	0,0586
150	2,0002	0,169		2,666	47,763	0,0597
180	2,0009	0,168		2,650	48,068	0,0601
Initial concentration of ammonium ions in solution 20 mg/L						
10	1,9980	0,366		19,104	6,414	0,0321
30	1,9992	0,305		15,940	21,914	0,1096
60	1,9989	0,238		12,465	38,937	0,1948
90	1,9989	0,197	1,5	10,338	49,354	0,2469
120	2,0008	0,162		8,523	58,248	0,2911
150	1,9980	0,156		8,212	59,771	0,2992
180	2,0006	0,155		8,160	60,026	0,3000
Initial concentration of ammonium ions in solution 50 mg/L						
10	2,0007	0,306		47,975	5,993	0,0749
30	2,0018	0,284		44,552	12,701	0,1586
60	2,0013	0,238		37,394	26,726	0,3339
90	1,9984	0,225	0,5	35,372	30,687	0,3839
120	2,0010	0,216		33,971	33,433	0,4177
150	1,9997	0,211		33,193	34,957	0,4370
180	1,9987	0,209		32,882	35,566	0,4449
Initial concentration of ammonium ions in solution 100 mg/L						
10	2,0000	0,374		97,592	4,383	0,1096
30	2,0018	0,338		88,257	13,531	0,3380
60	1,9995	0,309		80,736	20,898	0,5226
90	1,9996	0,302	0,3	78,921	22,676	0,5670
120	2,0016	0,289		75,550	25,981	0,6490
150	2,0015	0,286		74,772	26,743	0,6681
180	2,0017	0,284		74,253	27,251	0,6807

Fig. 1. Dependence of treatment efficiency E, %, on sorption duration τ, min,
at various initial values of ammonium ion concentrations in solution C_0, mg/L
(sorbent dose 2 g per 0.05 L of solution, pH 7, t = 25±2 ºC, v = 200 rpm)

Table 2

Pseudo-first-order model constants

Initial concentration of ammonium ions in solution C_0, mg/L	Equilibrium value of adsorption A_e, mg/g	Adsorption rate constant k_1, min^{-1}	Determination coefficient R^2
5	0.0619	0.0214	0.9719
20	0.3255	0.0159	0.9610
50	0.4614	0.0192	0.9922
100	0.6967	0.0212	0.9917

Table 3

Pseudo-second-order model constants

Initial concentration of ammonium ions in solution C_0, mg/L	Equilibrium value of adsorption A_e, mg/g	Adsorption rate constant k_2, g/(mg·min)	Determination coefficient R^2
5	0.0983	0.1088	0.9087
20	0.5605	0.0137	0.8922
50	0.6583	0.0202	0.9613
100	0.9344	0.0181	0.9774

Table 4

Intra-particle diffusion model constants

Initial concentration of ammonium ions in solution C_0, mg/L	Adsorption rate constant k_p, mg/(g·min$^{-1/2}$)	Parameter C, mg/g	Determination coefficient R^2
5	0.0054	- 0.0038	0.9106
20	0.0277	- 0.0368	0.9556
50	0.0382	- 0.0194	0.9269
100	0.0547	+ 0.0168	0.9214

external diffusion mechanism of physical adsorption and the applicability of the considered kinetics models for describing the adsorption of ammonium ions by a calcined sorbent based on ASW. The pseudo-first-order (Lagergren) model most adequately reflects the adsorption of ammonium ions.

Figure 2 shows the experimental data and calculated values of the adsorption value A, mg/g, from the sorption duration τ, min, cor-
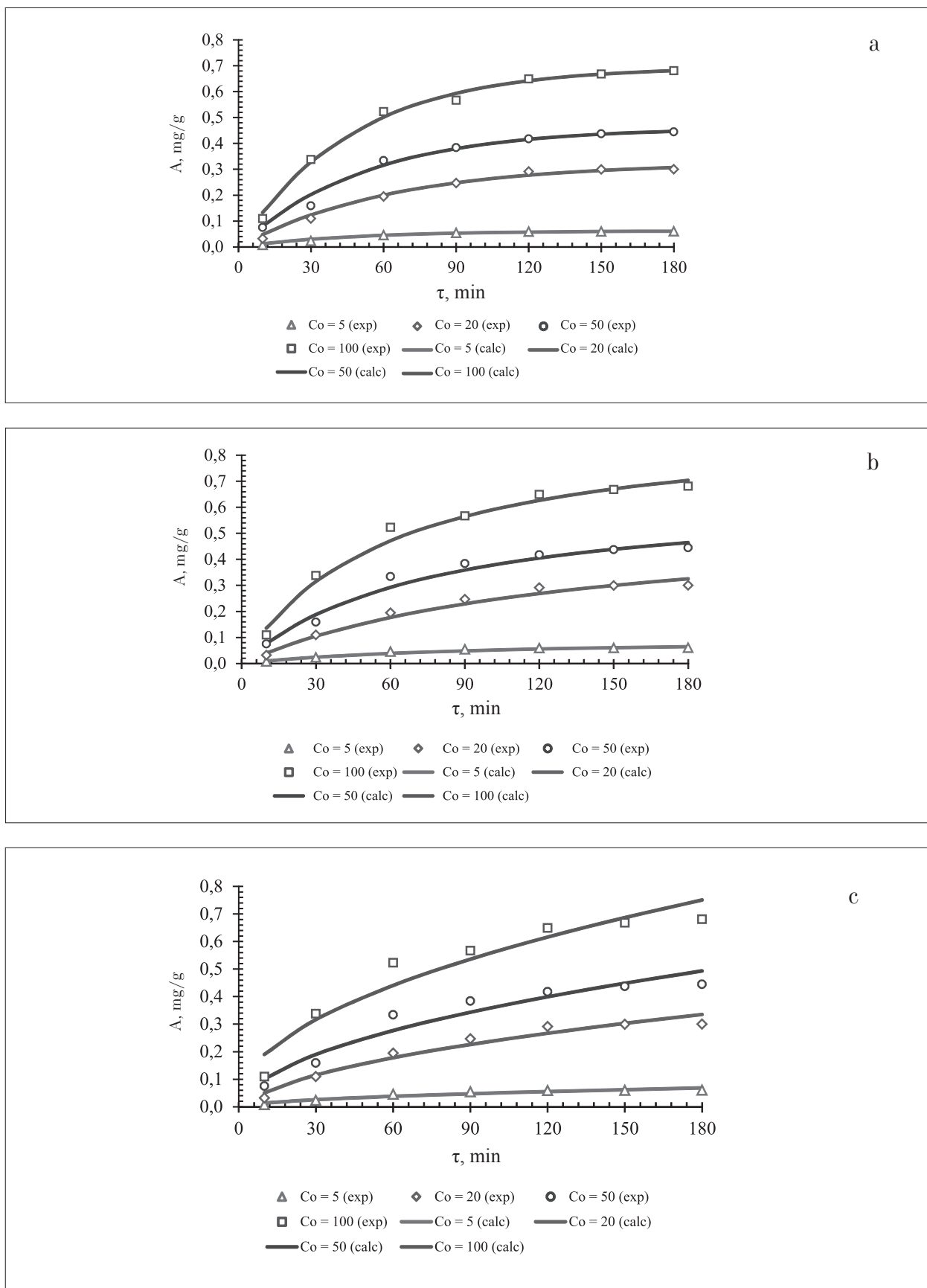
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Fig. 2. Dependence of the adsorption value on the contact time at different values
of the initial concentration of ammonium ions in the solution (sorbent dose 2 g per 0.05 L of solution,
pH 7, t = 25±2 ºC, ν = 200 rpm): a) pseudo-first-order model;
b) pseudo-second-order model; c) intra-particle diffusion

Table 5

Study of adsorption equilibrium in the system ammonium ions – calcined sorbent

Initial concentration of ammonium ions in solution C_0, mg/L	Mass of sorbent m, g	Solution optical density D	Aliquot of solution taken for analysis V, mL	Equilibrium concentration of ammonium ions in solution after sorption of C_e, mg/L	Treatment efficiency E, %	Equilibrium value of adsorption A_e, mg/g	Phase equilibrium constant, K_e, L/g
5	2.0009	0.168	5	2.650	48.068	0.0601	0.0227
20	2.0006	0.155	1.5	8.160	60.026	0.3000	0.0368
30	2.0057	0.201	1.0	15.819	48.341	0.3615	0.0229
50	1.9987	0.209	0.5	32.882	35.566	0.4449	0.0135
100	2.0017	0.284	0.3	74.253	27.251	0.6807	0.0092
200	2.0009	0.215	0.1	169.078	17.173	0.8583	0.0051
300	1.9987	0.169	0.05	266.583	12.936	0.9709	0.0036

Note: Sorption duration 180 min, magnetic stirrer speed 200 rpm, pH 7, temperature 25±2 °C.

responding to the initial concentration of ammonium ions, in mg/L: 5, 20, 50, 100 according to the pseudo-first, pseudo-second-order and diffusion models.

With an increase in the concentration of ammonium ions in the initial solution C_0, the adsorption value A increases and tends to the maximum value at a contact time of 150–180 min.

In equation (8), parameter C is a segment cut off on the ordinate axis by a straight line in coordinates $A_\tau = f(\tau^{1/2})$. This dependence, constructed using experimental points, has the greatest deviation from a straight line compared to the location of experimental points and straight lines constructed using equations (9) and (10). On the one hand, this explains the deviation of the experimental points from the calculated curve in Figure 2 c), the coefficients of which were found by the linearization method, on the other hand, it confirms the assumption about the limiting stage of the external diffusion mechanism.

In real household wastewater, the concentration of ammonium ions reaches about 20 mg/L. In this case, the maximum value of adsorption will be about 0.325 mg of ammonium ions per 2 g of calcined sorbent according to the pseudo-first-order model, which has the largest average value of the coefficient of determination.

Study of adsorption equilibrium in the system of ammonium ions – calcined sorbent. An additional series of solutions containing ammonium ions of 30, 200 and 300 mg/L were prepared. 2.0 g of calcined sorbent was placed in a container with a model solution with a volume of 50 mL. The container was placed on a magnetic stirrer. The solution was stirred for 180 minutes at pH=7 at a stirring speed of 200 rpm. The ad-

sorption equilibrium results are shown in Table 5, including the equilibrium data in Table 1.

Analyzing the data in Table 5, it can be noted that with adsorption equilibrium in the system of ammonium ions – calcined sorbent, the cleaning efficiency and phase equilibrium constant increase with an increase in the initial concentration of ammonium ions in the solution and reach a maximum at an initial concentration of ammonium ions of about 20 mg/L and then decrease.

We will process the experimental data on adsorption equilibrium on the basis of two-parameter adsorption isotherms [24, 25], relating the equilibrium adsorption value (sorption capacity) A_e, mg/g, with the equilibrium concentration of ammonium ions in the solution C_e after sorption, mg/L:

– Langmuir

$$A_e = A_{max} \frac{K_L C_e}{1 + K_L C_e};\qquad (11)$$

– Freundlich

$$A_e = K_F C_e^{1/n};\qquad (12)$$

– Temkin

$$A_e = \frac{RT}{B_T}\ln(K_T C_e).\qquad (13)$$

We determine the coefficients using the linearization method:

– Langmuir isotherms

$$\frac{C_e}{A_e} = \frac{C_e}{A_{max}} + \frac{1}{K_L A_{max}};\qquad (14)$$

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– Freundlich isotherms

$$\ln A_e = \ln K_F + \frac{1}{n}\ln C_e; \qquad (15)$$

– Temkin isotherms

$$A_e = \frac{RT}{B_T}\ln K_T + \frac{RT}{B_T}\ln C_e, \qquad (16)$$

where A_{max}, K_L are Langmuir constants; K_F, n – Freundlich constants; B_T, K_T – Temkin constants; $R = 8.314$ – universal gas constant, J/(g·K); T – temperature, К.

The Langmuir model is used to describe adsorption on a monomolecular layer. The A_{max} value shows the maximum (limiting) value of the adsorption value at the initial concentration of ammonium ions in the solution C_0, and the K_L constant is called the Langmuir adsorption equilibrium constant.

The Freundlich model characterizes unlimited adsorption on heterogeneous surfaces in several layers. The K_L constant is called the Freundlich adsorption equilibrium constant. The constant n (or $1/n$ – heterogeneity coefficient) shows the intensity of interaction between the adsorbent and ammonium ions at equilibrium.

The logarithmic Temkin adsorption isotherm was obtained taking into account the heterogeneity of the surface, which distinguishes it from the Langmuir isotherm, which describes adsorption on a homogeneous surface. Adsorption is monomolecular in nature.

Adsorption isotherm constants are given in Table 6.

The value of the coefficient of determination according to the Langmuir isotherm is the largest ($R^2 = 0.9904$). A comparison of experimental data and calculated adsorption isotherm curves (Figure 3) shows that the best description is achieved using the Langmuir model. It can be concluded that the adsorption of ammonium ions on a calcined sorbent based on ASW of thermal power engineering corresponds to the theory of monomolecular adsorption.

The relationship between the initial C_0 and equilibrium C_e concentrations of ammonium ions is almost a straight line with the coefficient of determination $R^2 = 0.9977$, when described by a quadratic dependence $R^2 = 0.9994$. A slight deviation from linearity is observed at small C_0. However, at low initial concentrations of ammonium ions in the C_0 solution, the calculated

Table 6

Langmuir, Freundlich, and Temkin isotherm constants

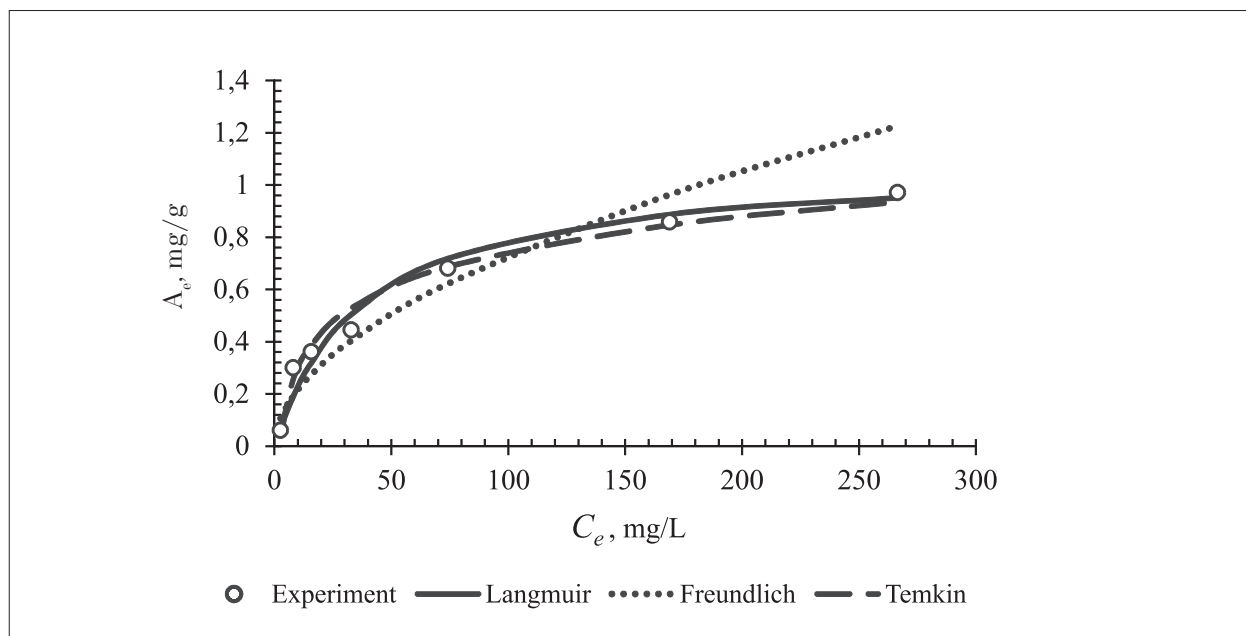| Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
A_{max}, mg/g	K_L, L/mg	R^2	n	K_F	R^2	B_T	K_T	R^2
1,0864	0,02624	0,9904	1,8823	0,06304	0,87255	12769,67	0,462	0,9822

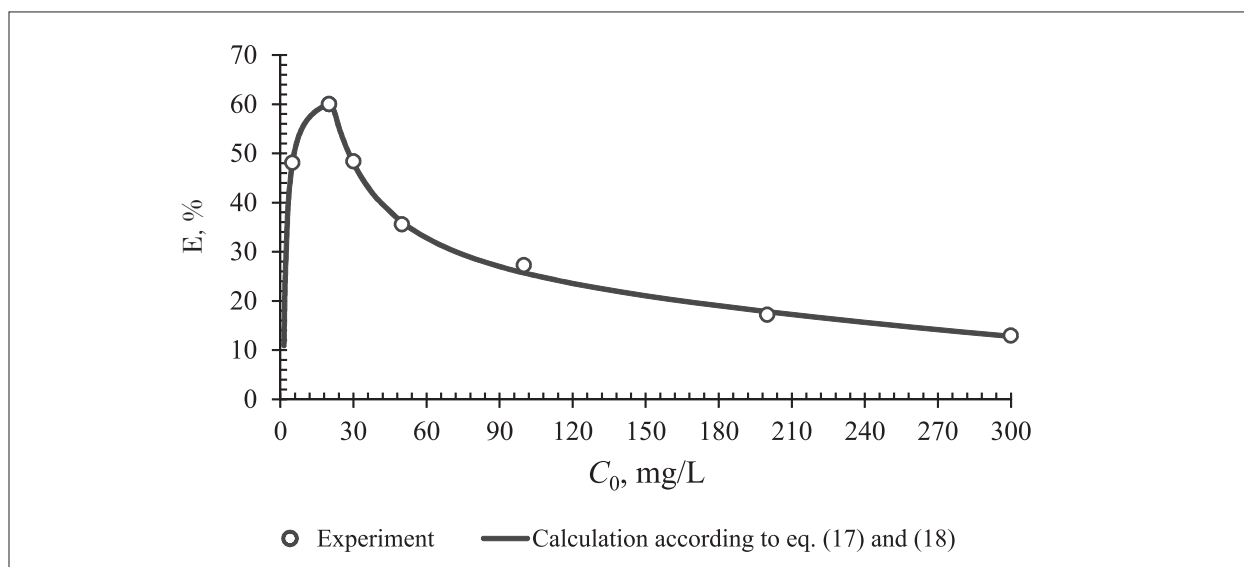**Fig. 3.** Langmuir, Freundlich, and Temkin isotherms

Fig. 4. Influence of the initial concentration of ammonium ions in the solution
on the efficiency of water treatment from ammonium ions by a calcined sorbent
(sorbent dose 2 g per 0.05 L of solution, pH 7, t = 25±2 ºC, τ = 180 min, ν = 200 rpm)

values of the equilibrium efficiency of water treatment from ammonium ions significantly exceed the experimental ones. The graphical shape of the efficiency curve is decreasing and does not have an extremum point. In this regard, we proposed to describe the relationship between the equilibrium C_e and initial C_0 concentrations of ammonium ions in solution by two approximating curves: for initial concentrations of ammonium ions from 0 to 20 mg/L – a linear dependence (equation (17)), above 20 mg/L –quadratic dependence (equation (18)).

$$C_e = 0.36733 \cdot C_0 + 0.81333 ; \qquad (17)$$

$$C_e = 0.00037 \cdot C_0^2 + 0.80857 \cdot C_0 - 8.69258 . \quad (18)$$

Figure 4 shows a comparison of calculated and experimental efficiency values at adsorption equilibrium. The efficiency was calculated using equation (4), where $C = C_e$. Analysis of the results shown in Figure 4 shows that a calcined sorbent based on ash-and-slag waste from thermal power engineering is most effective for removing ammonium ions from water at initial concentrations from 5 to 30 mg/L. Such values of ammonium ion concentrations are typical for domestic wastewater.

With an increase in the initial concentration of ammonium ions in the C_0 solution, the efficiency of treatment E at low concentrations of C_0 increases, and with an increase in the concentration of C_0 it decreases.

Conclusion

Based on the results of the research, we can conclude that the calcined sorbent based on ash-and-slag waste from thermal power engineering is applicable for the treatment of household wastewater from ammonium ions. The pseudo-first order kinetics model best describes the experimental data on the sorption of ammonium ions from water for all initial ammonium ion concentrations of 5, 20, 50 and 100 mg/L. Among the two-parameter adsorption isotherms, the best description is obtained using the Langmuir isotherm.

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