APPLICATION OF LOW-COST FLY ASH-BASED ADSORBENT FOR REMOVAL OF ACETOCHLOR HERBICIDE FROM WATER

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Abstract

In order to satisfy man's existential needs for food and energy, two major problems arise in the environment. Excessive use of herbicides based on acetochlor (ACT) in order to maximize food production causes surface water contamination. Its effect on endocrine disorders in humans and animals has been proven. By burning coal in thermal power plants, in addition to electricity, we also get huge amounts of by-products in the form of fly ash and boiler ash, the disposal of which requires large areas of land, a huge amount of water and energy.

These problems represent a major health, environmental and economic problem. In this work, the feasibility of using adsorbent based on fly ash as a cheap adsorbent for the removal of herbicide acetochlor from water was investigated instead of using commercial activated carbon. This study recognizes that fly ash (FA) is a promising adsorbent for the removal of various pollutants. Fly ash from the Morava thermal power plant was simply chemically treated with CaO and water to give modified fly ash (MFA), which proved to be an effective adsorbent for the removal of acetochlor (ACT) from water. The content of lime (CaO and water) in the fly ash was optimized in relation to the adsorption capacity of acetochlor using the D-Optimal Design method of response surfaces (RSM). For this purpose, the commercial software "Design expert 9" was used. The results showed that the pseudo-second-order rate equation effectively describes the adsorption kinetics and that the adsorption equilibrium is established after 60 minutes. The Freundlich model showed a better fit to the adsorption isotherm than the Langmuir model. The maximum Langmuir capacity of the adsorbent for ACT was 102.6mg g^{-1} at 25 °C at a solution pH of 8.

Key words: *fly ash, adsorbent, acetochlor, water, adsorption capacity*

1. INTRODUCTION

The energy dependence of a large number of countries in the world on fossil fuels (coal) has resulted in the generation of large amounts of fly ash, which is increasingly burdening the environment. Despite the fact that there are new applications of fly ash both in the production of building materials and in soil recultivation to increase soil fertility, it still represents a major ecological, economic and social problem (Karanac et al. 2018; Dai et al. 2020).

Also, a major environmental problem in the world is the drastic increase in the use of pesticides, which is conditioned by the increase in intensive agricultural production. This widespread use of pesticides in agricultural production results in the presence of their residues in various environmental matrices. The appearance of pesticides and their metabolites in rivers, canals, lakes, seas, air, soil, groundwater, even drinking water, indicates a high risk of these chemicals to human health and the environment. Pesticides are relatively stable chemical compounds and as such can accumulate after entering a living organism. They are also very harmful due to their toxicity and carcinogenic effect (Wang et al. 2020; Veličković et al. 2021). Pesticides can be classified according to their chemical structure, target organism and physical state.

Acetochlor, which is stable, non-volatile, and hydrophobic in nature, is the most representative pre-emergence selective systemic herbicide of amides. In addition, it has a certain water solubility (Dai et al. 2020). Since its successful development, acetochlor has been one of the most important and widely used herbicide varieties in the world. Acetochlor is primarily utilized in weed control of corn, soybean and other dryland crops (Dai et al. 2020).

Due to the potential genotoxicity of acetochlor, it is classified as a B2 carcinogen, and its use range is limited. Trace amounts of metolachlor are toxic to both human beings and animals (Wang et al. 2020; Dai et al. 2020).

In recent years, the adsorption method with low cost, high operability, and no secondary pollution has been widely used to remove herbicides in aqueous environments and soils.

The aim of this research was to examine the possibility of using cheap waste material fly ash from TE "Morava" modified by simple chemical activation to remove herbicide acetochlor from water, this type of adsorbent has already been used before to remove heavy metals from water.

2. MATERIALS AND METHODS

2.1 Chemicals and reagents

A large number of different chemicals were used during the research. Bearing in mind that the properties of the adsorbent, as well as the research results largely depend on the purity of the reagent, high purity chemicals were used:

- Analytical Acetochlor (purity of 99%) (Sigma-Aldrich, PA),

- CaO (extra pure ≥96 %) (Carl Roth GmbH)

- concentrated nitric acid HNO3 (Fluka, ultrapure) - used for digestion of FA in order to determine the elemental composition and adjust the pH level,

- sodium hydroxide - NaOH (Sigma Aldrich, PA) - used to adjust the pH of the solution in the adsorption process and titration during the synthesis of adsorbents,

- deionized water (resistance of 18 MΩ cm) - used for sample preparation and dilution of the solution,

- waste fly ash from thermal power plant "Morava" Serbia.

2.2 Activation of materials

The fly ash (FA) used in this research was obtained as a waste product from the TE (Morava, Serbia). In accordance with the standards of the American Society for Materials Testing, the above-mentioned material (FA) is classified as type F ash according to the content of silicon, aluminum and iron oxides (2-4). Chemical activation of FA was performed by dry mixing of FA (50 g) with a certain amount of calcium oxide (1.5 to 5 g) with the subsequent addition of a certain amount of water (2.5 to 25 ml). The resulting mixture was first dried in a vacuum, then dried for 4 hours in an oven at 105 °C and crushed by grinding in cutting mills. The resulting adsorption material (MFA) was further used in adsorption tests to remove the herbicide acetochlor from water.

2.3 Optimization of lime content in MFA adsorbent

The optimization of adsorbent synthesis in order to obtain an efficient adsorbent for the selected pollutant is based on the selection of the most influential factors (calcium oxide content and water content after mixing), which affect the efficiency of the adsorption process. The range of variable sizes is defined in relation to the highest adsorption capacity; therefore, the optimization goals are defined in relation to the adsorption efficiency (capacity).

Lime content in FA was optimized by response surface method (RSM) using D-optimal experimental design with 16 points of which five replicates (Table 1) (Veličković et al. 2021). In the experiment, the

input variables are: CaO content (2-10 %) and water content (5-50 %), and the response is the capacity of the adsorbent towards acetochlor.

Table 1. Experimental plan for optimization of MFA adsorbent using D-optimal design method of RSM response surfaces

Run	Factor 1 A: Content CaO (%)	Factor 2 B: Content H_2O (%)	Response: q_e (mg g^{-1})
1	10	5	51.1
2	6.5	24	73.1
3	10	5	51.1
4	10	28	61.5
5	4	50	78.2
6	10	50	50.2
7	2	5	48.2
8	10	50	50.2
9	2	35	64.1
10	6	5	55
11	2	5	48.2
12	3	20	60.3
13	7	49	66.3
14	2	35	64.1
15	9	16	66
16	4	50	78.2

2.4 Material characterization

The adsorbent was characterized in detail by various techniques (XRD, SEM, FTIR, BET and determination of the point of zero charge), more details of which are given in an earlier paper (Karanac et al. 2018).

2.5 Batch adsorption experiment

The adsorption of acetochlor on the MFA adsorbent, which was prepared as part of the experimental part of the work, was examined in a batch system as in similar research (Veličković et al. 2021). A certain mass of the material to be tested as an adsorbent (1, 2, 3, 4, 6, 8 and 10 mg) was measured and transferred to a glass bottle with a volume of 15 ml, and then 10 ml of Acetochlor solution with a concentration of 10.00 mg dm^{-3} was added. Before starting the research, based on the preliminary sorption results, the adsorbent MFA was selected for further research, which showed the best sorption results (with a content of 4% CaO) and it was used in further research.

During the experiment, the following parameters were varied: adsorbent mass, contact time and temperature. In order to improve the contact between the solid phase (adsorbent) and the liquid phase, the dispersion was treated with ultrasound. The eluent was separated from the adsorbent by vacuum filtration through a PTFA filter with a pore diameter of 0.45 μm.

The concentrations of acetochlor were determined by ultraviolet visible spectrophotometer V 1800 (Shimadzu Ltd., Tokyo, Japan) at 223 nm.

The influence of contact time on adsorption was examined by keeping the initial concentration, pH value and temperature constant during the specific duration of the adsorption process. The influence of pH value on the adsorption process experiments were performed in the range for the desired adsorbent mass at the initial concentration C_i=10.00 mg dm^{-3}. The effect of temperature (25, 35 and 45 °C) on adsorption was tested at pH 8 at the optimal contact time with the desired mass of adsorbent. The adsorbent capacity is calculated according to equation (1):

$$q = \frac{C_i - C_f}{m} V \quad (1)$$

where are they: q - adsorbent capacity in mg g^{-1}, C_i and C_f are the initial and equilibrium concentrations of acetochlor in mg dm^{-3}, V - volume of solution in dm^3 and m - mass of adsorbent in g.

2.5.1 Kinetic studies

The study of kinetics provides an insight into the possible mechanism of adsorption along with the reaction pathways. The adsorption data were analyzed by linear, non-linear least-squares and graphic method in the form of pseudo-first, pseudo-second-order (Lagergreen) and second order model (Table 2) (Veličković et al. 2021).

Table 2. Kinetic model equations

Kinetic model	Nonlinear form	Linear form	Equation
Pseudo-first-order equation (Lagergreen)	$q = q_e(1 - e^{-k_1 t})$	$\ln(q_e - q) = \ln q_e - k_1 t$	(3)
Pseudo-second order equation (Lagergreen)	$q = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	(4)
Second order	$q = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	$\frac{t}{C_t} = k_2 t + \frac{1}{C_0}$	(5)

Diffusion model as Weber-Morris, Dunwald-Wagner model and Homogenous Solid Diffusion Model (HSDM) were used for modeling diffusional processes/limiting step of overall process (Table 3) (Karanac et al.2018; Popović et al. 2022; Perendija et al.2020).

Table 3. Equations of kinetic models

Kinetic model	Nonlinear form	Equation
Weber-Morris	$\mathbf{q = k\sqrt{t} + C}$	(6)
Dunwald-Wagner model	$\frac{q}{q_e} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp[-n^2 K t]$ $\log\left(1 - \left(\frac{q}{q_e}\right)^2\right) = -\frac{K}{2.303}t$	(7)
Homogenous Solid Diffusion Model (HSDM)	$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right)$ $\frac{q}{q_s} = 1 + \frac{2R}{\pi r}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sin\frac{n\pi r}{R}\exp\left[\frac{-D_s t \pi^2 n^2}{R^2}\right]$	(8)

Activation energy for arsenate adsorption was calculated using Arrhenius equation (9):

$$k` = k_0 \exp\left[\frac{-E_a}{RT}\right] \quad (9)$$

Where k´ (g mg^{-1} min^{-1}) is the pseudo-second order rate adsorption constant, k_0 (g mmol^{-1} min^{-1}) is the temperature independent factor, Ea (kJ mol^{-1}) is the activation energy, R (8.314 J mol^{-1} K^{-1}) is the gas constant and T (K) is the adsorption absolute temperature. A plot of ln K' versus 1/T gave straight line with slope –Ea/R from which activation energy was calculated.

2.5.2 Isotherm models

The equilibrium adsorption data were fitted by the isotherm models Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isothermal models (Table 4) (Karanac et al. 2018; Popović et al. 2022; Perendija et al. 2020). The Langmuir equation is based on assumption that a point of maximum adsorption corresponds to a saturated mono-layer of adsorbate molecules on the adsorbent surface - where the energy of adsorption remains constant and no transfer of the adsorbate in the plane of the surface occurs. The Freundlich sorption isotherm, widely and reliably utilized as a mathematical determining expression, allows for a calculation encompassing surface heterogeneity and exponential distribution of active sites as well as their respective energies (Perendija et al.2020). Temkin, conceived this equation for subcritical vapours in micropore solids where the adsorption process follows a pore filling mechanism onto energetically non-uniform surface. Temkin isotherm is based on the assumption that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic. The Dubinin-Radushkevich model for subcritical vapours in micropore solids where the adsorption process follows a pore filling mechanism onto energetically non-uniform surface (Perendija et al. 2020).

Table 4. Adsorption isotherms equations

Isotherms	Nonlinear form	Equation
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	(10)
Freundlich	$q = K_F C^{1/n}$	(11)
Temkin	$q_e = \frac{RT}{b} \ln(AC_e)$	(12)
Dubinin-Radushkevich	$q_e = q_m \exp\left(-B(RT)^2 \left(\ln\left(1 + \frac{1}{C_e}\right)\right)^2\right)$	(13)

2.5.3. Thermodynamic studies

The feasibility of the experimental data obtained from the adsorption studies were analysed through the thermodynamic investigation. The parameters of free energy change (ΔG°, kJ/mol), enthalpy change (ΔH°, kJ/mol) and entropy change (ΔS°, J/mol/K) were calculated using the Van't Hoff equations (14) and (15) (Perendija et al.2020; Bajić et al. 2016):

$$\Delta G^0 = -RT \ln(b) \tag{14}$$

$$\ln(b) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{(RT)} \tag{15}$$

Separation factor (R_L) is in relation to Langmuir isotherm and it is used to assess adsorption feasibility on the given adsorbent. It is calculated using next equation (16):

$$R_L = \frac{1}{(1+bC_0)} \tag{16}$$

Where C_0 (mol dm^{-3}) is initial adsorbate concentration, b (dm^3 mol^{-1}) is Langmuir constant. Value of R_L points out to the isotherm type: irreversible (R_L = 0), favorable (0 < R_L <1), linear (R_L = 1), unfavorable (R_L > 1).

2.6. Examination of adsorbent leaching as a construction material

For the purpose of safe disposal - incorporation of spent adsorbent MFA / acetochlor in building materials, a test was performed on the leaching of hazardous substances from the used adsorbent by washing. The experimental procedure was performed according to the toxic characteristic leaching procedure (TCLP) and the EN12457-2003 standard, using acetic acid (sample 1) and deionized water (sample 2) as extraction liquids (Karanac et al. 2018)

2.7. Statistical analysis of experimental data (error analysis)

In order to choose and confirm which model fits with the adsorption data, the data was analyzed by error analysis, together with the values of correlation coefficient (r) from the regression analysis. All the experiments were performed in triplicates, and only the mean values are reported. All kinetic, isotherm and thermodynamic parameters and their standard errors were calculated, with linear and/or non-linear least-squares methods, using commercial software (Microcal Origin 8.0).

Within recent decades, linear regression has been one of the most viable tools defining the best-fitting relationship quantifying the distribution of adsorbents, mathematically analyzing the adsorption systems and verifying the consistency and theoretical assumptions of an isotherm model. Root mean

squared error test and non-linear chi-square test are two mathematical error functions used in this paper to determine the best fitting adsorption model. The non-linear isotherm modeling has numerous benefits over linearization models one of them is the involvement of the minimization or maximization of error distribution between the experimental data and the modeled isotherm based on its convergence criteria.

3. RESULTS AND DISCUSSION

3.1. Optimization of fly ash - CaO content in MFA adsorbent

Comparative adsorption study, performed with FA and MFA adsorbents, was conducted to distinguish the benefits of the CaO and water addition. The optimization procedure, performed according to experimental plan, presented in Table 1, revealed that the optimal adsorbent performance was deduced from results obtained using RSM method (Fig. 1).

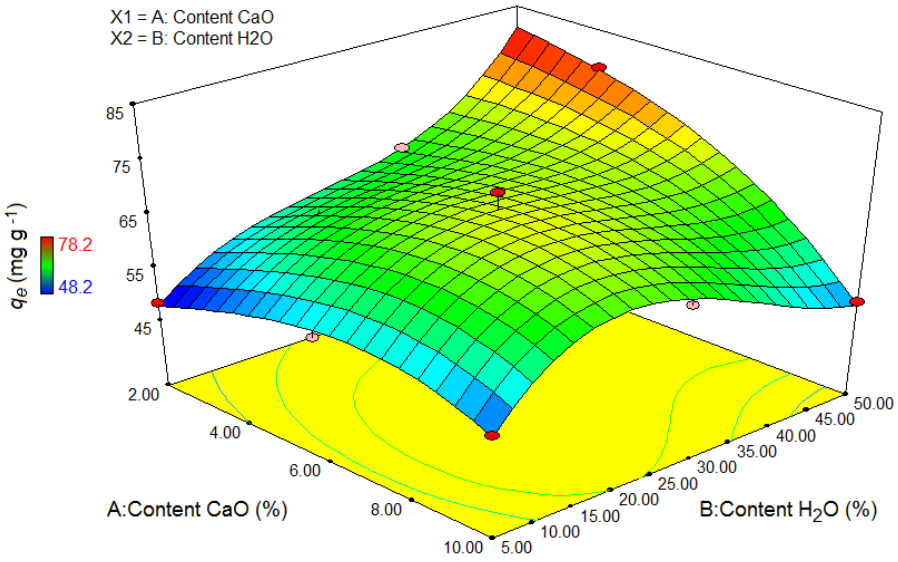

Fig. 1. Contour diagram representing relation between capacity (qe in mg g^{-1}) vs CaO and H_2O content (%) for MFA (C_i(ACh] = 10 mg L^{-1}, m/V = 100 mg L^{-1})

3.2 Effect of contact time

The influence of time on the sorption of acetochlor was analyzed in the range of 5-60 min (Figure 2). In this study, instead of classical mixing of the adsorbent-solution suspension, the reaction was stimulated by ultrasound. The presence of field ultrasound increases the rate of adsorption due to the reduction of resistance to mass transfer. Ultrasonic waves and the side effect of bubbles caused by cavitation in the solid substance (adsorbent) cause microdisruptions and thus reduce the boundary layer and increase effective mass transfer. In fact, they increase the affinity of the adsorbate for the adsorbent. In this case, ultrasound does not change the adsorption process but shifts the balance towards lower concentrations (Perendija et al. 2020; Popović et al. 2022).

The results (Figure 2) show the kinetics of the adsorption process. The kinetics for the first 30 minutes is fast, and then much slower until 60 minutes. Equilibrium is fully established in 120 minutes but the removal after 60 minutes is so small that for further research an equilibration time of 60 minutes has been taken as a compromise between theory and practice. Judging by regression coefficients (r), Δq values and calculated standard errors of parameters for all three models, the experimentally obtained kinetic data are best described by a pseudo-second-order equation (equation (4)).

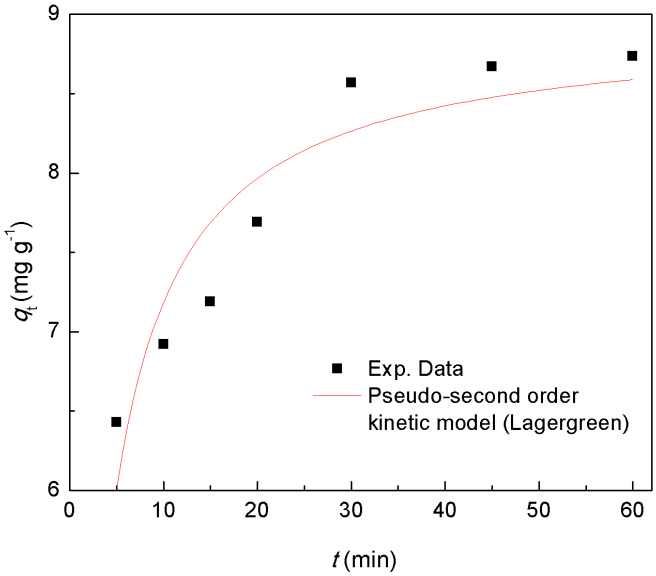

Fig. 2. Influence of time on the establishment of adsorption equilibrium (C_i=10.00 mg dm^{-3}, pH=8; V/m=1.00 g dm^{-3}, T=25 °C).

The results of fitting the experimental results with the most commonly applied kinetic models are given in table 5.

Table 5. Kinetic parameters of the model ($C_{i[ACh]}$=10 mg dm^{-3}, pH=8; V/m=1.0 g dm^{-3}, T=25 °C)

Kinetic parameters of the model	**Pseudo-first-order**	**Pseudo-second-order**	**Second order**
q_e	3.01	9.22	9.22
k (k_1, k_2)	0.046	0.03394	0.0104
R^2	0.910	0.998	0.895

The rate constants of diffusion kinetic models, intraparticle diffusion, Weber-Morris, Dunwald-Wagner and homogeneous solid diffusion models for the adsorption of acetochlor on MFA adsorbents under the same experimental conditions are shown in Table 6.

Table 6. Kinetic parameters of the W-M, D-W and HSDM models for the adsorption of acetochlor on MFA adsorbent ($C_{i[ACh]}$ =10.0 mg dm^{-3}; m/V=1.00 g dm^{-3}, pH=8, t=60 min., T=25 °C)

Intra-particle diffusion	**Constants**	**Value**
Weber-Morris	k_{p1} (mg g^{-1} min$^{-0.5}$)	0.541
(Step 1)	C (mg g^{-1})	5.198
	R^2	0.979
Weber-Morris	k_{p2} (mg g^{-1} min$^{-0.5}$)	0.0733
(Step 2)	C (mg g^{-1})	8.171
	R^2	0.996
Dunwald-Wagner	K	0.00322

	R^2	0.893
Homogenous Solid	D_s	$3.51E^{-11}$
Diffusion Model	R^2	0.890

The complex nature of the kinetics of the adsorption process can be described by considering the adsorption of molecules adsorbed on the adsorbent as a single step, as described by a pseudo-second-order equation, but it can also be described by successive / competing steps.

The Weber-Morris model reveals two linear steps that describe the adsorption process: fast kinetics in the first step and slower in the second. The first linear part describes the external mass transfer to the adsorbent surface, while the second part describes the process of material transfer into the porous structure of the adsorbent, and strictly depends on the size and shape of the pores as well as the density of their network on MFA adsorbent. Intra-particle and film diffusion slow down the transport of adsorbates. In the final phase of the process, adsorption takes place slowly until saturation is achieved on the entire available surface of the adsorbent.

3.3. Activation parameters

The activation parameters were obtained based on the Arrhenius equation (9) and are given in Table 7:

Table 7. Parameters of pseudo second-order kinetic model for acetochlor adsorption depending on temperature (C_i=10 mg dm^{-3}, pH=8; V/m=1.00 g dm^{-3}, T=25, 35 and 45 °C).

Temperature	**q_e (mg g^{-1})**	**k_2 (g (mg min)$^{-1}$)**	**R^2**
25 °C	4.129	0.0101	0.997
35 °C	4.166	0.0132	0.998
45 °C	4.228	0.0167	0.998

The calculated results give the value of Ea = 19.7 kJ mol^{-1}. The magnitudes of the activation energy can help in understanding the mechanism of adsorption of metal ions on the used adsorbent. Physosorption or physical adsorption usually has an activation energy below 40 kJ mol^{-1} (Perendija et al. 2020; Karanac et al.2018). While chemisorption requires more energy and an activation energy greater than 40 kJ mol^{-1} (Perendija et al. 2020; Bajić et al. 2016). According to this, it can be concluded that in this case we have a physisorption process. In practice, both physisorption and chemisorption can be expected on the surface of the adsorbent, for example, a layer of molecules can be physically adsorbed on a basic chemisorbed layer.

3.4. Adsorption isotherms

The state of interactions/bonds on the adsorbate/adsorbent surface can be observed by fitting the experimental data to different adsorption isotherms. The normalized correlation coefficient and standard deviation were used to assess the fit of the adsorption data. The experimental data were compared with the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models that have already been discussed, whose parameters and equations are shown in Table 4.

Table 8. Parameters of adsorption isotherms of acetochlor adsorption on MFA adsorbent

Isothermal models and parameters		Temperature		
		25 °C	35 °C	45 °C
Langmuir isotherm	q_m (mg g^{-1})	102.65	101.73	100.41
	K_L (L mg^{-1})	1.359	1.625	2.007
	b (L mol^{-1})	366782	438562	541527
	R^2	0.992	0.990	0.987
Freundlich isotherm	K_F (mg g^{-1}) (dm^3 mg^{-1})	53.40	57.01	60.65
	1/n	0.593	0.571	0.541
	R^2	0.994	0.994	0.995
Temkin isotherm	A_T (dm^3 g^{-1})	18.894	23.408	30.757
	b_T	130.62	138.54	149.41
	R^2	0.944	0.936	0.923
Dubinin-Radushkovich isotherm	q_m (mg g^{-1})	54.82	54.72	53.82
	K_{ad} (mol^2 kJ^{-2})	8.50	8.51	8.52
	Ea (kJ mol^{-1})	7.669	7.668	7.661
	R^2	0.906	0.894	0.872

By analyzing the experimental data on the adsorption of acetochlor molecules on the investigated adsorbent, the best fit is the Freundlich adsorbent model. The results of modeling the adsorption of acetochlor on the tested adsorbent are given in Table 8 and Figure 3.

According to the Freundlich isotherm, the adsorption mechanism on MFA can be described as heterogeneous adsorption, where adsorbed ions/molecules have different enthalpies and activation energies of adsorption. The value of n from the Freundlich isotherm is a measure of the intensity of adsorption or surface heterogeneity (Perendija et al. 2020; Popović et al. 2022)..

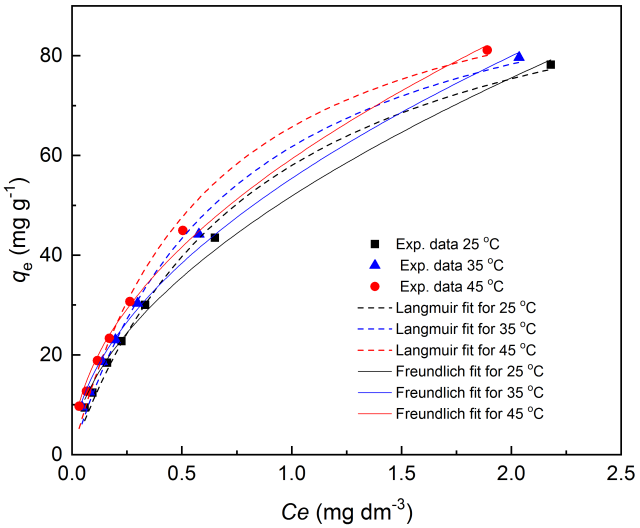

Fig. 3. Review of the results of adsorption experiments with the best-fitting models of isotherms (solid line) for the removal of acetochlor on adsorbent MFA

The calculation of the separation factor (R_L) according to equation (16) which is based on the parameter b of the Langmuir isotherm indicates the feasibility of adsorption on a given adsorbent. The R_L for adsorption of acetochlor on MFA ranges from 0.047 to 0.424 indicating that the adsorption process is favorable.

3.5 Thermodynamic studies

Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated by Van't Hoff equation (14 and 15), where T is the absolute temperature in R and b is the universal gas constant (8.314 mol^{-1} K^{-1}) and the adsorption constant b is calculated using the Langmuir isotherm (Table 7). ΔH° and ΔS° were calculated from the slope and sections in the diagram ln(b) - T^{-1}, assuming that the adsorption kinetics are stationary. The calculated thermodynamic parameters are shown in Table 9.

Table 9. Calculated Gibbs free adsorption energy, enthalpy and entropy for acetochlor adsorption on MFA at 25, 35 and 45 °C

ΔG° (kJ mol^{-1})			**ΔH°**	**ΔS°**	**R^2**
25 °C	35 °C	45 °C	**(kJ mol^{-1})**	**(J mol^{-1} K^{-1})**	
-41.72	-43.57	-45.54	15.34	191.32	0.996

Negative values of Gibbs free energy (ΔG°) and positive values of entropy (ΔS°) at all temperatures indicate that reactions in the adsorption process take place spontaneously. A decrease in the Gibbs free energy (ΔG°) with an increase in temperature also indicates that the spontaneity of the reaction increases.

Positive values of ΔS° indicate a tendency of greater disorder of the MFA surface systems and acetochlor solution. In Table 9 we can see that the Gibbs free energy values (ΔG°) for both adsorbents are approximate, and the positive entropy values (ΔS°) at all temperatures, while the positive enthalpy values (ΔH°) for MFA are noticeable, which indicates endothermic process. In general, the exchange of free energy in the case of physisorption is somewhere between -20 and 0 kJ mol^{-1}, for simultaneous hemisorption and physisorption between -20 and -80 kJ mol^{-1}, and hemisorption less than -80 kJ mol^{-1} (Veličković et al. 2021). The obtained results indicate that in these cases, hemisorption and physisorption are present at the same time.

3.6 Desorption study

An important property of any adsorbent is regeneration which can provide longevity of the tested adsorbent in a cyclic adsorption/desorption processes. Extension of the adsorbents' operating lifetime will reduce costs in real system applications. Hence, various alkaline and acidic-based regenerators are frequently employed in the regeneration process (Baskar et al., 2022). The bonding type between the adsorbate/surface functionalities has a strong influence on desorption rates. Aside from this, the deterioration of materials after desorption due to the effect of regenerators represents a negative impact and an undesirable phenomenon. Consequently, optimal regenerator dosage and acidity/basicity are important operative parameters that might lead to the efficient displacement of attached contaminants. Desorption experiments, in a column system, were therefore performed using MFA with an aim to minimize the level of material degradation, and enhance the desorption rate/efficiency by carefully selecting the desorption agent and operative parameters. The desorption process variables such as regenerator type, concentration, pH, and operating time were taken in the course of the optimization procedure. The best regeneration results, obtained using 500 mL of 2% NaOH solution at different flow rates (5.0, 10.0 and 15.0 mL/min), are given in Tabs. 10.

Table 10. The adsorption-desorption of the ACh onto MFA (Q_{des} = 5.0; 10.0 and 15.0 mL min^{-1}; m_{ads} = 0.525 g; $C_{i(ACh)}$ = 10.00 mg/L) using 2 wt.% NaOH

Cycle	Adsorption (mg g^{-1})*	Flow rate (mL min^{-1})	Desorption (mg g^{-1})*	Desorption efficiency (%)	C (ppm)**
I	74.2	5	70.77	95.4	74.31
		10	67.06	90.5	70.41
		15	65.1	87.8	68.35
III	63.7	5	58.8	92.4	61.74
		10	56.35	88.5	58.17
		15	54.67	85.8	57.40
V	55.3	5	49.98	90.4	52.48
		10	47.81	86.5	50.20
		15	46.83	84.8	49.17

* adsorption capacity and quantity of desorbed pollutants; ** concentration of the pollutant in effluent water;

The maximum desorption for MFA was 95.35% (Tab. 10) at Qdes = 5 mL min^{-1}, while increasing the flow rate the desorption percentage decreased to 90.5% and 87.8% at 10 and 15 mL min^{-1} flow rates, respectively. The concentration of ACh in the effluent was 74.31, 70.41 and 68.35 mg/L for flow rates of 5.0, 10 and 15 mL min^{-1}, respectively, after the first desorption cycle. After the fifth cycle, desorption efficiency decreases to 90.4%, 86.5% and 84.8% for flow rates of 5.0, 10 and 15 mL/min, respectively.

The findings from the reusability study reveal negligible loss of adsorption capacities for MFA, after five adsorption/desorption cycles leaving small amounts of the tightly bonded ACh (Tab. 10). Dual beneficial properties of produced MFA include relatively high adsorption capacities and desorption efficiency, and indicate high applicability in various wastewater purification systems. In general, optimized synthesis of both adsorbents provided their balanced structural and surface features which contribute to the high efficiency of ACh adsorption and desorption ability.

4. CONCLUSION

This research proved that fly ash from TE "Morava" after dry activation with CaO can be used as an effective adsorbent for removing herbicides (acetochlor) from wastewater solutions. It also showed that the optimization of the adsorbent synthesis through the response surface method can be successfully used to obtain the optimal input parameters of the synthesis, which significantly reduces the number of experiments. This additionally contributes to the preservation of the environment because in addition to economic savings due to the consumption of time and energy, there is also less consumption of dangerous chemicals that eventually end up in the environment. The results of the adsorption experiments showed us that two processes are represented during the binding of adsorbate to the adsorbent, physisorption and chemisorption. The best fit of the results to the Freundlich adsorption isotherm indicates an energetically heterogeneous surface of the adsorbent with interaction between adsorbed particles, that is, it indicates the fact that the adsorption energy decreases by filling the active centers of the adsorbent. Tests of the adsorbent for the leaching of hazardous substances using the TCLP test have shown that this adsorbent is environmentally friendly and that it can be incorporated into building materials after the end of its life cycle.

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