

UDK: 551.524.2; 541.183; 66.081

Investigation on the Adsorption of the Carbamate Pesticide Methomyl from Aqueous Solution using Modified Co-Beta Zeolite Particles

Predrag Stojisavljević¹, Nikolina Vulović¹, Zlate Veličković¹, Dušan Mijin², Stevan Stupar^{3*)}, Denis Dinić², Negovan Ivanković²

¹University of Defense, Military Academy, Pavla Jurišića Šturma 33, 11000 Belgrade, Serbia

²University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

³Military Technical Institute, Ratka Resanovića 1, 11132 Belgrade, Serbia

Abstract:

Adsorption of carbamate pesticide Methomyl by Co-Beta Zeolite particles prepared by wet ion-exchange method from aqueous solutions was studied. The effect of zeolite and pesticide concentrations, pH value, and sintering temperature on pesticide removal from an aqueous solution was studied. The change of methomyl concentration during the adsorption was followed using the UV-Visible spectrophotometer. Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDS) revealed the modified zeolite morphology and elemental structure. The change of the adsorbent surface before and after dye removal was observed using the Fourier Transformation-infrared spectroscopy (FT-IR). The adsorption kinetics follows the pseudo-second-order kinetics model, and at optimal condition adsorption rate is $k_1 = 0.0166 \text{ g mg}^{-1} \text{ min}^{-1}$. The Langmuir, Freundlich, Temkin and Dubinin-Radushkovich adsorption isotherm models were used to describe the adsorption process. Thermodynamic parameters were also determined using experimental data. The thermodynamic study indicates that during pesticide adsorption is, chemisorption and physisorption are present at the same.

Keywords: Adsorption; Pesticide removal; Adsorption kinetic; Diffusional processes; Isotherm models.

1. Introduction

Environmental pollution is a reality of modern human society, so in many countries around the world, constant efforts are being made to reduce the negative impact of this phenomenon on the health and quality of life of the human population, as well as the environment [1,2]. Human activities such as agricultural usage of herbicides, desiccants, and pesticides involving crop farming and industrial processes such as petroleum refining and combustion of fossil fuels, are contributing to the growing pollution of ground and surface water in amounts higher than the ecosystem can receive [3]. It has been proven that exposure of the organism to pesticides and their decomposition products can have carcinogenic and mutagenic effects, and the toxicity of pesticides certainly causes cell damage and the creation of metabolites harmful to the organism [4-7].

*) Corresponding author: stevan.stupar13@gmail.com

According to the broad spectra of the possibility of environmental and human contamination by pesticides from water and soil worldwide, extensive research and development of safe technologies for its effective removal was initiated. Adsorption is one of the most commonly used and most suitable considered methods as a simple, efficient, and highly effective method for pesticide removal from aqueous solutions [8-11]. The application of modern technologies in the production of materials in the field of water purification has enabled the development of various modified and functionalized high-capacity adsorbents, which should be thermostable, highly porous, with a good balance between micropores and macropores, and with the possibility of multiple applications, minimal environmental impact and financially viable in terms of exploitation [12-14]. According to many studies, the adsorption process is strongly influenced by the initial pollutant concentration, adsorbent concentration, presence of catalysts, and pH value of the solution (primarily solubility and pollutant concentration, adsorbent functional group concentration, and pollutant ionization in solution). In addition, the specific characteristics of the adsorbent (pore volume and size, specific surface area, zero filling point) can significantly impact the adsorption process [13,15]. This study aimed to investigate the performances of prepared adsorbents in terms of morphological characteristics, adsorption efficiency depending on pollutant pesticide and adsorbent concentration, capacity, and kinetics processes. As a pesticide model molecule, the carbamate pesticide methomyl was used.

Methomyl (Fig. 1) belongs to the broad-spectrum oxime carbamate pesticides with neurotoxic influence, used to protect agricultural goods from insects such as flies, crop pests, arthropods, and nematodes. However, extensive pesticide use in agricultural practices can lead to environmental pollution and human health issues [16].

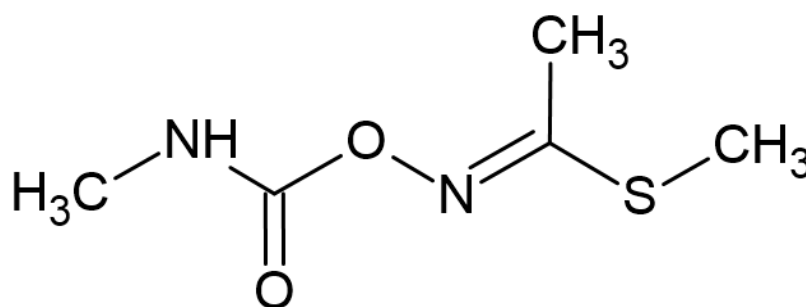


Fig. 1. Methomyl structure formula.

Many studies have proven that lethal and sub-lethal effects have been described following methomyl exposure in aquatic and soil organisms, even in more complex organisms such as rodents, amphipods, and fish. The high toxicity of the carbamate pesticide methomyl places it in the group of easily accessible chemical compounds that can be used in crises such as terrorist acts or war for water pollution, which is an essential resource for survival in addition to food [17].

Zeolites are crystalline microporous aluminosilicate minerals that are framework silicates built by SiO₄ and AlO₄ tetrahedrons. Zeolites have periodic one-to-three dimensional frameworks, unique porous structures, and satisfactory thermal and chemical stability [18]. Currently, zeolites are used in many industrial processes as adsorbents, carriers, separators, and catalysts [19]. Beta zeolite can be defined as a zeolite with high silicon content and a three-dimensional structure built by perpendicular 12-ring channel systems characteristic of the three polymorphs [20]. Modifying zeolite structure is essential to improve the characteristics of zeolite in some industrial processes. Modification of zeolite by metal is possible using isomorphic substitution and metal impregnation. In the first one, Al-centers can be replaced by 3-valent atoms and Si-centers by 4-valent atoms [21,22]. Cobalt-containing

materials are very efficient catalysts for total oxidation of Volatile Organic Compounds [23]. On the other hand, Vasiljević et al. synthesized a highly efficient adsorbent modifying the Beta zeolite particles for pesticide removal from the aqueous medium [24].

The zeolites are traditionally excellent adsorbent materials, significantly if their surface is modified. In our study, the adsorption of carbamate pesticide methomyl was investigated using the beta zeolite doped by cobalt. The adsorbent was prepared by the wet ion-exchange method, and one part of it was heated to investigate the influence of calcination temperature. The method used for surface modification improves the H-Beta zeolite adsorption capacity and the pesticide removal from aqueous solutions. Besides adsorption, Co-Beta zeolite particles can simultaneously contribute to pollutant removal from aqueous solutions as a catalyst in the degradation process. The morphology of adsorbent before and after calcination was investigated using Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy. Fourier Transformation-infrared spectroscopy was used to analyze the adsorbent surface before and after dye removal. Also, the influence of different initial parameters such as pesticide and adsorbent particles concentration, pH, and the temperature was studied. The kinetic study includes the pseudo-first, pseudo-second, and second-order kinetic models. The modeling diffusional processes/limiting step of the overall process is carried out using Weber-Morris, Dunwald-Wagner model, and Homogenous Solid Diffusion Model (HSDM). The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models and thermodynamic parameters were used to describe the adsorption process. Pesticide removal with time using Co-Beta Zeolite prepared by wet ion-exchange method, without and with calcination at 500°C, was followed by ultraviolet-visible (UV/Vis) spectroscopy.

2. Materials and Experimental Procedures

2.1. Materials and characterization methods

The carbamate pesticide methomyl was obtained from DuPont (USA). The zeolite material used for modification was H-Beta zeolite (CP811E-150, Si/Al=68) purchased from Zeolyst International (USA). Cobalt (II) chloride hexahydrate and hydrochloric acid were obtained by Centrohem (Serbia). The adjustment of an aqueous solution pH value was done by the addition of sulfuric acid and ammonium hydroxide (30% w/w) (Fisher Scientific (USA)). The Arium® Pro Ultrapure Water System (Sartorius, Germany) provided deionized water (18 MΩ). All the necessary chemicals used in the study were of analytical grade and used without further purification.

Morphology and microstructures of the adsorbent powder modified by the wet ion-exchange method before and after calcination were studied by scanning electron microscopy with Energy-Dispersive X-ray Spectroscopy (JEOL 6610LV, Japan).

Mettler Toledo pH Meter Seven Compact S220 (Switzerland) was used for the pH measurements. The solutions were stirred by an Ika (Germany) magnetic stirrer during adsorption experiments. A UV/Vis Shimadzu 3600 spectrophotometer (Japan) was used for UV-VIS analysis. Before measurements, all samples were filtered using the PVDF Millex-HV syringe filters with pore size 0.45 μm obtained from Merck (USA).

The infrared Fourier transform spectrum (FTIR) was recorded in the transformation mode between 400 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹ using an infrared (IR) spectrometer with Fourier transformation (FT) - Nicolet iS 50 manufactured by Thermo Scientific (USA).

2.2. Adsorbent preparation

The Co-BEA particles were prepared by the wet ion-exchange method. Firstly, the purchased 10g of H-Beta zeolite were mixed with 0.5 L of 0.01 mol L⁻¹ CoCl₂·6H₂O solution. All samples were mixed using a magnetic stirrer (Ika, Germany) at 500 rpm during the adsorbent preparations. The initial pH of the mixture was controlled to be around two by adding HCl solution. At these conditions (room temperature), H⁺ was exchanged with Co³⁺ during 24 h. Finally, the Co exchanged zeolite was washed using deionized water, filtrated, and dried at 110°C for 12 h. After zeolite modification by ion-exchange method, obtained powder was calcined at 500°C for four hours for experimental purposes.

2.3. Adsorption experiments

All adsorption experiments were carried out in a thermostatic water bath using glass reactor with the volume of 100 mL. The reactor contains methomyl solution and initial adsorbent amount (adjusted pH value). The influence of pH value, initial pesticide, and adsorbent concentration on adsorption efficiency was performed at 25°C. The study of adsorption efficiency dependence of the temperature was carried out at 25, 35, and 45 ±0.1°C. Kinetics of pesticide adsorption was followed by UV/Vis spectroscopy. The pH value at the initial reaction mixture was performed by the addition of 0.1 M H₂SO₄ or the same concentration of NaOH solution. During experiments, at least three measurements have been done for each determination of all evaluated parameters. The adsorbent samples were weighed to four-digit accuracy, and the solution concentrations were determined with four-digit accuracy.

The efficiency of methomyl removal using Co-Beta zeolite without calcination and after thermal threatening was calculated using Eq. (1):

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \cdot 100 \quad (1)$$

where C₀ and C_t represents the initial pesticide concentration and pesticide concentration at a specific time of the removal process.

The pH point of zero charge (pH_{PZC}) was determined by drift method [25].

The kinetics parameters obtained by modeling experimental data are necessary to design a wastewater treatment plant. The kinetics of methomyl removal by the adsorption was revealed using pseudo-first, pseudo-second and second order. Also, Weber-Morris, Dunwald-Wagner model, and Homogenous Solid Diffusion Model were used for diffusion modeling. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isothermal models were also used for adsorption modeling and characterization of adsorbent-adsorbate interactions.

2.4. Experimental conditions optimization

The adsorption conditions were optimized using the RSM (Response Surface Methodology) method. Optimization aims to determine optimal adsorption conditions with a smaller number of experiments. This method is maximally harmonized with the principles of environmental protection because it reduces: the number of experiments, the amount of used expensive and environmentally harmful chemicals, and the generation of waste [12].

Using the Response Surface Methodology (RSM) as a mathematical function, it is possible to examine the individual and interactive effects of different variables (adsorbent dose, solution pH value, contact time and temperature) in relation to different predictors. In this way, one get the optimal conditions that are needed to achieve the best results. The adsorption process itself was optimized by numerical and graphical optimization methods using the Bock-Behnken design. The capacity of the adsorbent was taken as the response. The

final optimized conditions were confirmed by additional experimental testing. The conditions of the adsorption experiment are given in Table I.

Tab. I Experimental plan of adsorption of methomyl performed using BBD design with four factors and three levels of values.

Run	A Dose adsorbent (mg L ⁻³)	B pH	C t(min)	D T (°C)	q _e (mg g ⁻¹)
1.	0.9	7	60	35	63.58
2.	0.9	7	60	35	63.58
3.	1.5	7	120	35	53.19
4.	0.3	7	5	35	42.02
5.	0.3	7	60	45	170.14
6.	0.9	11	5	35	9.44
7.	0.3	11	60	35	83.86
8.	0.9	7	5	45	16.66
9.	0.9	3	60	45	52.51
10.	0.3	7	120	35	216.38
11.	1.5	3	60	35	30.996
12.	1.5	7	5	35	10.45
13.	0.9	7	60	35	65.49
14.	0.9	7	60	35	65.49
15.	0.9	3	120	35	66.49
16.	0.3	7	60	25	205.3
17.	1.5	7	60	45	41
18.	1.5	11	60	35	19.04
19.	0.3	3	60	35	157.39
20.	1.5	7	60	25	51.22
21.	0.9	7	120	25	85.3
22.	0.9	3	5	35	13.21
23.	0.9	7	5	25	12.38
24.	0.9	11	60	25	39.21
25.	0.9	7	120	45	88.33
26.	0.9	11	120	35	40.51
27.	0.9	3	60	25	62.85
28.	0.9	11	60	45	34.23
29.	0.9	7	60	35	67.01

2.5. Methomyl adsorption research

Adsorption experiments were performed in a batch system where the initial concentration of methomyl solution was fixed $C_0 = 81.105 \text{ mg L}^{-1}$, and the dose of adsorbent was varied from 300 to 1500 mg L^{-1} . In order to examine the pH value influence on the adsorption process, the pH value was varied from 3.0 to 11.0. Thermodynamic and kinetic adsorption experiments were performed at temperatures of 25, 35 and $45 \pm 0.1^\circ\text{C}$, and the adsorption process was monitored in a time interval of 5 to 120 minutes. The amount of adsorbed molecules was calculated as the difference between the initial and equilibrium concentration.

The adsorbent capacity was calculated according to the Eq. (2):

$$q = \frac{C_i - C_f}{m} V \quad (2)$$

where q is adsorption capacity in mg g^{-1} , C_i and C_f are initial and final methomyl concentrations in mg L^{-1} ($\mu\text{g L}^{-1}$), respectively, V is volume of the solution in L, and m is the mass of adsorbent, expressed in g.

2.6. 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 II).

Tab. II Kinetic model equations.

Kinetic model	Nonlinear form	Model parameters	Equation
Pseudo-first-order equation	$q = q_e(1 - e^{-k_1 t})$	k_1 - pseudo first-order rate constant, (min^{-1}) q_e - adsorption capacity at time t , (mg g^{-1}) q - adsorption capacity, (mg g^{-1}) t - time, (min)	(3)
Pseudo-second order equation (Lagergreen)	$q = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	k_2 - pseudo-second order rate constant, ($\text{g mg}^{-1} \text{min}^{-1}$)	(4)
Second order	$q = \frac{t}{\frac{1}{k_2 q_e^2} + \frac{t}{q_e}}$	k_2 - second order rate constant, ($\text{L mg}^{-1} \text{min}^{-1}$)	(5)

Diffusion models as Weber-Morris, Dunwald-Wagner model and Homogenous Solid Diffusion Model (HSDM) were used for modeling diffusional processes/limiting step of overall process (Table III) [25,15].

Tab. III Equations of diffusion kinetic models.

Kinetic model	Nonlinear form	Equation
Weber-Morris	$q = k\sqrt{t} + C$	(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 methomyl adsorption was calculated using Arrhenius Eq. (9):

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

where k' ($\text{g mg}^{-1} \text{ min}^{-1}$) is the pseudo-second order rate adsorption constant, k_0 ($\text{g mmol}^{-1} \text{ min}^{-1}$) is the temperature independent factor, E_a (kJ mol^{-1}) is the activation energy, R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) 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 $-E_a/R$ from which activation energy was calculated.

2.7. Isotherm models

The equilibrium adsorption data were fitted by the isotherm models Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isothermal models [26,27]. The Langmuir equation assumes that a point of maximum adsorption corresponds to a saturated monolayer 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 an exponential distribution of active sites and their respective energies [26,28]. Temkin conceived this equation for subcritical vapors in micropore solids where the adsorption process follows a pore filling mechanism onto the 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 vapors in micropore solids where the adsorption process follows a pore filling mechanism onto an energetically non-uniform surface [29]. Equations of adsorption isotherms models are listed in Table IV.

Tab. IV Adsorption isotherms equations.

Isotherms	Nonlinear form	Model parameters	Equation
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	- q_m (mg g^{-1}) - maximum adsorbent capacity - q_e (mg g^{-1}) - adsorbent capacity in equilibrium	(10)
Freundlich	$q = K_F C^{1/n}$	- C (mg L^{-1}) - initial concentration - C_e (mg L^{-1}) - equilibrium concentration	(11)
Temkin	$q_e = \frac{RT}{b} \ln(AC_e)$	- K_L (L mol^{-1}) - Langmuir equilibrium constant - K_F (mg g^{-1}) ($\text{L mg}^{-1/1/n}$) - Freundlich constant - $1/n$ - Freundlich isotherm parameters - A_T (L g^{-1}) - Temkin isotherm constant - b_T (J mol^{-1}) - Temkin constant related to heat of sorption	(12)
Dubinin-Radushkevich	$q_e = q_m \exp\left(-B(RT)^2 \left(\ln\left(1 + \frac{I}{C_e}\right)\right)^2\right)$ $E = 1/\sqrt{2B}$	- T (K) - absolute temperature - B ($\text{mol}^2 \text{ kJ}^{-2}$) - Dubinin-Radushkevich model constant - E (kJ mol^{-1}) - free energy of adsorption	(13)

2.8. 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^{-1}) and entropy change (ΔS° , $\text{J mol}^{-1} \text{ K}^{-1}$) were calculated using the Van't Hoff equations (14) and (15) [28]:

$$\Delta G^0 = -RT \ln(b) \quad (14)$$

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

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 the following equation:

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

where C_0 (mol L^{-1}) is initial adsorbate concentration, b (Lmol^{-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 ($R_L > 1$).

2.9. Statistical analysis of experimental data

All adsorption experiments were repeated three times and mean values were taken for further processing and modeling. The obtained results were analyzed using the normalized standard deviation Δq (%), which is calculated using the following equation:

$$\Delta q(\%) = \sqrt{\sum \frac{[(q_{exp} - q_{cal})/q_{exp}]^2}{N - 1}} \times 100 \quad (17)$$

where q_{exp} and q_{cal} are the experimental and calculated values of adsorbed methomyl, N is the number of data used in the analysis. The maximum deviation is $< 3\%$, which is an experimental error. Standard errors for isothermal parameters, kinetic and thermodynamic parameters were determined using the commercial software Microcal Origin 8.0 [29].

In order to confirm the adsorption model that best corresponds to the experimental data, they were analyzed by ANOVA variance analysis, using the F value and the values of the correlation coefficient (R) from the regression analysis [29,30].

3. Results and Discussion

3.1. Adsorbent characterization

The morphological, structural, and semi-quantitative analyses of Co-Beta zeolite modified by wet ion-exchange before and after the annealing process were performed by Scanning Electron Microscopy coupled with Energy-Dispersive X-ray. Fig. 2 shows the SEM photographs of Co-Beta zeolite before and after annealing process at 500°C for two hours.

The SEM images (Fig. 2) show the interconnected grains by sub-spherical pores with the porous structure of both adsorbents. The highly porous surface of adsorbents confirms the large number of active sites that contribute to pesticide removal by adsorption. The SEM images also show the agglomeration of both Co-Beta particles. The distribution of examined particle sizes was obtained from the pictures where individual particles were distinguishable, and their diameters were measured using Image-pro's image analysis software. The distribution by Co-Beta particles is mainly in the range of $1.5\text{-}2.2 \mu\text{m}$. According to Energy Dispersive X-ray Spectroscopy, before annealing presence of silicon, oxygen, aluminum, and cobalt were 37.31, 61.92, 0.52, and 0.25 wt.% respectively. After annealing at 500°C for two hours the presence of the same elements was 34.47, 64.07, 0.60, and 0.86 wt.%, respectively. The EDS analysis confirms the high silicon content of both adsorbents. The difference after annealing noticeable difference in the weight percentage of cobalt, where after the sintering process weight percentage was increased from 0.25 to 0.86 wt.%.

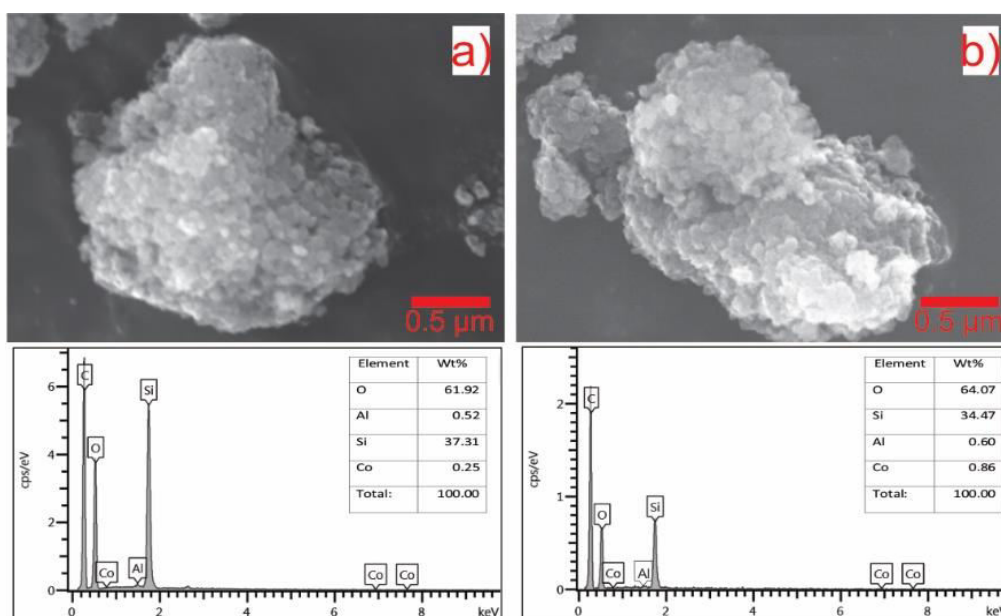


Fig. 2. SEM photographs and Energy-dispersive X-ray spectroscopy of Co-Beta zeolite (a) before and (b) after sintering.

The assesment of Co-Beta zeolite annealed at 500°C particles surface before and after pesticide removal was carried out by FTIR spectral analysis. Fig. 3 shows the FTIR spectra of Co-Beta zeolite annealed at 500°C before and after methomyl removal from aqueous solution.

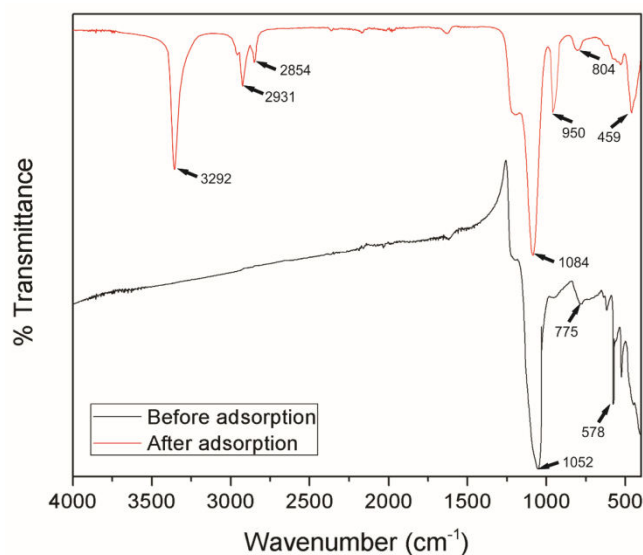


Fig. 3. FTIR spectrum of Co-Beta zeolite annealed at 500°C particles surface before and after pesticide removal.

According to obtained FTIR spectrum (Fig. 3) of Co-Beta zeolite annealed at 500°C particles surface before pesticide adsorption sharp peak at 1052 cm⁻¹ can be originated from internal linkages between SiO₄ and AlO₄ tetrahedra vibrations [31]. The pronounced low-intensity peak at 775 cm⁻¹ can be assigned to the symmetrical stretching of the internal tetrahedra. The peaks at 578 and 462 cm⁻¹ can be attributed to bending vibrations Si–O [32].

After methomyl adsorption by Co-Beta zeolite annealed at 500°C, changes were observed in the appearance of new peaks, decrease in intensity, disappearance, and displacement of peaks. After methomyl adsorption, a high-intensity peak at 3292 cm⁻¹ can be originated from N–H vibrations from the methomyl molecule. Also, low-intensity peaks at 2931 and 2854 cm⁻¹ can be attributed to C–H stretching vibrations. The absorption peaks at 955 and 804 cm⁻¹ can be assigned to twisting vibrations of C–H. There is no difference between FTIR spectra of adsorbents before and after annealing.

The pH value at which the net charge of the surface of the dispersed particle is zero, i.e., neutral, is called the pH point of zero charge (pH_{PZC}) [25]. The total charge is positive for pH values less than pH_{PZC} and negative if the pH is above the pH_{PZC} value. The pH_{PZC} value is determined from a wide range of initial pH values, and as can be seen in Figure S1 in Supplementary material, Co-Beta zeolite maintains its surface neutrality in a narrow range of pH values (7.5 < pH < 8). KNO₃ solution with 0.1, 0.01 and 0.001 mol L⁻¹ concentrations, respectively, was used to determine pH_{PZC}. The obtained results are given in Figure S1, with a determined pH_{PZC} value of 7.90.

The pH_{PZC} depends on the ion activity of the aqueous solution, but this dependence is negligible in the 7.5 < pH < 8 regions. The almost flat plateau is due to the extent of the ionization of surface functionalities at appropriate pH, i.e., proton-donating/accepting capability of primary groups present at the Co-Beta zeolite surface. Similar pH_{PZC} values were found for a comprehensive set of zeolite-based materials: various types of pure zeolites (4.5–8) as well as variously modified zeolites (4.9–8.1) [33–36]. The pH value for zero net charge is a valuable parameter for adsorption management since it may point to the optimal application of selected material. Used material should be oppositely charged from the pollutant on the selected pH value, promoting its adsorption on the surface. The isoelectric point of Methomyl is at pH 7.35. Above this value to the point of zero loading of the adsorbent, the sorption is enhanced due to the interaction of the negatively charged Methomyl and the positively charged surface of the adsorbent Figure S2. In accordance with this and the known fact that the pH of natural water is in the range of 6–8, pH 7.5 was chosen for the adsorption experiments.

Adsorption experiments showed that the adsorbent before sintering had a lower adsorption capacity compared to methomyl by about 44%. A comparison of the capacities of different zeolite-based adsorption materials for the removal of different pesticides is given in Table S1, supplementary material.

3.2. Influence of solution pH on adsorption

The influence of pH value on the system is manifested through surface tension, surface properties, degree of ionization of groups present on the surface of the adsorbent, and the speciation of ions in an aqueous solution at a specific pH value.

The effect of pH on methomyl removal is presented in Fig. 4. As mentioned above, methomyl retention depends on the nature of the pesticide and adsorbent. The examined pesticide efficiently hydrolyzes at a basic state (pH > 8), which negatively affects adsorption. The adsorption onto the zeolite surface of unhydrolyzed methomyl molecules is quicker due to its higher hydrophobicity than the hydrolyzed molecule. Also, in an acidic and basic aqueous environment, this pesticide efficiently hydrolyzes to more toxic metabolites, which is another reason why sorption experiments are performed at pH 7 [37]. The pesticide molecule could be more positively charged at a neutral state, with a cationic character, which can also explain this more significant adsorption. In an acidic state, H₃O⁺ ions attract surface oxygenated adsorbent groups, which could lead to the formation of a bond between H₃O⁺ and adsorbent [38].

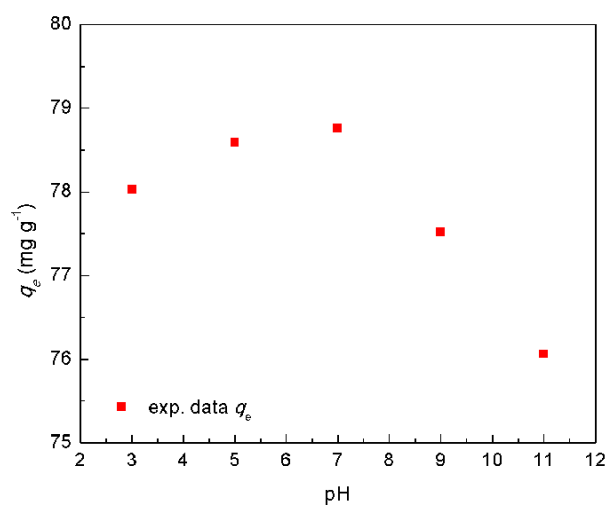


Fig. 4. Influence of the initial solution pH value on methomyl removal ($C_{i[\text{methomyl}]} = 81.105 \text{ mg L}^{-1}$, $m/V = 1000 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$).

3.3. Adsorption kinetics

The effect of time on methomyl adsorption was monitored in the range of 5 to 120 minutes. The final equilibrium was established after 240 minutes, but since the difference in the removal of methomyl from 120 to 240 minutes ranged from 2 to 5% to speed up the process, the final time of 120 minutes was chosen.

In order to determine the kinetic model that accompanies adsorption in order to interpret the adsorption mechanism, pseudo-first, pseudo-second-order, and second-order models were used (Table V). Table V shows the kinetic parameters for methomyl adsorption on Co-Beta zeolite adsorbent sintered at 500°C .

Tab. V The kinetic parameters for methomyl adsorption on Co-Beta zeolite adsorbent sintered at 500°C ($C_{i[\text{methomyl}]} = 81.105 \text{ mg L}^{-1}$, $\text{pH} = 7$; $m/V = 1000 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$).

Parameters / Model	Pseudo-first	Pseudo-second	Second-order
q_e	8.706	79.289	79.289
k (k_1, k_2)	0.05632	0.0166	0.00286
R^2	0.949	0.999	0.845

The results shown in Table V, according to the regression coefficient (R^2) and standard error for all model parameters, indicate that the kinetics for all adsorbents are best described using a pseudo-second order model.

The rate constants of diffusion kinetic models, intra-particle diffusion, Weber-Morris, Dunwald-Wagner and homogeneous solid diffusion models for methomyl adsorption on Co-Beta zeolite adsorbent sintered at 500°C under the same experimental conditions are presented in Table VI.

The complex nature of the kinetics of adsorption processes can be described by observing the adsorption of all ions adsorbed on the adsorbent as a single step, as described by a pseudo-second order equation, but can also be described by consecutive/competitive steps.

Tab. VI Parameters of intra-particle kinetic models (Ci[methomyl] = 81,105 mg L⁻¹, pH =7; m/V = 1000 mg L⁻¹, T = 25°C).

Model	Model parameters	Values
Weber-Morris Step 1 (Intra-particle diffusion)	k_{p1} (mg g ⁻¹ min ^{-0.5})	1.0726
	C (mg g ⁻¹)	70.566
	R^2	0.989
Weber-Morris Step 2 (equilibrium)	k_{p2} (mg g ⁻¹ min ^{-0.5})	0.0265
	C (mg g ⁻¹)	78.463
	R^2	0.949
Dunwald-Wagner model	K	0.02272
	R^2	0.851
Homogenous Solid Diffusion Model (HSDM)	Ds	2.33 10 ⁻¹¹
	R^2	0.850

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 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.

3.4. Evaluation of factors affecting adsorption: optimization of experimental conditions

The interactions between process variables and responses were determined by Analysis of variance (ANOVA). Polynomial model terms were evaluated at the 99% confidence level by P-value (probability). P-Values and q_m (mg g⁻¹) value were given in Table I for the adsorption of methomyl in the Co-Beta zeolite adsorbent. P-Value is the smallest significance level that allows rejection of the null hypothesis. When the P-value is <0.05, model and model terms are statistically significant with 95% of the pouch, and when the P-value <0.01 model and model term is significant with 99% reliability [30]. Since the adsorption process is very complex and a fixed initial concentration of methomyl is taken, other variables that affect the adsorption process were used in the statistical design of the experiment. A four-factor BBD with RSM was used to maximize the methomyl removal wastewater. Dosage adsorbent (A), pH (B), time adsorption (C), and temperature (D) were considered independent predictor parameters, while the methomyl removal (Y) was considered as the process response in the Design of the Experiment. Design Expert 9.0.1 statistical software (Stat-Ease, Minneapolis, MN, USA) was utilized to optimize the reaction conditions through numerical and graphical methods. The quadratic model (Eq. (18)) estimated the parametric coefficients of the statistical model by correlating both predictor parameters and responses using the least-squares regression:

$$q_e = 66.68 - 56.71A - 13.25B + 37.17C - 4.45D + 15.39AB - 32.56AC + 6.24AD - 5.30BC + 1.34BD - 0.040CD + 35.85A^2 - 23.05B^2 - 19.13C^2 + 8.12D^2 \quad (18)$$

In this model, negative coefficients corresponded to unfavorable effects on the methomyl removal for A, B, D, AC, BC, CD, B², and C², whilst positive coefficients corresponded to favorable effects on the methomyl removal for C, AB, AD, BD, A² and D². Parameters with coefficients close to zero indicated a lower effect on the methomyl removal

than that of larger coefficients under the same magnitude of change in that certain factor. Thus, CD did not significantly affect the methomyl removal when these factors were changed accordingly.

The statistical significance of the developed model and predictors was evaluated using the analysis of variance (ANOVA) with 95% confidence interval of the methomyl removal, as shown in Table VII. The significance of each factor coefficient was determined using probability values (p-values) from Fisher's (F) exact test, where values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case, A, B, C, AC, BC, BD, A², B², C² are significant model terms that affect the overall methomyl removal based on this model.

Tab. VII ANOVA of methomyl removal modeled by quadratic modeling in the optimization of adsorption of methomyl on Co-Beta zeolite adsorbent sintered at 500°C.

Source	Sum of Squares	d _f	Mean Square	F Value	p-value	
					Prob > F	
Model	79155.78	14	5653.984	15.16218	< 0.0001	significant
A-dose ads	38495.15	1	38495.15	103.2317	< 0.0001	significant
B-pH	2101.444	1	2101.444	5.635403	0.0324	
C-t	16579.31	1	16579.31	44.46041	< 0.0001	significant
D-T	237.0667	1	237.0667	0.635737	0.4386	
AB	947.8394	1	947.8394	2.541803	0.1332	
AC	4244.997	1	4244.997	11.38373	0.0045	
AD	155.5009	1	155.5009	0.417004	0.5289	
BC	112.4925	1	112.4925	0.301669	0.5915	
BD	7.1824	1	7.1824	0.019261	0.8916	
CD	0.006265	1	0.006265	1.68E-05	0.9968	
A²	8338.361	1	8338.361	22.36082	0.0003	
B²	3447.009	1	3447.009	9.243779	0.0088	
C²	2361.57	1	2361.57	6.332976	0.0247	
D²	427.8757	1	427.8757	1.147426	0.3022	

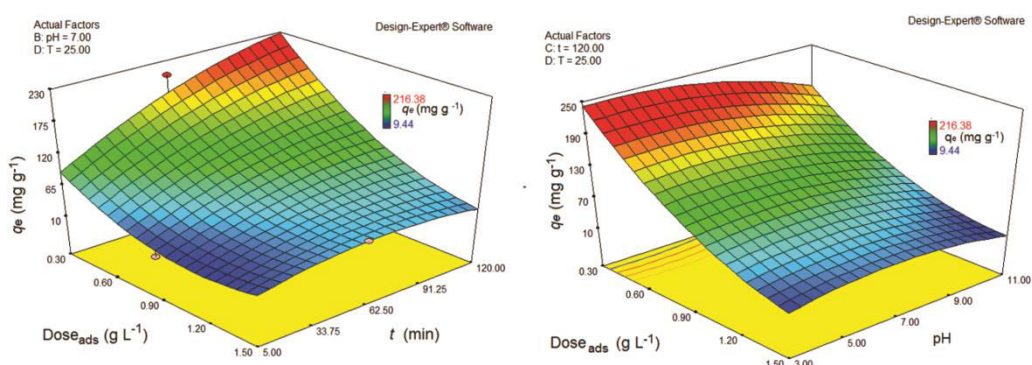


Fig. 5. 3D diagram of mutual dependence of the most influential variables of the adsorption process.

In Fig. 5 one can see mutual dependence - the interaction of the most influential variables on the adsorption process. The validity of the model is confirmed by the quality of

the fitting model, and the coefficient of determination (R^2). For an appropriate approach, R^2 should be greater than 0.90. R^2 for methomyl is 0.938. This value showed a high correlation between experimental and predicted results.

3.5. Adsorption activation energy

In relation to the results of kinetic research performed at temperatures of 298, 308 and 318 K, it is possible to determine the activation energy using the Arrhenius equation (Table VIII). Linear form of the Arrhenius equation is given:

$$\ln K' = -\frac{E_a}{RT} + \ln A \quad (19)$$

where K' is the reaction rate constant at a certain temperature, E_a shows the activation energy, R is the universal gas constant (8.314), T is the temperature in K and A is the Arrhenius factor (frequency for a given reaction).

Tab. VIII Pseudo-second order model parameters for methomyl adsorption on Co-Beta zeolite adsorbent sintered at 500°C ($C_{i[\text{methomyl}]} = 81,105 \text{ mg L}^{-1}$, $\text{pH} = 7$; $m/V = 1000 \text{ mg L}^{-1}$).

Temperature	$q_e \text{ (mg g}^{-1}\text{)}$	$k_2 \text{ (g (mg min)}^{-1}\text{)}$	R^2
25 °C	79.289	0.01660	0.999
35 °C	79.811	0.02065	0.999
45 °C	79.835	0.02291	0.999

Physisorption or physical adsorption generally possesses energy up to 40 kJ mol^{-1} , while chemisorption requires higher energy and activation energy over 40 kJ mol^{-1} [28]. Since E_a for Co-Beta zeolite adsorbent sintered at 500°C is 12.75 kJ mol^{-1} one can conclude that the main mechanism of adsorption is physical adsorption.

3.6. Adsorption isotherms

The state of interactions/bonds on the surface of the adsorbate/adsorbent can be observed by fitting the experimental data with different adsorption isotherms. The normalized correlation coefficient and standard deviation were used to estimate the fit of the adsorption data. The experimental data were compared with the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models already discussed, the parameters of which are shown in Table IX. By analyzing the experimental data on the adsorption of methomyl molecules on the tested adsorbents, the best fit for both adsorbents is given by the Freundlich isothermal model. The results of modeling methomyl adsorption on the tested adsorbents are given in Table IX. Fig. 6 shows the graphical review of the results of adsorption experiments with the best-fitting models of isotherms (solid line) for the removal of methomyl on Co-Beta zeolite adsorbent sintered at 500°C.

According to the Freundlich isotherm, the mechanism of adsorption on Co-Beta zeolite adsorbent sintered at 500°C can be described as heterogeneous adsorption, where the adsorbed ions/molecules have different enthalpies and adsorption activation energies. The value of n from the Freundlich isotherm is a measure of adsorption intensity or surface heterogeneity.

Tab. IX Parameters of adsorption isotherms of methomyl adsorption on Co-Beta zeolite adsorbent sintered at 500°C.

Isothermal models and parameters		Temperature		
		25 °C	35 °C	45 °C
Langmuir isotherm	q_m (mg g ⁻¹)	225.710	228.061	230.851
	K_L (L mg ⁻¹)	23.698	26.418	32.231
	K_L (L mol ⁻¹)	3844030	4285352	5228325
	R^2	0.997	0.997	0.996
Freundlich isotherm	K_F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	299.061	305.792	318.207
	1/n	0.354	0.346	0.335
	R^2	0.933	0.942	0.934
Temkin isotherm	A_T (Lg ⁻¹)	331.901	376.95	329.44
	b_T (kJmol ⁻¹)	41.57	41.04	40.22
	R^2	0.973	0.981	0.973
Dubinin-Radushkovich isotherm	q_m (mg g ⁻¹)	228.54	230.42	235.68
	K_{ad} (mol ² kJ ⁻²)	6.5649	6.5567	6.5342
	Ea (kJmol ⁻¹)	8.727	8.732	8.747
	R^2	0.985	0.990	0.982

Values of n near zero indicate a highly heterogeneous surface. Values of $n < 1$ (Table IX) imply a chemisorption process, and higher values indicate combined adsorption, e.g. physisorption and chemisorption with different process system balancing steps. The values given in table indicate that the adsorption was combined in all cases.

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 methomyl on Co-Beta zeolite adsorbent sintered at 500°C ranges from 0.011 to 0.072 indicating that the adsorption process is favorable.

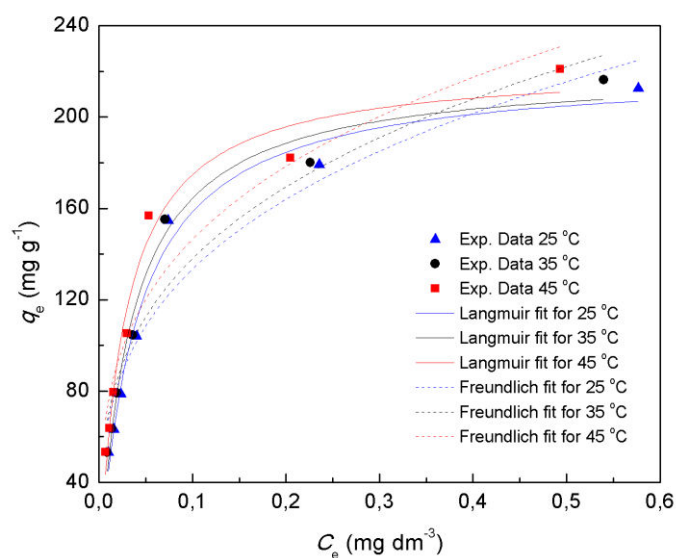


Fig. 6. Review of the results of adsorption experiments with the best-fitting models of isotherms (solid line) for the removal of methomyl on Co-Beta zeolite adsorbent sintered at 500°C.

3.7. Thermodynamic studies

Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated by Van't Hoff equation (14) and (15). The calculated thermodynamic parameters are shown in Table X.

Tab. X Calculated Gibbs free adsorption energy, enthalpy and entropy for methomyl adsorption on adsorbent at 25, 35 and 45°C.

ΔG^0 (kJ mol ⁻¹)			ΔH^0	ΔS^0	R^2
25 °C	35 °C	45 °C	(kJ mol ⁻¹)	(J mol ⁻¹ K ⁻¹)	
-47.54	-49.41	-51.54	12.09	199.85	0.966

Negative values of Gibbs free energy (ΔG^0) and positive values of entropy (ΔS^0) at all temperatures indicate that reactions in the adsorption process take place spontaneously. A decrease in the Gibbs free energy (ΔG^0) with an increase in temperature also indicates that the spontaneity of the reaction increases.

Positive values of ΔS^0 indicate a tendency of greater disorder of the Co-Beta zeolite adsorbent sintered at 500°C surface systems and methomyl solution. In Table X we can see that the Gibbs free energy values (ΔG^0) for both adsorbents are approximate, and the positive entropy values (ΔS^0) at all temperatures, while the positive enthalpy values (ΔH^0) for Co-Beta zeolite adsorbent sintered at 500°C 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 chemisorption and physisorption between -20 and -80 kJ mol⁻¹, and chemisorption less than -80 kJ mol⁻¹. The obtained results indicate that in these cases, chemisorption and physisorption are present at the same.

4. Conclusion

Based on the obtained results during the investigation of carbamate pesticide methomyl removal from aqueous solution, it can be concluded following:

- The SEM images show the interconnected grains by sub-spherical pores with the porous structure of both adsorbents and the EDS analysis confirms the high silicon content of both adsorbents,
- After methomyl adsorption by Co-Beta zeolite sintered at 500 °C, changes were observed in the appearance of new peaks, decrease in intensity, disappearance, and displacement of peaks - a high-intensity peak at 3292 cm⁻¹ can be originated from N-H vibrations from the methomyl molecule,
- The obtained results, according to the regression coefficient (R^2) and standard error for all model parameters, indicate that the kinetics for all adsorbents are best described using a pseudo-second order model - the Weber-Morris model, which 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 adsorbent,
- The statistical significance of the developed model and predictors can be evaluated using the analysis of variance (ANOVA) with 95% confidence interval of the methomyl removal,

- Based on the obtained results that the activation energy for Co-Beta zeolite adsorbent sintered at 500°C is up to 40 kJ mol⁻¹, one can conclude that the main mechanism of adsorption is physical adsorption; according to the Freundlich isotherm, the mechanism of adsorption on Co-Beta zeolite adsorbent sintered at 500°C can be described as heterogeneous adsorption, where the adsorbed ions / molecules have different enthalpies and adsorption activation energies,
- The values of n near zero indicate that the adsorption was combined in all cases - physisorption and chemisorption with different process system balancing steps.

According to all the above, it can be noted that the Co-Beta zeolite adsorbent sintered at 500°C showed satisfactory adsorption performance and can be successfully used to remove pesticides from aqueous solution.

Acknowledgments

This work was financially supported by The Ministry of Education, Science and Technological Development of the Republic of Serbia (Contracts No. 451-03-68/2021-14/200135, 451-03-9/2021-14/200017, 451-03-68/2022-14/200326 and the University of Defense, Project No. VA TT/1/22-24).

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Сажетак: Адсорпција карбаматног пестицида метомила вршена је помоћу Со-Бета зеолита припремљеног методом влажне јонске размене. Испитиван је утицај концентрација зеолита и пестицида, рН вредности и температуре синтеровања на уклањање пестицида из воденог раствора. Промена концентрације метомила током адсорпције је праћена коришћењем УВ-вис спектофотометра. Скенирајућа електронска микроскопија-енергетска дисперзивна рендгенска спектроскопија (SEM-EDS) открила је модификовану морфологију зеолита и елементарну структуру. Промена површине адсорбента пре и после уклањања боје примећена је помоћу Фуријеове трансформације-инфрацрвене спектроскопије (ФТ-ИР). Кинетика адсорпције следи модел кинетике псеудо-другог реда, при оптималним условима константа брзине реакције је $k_1 = 0.0166 \text{ g mg}^{-1} \text{ min}^{-1}$. За опис процеса адсорпције коришћени су модели изотерме адсорпције Лангмуир, Фројндлих, Темкин и Дубинин-

Радушкович. Термодинамички параметри су такође одређени експерименталним подацима.

Кључне речи: *адсорпција, уклањање пестицида, кинетика адсорпције, дифузиони процеси, модели изотерме.*

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