

# Removal of Methomyl from Aqueous Solutions Using Reactivated Carbon Microspheres

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The removal of methomyl, one of the most frequent pesticides, from aqueous solutions has been studied by adsorption using the reactivated carbon microspheres separated from worn filtering protective suits. This study is significant in two aspects – the first is the in-situ adsorption of pesticides from aqueous solutions, and the second is recycling protective equipment as an effective material for water decontamination. Carbamate pesticide, methomyl is aimed to control foliage and soil-borne insect pests on various agricultural product. Also, due its toxicity, it has a great potential for usage in terroristic acts and tactical purposes during military operations. The reactivated carbon (RAC) microspheres were characterized by Scanning Electron Microscopes (SEM). The changes in relative concentration of methomyl during the adsorption onto the surface of the RAC microspheres was determined using the UV-Visible spectrophotometer. The adsorption process is described by Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich adsorption isotherm models. The adsorption kinetics follows the second-order kinetics model, and the thermodynamics study confirms that the adsorption is exothermic and spontaneous. At optimal conditions, the adsorption capacity was  $q_e = 8.631 \text{ mol g}^{-1} \times 10^{-3}$  and the adsorption rate was  $k = 0.749 \text{ g mmol}^{-1} \text{ min}^{-1}$ . The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich adsorption isotherm models were used to describe the adsorption process. The thermodynamic study of adsorption proves the process is spontaneous with exothermic nature.

*Key words:* insecticide, adsorption, carbon microspheres, recycling, water pollution.

## Introduction

THE increasing world population and living standards have initiated the increase in water demands in the last few decades. The primary pollution sources are industry processes such as petroleum refining and combustion of fossil fuels, agriculture, and households [1]. Second, population growth increases food production. For that purpose, pesticides significantly influence food produced per unit area. Agriculturists used them to control insects and weeds, and their significant increase in agricultural products was recorded. However, the increases of these chemicals in recipients was initiated by their excessive use in agriculture [2]. Many studies prove the side effects of organism exposure to pesticides and their decomposition products can have many side effects such as high toxicity, carcinogenic and mutagenic effects. Also, pesticides certainly cause cell damage and the creation of metabolites harmful to the organism [3, 4]. Carbamates are highly toxic pesticides similar as organophosphates. They are not persistent in the environment but are enough to affect the environment and living system. Due to the high toxicity and hazardous behaviors, similar to organophosphates, the World Health Organization categorized these pesticides as restricted for use. Examples of carbamates

pesticides include Carbaryl, Aldicarb, Carbofuran, Propoxur, and Methomyl and they usually belong to the family of insecticides [5-6]. Methomyl can easily cause soil and water contamination due to its high solubility in aqueous solutions and low affinity of soil to adsorb their particles. The presence of insecticides in groundwater can potentially cause health problems and contaminate the environment because of pesticide and residuals' moderate toxicity and carcinogenicity [7]. In case of methomyl ingestion or inhalation, the cholinesterase enzymes are irreversibly inhibited and cause the increase of acetylcholine in nerve cells resulting in many health problems such as nausea, dizziness, confusion, respiratory paralysis, and death [8].

Beside the direct negative effects on organisms, there are reports that show that pesticides sustain in the environment for a long time as they are resistant to biological treatment of wastewater [9]. Choosing the appropriate wastewater treatment method for pollutant removal depends on the type and pollutant's characteristics and efficiency of the selected process. There are various chemical treatment techniques to remove pesticides from water, such as advanced oxidation process (AOPs) [10], electrochemical oxidation [11, 12], photochemical degradation [13], ozonation [14] and adsorption [15, 16]. Adsorption was widely investigated as a

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process for dissolved or dispersed pollutants in untreated effluent. In order to select an effective material that would be used as an adsorbent, the effectiveness depends on the porosity, surface area, number of available sites, and possible interactions with the target contaminant. The various possible adsorbents were used for wastewater treatment: activated carbon, nanomaterials, composite and nanocomposite, non-conventional low-cost zeolites and clay and zeolites, and miscellaneous adsorbents [17].

The effectiveness of materials based on activated carbon is well known, but finding an efficient way to reuse the used materials is a big problem. Their high specific surface area contributes to the effective removal of organic pollutants from wastewater. Various studies have been reported previously for the adsorption and removal of pesticides from water by the activated carbon materials [18–20].

In recent years, intensive studies have been carried out to find new high-efficient treatment techniques and materials for wastewater treatment. A potential material for pesticide removal is spent activated carbon microspheres from protective suits in use by chemical, biological, radiological and nuclear (CBRN) defense units. The concept of the CBRN protection introduced the requirement to equip soldiers with a personal protective equipment (PPE). Level C of PPE consists of a protective mask, protective gloves, resistant boot covers (overboots) and a filtering protective suit. After Chemical Reconnaissance or Chemical Live Agent Training (C LAT), the suits are usually destroyed by incineration. However, it is possible to partially recycle the suit, that is, to remove the activated carbon microspheres and reactivate it, and use to remove pesticides from water.

Blucher GmbH/Germany developed the last generation of the filtering protective suits under the brand name Saratoga™ with excellent characteristics for adsorption and the best possible comfort for the user under all climatic conditions. Examined protective equipment is based on highly porous activated carbon microspheres freely accessible to harmful gases, resulting in extraordinarily rapid and firm adsorption with high absorption capacity for chemical weapon agents (CWA) adsorption bonded to a textile carrier fabric. Based on the manufacturer's instructions, the density of used activated carbon is between 180 g m<sup>-2</sup> to 220 g m<sup>-2</sup>. These suits provide a minimum of one-day protection and more than 40 days of wear under battlefield conditions, including several washings cycles [21].

This study investigated the adsorption of methomyl using the reactivated carbon (RAC) microspheres obtained from Saratoga™ filtering protective suit. The morphology of the adsorbent was investigated using Scanning Electron Microscopy. The dependence of wastewater treatment efficiency 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 (PSO), and second-order kinetic models. The Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models and thermodynamic parameters were used to describe the adsorption process. Methomyl removal using reactivated carbon was followed by ultraviolet-visible (UV-Vis) spectroscopy.

## Experimental Part

### Materials and characterization methods

Activated carbon (AC) microspheres from filtering protective suit (used in C LAT) brand name Saratoga™ was

used as a sorbent for water treatment. The commercial pesticide Lannate® with 90% of methomyl pesticide (Dupont) was used as an organic pollutant without further purification. Nitric acid an (65% v/v) and hydrogen peroxide solution (30% v/v) provided by Centrohem were used for reactivation of AC microspheres.

For pH value adjustment of an aqueous solution, sulfuric acid and ammonium hydroxide (Fisher Scientific (USA)) were used. The Millipore Waters Milli-Q (USA) system provided deionized water.

Morphology and microstructures of the AC 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 degradation experiments. A UV-Vis spectrophotometer LLG-uniSPEC 2 (Germany) was used for measuring the changes of pesticide concentration during time.

### Reactivation of carbon microspheres

The protective filtering suit used in C LAT was decontaminated in the washing machine at 90 °C and dried in the air for 24 h. After drying, the filter protective suit was cut into pieces of 5×5 cm dimensions. In the second step, the pieces were mixed in nitric acid on a magnetic stirrer at the room temperature for 24 h to separate the AC spheres from the textile. Then the separated spheres were washed with distilled water and left in 30% hydrogen peroxide for 24 hours to remove organic compounds residues. In the last step, the microspheres were washed with distilled water and left to dry at 200 °C in thermostatic chamber (G209A, SDL Atlas, UK) for 24 h. The particles of microspheres and textile scraps were separated by the sieving method.

### Adsorption experiment

All pesticide removal experiments were carried out in a thermostatic water bath with a shaker (WNB 14, Memmert, Germany) using open glass reactors with 100 ml. The reactor contains methomyl solutions and initial adsorbent concentrations with adjusted pH values. The influence of pH value, initial pesticide, and adsorbent concentration on adsorption efficiency was performed at 25 °C. The dependence of adsorption efficiency on the temperature was carried out at 25, 35, and 45 ± 0.1 °C. The kinetics of pesticide removal by adsorption was followed by UV-Vis Spectrophotometer at  $\lambda_{max} = 235$  nm. In all experimental systems, equilibrium was established within three hours. The initial pH value at every reaction system was performed by adding 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> for acidification or the same concentration of NaOH solution for an alkaline solution. During the experiments, at least three measurements have been done for each determination of all evaluated parameters.

The efficiency of pesticide removal using RAC microspheres were calculated using the following equation:

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

where  $C_0$  and  $C_t$  represent the initial methomyl concentration and methomyl concentration at a specific time of the removal process.

The kinetics parameters originated by modeling experimental data are necessary to design highly effective wastewater plants. The kinetics of pesticide removal by adsorption was revealed using pseudo-first, pseudo-second,

and second order. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isothermal models were also used for adsorption modeling and characterization of adsorbent-adsorbate interactions.

### Optimization of adsorption conditions

Response Surface Methodology (RSM) was used to optimize the adsorption conditions. Using RSM, it is possible to obtain complete modeling of the adsorption process from a few results. Also, it is possible to reduce the number of experiments, thus saving the resources used during the experiments [23].

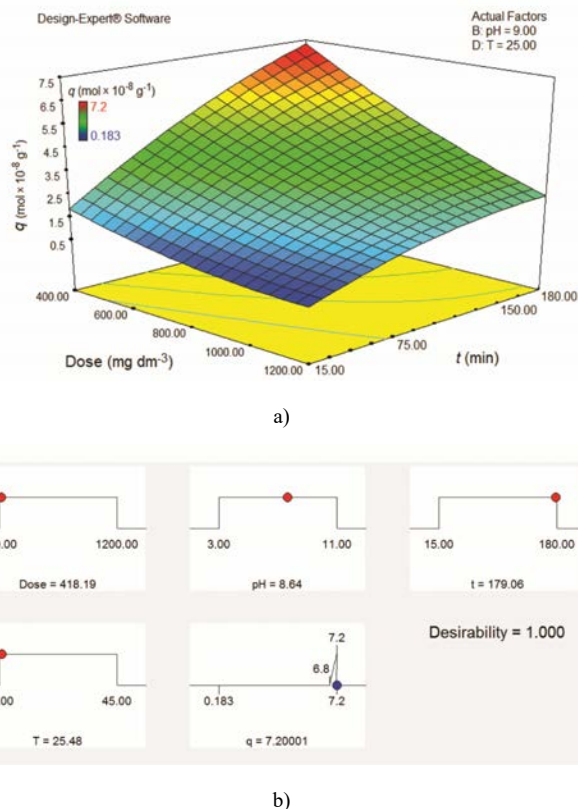
Using the Desing Expert 9 software for the methomyl adsorption process optimization, it is possible to examine the individual and interactive effects of adsorbent dose, solution pH value, contact time, temperature, and other variables contributing to pest removal. Also, this software package gives various predictions and conclusions that can be used to obtain optimal conditions needed to achieve the best results. The process was optimized by numerical and graphical optimization methods using the Bock-Behnken design (BBD). The capacity of the adsorbent was taken as the response. The conditions of the adsorption experiment are given in Table 1.

**Table 1.** Experimental plan of adsorption of methomyl performed using BBD with four factors and three levels of values

Run	A Dose adsorbent (mg L <sup>-1</sup> )	B pH	C t (min)	D T (°C)	q <sub>e</sub> (mol g <sup>-1</sup> × 10 <sup>-8</sup> )
1.	400	7	15	35	1.144
2.	800	7	180	25	4.246
3.	800	7	180	45	4.215
4.	400	3	100	35	4.61
5.	1200	3	100	35	0.183
6.	800	7	15	45	0.67
7.	800	11	100	25	2.394
8.	400	7	100	45	5.11
9.	800	7	100	35	3.03
10.	800	7	100	35	3.03
11.	1200	7	100	45	2
12.	400	7	180	35	7.2
13.	1200	7	180	35	2.99
14.	1200	11	100	35	1.62
15.	800	3	100	25	3.03
16.	800	11	180	35	3.35
17.	400	7	100	25	5.172
18.	800	7	100	35	3.03
19.	1200	7	15	35	0.444
20.	800	7	15	25	0.694
21.	800	11	15	35	0.52
22.	800	3	180	35	3.79
23.	800	7	100	35	3.03
24.	800	3	100	45	2.69
25.	400	11	100	35	4.04
26.	800	3	15	35	0.582
27.	800	11	100	45	2.35
28.	800	7	100	35	3.03
29.	1200	7	100	25	2.08

The adsorbent's highest capacity for methomyl was obtained using BBD design within the RSM method. The presentation of the optimization results with the prediction of the most desirable experimental conditions to achieve maximum results is given in Figures 1 and 2. The red field on the 3D graphic shows the optimal experimental conditions for obtaining the target capacity of 6.8 to 7.2 × 10<sup>-8</sup> mol g<sup>-1</sup>. Fig. 1 shows a (a) 3D graph of the optimization of the conditions of

examined pesticide adsorption using the BBD design and (b) prediction of optimal condition using the Desing Expert 9 software.



**Figure 1.** (a) 3D graph of the optimization of the conditions of examined pesticide adsorption using the BBD design and (b) prediction of optimal condition using the Desing Expert 9 software

### Methomyl adsorption research

A study of methomyl adsorption effectiveness was performed in a batch system. The initial concentration of methomyl solution was fixed  $C_0 = 10.01 \text{ mg L}^{-1}$ , and the dose of adsorbent ranged from 0.4 to 1.2 g L<sup>-1</sup>. The investigation of pH value influence on pesticide removal was examined at a range of pH values from 3.0 to 11.0. Thermodynamic and kinetic adsorption experiments were performed at temperatures of 25, 35 and 45 ± 0.1 °C, and the adsorption process was monitored in a time interval of 15 to 180 minutes. The amount of adsorbed molecules was calculated as the relative concentration of the initial and equilibrium concentration.

The adsorbent capacity was calculated according to the following equation:

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

Where  $q$  is adsorption capacity in mg g<sup>-1</sup>,  $C_i$  and  $C_f$  are initial and final methomyl concentrations in mg L<sup>-1</sup> (µg L<sup>-1</sup>), respectively,  $V$  is volume of the solution in L, and  $m$  is the mass of adsorbent, expressed in g.

### Kinetic studies

A kinetics study is unavoidable to describe possible mechanisms and pathways of pesticide adsorption. Previously described kinetics models analyzed the experimental results obtained during the methomyl removal by adsorption effectiveness using the linear, non-linear least-squares, and graphic methods.

**Table 2.** Kinetic model equations

Kinetic model	Nonlinear form	Model parameters	Eq.
Pseudo-first-order	$q = q_e (1 - e^{-k_1 t})$	$k_1$ - pseudo first-order rate constant, ( $\text{min}^{-1}$ ) $q_e$ - adsorption capacity at time $t$ , ( $\text{mg g}^{-1}$ ) $q$ - adsorption capacity, ( $\text{mg g}^{-1}$ ) $t$ - time, ( $\text{min}$ )	(3)
Pseudo-second order (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)

### Isotherm models

The results obtained during the study were used in

**Table 3.** Adsorption isotherms equations

Isotherms	Nonlinear form	Model parameters	Eq.
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$q_m$ ( $\text{mg g}^{-1}$ ) - maximum adsorbent capacity $q_e$ ( $\text{mg g}^{-1}$ ) - adsorbent capacity in equilibrium $C$ ( $\text{mg L}^{-1}$ ) - initial concentration	(6)
Freundlich	$q = K_F C^n$	$C_e$ ( $\text{mg L}^{-1}$ ) - equilibrium concentration $K_L$ ( $\text{L mol}^{-1}$ ) - Langmuir equilibrium constant	(7)
Temkin	$q_e = \frac{RT}{b} \ln(AC_e)$	$K_F$ ( $\text{mg g}^{-1}$ ) ( $\text{L mg}^{-1}$ ) $1/n$ - Freundlich constant - $1/n$ - Freundlich isotherm parameters $A_T$ ( $\text{L g}^{-1}$ ) - Temkin isotherm constant $b_T$ ( $\text{J mol}^{-1}$ ) - Temkin constant related to heat of sorption	(8)
Dubinin-Radushkevich	$q_e = q_m \exp\left(-B(RT)^2 \left(\ln\left(1 + \frac{1}{C_e}\right)\right)^2\right)$ $E = 1/\sqrt{2B}$	$R$ - gas constant $T$ (K) - absolute temperature $B$ ( $\text{mol}^2 \text{kJ}^{-2}$ ) - Dubinin-Radushkevich model constant $E$ ( $\text{kJ mol}^{-1}$ ) - free energy of adsorption	(9)

### Thermodynamic studies

Thermodynamic parameters describe the feasibility of methomyl adsorption by RAC spheres based on the results of experimental tests of adsorption efficiency. Values of Gibbs free energy change ( $\Delta G^\circ$ ,  $\text{kJ mol}^{-1}$ ), enthalpy change ( $\Delta H^\circ$ ,  $\text{kJ mol}^{-1}$ ) and entropy change ( $\Delta S^\circ$ ,  $\text{J mol}^{-1} \text{K}^{-1}$ ) were calculated using the Van't Hoff equations [26]:

$$\Delta G^\circ = -RT \ln(b) \quad (10)$$

$$\ln(b) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{(RT)} \quad (11)$$

### Statistical analysis of experimental data

During the study, all experiments were repeated three times and mean values were taken for further data processing previously described. The obtained results were analyzed using the normalized standard deviation  $\Delta q$  (%), which is calculated using the following equation:

$$\Delta_q = \sqrt{\frac{\left[ \frac{(q_{\text{exp}} - q_{\text{cal}})^2}{q_{\text{exp}}} \right]}{n-1}} \times 100 \quad (12)$$

where  $q_{\text{exp}}$  and  $q_{\text{cal}}$  are the values obtained by experiments and theoretic calculation of adsorbed methomyl,  $N$  is the number of data used in the analysis. The maximum deviation is  $<3\%$ , which is an experimental error. A commercial software package Microcal Origin 8.0 was used to determine the

thermodynamic and isotherm studies using the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isothermal models [24, 25]. The first of the above isotherm model is based on the assumption that a point of maximum adsorption corresponds to forming of mono-layer of metomyle particles on the RAC surface - where the energy of adsorption remains constant and no transfer of the adsorbate in the plane of the surface occurs. The second model is widely and reliably utilized as a mathematical method for a determination of surface heterogeneity and exponential distribution of active sites as well as their respective energies [24, 26]. The third model describes the behavior of subcritical steam in solids with micropores, where the adsorption process follows pore filling on an energetically uneven surface. This isotherm model is based on the assumption that the decay of the heat of sorption as a function of temperature is linear. The fourth model is intended to describe the behavior of subcritical steam in solid micropores [27]. The equations of adsorption isotherms models are listed in Table 3.

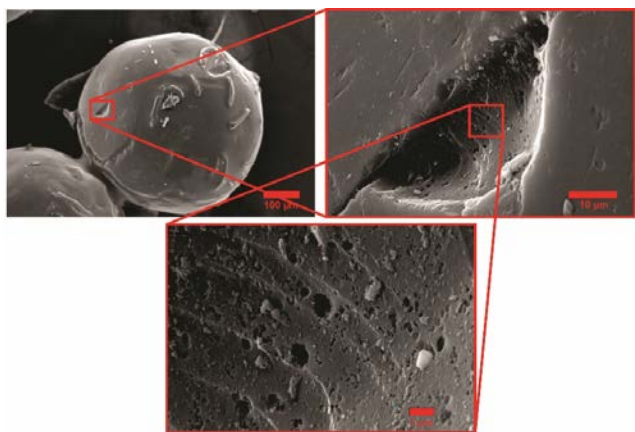
standard error of the parameters obtained from the experiments [27]. In order to confirm the model that best describes the methomyl adsorption process, the test results were processed by ANOVA analysis of variance, using the  $F$  value together with the values of the reduced chi-square  $\chi^2$  statistic and the correlation coefficient ( $R$ ) from the regression analysis [27, 28].

## Results and Discussion

### Adsorbent characterization

The morphological and structural analyses of RAC microspheres after drying at  $200^\circ\text{C}$  in thermostatic chamber for 24 h was performed by Scanning Electron Microscopy. Fig.3 shows the micrographs of RAC microspheres after reactivation process obtained by SEM analysis.

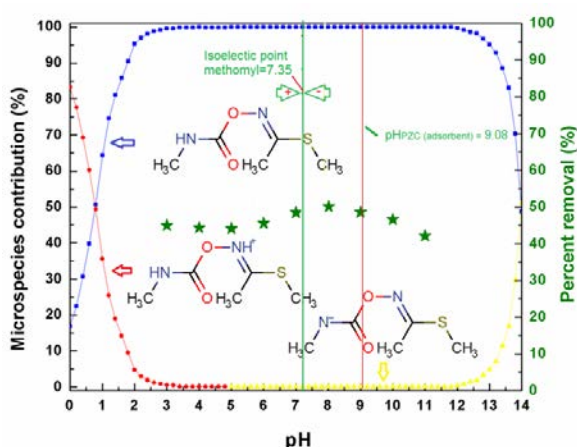
The micrographs obtained at different magnifications (Fig.3) show the uniform distribution of microsphere particle size without agglomeration, confirming AC particles' excellent separation during protective suit recycling. The particle size distribution of RAC was defined using the pictures where individual adsorbent particles were distinguishable, and their diameters were measured using Image-pro's image analysis software. The distribution by the RAC microspheres are mainly in the range of  $450\text{--}570\ \mu\text{m}$ . According to the SEM micrographs at higher magnification, the RAC microspheres have a highly porous surface, confirming a large number of active sites that contribute to pesticide removal by adsorption.



**Figure 3.** SEM photographs of RAC at different magnification ((a) 150, (b) 2000, and (c) 10000 times)

#### Influence of solution pH on adsorption

Beside the adsorbent characteristics, the pH value significantly impacts the adsorption efficacy due to the surface tension and properties, the degree of ionization of groups present on the active site's surface, and the speciation of ions in an aqueous solution at a specific pH value. The effect of pH on methomyl removal is presented in Figure 4. As mentioned above, methomyl retention depends on the nature of the pesticide and RAC spheres. The adsorption onto the RAC surface of unhydrolyzed methomyl molecules is quicker due to its higher hydrophobicity than the hydrolyzed molecule. Also, in an acidic aqueous environment, this pesticide efficiently hydrolyzes to more toxic metabolites, which is another reason why sorption experiments are performed at pH 9 [29]. The second reason for better pesticide adsorption at pH 9 is a value of the point of zero charges for adsorbent, where  $pHPZC$  is 9.08. According to the isoelectric point of pesticide and  $pHPZC$ , an optimal ratio of adsorbent and pesticide charge is at a moderately alkaline state. 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,  $H_3O^+$  ions attract surface oxygenated adsorbent groups, which could form a bond between  $H_3O^+$  and adsorbent [30].



**Figure 4.** pH-dependent methomyl microspecies distribution and pH-dependent pesticide removal. Initial conditions: ( $C_{i[\text{methomyl}]}$ ) = 10.01 mg L<sup>-1</sup>,  $m/V$  = 2000 mg L<sup>-1</sup>,  $T$  = 25 °C)

#### Adsorption kinetics

The kinetics parameters of methomyl adsorption were monitored for 5 to 120 minutes. After 3 hours of the

methomyl removal, an equilibrium was established. The difference in pesticide removal between 120 and 180 minutes increases from 20 to 3 percent. In order to speed up the process, the last sample in the process was taken after 120 minutes. The determined kinetics parameters of pesticide adsorption on RAC microspheres of pseudo-first, pseudo-second-order (PSO), and second-order models are shown in Table 4.

**Table 4.** Pseudo-first, PSO and second order model parameters for the adsorption of Methomyl on AC adsorbent

Equation parameter	Pseudo-first	PSO	Second order	$E_a$ (kJ mol <sup>-1</sup> )
$q_e$ (mol g <sup>-1</sup> × 10 <sup>-8</sup> )	8.014	8.631	8.631	
$k$ ( $k_1, k_2$ )	0.0247	0.4254	0.749	
$\chi^2$ (× 10 <sup>-8</sup> )	0.00122	1.34	0.781	42.26
F value	765	2343	1543	
Prob>F (× 10 <sup>-10</sup> )	15.1	0.911	2.21	
$R^2$	0.897	0.993	0.999	

The results shown in Table 4, according to the presented parameters, indicate that the kinetics for all adsorbents are best described using a pseudo-second and second order kinetics models. According to the kinetics parameters of pesticide adsorption it can be concluded that the adsorption of methomyl particles on the RAC surface is a single step, as described by a pseudo-second-order equation, but can also be described by consecutive/competitive steps. The activation energy for the adsorption of methomyl was calculated using the Arrhenius equation:

$$k' = k_0 \exp\left[\frac{-E_a}{RT}\right] \quad (13)$$

Where  $k'$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the PSO rate adsorption constant,  $k_0$  (g mmol<sup>-1</sup> min<sup>-1</sup>) is the temperature independent factor,  $E_a$  (kJ mol<sup>-1</sup>) is the activation energy,  $R$  (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) is the gas constant and  $T$  (K) is the adsorption absolute temperature. A plot of  $\ln k'$  versus  $1/T$  gave a straight line with slope  $-E_a/R$  from which activation energy was calculated. Physisorption or physical adsorption generally has an energy up to 40 kJ mol<sup>-1</sup>, while chemisorption requires a higher energy and activation energy over 40 kJ mol<sup>-1</sup>. Based on the obtained results, where  $E_a$  for methomyl adsorption is 42.26 kJ mol<sup>-1</sup>, we can conclude that the main mechanism of adsorption is chemical adsorption.

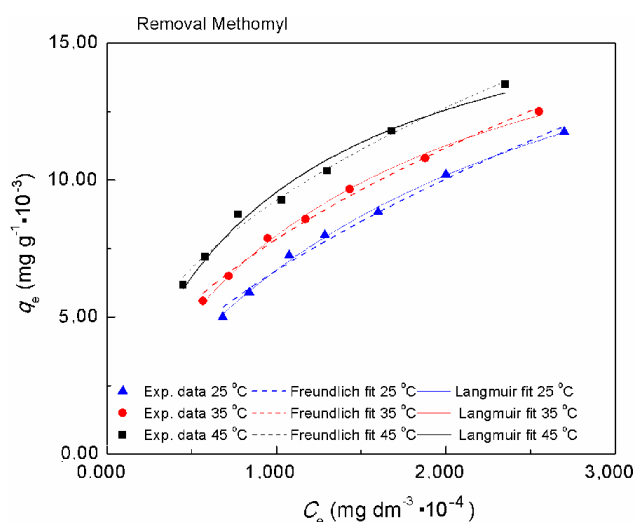
#### Thermodynamic study

For the design of the adsorption system, the equilibrium adsorption isotherm is valuable data that describes the way of interaction between adsorbates and adsorbents. The parameters obtained from the isotherm study are shown in Table 5.

The fitting of the isotherm parameters obtained by processing the experimental results with the Langmuir isotherm model confirms the occurrence of a single-layer adsorption. In contrast, the Freundlich isotherm describes adsorption characteristics for a multi-layer adsorbent surface [31, 32]. The parameters of the adsorption isotherms given in Table 5 were obtained by non-linear regression (Figure 5) using Origin 8 software.

**Table 5.** The isotherm parameters for methomyl adsorption on RAC

Equation parameter		25 °C	35 °C	45 °C
Langmuir isotherm	$q_m$ (mol g <sup>-1</sup> ×10 <sup>-7</sup> )	1.293	1.179	1.130
	$K_L$ (dm <sup>3</sup> mol <sup>-1</sup> )	764009100	1158828284	1767115740
	$\chi^2$ (×10 <sup>-8</sup> )	1.89	2.32	0.977
	F value	13109	14210	11422
	Prob>F(×10 <sup>-10</sup> )	9.64	5.76	11.4
	$R^2$	0.997	0.997	0.990
Freundlich isotherm	$K_F$ (mg g <sup>-1</sup> )(dm <sup>3</sup> mg <sup>-1</sup> ) <sup>1/n</sup>	1.902	1.038	0.664
	1/n	0.615	0.531	0.460
	$\chi^2$ ×10 <sup>-18</sup>	2.68	1.82	2.82
	F value	3508	6005	4573
	Prob>F (×10 <sup>-8</sup> )	2.594	0.677	1.34
	$R^2$	0.987	0.991	0.987
Temkin isotherm	$A_T$ (dm <sup>3</sup> g <sup>-1</sup> )	40261	58376	91089
	$B$ (J mol <sup>-1</sup> )	0.0049	0.0046	0.0043
	$\chi^2$ ×10 <sup>-14</sup>	3.17	4.65	1.22
	F value	7304	8201	7798
	Prob>F (×10 <sup>-9</sup> )	3.55	6.54	9.92
	$R^2$	0.997	0.997	0.988
Dubinin-Radushkevich isotherm	$q_m$ (mol g <sup>-1</sup> ×10 <sup>-7</sup> )	7.68	5.88	4.82
	$K_{ad}$ (mol <sup>2</sup> KJ <sup>-2</sup> )	14.079	14.346	14.544
	$E_a$ (KJ mol <sup>-1</sup> )	5.959	5.903	5.863
	$\chi^2$ ×10 <sup>-19</sup>	6.67	4.86	1.87
	F value	76.6	98.1	34.2
	Prob>F (×10 <sup>-3</sup> )	0.821	1.34	4.45
R2	0.991	0.995	0.989	

**Figure 5.** Presentation of the results of adsorption experiments with the best fitted isotherm models (solid line) for the removal of methomyl

The dimensionless separation factor ( $R_L$ ) is used to evaluate the feasibility of adsorption on a given adsorbent and can be calculated by the following reaction (Eq. 14):

$$R_L = \frac{1}{1+bC_i} \quad (14)$$

Value of  $R_L$  points out to the isotherm type: irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), unfavorable

( $R_L > 1$ ) [33]. The  $R_L$  for the adsorption of methomyl on RAC ranges from 0.156 to 0.560, which indicates that the adsorption process is favorable.

The thermodynamic parameters of pesticide adsorption were calculated using the equations 10 and 11. The calculated thermodynamic parameters for methomyl adsorption onto AC adsorbent are presented in Table 6.

**Table 6.** Thermodynamic parameters for methomyl adsorption onto AC adsorbent

Ion/pesticide	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )			$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$R^2$
	298 K	308 K	318 K			
RAC/methomyl	-60.66	-63.76	-66.94	33.05	314.26	0.999

According to the negative values of Gibbs free energy and positive values of entropy at all temperatures, pesticide adsorption is spontaneously processed. The decrease in  $\Delta G^\circ$  initiated by temperature increase also indicates that the reaction's spontaneity is increasing. Positive values of entropy indicate a tendency for a more significant disorder of the RAC surface system and the solution of methomyl.

The calculated enthalpy values at all temperatures are noticeable, indicating an endothermic process. In general, the obtained results of Gibbs free energy indicate that both mechanisms of adsorption (chemisorption and physisorption) are presented simultaneously in these cases.

## Conclusion

Based on the obtained results during the investigation of carbamate pesticide methomyl removal from simulated wastewater using the RAC microspheres, the following can be concluded:

- The SEM images show the uniform distribution of adsorbent particles without agglomerations. The distribution of particles is in the range of 450–570  $\mu\text{m}$  with a highly porous surface.
- The optimal pH value for pesticide removal by adsorption using the RAC microspheres is pH 9 as an effect of excellent ratio of the pesticide and adsorbent surface charge and faster adsorption than electrolysis of pesticide at moderate alkaline state.
- According to the reduced chi-square  $\chi^2$  statistic, regression coefficient ( $R^2$ ), and standard error for all model parameters, pesticide adsorption can be satisfactorily described by the pseudo-second-order and second-order kinetics models.
- According to the thermodynamic study, the chemisorption and physisorption mechanisms are simultaneously presented in the adsorption of methomyl pesticide adsorption using the reactivated AC microspheres. The activation energy indicates that the primary mechanism is chemical adsorption. The values of  $\Delta G^\circ$  and  $\Delta S^\circ$  indicate that the reactions in the pesticide removal by spontaneous adsorption take place simultaneously.
- The results of methomyl adsorption show good fitting with the Langmuir isotherm model, which confirms that the pesticide particles form a monolayer on the adsorbent homogenous surface at equilibrium.

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Received: 20.02.2023.

Accepted: 19.06.2023.

## Uklanjanje metomila iz vodenih rastvora korišćenjem mikrosfera reaktiviranog aktivnog uglja

U ovoj studiji prikazano je uklanjanje metomila, jednog od najčešće upotrebljivanih pesticida, iz vodenih rastvora adsorpcijom na mikrosferama reaktiviranog aktivnog uglja dobijenog iz iznošenog filtrujućeg zaštitnog odelca. Ova studija je značajna sa dva aspekta – prvi je *in-situ* uklanjanje pesticida iz vodenih rastvora, a drugi je reciklaža zaštitne opreme kao efikasnog materijala za dekontaminaciju vode. Metomil je karbamatni pesticid namenjen za kontrolu štetočina na različitim usevima. Takođe, zbog svoje visoke toksičnosti, ima potencijalnu primenu u terorističkim aktima i u taktičke svrhe tokom vojnih operacija. Mikrosfere reaktiviranog aktivnog uglja su okarakterisane skenirajućom elektronskom mikroskopijom (SEM). Promena koncentracije metomila tokom adsorpcije praćena je UV-vidljivom spektrofotometrijom. Kinetika adsorpcije odgovara kinetičkom modelu drugog reda. Pri optimalnim uslovima, adsorpcioni kapacitet bio je  $q_e = 8.631 \text{ mol g}^{-1} \times 10^{-8}$  i brzina adsorpcije je  $k = 0.749 \text{ g mmol}^{-1} \text{ min}^{-1}$ . Za opisivanje procesa adsorpcije korišćeni su modeli Langmuirove, Frojndlihove, Temkinove i Dubinin-Radushkevič izotermnim modelima. Termodinamička studija adsorpcije dokazuje da je proces spontan i egzotermne prirode.

*Ključne reči:* insekticid, adsorpcija, mikrosfere uglja, recikliranje, zagađenje vode.