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UKLANJANJE METOMILA IZ VODENIH RASTVORA UPOTREBOM TERMIČKI REGENERISANIH UGLJENIČNIH MIKROSFERA

REMOVAL OF METHOMYL FROM AQUEOUS SOLUTIONS USING THERMAL REGENERATED CARBON MICROSPHERES

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Metomil je široko rasprostranjen karbamatni pesticid, koji je u velikoj meri korišćen u poslednjih 60 godina prvenstveno kao insekticid, ali i kao herbicid i fungicid. Proizvodnja metomila uključuje niz složenih reakcija. Tokom njegove sinteze, otpadne vode iz fabrika za proizvodnju pesticida mogu kontaminirati vodene tokove. U ovom radu prikazani su rezultati ispitivanja efikasnosti uklanjanja metomila iz vodenih rastvora, adsorpcijom, korišćenjem termički regenerisanih mikrosfera aktivnog uglja (RAC). Mikrostruktura površine adsorbenta ispitana je skenirajućom elektronskom mikroskopijom (SEM). Promena relativne koncentracije pesticida u vodenom rastvoru praćena je pomoću UV vidljive spektrofotometrije. Kinetika adsorpcije metomila i izoterme regenerisanih mikrosfera aktivnog uglja odgovaraju modelima pseudo-prvog reda i Frojndlihovog modela. Konstanta brzine pseudo-prvog reda iznosi 0.0105 min^{-1} na temperaturi od 25 °C. Određivanjem termodinamičkih parametara adsorpcije može se zaključiti da je proces spontan i egzotermne prirode.

***Ključne reči:** prečišćavanje vode; adsorpcija; metomil; termalna regeneracija; mikrosfere*

Methomyl is a widely used carbamate pesticide, which has been extensively used over the past 60 years, primarily as an insecticide, but also as an herbicide and fungicide. Methomyl production involves a series of complex reactions. During its synthesis, wastewater from pesticide manufacturing plants can contaminate aqueous media. This study provides the results of investigation of effectiveness of methomyl removal from aqueous solutions by adsorption using the thermally regenerated microspheres of activated carbon (RAC). The microstructure of the adsorbent surface was examined by scanning electron microscopy (SEM). The change in the relative concentration of the pesticide in the aqueous solution was monitored using UV-Vis spectrophotometry. Methomyl adsorption kinetics and isotherms of regenerated activated carbon microspheres fit the pseudo-first-order and Freundlich models. The pseudo-first-order rate constant is 0.0105 min^{-1} at a temperature of 25 °C. By

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determinig the thermodynamic parameters of adsorption, it can be concluded that the process is spontaneous and exothermic.

Key words: *water purification; adsorption; methomyl; thermal regeneration; microspheres*

1. Introduction

Water is an essential compound for life on Earth and its quality is crucial for the future of humanity. The demand for clean water is expected to increase by midcentury. Only a small fraction of the available surface water has the quality necessary for human and industrial use, and improvement of technologies for treatment of wastewater, remediation of polluted water and elimination of micropollutants from water, are very important. Removing pesticide residues from water is very difficult and pesticide pollution in surface and groundwater has been recognized many years ago as an important issue in a number of countries. There are two sources of pesticides that contaminate aqueous media: (1) wastewaters from pesticide manufacturing plants, agricultural fields, and equipment rinsing operations and (2) surface water and groundwater. Whereas wastewaters often contain very high level of pesticides (a mg L^{-1} or more), surface water and groundwater usually contain only trace amounts of pesticides (µg L^{-1} or less), but these often occur as a more complex mixture [1].

Currently, organophosphates (OPs) and carbamates (CMs) are the most commonly used pesticides in agriculture, floriculture, and forestry around the world. This trend is partly due to their lack of residue persistence in the environment and in mammalian species, and also due to the development of lesser resistance in insects compared with the organochlorine pesticides. However, these pesticides lack species selectivity and being extremely toxic chemicals, they pose a serious threat to the environment as well as to the health of humans, domestic animals, wildlife, and aquatic species. OPs and CMs produce toxicity primarily by virtue of the inhibition of the acetylcholinesterase (AChE) enzyme [2].

Methomyl is a white, crystalline solid with a slight sulfurous odor. Methomyl dust is combustible and can form explosive mixtures when dispersed in air. It was introduced in 1966 as a carbamate insecticide and registered by the U.S. Environmental Protection Agency (EPA) in 1968 as a restricted use pesticide to its high human toxicity. Methomyl is an oxime carbamate insecticide that is formulated as a soluble concentrate, a wettable powder or a water-soluble powder and is the active ingredient of Du Pont 1179™, Flytek™, and Kipsin™, among other trade formulations. Methomyl is weak-to-moderately persistent, with a soil half life ranging from a few to more than 50 days [3,4]. Methomyl has a melting point of 77 °C and a vapour pressure of 0.72 mPa at 25 °C. Its solubility in water is 54.7 g L^{-1} and its octanol/water partition coefficient (K) is 1.24. It is stable in sterile water at pH 7, but is broken down at higher pH values. Under natural environmental conditions, abiotic degradation of methomyl by hydrolysis or photolysis is slow or absent [5].

Most of the past studies have focused on the removal of pesticides from water by the more traditional and more expensive methods such as cation exchange, and dialysis. Advanced oxidation processes using hydrogen peroxides are, often ineffective because carbonate and bicarbonate ions, which are abundant in all natural water, react as strong free radical scavengers. Pesticides are not completely degraded into inorganic compounds such as CO_2 by ozonation. These findings suggest that the breakdown products of pesticides remain in water after treatment, need complementary operations and are not economical. The use of enzymes to detoxify wastewater failed to attract much attention due to the high cost of enzyme-based systems. Filtration through membranes needs another method such as oxidation reaction catalyzed by enzyme to transform the pesticide into an insoluble product, so that this method is highly expensive. Compared with the above methods, adsorption of different pesticides onto activated carbon has demonstrated efficiency and economic feasibility and gained high favorability for removing pesticides that are chemically and biologically stable [6].

Adsorption is a surface phenomenon involving the adsorption of adsorbate molecules onto adsorbent. Basic principle involving the adsorption process is the variable surface energy. Urge to stabilize the surface energy results into interactions between the adsorbent surface and adsorbate molecules. Adsorption can be classified into two categories: physical and chemical based on the type of interactions between adsorbate and adsorbent molecules. Activated carbon (AC) is one of the most utilized adsorbents, AC and its composites can be utilized as a catalyst or catalyst support for various chemical reactions, AC and its various derivatives have found to be used in food and pharmaceutical industries, it is also used as a storage system for gases and of course for the adsorption of various pollutants.

The regeneration of AC is a very important process, as it helps in increasing the productive life of the adsorbent and enhances its practical utility. Considering the regeneration of AC, it can be done by various methods, Typically, physical and chemical approaches are used in the regeneration process to obtain the desired surface area and porosity. Physical regeneration involves the activation of carbonized char using oxidizing gases such as air, carbon dioxide, and steam at high temperatures (between 650 and 900°C). The chemical approach involves the mixing of precursor with activating agents (NaOH, KOH, and $FeCl_3$, etc.). These activating agents acts as oxidants as well as dehydrating agents. In this approach, carbonization and regeneration is carried out simultaneously at comparatively lower temperature 300-500°C as compared to the physical approach [7].

A few studies have been carried out on the removal of methomyl pesticide onto activated carbon microspheres (Watcharenwong et al. 2024 and Dinić et al. 2023) [8,9]. Therefore, the objective of the present work was to investigate the adsorption performance of regenerated activated carbon (RAC) microspheres used for the removal of methomyl from water. Dinić et al. 2023 regenerated AC by treating it with aggressive chemicals at room temperature for 24 h. On the other hand, in the present study, AC regeneration was conducted by heating at 650 °C in air for 30 min at a heating rate of 10 °C min^{-1}. This procedure represents a more environment-friendly method that leads to an equally satisfactory adsorption performance.

2. Experimental Part

2.1. Materials and characterization methods

Activated carbon (AC) microspheres from filtering protective suit produced by Trayal Corporation used as sorbent for adsorption. Commercial grade methomyl (Dupont) was used as an organic pollutant without further purification. For pH value adjustment an aqueous solutions, (0.1 M) of sulfuric acid, H_2SO_4, and ammonium hydroxide, NaOH, (Fisher Scientific (USA)) were used. 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 LLG-uniSPEC 2 spectrophotometer (Germany) was used for UV/VIS analysis.

2.2. Reactivation of carbon spheres

The old protective filtering suit was washed 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 dimension 10×10 cm. In the second step, carbon microspheres were mechanically taken from a peace of suit. Then the separated spheres were heated into a furnace (Muffle Furnace LE 6/11/B150 LE060K1BN, Nabertherm, Germany) at 650 °C in air for 30 min with a heating rate of 10 °C min^{-1}, and cooled with a cooling rate of 10 °C min^{-1}. 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.

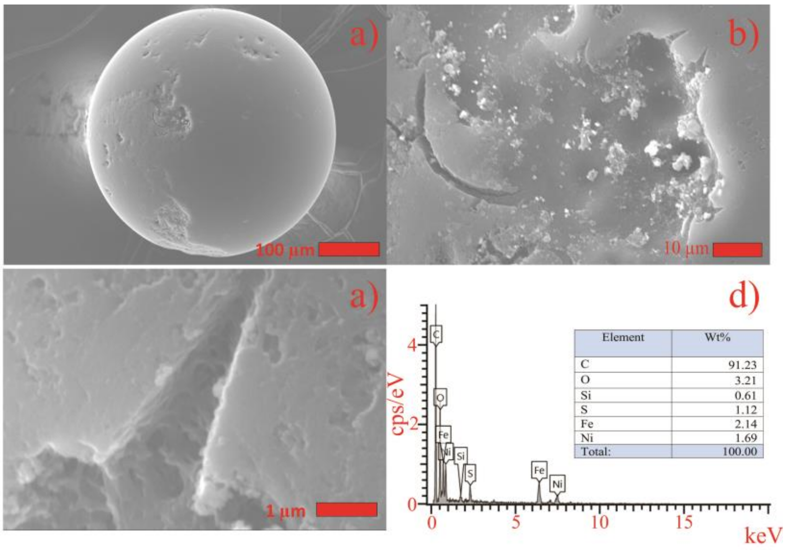
2.3. Adsorption experiment

All adsorption experiments were carried out in a thermostatic water bath with a shaker (WNB 14, Memmert, Germany) using open glass reactors of 50 ml volume. The influence of pH value, initial pesticide concentration, and adsorbent concentration on adsorption efficiency was performed at 25 °C. Also the value of the point of zero charge for the adsorbent pH_{PCZ} was calculated. The pH value at the beginning of adsorption was performed by adding 0.1 M H_2SO_4 for acidification or the same concentration of NaOH solution for an alkaline solution. The dependence of adsorption efficiency on the temperature was carried out at 25, 35, and 45 ±0.1 °C. The kinetics of pesticide adsorption was followed by a UV-Vis Spectrophotometer at $\lambda_{max} = 235$ nm. The kinetics of pesticide removal by the adsorption was revealed using pseudo-first and pseudo-second order. Langmuir, Freundlich, and Temkin isothermal models were also used for adsorption modeling.

3. Results and discussion

3.1. Adsorbent characterization

The morphological and structural analyses of reactivated AC microspheres, after thermally re-activation in thermostatic chamber for 2 h, were performed by Scanning Electron Microscopy (SEM). Figure 1 shows the SEM micrographs of reactivated AC microspheres after reactivation process.



Element	Wt%
C	91.23
O	3.21
Si	0.61
S	1.12
Fe	2.14
Ni	1.69
Total:	100.00

Figure 1. SEM photographs of reactivated AC at different magnification (a) 200 (b) 1600 and (c) 20000 times) and EDS spectra

The SEM micrographs obtained at different magnifications and EDS spectra (Figure 1) shows the uniform distribution of microsphere particle size without agglomeration, confirming AC particles excellent separation during protective suit recycling. 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 reactivated AC is mainly in the range of 170-290 µm. According to SEM micrographs at higher magnification, reactivated AC microspheres have a highly porous surface, confirming the large number of active sites that contribute to pesticide removal by adsorption.

3.2. Effect of solution pH on methomyl adsorption

The effect of pH on methomyl removal is shown in Fig. 2 As previously stated, methomyl retention depends on the nature of the adsorbent. The experimental data show that the surface of the RAC was neutrally charged in the pH_{PZC} 8.82 phase solution. Based on the obtained results, for the practical reason the following experiments were performed at pH 9.

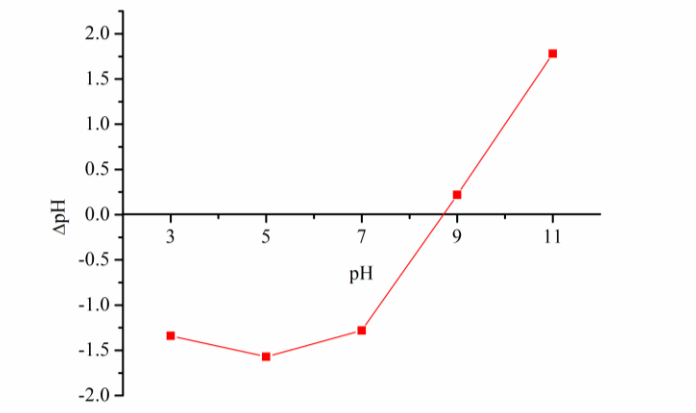


Figure 2. The effect of pH on methomyl removal

3.3. Adsorption kinetics

The influence of time on methomyl adsorption was monitored in the range of 10–180 min. The final balance was established after 400 min but considering that the difference in methomyl removal from 180 to 400 min ranged from 3 to 7%, to speed up the process, we took 180 min as the final time.

The kinetic study provides an insight into the possible mechanism of adsorption along with the reaction pathways. The adsorption data were analyzed by non-linear least-squares method in the form of pseudo-first-order and pseudo-second-order (Table 1).

Table 1. Kinetic model equations

Kinetic model	Nonlinear form	Model parameters	Equa-tion
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)	(1)
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, (g mg^{-1} min^{-1})	(2)

In Table 2, the pseudo-first order adsorption kinetic equation has a correlation coefficient (R^2) value of 0.931, which is closer to 1 than that of the pseudo-second order adsorption kinetic equation. The experiments showed a great adsorption capacity. This high adsorption capacity indicates that RAC could be used to adsorb methomyl from wastewater. The results of this study are consistent with Watcharenwong et al. 2024 [8] research in which AC is used as an adsorbent for methomyl, without any modification. In addition we obtained a slightly less adsorption capacity then that obtained in the previous study, which indicates that our regeneration process was successful.

Table 2. The kinetic parameters for adsorption of methomyl on RAC.
(Ci[methomyl] = 9,895 mg L^{-1}, pH = 9; m/V = 200 mg L^{-1}, T = 25 °C)

Parameters	Pseudo-first order	Pseudo-second order
q_e	28.12	36.04
k (k_1, k_2) (min^{-1}, g mg^{-1} min^{-1})	0.0105	0.00022
R^2	**0.931**	0.896

3.4. Adsorption isotherms

The state of the interactions/bonds on the adsorbate/adsorbent surface can be recorded by fitting the experimental data with different adsorption isotherms. Equations of adsorption isotherms models are listed in Table 3.

Table 3. Adsorption isotherms model 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 −C (mg L^{-1}) - initial concentration −C_e (mg L^{-1})-equilibrium concentration −K_L(L mol^{-1}) – Langmuir equilibrium constant −K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$ – Freundlich constant – $1/n$ –Freundlichisotherm parameters −A_T (Lg^{-1})- Temkin isotherm constant −b_T (J mol^{-1})- Temkin constant related to heat of sorption −R - gas constant −T (K)-absolute temperature	(3)
Freundlich	$q = K_F C^{1/n}$		(4)
Temkin	$q_e = \frac{RT}{b} \ln(AC_e)$		(5)

The adsorption experiments results and the Langmuir, Freundlich and Temkin isotherm curves are shown at Fig. 3, and their parameters are listed in Table 4.

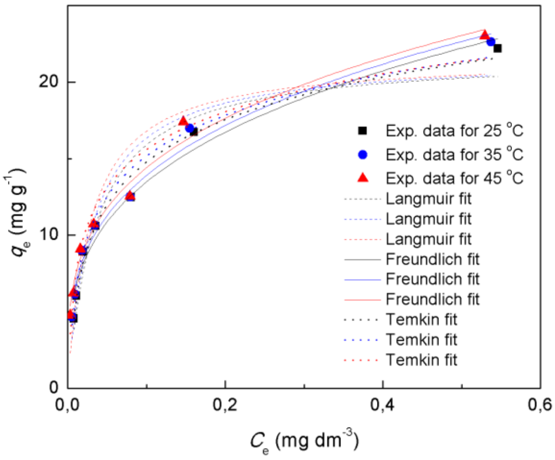


Figure 3. Presentation of the adsorption experiments results with best-fit isotherm models (solid line) for the removal of methomyl on the RAC.

Table 4.The isotherms parameters for adsorption of methomyl on RAC

Isotherms model and parameters		Temperature		
		25 °C	35 °C	45 °C
Langmuir	q_m (mg g^{-1})	23.63±1.67	23.92±1.96	24.15±2.33
	b (L mg^{-1})	22.20±6.71	24.20±9.36	26.96±13.41
	R^2	0.928	0.898	0.854
Freundlich	K_F (mg g^{-1}) (dm^3 mg^{-1})$^{1/n}$	27.56±1.50	27.96±1.28	28.21±1.17
	N	3.22±0.25	3.30±0.22	3.43±0.21
	R^2	**0.968**	**0.978**	**0.982**
Temkin	A_T (dm^3 g^{-1})	395.89±65.02	522.43±116.65	791.63±266.15
	b_T	4.014±0.20	3.835±0.25	3.566±0.32
	R^2	0.964	0.975	0.953

According to the results presented in Table 4, the Freundlich model provided higher correlation coefficients than the Langmuir model at all temperatures. According to the Freundlich isotherm, the mechanism of adsorption on RAC can be described as heterogeneous and multi-layer adsorption [10], where the adsorbed molecules have different enthalpies and adsorption activation energies [9]. It is characteristic that in the **El-Geundi et all.** [6] **study, when clay was used as one adsorbent in the process of removing methomyl isotherm process was described using** the Langmuir model. Considering that differnt types of adsorbent were used, their results were not in agreement with does obtained in our study.

The magnitude of the exponent n indicates the favorability and capacity of the adsorbent-adsorbate system; values of n > 1 represent favorable adsorption [6]. In this study, the values of n are greater than one (n > 1), which indicates that methomyl shows favorable adsorption by RAC.

3.5. Thermodynamics study

Gibbs free energy (Δ*G*°), enthalpy (Δ*H*°), and entropy (Δ*S*°) were calculated using the Van't Hoff equation (6) and (7):

$$\Delta G^0 = -RT\, ln(b) \tag{6}$$

$$ln(b) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{(RT)} \tag{7}$$

where T is the absolute temperature in K, R is the universal gas constant (8.314 mol^{-1} K^{-1}) and the adsorption constant b was calculated using the Langmuir isotherm (Table 4). The calculated thermodynamic parameters are listed in Table 5.

Negative values of Gibbs free energy (Δ*G*°) and positive values of entropy (Δ*S*°) at all temperatures indicate that the reactions in the adsorption process occurs spontaneously. The decrease in the Gibbs free energy (Δ*G*°) with increasing temperature also indicates that the spontaneity of the reaction increases. Positive values of Δ*S*° indicate a tendency for greater disorder of the surface system of RAC and the methomyl solution. Also, positive values of entropy (Δ*S*°) and positive values of enthalpy (ΔH°) indicate an endothermic process. In general, for simultaneous chemisorption and physisorption between -20 and -80 kJ mol^{-1} [11]. This behavior of RAC adsorbents in this study is in agreement with the results obtained by Dinić et al. 2023 [9] study in which they studied metomyl adsorption on chemically reactivated carbon microspheres with an optimum pH of 9. The obtained results indicated that chemisorption and physisorption were simultaneously represented in these study.

Table 5. Calculated Gibbs free energy of adsorption, enthalpy, and entropy for methomyl adsorption on RaAC at 25, 35, and 45 °C

Adsorbent	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K^{-1})	R^2
	25 °C	**35 °C**	**45 °C**			
RAC	-50.33	-52.24	-54.22	7.66	194.48	0.993

4. Conclusion

In this study, regenerated activated carbon (RAC) microspheres used for the removal of methomyl from water were investigated.

The SEM images show a uniform distribution of the adsorbent particles without agglomeration. The distribution of the particles was in the range of 170–290 µm with a highly porous surface. Also, SEM-EDS analysis confirms the high degree of purity of RAC after the recycling of used protective suits

The obtained results, according to the correlation coefficient (R^2) and standard error for all model parameters, indicated that the kinetics for all adsorbents were best described using a pseudo-first-order model.

Adsorption isotherms were plotted to obtain the Langmuir, Freundlich, and Temkin parameters. Theoretical isotherms were compared with experimental adsorption data, and the general results of this study revealed that the Freundlich model can be used to describe the system adequately. Freundlich isotherm, the mechanism of adsorption on RAC adsorbent can be described as heterogeneous adsorption.

Thus, RCA exhibited satisfactory adsorption performance and could be successfully used to remove pesticides from water.

5. Nomenclature

AchE – Acetylcholinesterase
AC – Activated carbon
CMs – Carbamates
EPA – U.S. Environmental Protection Agency
Ops – Organophosphates
RAC – Regenerated active carbon
SEM – Scanning electron microscopy

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