



Removal of carbendazim from aqueous solutions by adsorption on different types of zeolite

Anica Pavlinović¹ ,
Mladenka Novaković² ,
Ivona Nuić¹ 

¹Faculty of Chemistry and Technology,
University of Split, Split, Croatia

²Faculty of Technical Sciences,
University of Novi Sad, Novi Sad, Serbia

Objective: Due to the avid interest in devising economically and environmentally viable and readily available materials for pesticide-contaminated water treatment, the effectiveness of clinoptilolite, a natural zeolite, its modified Na-form, as well as ZSM-5, a synthetic zeolite, was investigated for the removal of the fungicide carbendazim from aqueous solutions.

Methods: The removal was investigated using batch adsorption by mixing zeolite and the carbendazim solution at different contact times. At the end of each experiment, the suspensions were filtered, and the residual concentration of carbendazim in the filtrates was measured using high-performance liquid chromatography (HPLC). The experimental results were used to calculate the efficiency of tested zeolite types for the removal of carbendazim from aqueous solutions.

Results: Synthetic zeolite was highly effective (94.5%) in removal of carbendazim from aqueous solutions when compared to natural zeolite (19.5–23.3%) and its Na-form (22.5–29.0%). However, the residual carbendazim concentration for all three zeolites tested was above the maximum allowable concentration (MAC).

Conclusion: Zeolite ZSM-5 exhibited outstanding properties for the removal of the carbendazim fungicide from aqueous solutions; however, high production costs could be a limiting factor for a wider application in water treatment. For practical applications, natural zeolite may be a more economically viable choice, regardless of its significantly lower removal efficiency. Its surface properties would need to be modified and improved by organic surfactants, which would require additional experiments. Finally, the cost-effectiveness of modified natural zeolite should be compared to the production cost of synthetic zeolite to determine the most effective, economically advantageous, and environmentally friendly solution for the treatment of pesticide-contaminated water.

Correspondence to:

Anica Pavlinović
Faculty of Chemistry and Technology,
University of Split, Ruđera Boškovića 35,
21000 Split, Croatia
anicapavlinovic@gmail.com

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Introduction

Agricultural intensification aided by the irrational use of plant protection products (PPPs), also known as pesticides, has contributed environmental (air, soil, and water) pollution and jeopardized natural resources [1]. Overuse, misuse, and ill-informed use of pesticides resulted in high concentrations of pesticide residue in the environment. Moreover, pesticides can reach areas far from the site of application by air. It has been estimated that as much as 20% of applied pesticides end up dispersed outside the target areas [2]. Through contact with soil components, the active substance in a PPP may enter a number of physicochemical and biological processes that may directly affect its behavior in the environment. The most significant influencing factors are the physicochemical properties of the active substance, method of application, time of year of PPP application, weather conditions prior to, during, and following the application, as well as soil properties. By drifting due to wind, by rainfall and irrigation, pesticides may enter surface and groundwater. Karst areas, light and sandy soils, as well as soils with low organic matter levels are the most vulnerable areas for groundwater contamination. Water supplies are finite and the environmental awareness of every individual plays an important role in their conservation and protection [3]. Pesticides can easily enter the food chain and may have a harmful effect on human health, disrupt organ function, or cause organ damage due to acute or chronic pesticide poisoning [2]. The maximum allowable concentrations (MAC) are consequently very low, and equal 0.50 µg/L for total and 0.10 µg/L for individual pesticide concentrations [4]. Carbendazim is an active substance in benzimidazole fungicides [5]. Due to its biodegradation resistance and poor-to-moderate water solubility, it will remain in the soil for a long period of time (6–12 months) after use. Based on the groundwater ubiquity score (GUS) index, used to describe the mobility of pesticides, with $GUS < 1.8$ indicating low mobility, carbendazim is a moderately mobile pesticide ($GUS = 2.22$) [6–8]. According to the World Health Organization (WHO) classification, carbendazim is a hazardous chemical and one of the major contaminants in food, soil, and water [9]. It may have a mutagenic effect on health, cause liver toxicity, and affect estrogen production [8]. Although PPPs containing carbendazim have not been approved for use since 2015, their residues still remain detectable in the environment due to their non-biodegradability. It is, therefore, crucial to develop effective and economically viable methods for removing pesticides from the environment, especially from water for human consumption and irrigation. The most commonly used remediation methods for pesticide-contaminated soils are low-temperature thermal desorption and incineration. Bioremediation is a natural self-purification process through the microbiological decomposition of organic matter. Phytoremediation is an environmentally friendly soil and sediment purification technology that employs plants to decompose, assimilate, metabolize, or detoxify pollutants [10]. Adsorption on activated carbon is one of the most common methods for removing pesticides and other hazardous chemicals from contaminated water. However, due to the high costs of activated carbon, there is an increased interest in using readily available, more cost-effective materials [7]. One such example are zeolites, aluminosilicate minerals of alkali and alkaline earth metals with a lattice structure composed of interconnected tetrahedral SiO_4 and AlO_4 units. The resulting cavities and channels of various shapes and sizes may contain exchangeable Na, K, Ca, and Mg cations [11]. Due to their chemical, physical,

and structural properties, zeolites are highly selective and have a high sorption capacity for hazardous substances. The number of adsorption sites in the zeolite depends on the Si/Al ratio, so different types of zeolites have different sorption properties [12, 13]. In this study, the effectiveness of different types of zeolites – natural zeolite (NZ) clinoptilolite, its homoionic sodium form (NaZ), and the synthetic zeolite ZSM-5 (Zeolite Socony Mobil-5) were tested for the removal of carbendazim from aqueous solutions. The obtained results may contribute to the development of effective, environmentally and economically viable methods of pesticide-contaminated water treatment.

Materials and Methods

In this study, three samples of zeolite – natural zeolite (**Figure 1a**), its homoionic sodium form (**Figure 1b**), and a synthetic zeolite, ZSM-5 (**Figure 1c**) were utilized.



Figure 1. a) Natural zeolite (NZ) with particle sizes of 0.09–0.56 mm, b) the Na-form of natural zeolite (NaZ) with particle sizes of 0.6–0.8 mm, and c) a synthetic zeolite, ZSM-5, with 0.0045 mm particles.

Clinoptilolite is the most common naturally occurring zeolite. The sample of natural zeolite in this study originated from the Zlatokop deposit in Vranjska Banja (Serbia). Based on the results of a chemical analysis and a semi-quantitative mineralogical analysis, this natural zeolite contained $\approx 80\%$ clinoptilolite as the main mineralogical component, with quartz as impurities. The Si/Al ratio equals to 4.8 [14, 15], which identifies it as a mineral of the heulandite (HEU) group, where the Si/Al ratio amounts to ≥ 4 [16]. As for exchangeable cations, the Ca^{2+} content was greater than the total content of the Na^+ and K^+ , marking it as the Ca-form of clinoptilolite [14, 15]. As a natural zeolite, clinoptilolite has excellent adsorption and ion exchange properties. It is being increasingly physically or chemically modified to improve its sorption properties and discover new applications [17]. Therefore, natural clinoptilolite was chemically converted to its homoionic Na-form with NaCl solution. Since certain synthetic zeolites have been shown to be effective adsorbents for removing pesticides from aqueous solutions [7], the synthetic zeolite ZSM-5 (manufactured by Acros Organics, Geel, Belgium) was used in this study in order to compare its efficiency with that of the natural zeolite and its homoionic form. ZSM-5 (Na-form) is a MFI zeolite ($\text{Si/Al} > 5$), with the Si/Al ratio = 37 [18].

Natural clinoptilolite was first pulverized in a ball mill, sieved to different particle sizes, and washed in ultrapure water to remove any impurities. It was then dried in the oven at 60°C to its constant weight and stored in a desiccator. This study used the following

chemicals: silver nitrate (AgNO_3 , p.a., Kemika, Croatia), sodium chloride (NaCl , p.a., Merck, Germany), carbendazim ($\text{C}_9\text{H}_9\text{N}_3\text{ON}_2$, PESTANAL®, analytical standard, Sigma-Aldrich, USA), and methanol (CH_4OH , Sigma Aldrich, HPLC purity $\geq 99.9\%$, USA).

Chemical modification of natural zeolite with NaCl solution

Natural zeolite was converted to its homoionic Na-form through chemical activation with a sodium chloride (NaCl) solution. Over 5 days, 2 g of natural zeolite (NZ) with particle sizes 0.6–0.8 mm were equilibrated with 100 mL of the NaCl solution ($c = 2 \text{ mol/L}$) at 37°C and stirred in an incubator shaker at $\approx 230 \text{ rpm}$. After equilibration, the solution was filtered and the precipitate was washed thrice with $c(\text{NaCl}) = 0.1 \text{ mol/L}$, twice with $c(\text{NaCl}) = 0.05 \text{ mol/L}$, and finally four times with ethanol. The product was then tested for complete removal of NaCl using an AgNO_3 ($c = 0.1 \text{ mol/L}$) solution up to a negative reaction to chlorides. Finally, the zeolite was dried in the oven at 60°C and stored in a desiccator.

Preparation of the stock solution of carbendazim

The aqueous solution of carbendazim (an active substance in fungicides) with an initial concentration $\gamma_0 \approx 5 \text{ mg/L}$ was prepared by diluting the standard 200 mg/L carbendazim solution in ultrapure water. The standard carbendazim solution ($\gamma = 200 \text{ mg/L}$) was prepared by dissolving 10 mg of carbendazim, precisely measured using an analytical balance, in 50 mL of methanol. The exact initial carbendazim concentration and initial pH

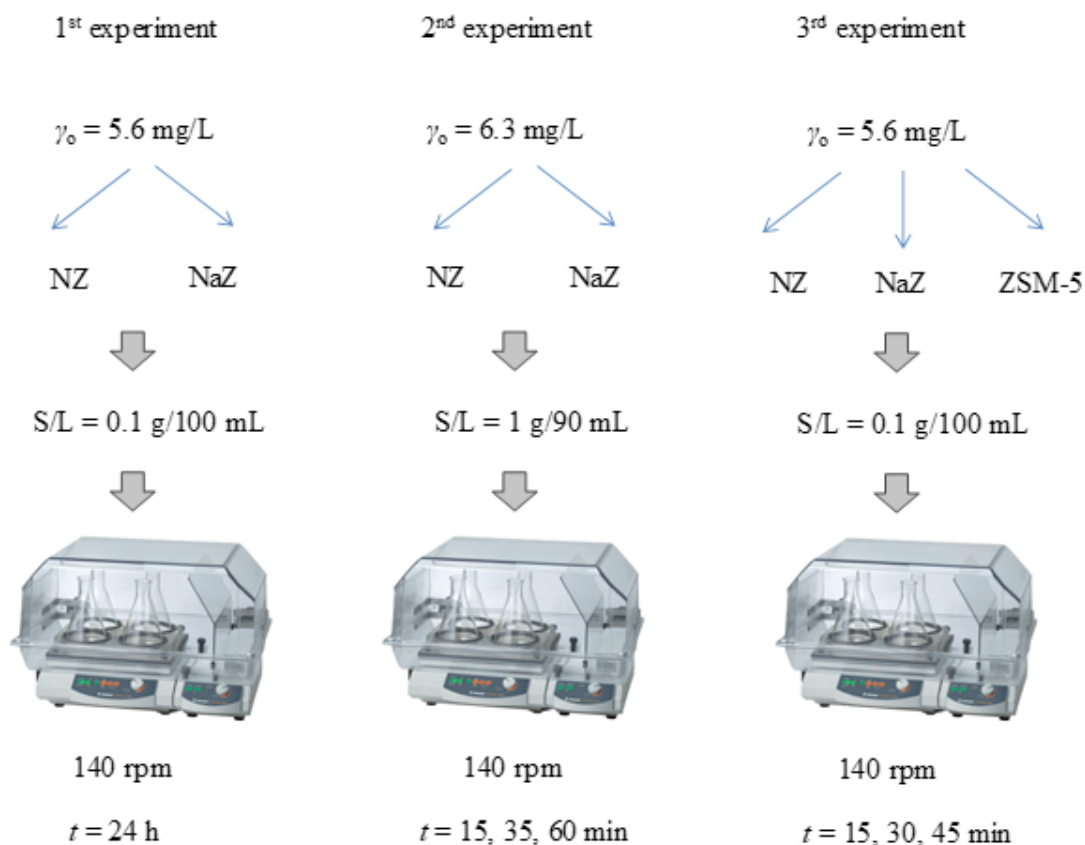


Figure 2. A scheme of the batch performance of carbendazim removal from aqueous solutions with corresponding experimental conditions.

were measured for the prepared stock solution. The initial carbendazim concentration (γ_0) in the solution and the residual carbendazim concentration (γ_e) after adsorption were measured in all samples using high-performance liquid chromatography (HPLC).

Removal of carbendazim from the aqueous solution

Carbendazim was removed from the prepared solution by batch adsorption on three different zeolite samples – natural clinoptilolite (NZ), its sodium form (NaZ), and synthetic ZSM-5. The batch process was performed at room temperature ($T = 23 \pm 2^\circ\text{C}$), by mixing zeolite and the aqueous carbendazim solution in varying solid/liquid (S/L) ratios in the incubator shaker at 140 rpm at different contact times (t). A schematic of the experiments and experimental conditions is shown in **Figure 2**.

The pH value of the suspensions was measured at defined time intervals. At the end of each experiment the suspensions were filtered, and the residual carbendazim concentrations were measured in all filtrates with an HPLC device. All experiments were carried out in two parallel assays, and the residual carbendazim concentrations and pH values were expressed as mean.

Results

Suspension pH values during the adsorption process, as well as residual carbendazim concentration in the filtrates for all three experiments are shown in **Tables 1–3**.

Table 1. Residual pH and carbendazim concentrations in the first experiment

Zeolite sample	pH		$^*\gamma_e$, mg/L $t = 24$ h
	$t = 0$ min	$t = 24$ h	
Natural zeolite	7.59	7.16	4.46
Na-form natural zeolite	7.98	6.32	4.19

$^*\gamma_e$ – residual carbendazim concentration after 24 h adsorption.

Table 2. Suspension pH values at time intervals and residual carbendazim concentrations after 60 min, in the second experiment

Zeolite sample	pH				$^*\gamma_e$, mg/L $t = 60$ min
	$t = 0$ min	$t = 15$ min	$t = 35$ min	$t = 60$ min	
Natural zeolite	7.43	6.49	6.27	6.15	4.83
Na-form natural zeolite	7.99	7.06	7.01	7.05	4.88

$^*\gamma_e$ – residual carbendazim concentration after 60 min adsorption.

Table 3. Suspension pH values at time intervals and residual carbendazim concentrations after 45 min, in the third experiment

Zeolite sample	pH				$^*\gamma_e$, mg/L $t = 45$ min
	$t = 0$ min	$t = 15$ min	$t = 30$ min	$t = 45$ min	
Natural zeolite	7.59	6.32	6.08	6.73	4.51
Na-form natural zeolite	7.98	6.45	6.14	7.15	3.98
Synthetic zeolite ZSM-5	7.57	6.18	5.66	6.21	0.31

$^*\gamma_e$ – residual carbendazim concentration after 45 min adsorption.

In order to quantify the effectiveness of the tested zeolites, the efficiency of carbendazim removal α (%) was calculated using the following equation:

$$\alpha = \frac{(\gamma_o - \gamma_e)}{\gamma_o} \cdot 100 \quad (1)$$

where γ_o and γ_e are the initial and residual concentrations of carbendazim in the aqueous solution.

The efficiency of carbendazim removal in the first experiment amounted to 20.4% for NZ and 25.2% for NaZ. In the second experiment, it was 23.3% for NZ and 22.5% for NaZ. In the third experiment, the efficiency amounted to 19.5% for NZ and 29.0% for NaZ, whereas ZSM-5 was 94.5% effective. The calculated removal efficiency values for all three experiments are shown in Figure 3.

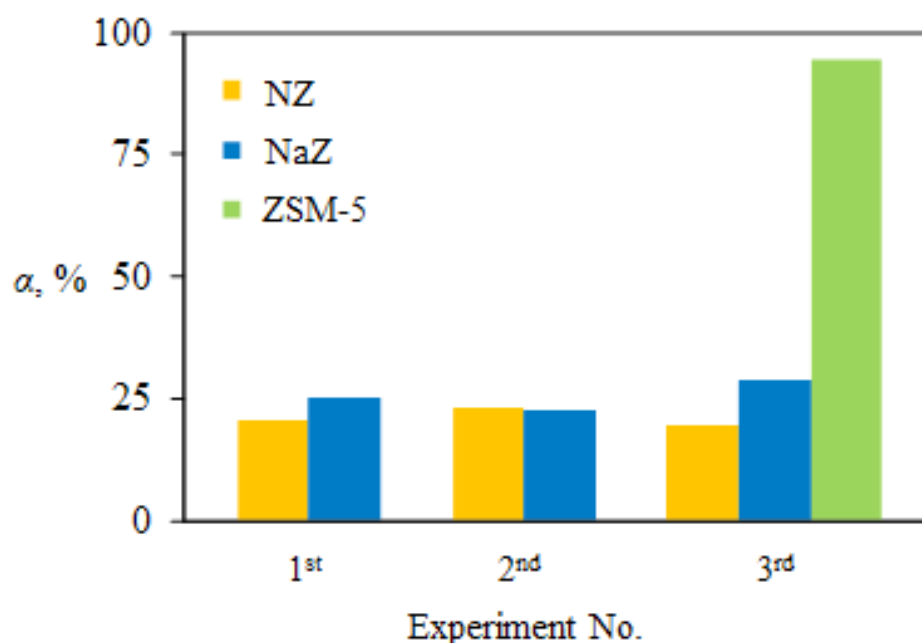


Figure 3. The efficiency of carbendazim removal on different types of zeolites in all three experiments. NZ stands for “natural zeolite”, NaZ “sodium homoionic form of natural zeolite”, and ZSM-5 is a synthetic zeolite.

Discussion

When comparing the removal efficiency of NZ (19.5–23.3%) and NaZ (22.5–29.0%) in **Figure 3**, the Na-form of natural zeolite was insignificantly more effective in the first and third experiments. Specifically, the aim of converting natural zeolite into the homoionic Na-form is to improve the ion-exchange properties of zeolite by modifying the exchangeable cations (K^+ , Mg^{2+} , and Ca^{2+}) in its structure by Na^+ , which is more readily exchangeable with cations in aqueous solutions. However, since this study involves the removal of an organic compound from water, this chemical activation had no significant effect. Such a modification does not increase the specific surface area of zeolite and thus does not increase the number of active sites, ultimately having no significant effect on its sorption capacity [19]. Furthermore, natural zeolites are known to have a negatively charged, hydrophilic surface, which is favorable for the adsorption of positive ions and polar organic molecules [20]. However, they have no affinity for hydrophobic, non-polar and weakly polar organic molecules or anions, so their outer crystal surface has to be modified with surfactants, surface-active organic substances that can change the surface charge from negative to neutral or positive (hydrophobic) [21, 22]. The synthetic ZSM-5 zeolite had an excellent removal efficiency as high as 94.5%, when compared to NZ and NaZ. The most likely reason lies in the primary microporous lattice structure of ZSM-5, which is the basis of most of its successful applications, as well as its higher Si/Al ratio and smaller particle size. ZSM-5 has a significantly higher Si/Al ratio compared to clinoptilolite (37 vs. 4.8) and thus a higher hydrophobicity. The selectivity of zeolites largely depends on the Si/Al ratio. Accordingly, zeolites may be divided into low-silica/hydrophilic zeolites with $Si/Al \leq 2$, medium-silica/moderately hydrophobic zeolites ($2 < Si/Al \leq 5$), and high-silica/hydrophobic zeolites ($Si/Al > 5$). Zeolites with a higher aluminum content, i.e. hydrophilic zeolites, have a higher affinity for polar molecules and cations. As the silicon content in the structure increases, the exchange properties decrease due to a decrease in the hydrophilic character; at $Si/Al \geq 20$, a zeolite becomes hydrophobic [23, 24]. Due to its higher hydrophobicity, ZSM-5 has a higher affinity for carbendazim compared to NZ. In addition, smaller particle size of ZSM-5 contributed to its sorption capacity. The specific surface area of natural clinoptilolite measured using the BET method [25] usually ranges from 15 to 40 m^2/g (depending on the mining site) [26, 27]. The specific surface area of natural clinoptilolite (the Vranjska Banja deposit in Serbia) with particle sizes 0.6–0.8 mm is 17.9 m^2/g [14, 15], while for ZSM-5 it amounts to 390 m^2/g [18], indicating its significantly better pore availability for various ions and molecules. Based on pore size, zeolites are generally classified into small-pore (0.4 nm pore diameter), medium-pore (0.55 nm pore diameter), and large-pore zeolites (0.75 nm pore diameter). Zeolites with ultra-large pores are still quite rare [23]. The differing arrangement of structural units in zeolites gives rise to pores and cavities of various sizes, which can be a limiting factor in the adsorption of molecules. Two values of particular interest in pore classification are the largest cavity diameter (LCD) and pore-limiting diameter (PLD). More specifically, the pore-limiting diameter (PLD) is the smallest opening along the pore for a molecule to penetrate and diffuse into the material, and the largest cavity diameter (LCD) is the largest opening along the pore [7]. The illustration of the channel cross-section (**Figure 4**) vertical to the central axis best shows the difference in channel topology of zeolites with the same pore-limiting diameter (PLD) [28, 29].

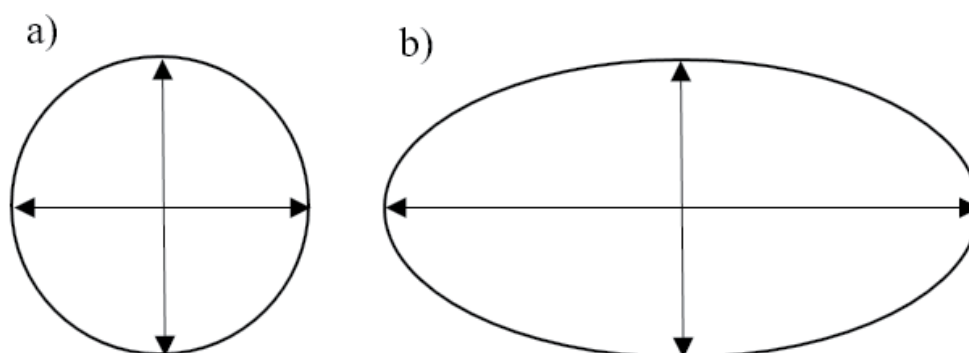


Figure 4. A cross-section of (a) a circular and (b) elliptical channel in zeolites with the same pore-limiting diameter (PLD). Elliptical pores have a visibly larger cross-section compared to circular pores with the same PLD [28, 29].

Vertical arrows represent the vertical diameter of the channel, which equals the pore-limiting diameter. In the circular cross-section (**Figure 4a**), this arrow equals the horizontal arrow. In the elliptical cross-section (**Figure 4b**), the vertical diameter is the same as the circular channel diameter, but the horizontal diameter is longer. Elliptical pores have a visibly larger cross-section compared to circular pores with the same PLD [7, 30]. According to the data available in the literature, the LCD of ZSM-5 amounts to 0.7 nm, and PLD amounts to 0.5 nm, while the clinoptilolite has an LCD of 0.66 nm and a PLD of 0.43 nm [31]. ZSM-5 has a greater largest cavity diameter and a larger maximum distribution of pore sizes, and thus a better ability to adsorb larger organic molecules.

The duration of adsorption (45 min, 60 min, and 24 h) under the examined experimental conditions did not significantly affect the removal of carbendazim. Equilibrium was likely reached even before the shortest contact time of 45 min; however, additional research is needed for more concrete conclusions. The residual concentration of carbendazim in the aqueous solution after treatment on ZSM-5 amounted to 0.31 mg/L, while for NZ it was in the range 4.46–4.83 mg/L, and for NaZ, in the range between 3.98 and 4.88 mg/L. All residual concentrations were above the prescribed maximum allowable values in water, meaning 0.10 µg/L for individual pesticides and 0.50 µg/L for total pesticides [4].

Multistage batch adsorption on zeolite should be used to reduce residual concentrations of carbendazim in water to below the MAC, and, if necessary, followed by the column adsorption method. The batch adsorption process is discontinuous and thus suitable for the treatment of smaller amounts of water with high pollutant concentrations. The column process is continuous and, therefore, suitable for treating larger volumes of water. It is more economically viable and can reduce pollutant concentrations to below the maximum allowable concentrations.

ZSM-5, a synthetic cationic zeolite, exhibited outstanding properties for the removal of carbendazim from aqueous solutions; however, its high production cost may be a limiting factor for a wider application in the treatment of larger quantities of contaminated water. Consequently, natural zeolite would be a more economically viable choice for practical applications owing to the lower water treatment cost, regardless of its significantly lower removal efficiency. However, seeing as natural zeolite has a low adsorption capacity for

negatively charged organic components in aqueous solutions due to the negative charge of the zeolitic structure, its surface properties would have to be improved through modification with organic surfactants [21, 22], which would require additional experiments. Finally, the cost-effectiveness of modifying natural zeolite should be compared to the production cost of synthetic zeolite to determine the most effective, economically advantageous, and environmentally friendly solution for the treatment of pesticide-contaminated water.

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ORCID

Anica Pavlinović  <https://orcid.org/0000-0002-4909-3709>

Mladenka Novaković  <https://orcid.org/0000-0001-5036-6682>

Ivona Nuić  <https://orcid.org/0000-0002-8921-6224>

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