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Preliminary Investigation of Various Low-cost Organic and Inorganic Materials for Carbendazim Sorption – Advantages, Disadvantages and Significance of pH

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Abstract

Carbendazim, a widely used fungicide, is frequently detected in agricultural runoff and in surface and groundwater, raising environmental and public health concerns. The efficient removal of carbendazim from water sources remains a significant challenge, especially at different pH conditions. This study evaluates the sorption performance of several organic and inorganic materials for the removal of carbendazim ($\approx$ 1 mg l^{-1}) from aqueous solutions across a pH range of 3–6. A series of batch experiments was conducted using fruit-processing by-products (olive, cherry, and sour cherry pits) and various zeolite samples (natural zeolite clinoptilolite and its modified forms enriched with sodium, iron or sulphur). The results showed that only sodium-rich natural zeolite and sour cherry pits achieved notable removal efficiencies. Sodium-rich natural zeolite exhibited maximum performance of up to 99.0 % at $pH_o = 3.02$, while sour cherry pits achieved 58.4 % efficiency at $pH_o = 5.81$. The findings demonstrate that both sorbent type and solution pH are key factors affecting carbendazim removal. These findings provide a basis for the development of optimised, pH-sensitive sorption-based treatment strategies for pesticide-contaminated waters using environmentally friendly and readily available materials.

Keywords

Fungicide carbendazim, low-cost sorbents, fruit-processing by-products, natural zeolite, sustainable water treatment

1 Introduction

With water stress already affecting approximately 20 % of European territory, and is expected to increase, aquatic ecosystems remain under significant pressure due to persistent pollution from various human activities. According to recent reports from the Environmental Protection Agency and the European Environment Agency, agriculture represents the most significant pressure for water bodies identified as being at risk, primarily due to nitrate and pesticide contamination.[1,2] Modern agricultural practices rely heavily on pesticides to sustain intensive food production,[3,4] and their global use is expected to rise further due to population growth and increased food demand. In addition to agriculture, pesticides are also used in forestry and livestock farming, with herbicides, insecticides, rodenticides, and fungicides being the most common types. In this study, the synthetic fungicide carbendazim [methyl-1H-benzimidazol-2-ylcarbamate] was selected as a model organic pollutant due to its low cost and widespread global use for controlling fungal infections on agricultural crops. As an active substance in biocidal products, it is also applied to lawns, tennis courts, and golf courses, as well as in the textile, leather, and paper industries, and for protecting building facades from fungal growth.[5–8] A study by *Merel et al.*[7] detected carbendazim in all twenty-two effluent samples collected from wastewater treatment plants in Germany, indicating households as an additional source of this fungicide. Consequently, carbendazim is found in surface waters worldwide, with reported concentrations ranging from 0.01 to 6 µg l^{-1}, and reaching up to 180 µg l^{-1} in paddy field water.[7,9] Although carbendazim-containing products are no longer approved in the European Union and remain currently under the review programme, illegal procurement from neighbouring countries contributes to its continued use.[7,10] Pesticide residues pose a significant threat to the quality of aquatic environments and consequently to living organisms due to their carcinogenic, reproductive, and developmental toxicity, neurotoxicity, and endocrine-disrupting effects. Thus, the development of an effective and environmentally friendly water treatment protocol is crucial.[8,11] Numerous treatment methods are available for the removal of pesticides, such as biological processes, chemical methods (*e.g.*, advanced oxidation processes), and physical techniques (*e.g.*, membrane processes and adsorption), but no single method is fully effective for removing complex organic molecules such as pesticides. Among these methods, adsorption is the most widely used due to its simple design, feasibility, and high efficiency in removing organic pollutants, especially when using activated carbon and modified adsorbents. However, high costs are often a limiting factor for wider application.[12,13] To reduce costs, activated carbon derived from agricultural waste is also used for pesticide removal.[14] Although waste represents an economical source of this adsorbent, its production still requires high temperature in the pyrolysis process. Therefore, in order to find and develop more affordable and greener alternatives, the aim of this paper was a preliminary investigation of the

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effectiveness of readily available natural materials - zeolites (native and modified forms) widely recognised as effective sorbents, as well as local fruit-processing by-products in their native form (olive, cherry, and sour cherry pits) in removing the fungicide carbendazim from water. Evaluating these readily available by-products aligns with practical local needs and circular-economy principles. In this context, the advantages and disadvantages of using these materials are discussed, with the main goal of further development and optimisation of the successful removal of carbendazim from water, with special emphasis on the influence of pH, as a key parameter in the sorption process. Ultimately, this approach promotes sustainability not only by enabling greener water treatment but also by utilising locally available by-products from food processing at no cost, thereby contributing to several United Nations Sustainable Development Goals, particularly Goal 6 (Clean Water and Sanitation), Goal 11 (Life Below Water), and Goal 12 (Ensure Sustainable Consumption and Production Patterns).[15]

2 Experimental

2.1 Preparation of the carbendazim-contaminated water

A carbendazim stock solution ($\approx$ 200 mg l^{-1}) was prepared by dissolving 10 mg of carbendazim (PESTANAL™, Sigma-Aldrich) in 50 ml of methanol (LC-MS Grade Chromasolv, Honeywell). This stock was subsequently diluted with ultrapure water (Purelab Flex 3, Elga) to obtain an aqueous carbendazim solution of 0.992 mg l^{-1} used as the model wastewater.

2.2 Preparation of sorbent materials

Raw natural zeolite (NZ) obtained from the Zlatokop mine (Serbia) is a clinoptilolite-type zeolite (up to 80 %) with calcium as the main exchangeable cation.[16] Its sorption properties were enhanced by chemical modification using three approaches. Sodium-rich zeolite (Na-NZ) was obtained by chemical activation with NaCl solution.[17] Iron-rich zeolite (Fe-NZ) was prepared by mixing NZ successively with $Fe(NO)_3 \cdot 9H_2O$, NaOH, and $NaNO_3$ solutions.[18] The sulphur-rich zeolite (S-NZ) was obtained by mixing NZ with Na_2S at 150 °C.[19] Fruit-processing by-products, *i.e.*, olive pits (OP), cherry pits (CP), and sour cherry pits (SCP) were collected in nearby fruit-processing plants. All collected materials were washed with distilled water to remove impurities, dried at 40 °C to constant weight in an oven (Binder IP-20), ground in a mill (Retsch MM 200), and sieved (Retsch AS 200 basic). For the purposes of the experiment, a particle size fraction of 0.56–1.00 mm was chosen. It is worth noting that the pits were used without separating the hard outer shell from the inner kernel, simplifying their recycling.

2.3 FTIR analysis

The pit samples were prepared in KBr pellet and analysed using Fourier transform infrared (FTIR) spectrometer IRAffinity-1 (Shimadzu, Kyoto, Japan). Spectra were collected over the mid-infrared range of 4000–400 cm^{-1}, with 16 scans averaged at a resolution of 4 cm^{-1}.

2.4. Zeta potential analysis

Zeta potential measurements were performed in an aqueous carbendazim solution at $pH_o = 5.81$ using a Malvern Zetasizer Ultra device. Approximately 1 mg of each sample was suspended in 2 ml of solution. The resulting suspensions were mixed in an ultrasonic bath for 2 min and the zeta potential was measured in triplicate. The results for each sample are expressed as mean values.

2.5. Sorption experiments

To optimise the sorption process, the influence of pH_o of carbendazim-contaminated water was tested at $pH_o = 5.81$ (unaltered), $pH_o = 4.03$ and $pH_o = 3.02$ (adjusted with glacial acetic acid, 99.8–100.5 % AnalaR NORMAPUR). Batch sorption experiments were performed by mixing 0.50 g of each sorbent with 50 ml of carbendazim-contaminated water on an orbital shaker (ES-20/60) at a temperature of 25 ± 2 °C and 230 rpm for 24 h. These process conditions were selected based on prior research of tested materials with other pollutants to allow for an initial screening ahead of detailed parameter optimisation. For each sorbent, the experiment was performed in triplicate. After 24 h, the suspensions were fast filtered through folded qualitative paper, and pH (Mettler Toledo SevenEasy pH-meter), and residual carbendazim concentration were measured. The batch experiment allowed for a simple, fast, and reliable assessment of the effectiveness of the selected material for the target pollutant by calculating the removal efficiency (α, %) using the following equation:

$$\alpha = \frac{\left(c_o - c_r\right)}{c_o} \cdot 100 \tag{2}$$

where c_o and c_r are the initial and the residual concentration of carbendazim (mg l^{-1}), respectively.

2.6 Quantitative determination of carbendazim

Carbendazim concentrations were determined using ultra-high performance liquid chromatography coupled with mass spectrometer, UHPLC-MS/MS (UltiMate 3000RS – TSQ Quantis) equipped with AccucoreTM C18 (150 mm × 2.1 mm, 2.6 µm) column (Thermo Fisher Scientific, Waltham, Massachusetts, SAD). The mobile phase consisted of 0.05 % acetic acid in water and methanol in gradient mode, at a flow rate of 0.4 ml min^{-1}. Total run time was 15 min, and injection volume was 5 µl. The concentration range of the method was from 10 to 1000 µg l^{-1}.

2.7 Chemical oxygen demand analysis

To assess the water quality in terms of oxidisable compounds, both inorganic and organic (biodegradable +

non-biodegradable), the chemical oxygen demand (COD) test was performed before and after sorption (filtrates) at pH_o = 5.81. The standard procedure for COD involves boiling the sample with a strong oxidising agent (potassium dichromate) under reflux and subsequently titrating the residual oxidant with ferric ammonium sulphate.[20]

3 Results and discussion

3.1 Sorption results

The calculated removal efficiencies of the tested materials depending on pH_o of carbendazim-contaminated water are presented in Fig. 1. A distinctly different behaviour was observed between the organic and inorganic low-cost materials. For all zeolite samples, decreasing pH_o led to a significant increase in removal efficiency, whereas the fruit-processing by-products (pits) exhibited the opposite trend. Among the fruit-processing by-products, sour cherry pits (SCP) showed the highest removal efficiency, achieving 58.4 % at pH_o = 5.81. Olive pits (OP) and cherry pits (CP) showed similar behaviour with their highest efficiencies at pH_o = 4.03 (45.2 % for OP, and 51.8 % for CP). All zeolite samples showed significant increase in sorption properties at lower pH_o values, with the best results observed at the lowest pH_o = 3.02. Sodium-rich zeolite (Na-NZ) exhibited the highest removal efficiency of 99.0 %, followed by natural zeolite (NZ) and iron-rich zeolite (Fe-NZ), both reaching 95.1 %, while sulphur-rich zeolite (S-NZ) was the least effective (69.2 %).

Sorption performance is influenced by several parameters, such as the pH of the medium, surface charge of the material, pore size and volume, but also the charge of the pollutant. Therefore, to gain a closer insight and explain the observed results, additional parameters were considered, namely the equilibrium pH_e, zeta potential and functional groups of the materials, as well as the charge of the carbendazim molecule.

Some studies on pesticide removal using untreated, low-cost adsorbents are available in the literature. *Rojas et al.*[21] achieved a 74 % removal efficiency of several pesticides using rice husks as adsorbent, although their solid-to-liquid ratio was twice that applied in this study. *Huguenot et al.*[22] achieved 49 % and 50 % removal of the pesticide glyphosate using sugar beet pulp and corn cob, respectively, at pH = 4.8, values comparable to those obtained with OP, CP, and SCP (≈ 45–58 %). However, their experiments also used a higher solid-to-liquid ratio of 20 g l^{-1}. In contrast, corn-cob-derived char showed a higher removal efficiency of 74 %.[22] There are many studies on the use of biochar for pesticide removal, but because its production requires pyrolysis of bio-waste, its classification as a low-cost and environmentally friendly absorbent becomes questionable, both in terms of energy consumption, environmental pollution, and yield. Consequently, using materials in their native form still offers certain advantages, despite their lower efficiencies.

3.2 Equilibrium pH_e and zeta potential results

The zeta potentials of OP (−40.7 mV), CP (−35.1 mV), and SCP (−28.5 mV) measured in native carbendazim-contaminated water at pH_o = 5.81 indicate a negative surface. Carbendazim, at pH values below the first equilibrium constant (pK_{a1} = 4.20), exists predominantly in a protonated, cationic form; at pH values above the second equilibrium constant (pK_{a2} = 9.60), the deprotonated, anionic form dominates; and between these two constants (4.20 < pH < 9.60), the neutral form of the molecule is predominant.[23] Although SCPs exhibit a less negative surface charge, they nevertheless showed the best sorption properties, suggesting that, in addition to zeta potential, the pH of the aqueous medium plays a critical role. The pH influences the sorption because it affects the protonation-deprotonation of the carbendazim molecule. As shown in Fig. 2a, which represents the equilibrium pH_e values, at pH_o = 5.81 the lowest equilibrium pH_e value (pH_e = 5.63) was observed after binding carbendazim to SCPs, where carbendazim was present predominantly in its neutral form, favouring electrostatic attraction, which resulted in the highest removal efficiency among the pit samples. According to literature data, the concentration of protonated carbendazim decreases with increasing pH, as follows: at pH = 4.2, 50 % of carbendazim is in its protonated form (positively charged); at pH = 5.0, this drops to 14 %; and at pH = 6.0, only 2 % remains protonated.[6,23]

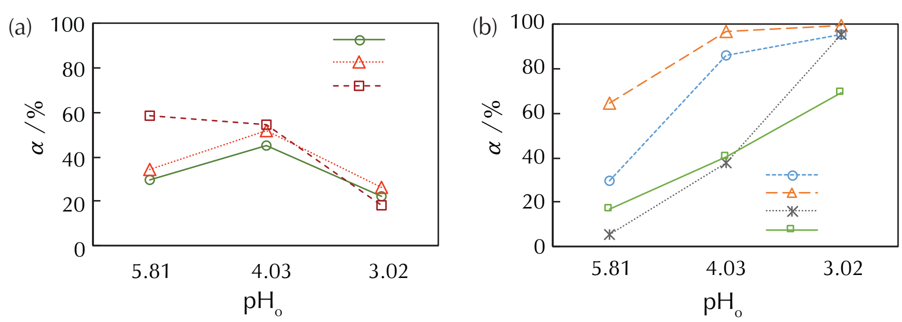

Fig. 1 – Carbendazim removal efficiencies using fruit-processing by-products (a), and zeolite samples (b) as a function of pH_o

Slika 1 – Učinkovitosti uklanjanja karbendazima na nusproizvodima prerade voća (a) i uzorcima zeolita (b) u ovisnosti o pH_o

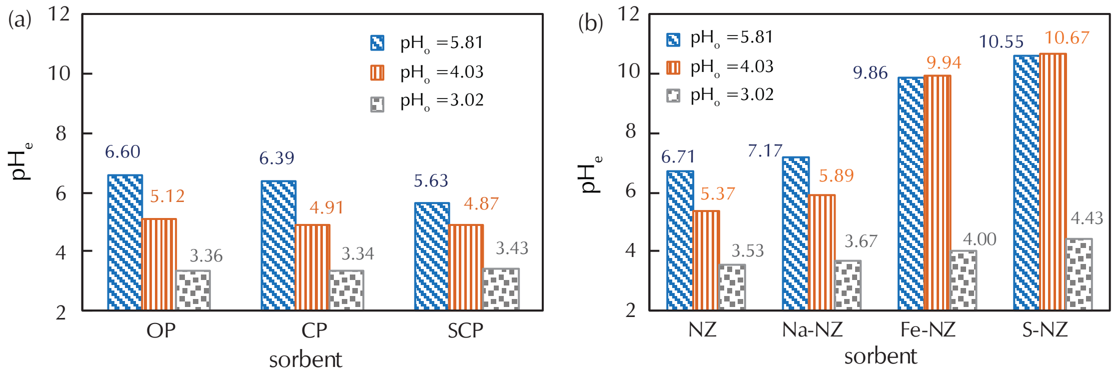

Fig. 2 – pH_e values after sorption of carbendazim on fruit-processing by-products (a), and zeolite samples (b)
Slika 2 – pH_e vrijednosti nakon sorpcije karbendazima na nusproizvodima prerade voća (a) i uzorcima zeolita (b)

Although lowering the initial pH_o also lowers the equilibrium pH_e, thereby making carbendazim more protonated, at $pH_o = 3.02$, the removal efficiencies of all pit materials significantly dropped, especially in the case of SCPs. In contrast, sorption onto zeolite samples was far more influenced by pH_o.

All zeolite samples carry a negative surface charge in aqueous solution, even under very acidic conditions. Their modification with inorganic salts generally leads to changes in physicochemical properties, such as an increase in specific surface area, porosity, negative surface charge, functional groups, etc.[24–28] The zeta potential of NZ at pH = 5.8 is −22.8 mV, while for Na-NZ, Fe-NZ and S-NZ it is −25.7 mV, −29.7 mV, and −39.9 mV, respectively.[19] Modification increases the negative charge through Fe oxo- and hydroxo-complexes in Fe-NZ, and sulphide and hydrosulphide complexes in S-NZ, and due to the presence of highly hydrated monovalent Na^+, which is less effective at neutralising the negative framework compared to multivalent cations (Ca^{2+} and Mg^{2+}).[19,24–26] This indicates that in an acidic medium, S-NZ should be the most effective in binding carbendazim, which was not the case according to the results in Fig. 1b. Although zeolites possess a negative charge across the entire pH range, decreasing pH_o makes the charge less negative due to protonation of the functional groups, leading to an increase in pH_e. In an aqueous medium, the zeolite structure tends towards electroneutrality, which results in the neutralisation of the surrounding medium. In the case of carbendazim binding to zeolites, at all pH_o an increase in pH_e was observed in the order S-NZ > Fe-NZ > Na-NZ > NZ (Fig. 2b). This sequence is consistent with the measured zeta potentials, *i.e.*, the zeolite with the most negative zeta potential exhibited the highest increase in pH_e. On the other hand, the smallest increase in pH_e was observed at $pH_o = 3.02$, where the zeolite is less negatively charged than at $pH_o = 5.81$. This indicates competition between carbendazim and H^+ ions for the available negative active sites at all pH_o. Namely, H^+ ions, are smaller compared to the carbendazim molecule and therefore more mobile. In addition, although the carbendazim becomes protonated in acidic media, its concentration is lower compared to the concentration of H^+, which further contributed to the prevalent binding of H^+ ions. At pH_o of 4.03 and 5.81, pH_e increased significantly for Fe-NZ (> 9.86) and S-NZ (> 9.94), conditions under which carbendazim is present in its neutral as well as deprotonated anionic forms. This prevented its binding to the negative surface of the zeolite. Consequently, the highest removal efficiencies for all zeolites were achieved at the lowest $pH_o = 3.02$, where pH_e remained within the range in which carbendazim in cationic form, enabling electrostatic attraction to the negatively charged zeolite surface. Across all pH_o values, Na-NZ proved to be the best sorbent among zeolites, likely due not only to its more negative charge compared to NZ and greater number of functional groups, but also to the pH_e of the surrounding medium, which did not significantly increase as with Fe-NZ and S-NZ.

3.3 FTIR results

FTIR spectra of OP, CP and SCP (Fig. 3) provided insight into surface functional groups responsible for interactions with carbendazim. All tested pits showed similar FTIR spectra with characteristic peaks: broad O−H stretch (3500–3200 cm^{-1}), aliphatic C−H stretch (≈ 2950 cm^{-1}

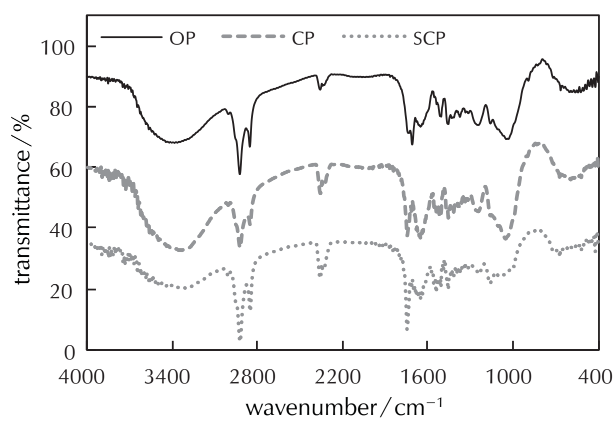

Fig. 3 – FTIR spectra of fruit-processing by-products
Slika 3 – FTIR spektri nusproizvoda prerade voća

and ≈ 2850 cm^{-1}), atmospheric CO_2 vibrations (2330–2360 cm^{-1}), carbonyl C=O stretch (≈ 1745 cm^{-1}), lignin aldehyde groups (≈ 1610 cm^{-1}), methyl, methylene C−H deformations (≈ 1500 cm^{-1}), aromatic skeletal vibration (≈ 1440 cm^{-1}) and C−O and C−O−C stretch (1250–1030 cm^{-1}).[29–31] Despite their similar reported composition: lignin, cellulose, and hemicellulose, proteins and polyphenols, as well as traces of lipids, functional group differences were observed. SCP shows the most intense O−H, C=O and aromatic C=C groups, indicating a higher content of hydrophilic and polar functional groups such as carboxylic and hydroxyl groups.[32–35]

FTIR analysis of zeolite samples has been previously published and explained in detail.[18,19] The results showed similar FTIR spectra of natural and modified zeolites, with characteristic bands corresponding to aluminosilicate minerals, indicating that the zeolite structure was preserved after modification. Significant increase in the intensity of absorption bands associated with hydroxyl groups was observed for Fe-NZ, and especially for S-NZ. This was attributed to partial desilication, formation of Fe(oxy)hydroxide and sulphide active groups, increase in negative charge and higher content of hydrated sodium ions. FTIR analysis was also performed after sorption; however, no visible changes were observed, most likely due to the very low initial concentration of carbendazim.

3.4 Mechanism of sorbent-carbendazim interactions

Changing the pH_o of the solution also changes the surface charge of the sorbents, as well as the speciation of carbendazim, which consequently affects sorption. As already mentioned, at pH < 4.20 the carbendazim dominant form is cationic[23], while according to *Paszko et al.*[6], at pH = 6, almost 98 % of carbendazim is in uncharged, neutral form. At pH values greater than 9.6, carbendazim exists in an anionic form.[36] Carbendazim contains a benzimidazole ring with nitrogen atoms that can undergo protonation and possibly interact with functional groups on the pits surface through hydrogen bonding (H-bonding), π–π interactions, and electrostatic attraction or repulsion. However, a single mechanism can dominate depending on surrounding conditions. At the highly acidic pH_o = 3.02, all pits performed poorly because both the material surface and carbendazim were protonated, which suppressed electrostatic interactions and H-bonding, leaving only weak π–π interactions. At less acidic pH_o of 4.03, the pit surfaces were partially protonated and, although carbendazim remained mostly in its cationic form, many hydroxyl and carboxyl groups were still active for H-bonding. At near neutral pH (pH_o = 5.81), the pit surfaces were less protonated, i.e., the carboxylic groups were deprotonated (−COO^-), enabling stronger electrostatic interactions and H-bonding capacity with predominantly neutral carbendazim, with π–π stacking contributing to the overall removal efficiency. Therefore, due to its higher content of hydroxyl, carboxyl, and aromatic groups and their greater capacity for H-bonding, electrostatic attractions and π–π stacking, the SCP overall exhibited superior sorption properties compared to OP and CP, especially at pH_o = 5.81. Very similar findings were reported by *Nagdhi et al*[37], who found that at low pH, the establishment of H-bonds between the pine-wood-derived nanobiochar and pharmaceutical carbamazepine was prevented due to the interaction of their functional groups with high concentration of H^+ in the solution, which ultimately reduced the removal efficiency. In contrast, with reduced H^+ concentration in the solution, the amide functional group of carbamazepine more easily associated via H-bonds with the oxygen-containing functional groups of the adsorbent, leading to enhanced adsorption efficiency.[37] The main mechanisms of carbamazepine removal were H-bonds and π-π interactions, since it contains aromatic rings and is non-ionisable, *i.e.,* it is neutral in the entire pH range.[37] *Wang et al.*[38] performed removal of carbendazim by activated carbon obtained from rape straw. At low pH_o, electrostatic interactions were more dominant in the adsorption process, while with increased pH_o, hydrophobic interactions became more significant. Thus, at pH < 3.00, the electrostatic repulsion between prevalently positively charged carbendazim and positive surface of activated carbon was dominant due to the high concentration of H^+, resulting in decreased removal efficiency. Certain capacity was obtained probably through the π–π bond between the aromatic ring of activated carbon and carbendazim. By increasing the pH above 4.53, the main sorption mechanism of mostly neutral carbendazim occurred through hydrophobic/π–π interactions and pore-filling.[38] Studies of the adsorption of carbendazim on soil constituents also showed similar observations related to pH conditions.[6,39,40] In the acidic to neutral pH range of 3–5.5, carbendazim is found in predominantly cationic form, leading to increased adsorption on clay minerals. At pH > 5.5, its neutral form becomes prevalent, increasing its adsorption through non-ionic interactions onto clays and organic matter.[6] Scientific literature on the pH-dependent adsorption of carbendazim was mainly carried out on modified materials or biochar, while studies on use of untreated bio-based materials remain scarce, making current research even more important and desirable. The sorption efficiency among zeolite samples was as follows: Na-NZ > NZ > Fe-NZ > S-NZ. As stated previously, at highly acidic pH, where the zeolite surface is protonated, the sorption is mainly governed by π–π stacking and van der Waals forces. This is in contrast with the less acidic pH, where less protonated −OH groups at the zeolites surface slightly enabled interaction with carbendazim (partially neutral, partially protonated) through H-bonds and electrostatic attraction. At near-neutral pH, the best interactions *via* H-bonds are possible among predominantly neutral carbendazim and fully available surface −OH groups. However, at investigated experimental conditions, it was found that these interactions were predominantly a consequence of pH changes during sorption, rather than the initial pH_o, which was explained earlier. Similar findings were obtained by *Andrunik et al.*[13] who reported a very complex sorption mechanism, with physisorption as dominant due to the electrostatic interactions. Also, less effective removal of carbendazim was observed on surfactant-modified zeolite-carbon composites compared to the unmodified ones.

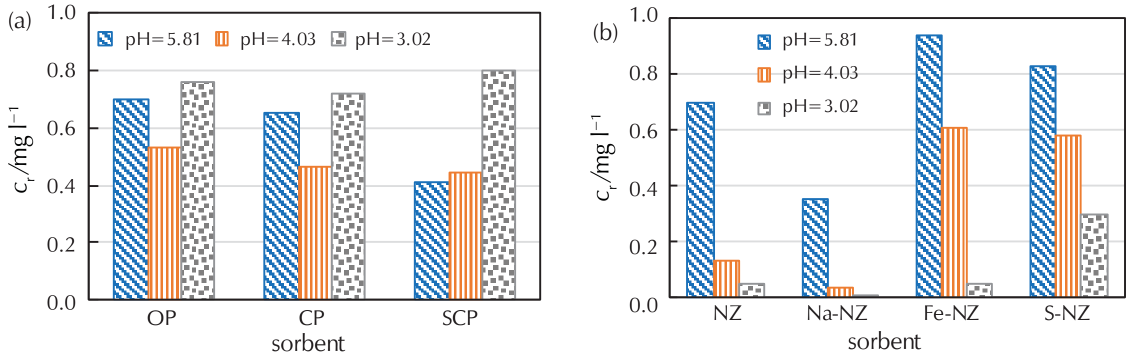

Fig. 4 – Residual concentration of carbendazim after sorption on fruit-processing by-products (a), and zeolite samples (b)

Slika 4 – Ostatna koncentracija karbendazima nakon sorpcije na nusproizvodima prerade voća (a) i uzorcima zeolita (b)

3.5 The residual carbendazim concentration

In addition to evaluating the effectiveness of the tested materials, it is essential to consider the residual concentration of carbendazim (Fig. 4) in the aqueous phase, since very often high effectiveness does not necessarily lead to complete pollutant removal, requiring additional treatment steps.

The lowest residual carbendazim concentration among the fruit-processing by-products (Fig. 4a) was obtained using SCP (413 µg l^{-1}), which is far above the limit values in water for human consumption of 0.1 µg l^{-1} for individual pesticides and 0.5 µg l^{-1} for total pesticides, as well as for wastewater emission (3–40 µg l^{-1}).[41,42] Nevertheless, this material was still able to significantly reduce the quite high carbendazim concentration of 992 µg l^{-1}, highlighting its potential to address the widespread presence of this contaminant, especially considering its environmental friendliness and low cost. Regarding zeolites (Fig. 4b), the lowest residual concentration was obtained with Na-NZ, being below the quantification limit of 10 µg l^{-1}. This is an exceptional result, which again highlights Na-NZ as the best among all tested materials.

3.6 Chemical oxygen demand results

Assessment of the chemical oxygen demand (COD) in the filtrates after sorption on the fruit-processing by-products provided insight into the potential release of organic matter, which is important for determining the effluent disposal requirements or the need for COD reduction. Only the difference (ΔCOD) between the COD value in the filtrate after sorption and the initial COD_o is considered, since the high initial COD_o of 3654.7 mg O_2 l^{-1} can be attributed not only to carbendazim, but to the methanol used in preparing the carbendazim-contaminated water. Similar observations are reported in the study by *Wehbe et al.*[43] Fig. 5 shows an increase in the COD value for CP, and especially OP, while SCP was less prone to leaching. It is likely that, in the case of SCP, which at pH_o = 5.81 showed the highest removal efficiency among the tested fruit-processing by-products, sorption overcame leaching.

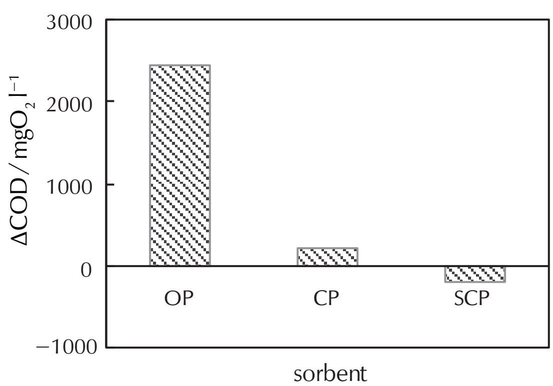

Fig. 5 – Change in COD after sorption on fruit-processing by-products compared to initial COD_o

Slika 5 – Promjena KPK nakon sorpcije na nusproizvodima prerade voća u odnosu na početnu KPK_o

An increase in COD was also reported by *Ramírez-Godínez et al.*,[44] where organic matter leached from barley grains, peanut shells, and woodchips resulted in values exceeding 10000 mg O_2 l^{-1}. Such findings are important for future research, but may also be a limiting factor in the use of certain fruit-processing by-products: instead of removing pollutants, such materials become secondary sources of pollution. To address this challenge, a combined approach to water treatment is required to manage both the target pollutant and the associated COD. In addition, the literature suggests that surface modification of raw biomaterials could reduce the release of organic matter.[45,46] A further constraint is the seasonal availability of fruit-processing by-products, which limits supply on a yearly basis. Nevertheless, any utilisation of agricultural and food-processing residues is desirable to support circular economy principles and more sustainable solid waste management.

4 Conclusion

This study evaluated fruit-processing by-products and zeolite samples for their efficiency in removing pesticide carbendazim from aqueous solution. Sour cherry pits among the organic materials, and the sodium-rich form of natural zeolite among the inorganic materials demonstrated highest removal efficiency of 58.4 and 99.0 %, respectively, with performance strongly influenced by the pH_o of the solution. Moreover, sorption onto sodium-rich natural zeolite resulted in residual carbendazim concentration below the quantification limit (10 μg l^{-1}). These two materials offer additional advantages over the others. Among the modified zeolites, the sodium-rich natural zeolite was produced using an economical and environmentally friendly method, while among the pits, only sour cherry pits did not increase the organic load of the effluent under the tested conditions. This is an essential consideration in terms of preventing secondary pollution, especially in large-scale applications. These findings highlight the importance of selecting appropriate sorbents and optimising operating conditions when designing treatment technologies for pesticide-contaminated water. While the results are promising, the study was limited to batch experiments under controlled laboratory conditions.

Future research should focus on the long-term performance of these two most effective sorbents in real wastewater systems, as well as explore potential regeneration and reuse strategies, with particular attention to preventing secondary pollution.

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List of abbreviations and symbols
Popis kratica i simbola

NZ – natural zeolite
– prirodni zeolit

Na-NZ – sodium-rich natural zeolite
– natrijem obogaćen prirodni zeolit

Fe-NZ – iron-rich natural zeolite
– željezom obogaćen prirodni zeolit

S-NZ – sulphur-rich natural zeolite
– sumporom obogaćen prirodni zeolit

OP – olive pits
– koštice maslina

CP – cherry pits
– koštice trešanja

SCP – sour cherry pits
– koštice višanja

COD – chemical oxygen demand
– kemijska potrošnja kisika

α – removal efficiency
– učinkovitost uklanjanja

c_o – initial concentration of carbendazim
– početna koncentracija karbendazima

c_r – residual concentration of carbendazim
– ostatna koncentracija karbendazima

pH_o – initial pH value
– početna pH vrijednost

pH_e – pH value after sorption
– pH vrijednost nakon sorpcije

pK_{a1} – first equilibrium constant
– prva konstanta ravnoteže

pK_{a2} – second equilibrium constant
– druga konstanta ravnoteže

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SAŽETAK

Preliminarno ispitivanje različitih *low-cost* organskih i anorganskih materijala za sorpciju karbendazima – prednosti, nedostaci i značaj pH vrijednosti

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Karbendazim, široko upotrebljavan fungicid, često se detektira u površinskim i podzemnim vodama diljem svijeta, uzrokujući zabrinutost za okoliš i zdravlje ljudi. Učinkovito uklanjanje karbendazima iz vode predstavlja velik izazov, posebice pri različitim pH uvjetima. Ovo istraživanje procjenjuje sorpcijsku sposobnost nekoliko organskih i anorganskih materijala za uklanjanje karbendazima iz vodene otopine (≈ 1 mg l^{-1}) pri različitim pH vrijednostima u području od 3 do 6. Šaržni eksperimenti provedeni su na nusproizvodima prerade voća (košticama maslina, trešanja i višanja) i različitim uzorcima zeolita (prirodnim zeolitom klinoptilolit te njegovim modificiranim oblicima – obogaćenim natrijem, željezom i sumporom). Rezultati su pokazali zadovoljavajuće učinke uklanjanja jedino na natrijem obogaćenom prirodnom zeolitu te na košticama višanja. Natrijem obogaćen prirodni zeolit postigao je maksimalnu učinkovitost uklanjanja od čak 99,0 % pri $pH_o = 3{,}02$, dok su koštice višanja bile 58,4 % učinkovite pri $pH_o = 5{,}81$. Ovim istraživanjem utvrđeno je da su i vrsta sorbenta i pH uvjeti ključni faktori koji utječu na uklanjanje karbendazima, a dobiveni rezultati mogu poslužiti kao temelj za razvoj i optimizaciju metoda obrade voda onečišćenih pesticidima uporabom ekološki prihvatljivih i lako dostupnih materijala.

Ključne riječi
Fungicid karbendazim, low-cost sorbensi, nusproizvodi prerade voća, prirodni zeolit, održiva obrada voda

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