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## Cost-effective method of simultaneous removal of copper and phosphate on environmentally friendly nanomaterial

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**Abstract:** Environmentally friendly and economically viable methods are essential in the selection of materials and techniques for the synthesis of nano-zero-valent iron. Plants, with their high polyphenol content and antioxidant capacity, have found application in eco-friendly synthesis processes. The definitive screening design (DSD) monitored four key process parameters for the concurrent removal of copper and phosphate: copper concentration (ranging from 1 to 9 mg L<sup>-1</sup>), phosphate concentration (ranging from 1 to 9 mg L<sup>-1</sup>), initial pH values (ranging from 2 to 10), and the dosage of nano-zero-valent iron (ranging from 2 to 16 mL). The analysis results provide valuable insights into the significant individual factors influencing the process, along with the potential for their interactions. The model also proposes process optimization to attain maximum removal efficiency, and subsequent verification confirmed its superiority among the alternatives. Mechanisms such as sorption, reduction, complexation, electrostatic attraction, and ligand exchange play pivotal roles in the effective removal of copper and phosphate using nano-zero-valent iron. In summary, this research yields several benefits: the utilization of environmentally sustainable materials, a substantial reduction in experimental complexity, coupled with the ease of the entire procedure, simultaneous and highly efficient copper and phosphate removal, favorable pH levels and, notably, no requirement for additional treatment.

**Keywords:** eco-friendly green synthesized nano zero-valent iron; metal ions; definitive screening design.

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## INTRODUCTION

A decade behind us, nanoscale iron particles (nZVI) are being tested for water treatment, primarily potentially toxic metals, but also other pollutants of interest, because the most important thing is to choose remediation technology that will ensure the desired water quality at acceptable process costs. Compared to materials in macro dimensions, nanomaterials are characterized by multiplied specific surface area as a function of mass, and the advantage is manifested by achieving the same goals, which theoretically leads to savings in the amount of material used, reduced energy consumption, and thus reduced remediation costs.<sup>1,2</sup>

One of the aspects of the nano revolution is the use of synthesized nanomaterials with “green” solvents in the process of remediation of contaminated water. The synthesis of nanomaterials performed in this way is considered cheaper, environmentally friendly because it uses extracts of natural products such as plants that are less toxic and biodegradable.<sup>1</sup> Another important fact when using plants, primarily leaves, that the content of polyphenols and antioxidant capacity are very significant factors for the production of nZVI. The nZVI particle is composed of a Fe<sup>0</sup> nucleus and a shell layer, *i.e.*, different forms of Fe oxide. The core has the potential for reduction, while the surface has reaction site properties and affinity for chemisorption and electrostatic interactions, and based on that it is concluded that mechanisms of removal of potentially toxic metals can be reduction, absorption, precipitation, and mineralization.<sup>3</sup>

Copper ion, when present in trace amounts, is considered an essential micro-nutrient due to its direct involvement in hemoglobin formation, collagen constitution, and hair keratin. However, elevated concentrations of this metal resulting from anthropogenic sources can lead to increased levels of copper, thereby causing undesired effects.<sup>4</sup> Cu<sup>2+</sup> is widely used in the household, as well as in industries, technological aids, agriculture and many other spheres of life. Good conductive properties, lower prices compared to silver and gold, and possible recycling and reuse are some of the advantages of using copper.<sup>5</sup> The reason for choosing copper as a metal of interest for the purposes of this study is the detection of increased concentrations of copper in watercourses and seas, as a consequence of its prevalence and wide application.

Phosphorus is considered a autotrophic element in water resources, which leads to the deterioration of water quality and reduction of biodiversity. Excessive non-selective use of fertilizers, industrial waste, municipal waste in landfills are just some of the ways to get phosphorus into the environment. In order to resist this problem, it is necessary to apply some of the available methods for phosphorus removal, which include biological methods, adsorption and precipitation.<sup>6,7</sup> Since nZVI has already been mentioned as a suitable adsorbent for the removal of various pollutants, adsorption is imposed as suitable for the removal of phosphates and is considered a very efficient, easy to perform and cheap

method. Nanoparticles of zero-valent iron (nZVI) were applied using sodium borohydride in the treatment of wastewater with an elevated content of copper ions, and the removal efficiency was 96 %.<sup>8</sup> The removal of phosphates using zero-valent iron nanoparticles (nZVI) has been investigated in several studies. Most of them have focused on the adsorption of phosphates on the surface of nZVI.<sup>9</sup>

Given that optimizing a process involves conducting a considerable number of experiments, the utilization of definitive screening design (DSD) was deemed beneficial for design of experiments (DoE), developing mathematical models, and statistically interpreting the obtained results. The DSD statistical method operates on the principle of employing a numerical algorithm to maximize the matrix determinant of the main effect model. This analysis helps identify significant factors, predict their two-factor interactions and estimate the coefficients of the equation model describing the total experiments conducted. In contrast to traditional statistical methodologies like Response surface methods with Box-Behnken or central composite design, this approach enables a substantially reduced number of experiments while maintaining maximum precision.<sup>10</sup> Therefore, DSD might be used as powerful experimental design technique applied in the adsorption process to efficiently investigate and optimize various factors influencing adsorption efficiency. In this context, DSD allows researchers to systematically vary multiple factors, such as adsorbent dosage, contact time, pH, temperature or initial concentration of adsorbate, in a structured and resource-efficient manner. By conducting a series of experiments based on the DSD, researchers can identify key factors and their interactions that significantly impact the adsorption process. This approach aids in the development of robust and cost-effective adsorption systems by minimizing the number of experimental runs required while maximizing the amount of information obtained.<sup>11</sup>

The focus of this paper is to examine the influence of various factors on the removal of copper in the presence of phosphate, i.e. phosphate in the presence of copper from the synthetic wastewater matrix. Parameters of interest for this study were: copper concentration, phosphate concentration, dose nZVI and pH value. Their individual influences were monitored, as well as two-factor interactions. The process has been optimized, and a possible mechanism for removing pollutants of interest has been proposed.

## EXPERIMENTAL

### *Preparation of "green" zero-valent iron nanoparticles*

Oak leaves were used for the preparation of the extract for further synthesis of nanomaterials due to their antioxidant capacity as an important factor in the production of nZVI. Also, the advantage of using oak leaves is its distribution in Vojvodina. Drying at 50 °C for 48 h as well as grinding the material to a size of <2 mm are indispensable steps in preparing the leaves for extraction. The guide for the preparation of the extract was the study<sup>12</sup> according to which 3.7 g of prepared leaves were weighed in 100 ml of water. During 20 min, it is neces-

sary to heat the extract with 80 °C with continuous stirring, after which it is cooled and filtered. A 3:1 ratio was chosen for the ratio in which the leaf extract and 0.1 M Fe(III) are mixed.

#### *Definitive screening design (DSD)*

Definitive screening design (DSD) is still a young statistical method for constructing experiments based on a numerical algorithm.<sup>13</sup> For the purposes of this study, four operational parameters were monitored: copper concentration from 1 to 9 mg L<sup>-1</sup>, concentration phosphate from 1 to 9 mg L<sup>-1</sup>, nanomaterial dose from 2 to 16 mL, and pH value from 2 to 10. The concept of the analysis is based on determining significant process parameters and predicting their two-factor interactions. The advantage of using this concept is the reduced number of experiments because based on operational factors we get 13 experiments performed in duplicate and plus two central points, we come to the number of 28 experiments (Supplementary material to this paper, Table S-I).

#### *Experimental procedure*

Based on known parameter values, the experiment followed the following procedure. First, a base solution with a concentration of 100 mg L<sup>-1</sup> was prepared by dissolving the appropriate amounts of CuSO<sub>4</sub>·5H<sub>2</sub>O and KH<sub>2</sub>PO<sub>4</sub>. In order to meet the initial copper and phosphate concentrations, required by the model (1, 5 and 9 mg L<sup>-1</sup>), the base solution was subjected to dilution with deionized water to achieve the desired concentration. The efficiency of removing selected pollutants was monitored by adding nZVI in doses of 2, 9 and 16 mL. The final volume of the reaction mixture was 0.1 L. pH adjustments were made by adding 0.1 M HNO<sub>3</sub> or NaOH (2, 6, 10). After adjusting the pH values, the samples were placed on a horizontal shaker (IKA-Werke KS501 digital) at 180 rpm for 60 min, at a constant temperature of 23±1 °C. After mixing, it was necessary to centrifuge the samples at 4000 rpm for 12 min. To determine the residual concentrations of metal ions or anions, samples had to undergo the proper preparation procedure for future analysis. The samples were filtered through a 0.22 µm filter, after which the residual concentrations of metal ions were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS). Residual phosphate content was determined using the SRPS EN ISO 6878: 2008 methods.

#### *Characterization*

Application of a TEM model apparatus (TEM-EDX; JEOL-JEM 2100, Jeol, Italy) produced a more concrete picture of the morphological features of the examined nanomaterial. Sample, received as suspension were diluted 1:100 in Milli-Q water. Three µL of each suspension were manually drop on 200 mesh Cu-formvar carbon coated grids (Ted Pella, Inc.). Grids were left to dry in desiccator overnight and analysed in TEM mode to assess morphology and primary size distribution.

## RESULTS AND DISCUSSION

#### *Characterization oak-nZVI*

Fig. 1 shows TEM analysis to understand the shape and dispersity of the synthesized nZVI particles. The particles take a spherical shape together with irregular shapes and tend to form chain-like aggregates. The surface of the layer is covered with a transparent layer, which serves as a sealing and stabilizing agent and plays a key role in improving its dispersion and stability as the basic

ingredient of green nZVI. The structural information obtained by TEM analysis is in accordance with the observations of other authors.<sup>3</sup>

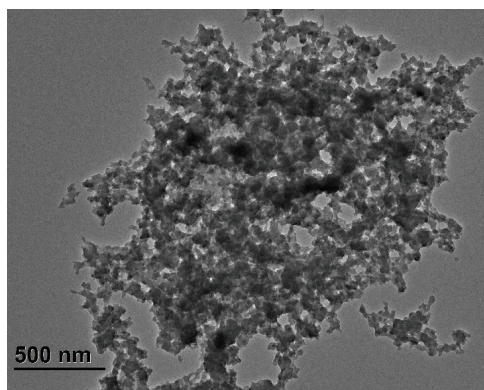


Fig. 1. Characteristics of oak-nZVI, TEM image.

#### *Statistical analysis for the removal of copper and phosphate*

*DSD model evaluation – copper/phosphate.* In order to remove copper in the presence of phosphate, the removal efficiency was monitored at different process parameters: nanomaterial dose, copper concentration, phosphate concentration and pH value, using statistical analysis of DSD. The efficiency results are shown in Table S-II of the Supplementary material, and the established efficiency range is from 2.25 to 98.98 %, while the percentage of phosphate removal in the presence of copper ranges from 54.70 to 91.50 %.

Descriptive factors for the selected statistical models that best approximate the experimental data are shown in Table I. A lower value of the correlation factor (0.859 and 0.750) was found, but the results in Table S-III of the Supplementary material confirm the validity of the selected model based on the results of the ANOVA test ( $F < 0.0001$ ) and the “lack of fit” test ( $F > 0.05$ ). Approximate values of *AIC* and *BIC* parameters imply a good approximation of experimental data.

TABLE I. Standard selection criteria for the regression models (copper and phosphate)

Descriptive factor	Copper	Phosphate
$R^2$	0.859	0.750
$R^2$ adj	0.809	0.703
<i>AIC</i>	234.407	220.997
<i>BIC</i>	236.396	223.374
<i>RMSE</i>	11.417	6.121

Based on the approximated parameter values and standard error, the factors with statistical significance shown in Table II (bold values) were singled out,

which in turn contributed to the efficiency of copper removal in the presence of phosphate and phosphate removal efficiency in the presence of copper.

TABLE II. Estimated regression coefficients sorted by statistical significance

Parameter	Estimate	Std Error	<i>t</i> ratio	Prob >   <i>t</i>
Copper				
nZVI (mL) * copper (mg L <sup>-1</sup> )	17.924	2.948	6.080	<0.0001*
Copper (mg L <sup>-1</sup> )	16.879	2.553	6.610	<0.0001*
Phosphate (mg L <sup>-1</sup> )	-11.447	2.553	-4.480	0.0002*
nZVI (mL)	-10.401	2.553	-4.0700	0.0006*
Copper (mg L <sup>-1</sup> ) * pH	7.322	2.948	2.48	0.0220*
pH	-0.523	2.553	-0.200	0.8398
Phosphate				
Copper (mg L <sup>-1</sup> ) * Phosphate (mg L <sup>-1</sup> )	-6.032	1.829	-3.300	0.0038*
Phosphate (mg L <sup>-1</sup> ) * pH	4.124	1.716	2.400	0.0266*
pH	-2.918	1.369	-2.130	0.0463*
nZVI (mL) * Phosphate (mg L <sup>-1</sup> )	3.293	1.716	1.920	0.0701
nZVI (mL) * pH	-3.498	1.829	-1.910	0.0710
Copper(mg L <sup>-1</sup> )	2.485	1.369	1.820	0.0852
nZVI (mL)	0.924	1.369	0.680	0.5077
Phosphate (mg L <sup>-1</sup> )	0.162	1.369	0.120	0.9073

Copper and phosphate concentration, as well as nZVI dose exhibit statistical significance for copper removal, which also reflects in the magnitude of their estimates. A positive sign before the linear term of copper concentration (16.879) suggests that the increase of this parameter contributes to the copper removal efficiency up to a certain point, after which further increase has an adverse effect on the removal process.<sup>14</sup> This is corroborated by the optimization plot (Figure 3) which shows that, within the adopted regression model, the optimal removal efficiency lies between the center and high level, equaling approximately 7.4 mg L<sup>-1</sup> of copper concentration. In contrast, the negative regression estimation coefficient is interpreted in such a way that the two variables tested have opposite associations. Referring to the case study, the negative estimated phosphate (-11.447) and nZVI (-10.401) coefficient affects the copper removal efficiency in a negative direction. Interpretation can be that if the phosphate concentration and nZVI dose are increased, it will affect the copper removal efficiency to decrease and *vice versa*. The value of significance 0.0002 and 0.0006 for phosphate concentration and nZVI dose, respectively indicates that the *p*-value <0.05, so it can be concluded that the both parameters have a significant effect on copper removal efficiency with a negative sign.

Copper concentration and dose of nZVI have an individual influence and mutual interaction, while the other is a two-factor interaction between copper concentration and pH value. In the following text, two-factor interactions will be

presented using 3D diagrams and more will be said about them. Phosphate concentration has only a single effect.

On the efficiency of phosphate removal, pH has a single effect and a two-factor interaction with the phosphate concentration. In addition to pH, the phosphate concentration builds another significant interaction, and that is the copper concentration.

By increasing the concentration of copper, at a constantly high dose of nano-materials, the efficiency of copper removal increases, because by increasing the dose of adsorbent, new active centers appear on the surface of the adsorbent (Fig. 2a).

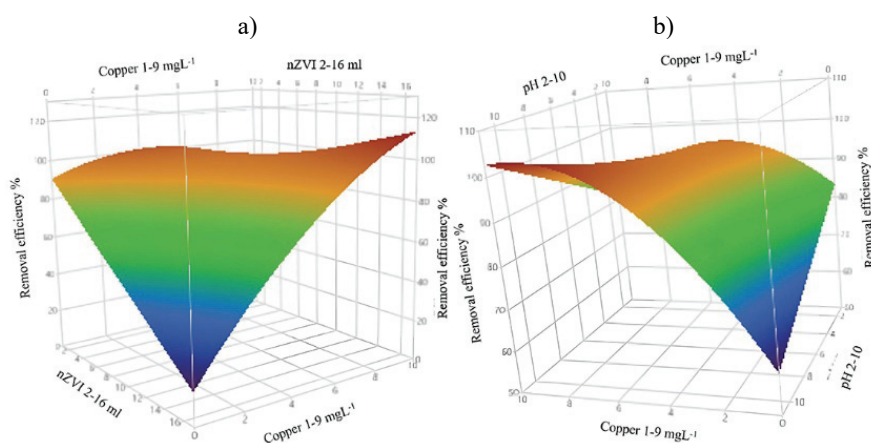


Fig. 2. Statistically significant two-factor interactions in the copper removal process: a) nZVI and copper; b) copper and pH.

The interaction of copper concentration and pH value (Fig. 2b) can be explained in 2 different ways, *i.e.*, two mechanisms of copper removal differ. To explain the mechanisms, it is first necessary to know the forms in which copper can be found in water depending on the pH conditions.  $\text{pH} < 6$ ,  $\text{Cu}^{2+}$ , between 6 and 8.5  $\text{Cu}_2\text{Cl}(\text{OH})_3$ , 8.5 and 12  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ , 12 and 13  $\text{HCuO}_2^-$  and  $>13$   $\text{CuO}_2^{2-}$ .<sup>15</sup> By fixing the pH value at a low level of  $\approx 2$ , the copper form is  $\text{Cu}^{2+}$  and the removal takes place via a redox mechanism up to  $\text{Cu}^0$ , and the remaining  $\text{Cu}^{2+}$  is adsorbed on the nZVI surface and complexed with available  $\text{FeOOH}$ . The second mechanism is related to the pH value of  $\approx 8$ . Above pH 6, the present forms of copper are poorly soluble hydroxides, which leads to the conclusion that the main mechanism of copper removal under such conditions is precipitation.

The interaction of copper concentration and phosphate concentration is shown in Fig. 3a. By keeping the copper concentration at a low level, and by increasing the phosphate concentration, the efficiency of phosphate removal increases. The same observation is in the opposite case. The reason for this is that

copper on the surface of the nanomaterial can solidify as zero valence copper, which accelerates the corrosion of iron and releases Fe(III) into solution and as a result, improves phosphate removal.<sup>8</sup>

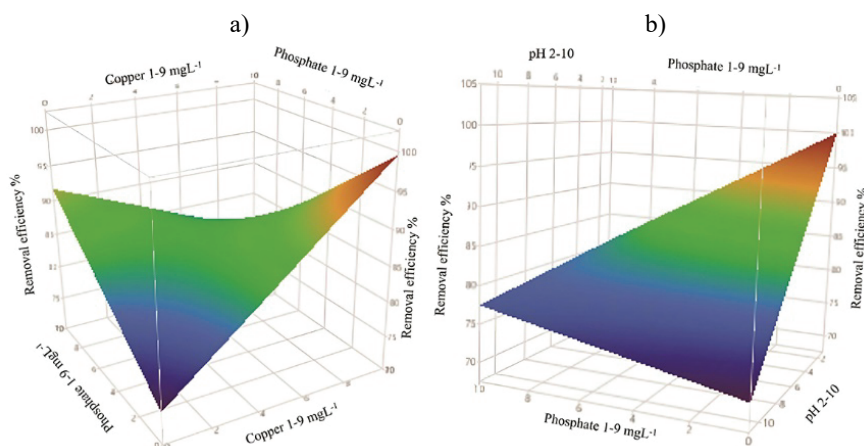
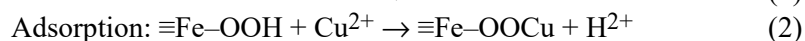
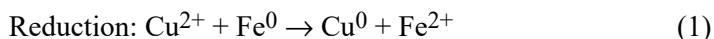


Fig. 3. Statistically significant two-factor interactions in the phosphate removal process: a) copper and phosphates; b) phosphates and pH.

The second diagram (Fig. 3b) shows a large dependence of phosphate removal efficiency on pH values. Acidic conditions are more suitable for phosphate removal because in that case the surface of the nanomaterial is positively charged and electrostatic attraction occurs with the phosphate ion. By changing the pH of the medium from acidic to basic, there is a decrease in the removal efficiency for two reasons. The first is because there is competition between  $\text{OH}^-$  and phosphates for adsorption sites on the adsorbent surface, and the second is that the adsorbent surface is more negatively charged and as such has a lower affinity for attracting phosphate species.

*Process optimization of copper and phosphate adsorption.* In order to achieve the most efficient results, the optimization of the entire process is carried out. To achieve the maximum efficiency of 97.71 %, it is necessary to apply the following conditions: dose of 5.64 mL, copper concentration  $7.4 \text{ mg L}^{-1}$ , phosphate concentration  $3.16 \text{ mg L}^{-1}$  and pH value of 6 (Fig. 4). Based on knowledge of the pH of the medium and form of copper, ( $\text{pH} \geq 6$ ,  $\text{Cu}^{2+}$ ), it is clear that the mechanisms of copper removal are reduction to  $\text{Cu}^0$  and adsorption of residual  $\text{Cu}^{2+}$ ,<sup>1</sup> and this can be shown as:



The second model (Fig. 5) represents the optimization of the phosphate removal process in the presence of copper which proposes a phosphate removal effi-



ciency of 95.38 %: dose nZVI 16 mL, copper concentration 9 mg L<sup>-1</sup>, phosphate concentration 1 mg L<sup>-1</sup> and pH value of 2. At the proposed pH value, phosphate is found in the forms H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, so the removal mechanism may include the possibility of removal by physical sorption on the surface of the nano-material, while the other is chemical sorption, *i.e.*, the construction of the inner spherical complex with (hydro) iron oxides.

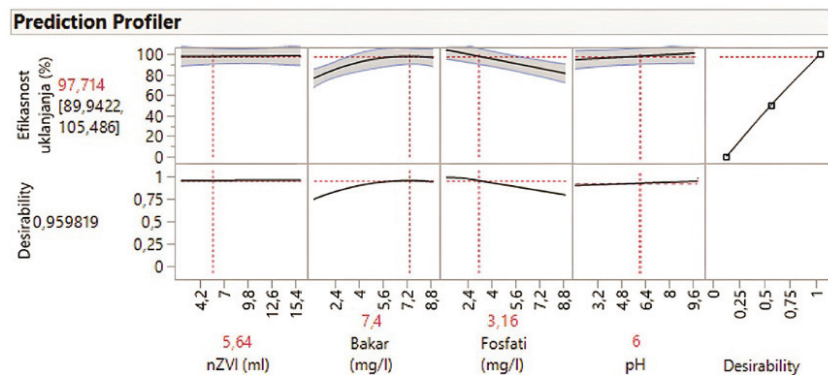


Fig. 4. Diagram of optimization of copper removal in the presence of phosphate.

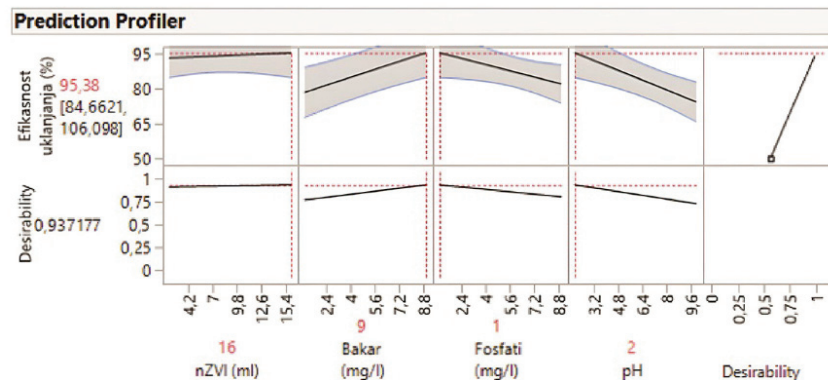


Fig. 5. Diagram of phosphate removal optimization diagram in the presence of copper.

In order to propose a phosphate removal mechanism, it is necessary to consider other factors of this medium. Under the given pH conditions, H<sub>3</sub>PO<sub>4</sub> dissociated, which further led to the protonation of nZVI-FeOH as described by the following reactions:



The positively charged surface facilitates the electrostatic attraction of anionic phosphate due to the formation of new active sites and surface complexation, which explains the dominant role of acidic environmental conditions in the highly efficient phosphate adsorption process:



#### *Experimental verification*

Verification of optimized processes was performed to realize a set of eight-point experiments. Based on this, the confidence interval was calculated with 95 % confidence (Table III). The proposed efficiencies in the process of removing copper, *i.e.*, phosphate using nZVI, fit into the confidence interval proposed by the process optimization, which confirmed that the models have passed the validation test for this phase of research.

TABLE III. Experimental verification of optimized processes

Run	Copper	Phosphate
1	97.55	96.70
2	96.78	95.90
3	98.00	95.50
4	97.45	94.80
5	98.12	95.40
6	97.69	95.20
7	98.35	95.80
8	99.09	96.00
95 % Confidence interval	97.31–98.45	95.18–96.14

#### *Possible removal mechanism*

Observing the model for removing copper in the presence of phosphate at pH 6 and removing phosphate in the presence of copper at pH 2 based on knowledge of the chemistry of monitored pollutants, it can be pointed out that pollutants of interest for both operating conditions are in the same forms. This would further mean that in both cases we have copper in the form of  $\text{Cu}^{2+}$  which is reduced to  $\text{Cu}^0$  and the residual  $\text{Cu}^{2+}$  sorbs on the surface of the nanomaterial. Phosphate is up to  $\text{pH} \geq 7.2$  in the form of  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$  and as such is complexed on the surface of nanomaterials. Fig. 6 shows the mechanism of removal of copper and phosphate on nZVI.

#### *Consideration for environmental applicability*

The merged wastewater represents the bulk of industrial and domestic wastewater, so the urgent need for simultaneous removal of coexisting different kinds of heavy metals (in our case, Cu) and anions (*e.g.*,  $\text{PO}_4^{3-}$ ) is indispensable. Many scientific results, gathered by authors,<sup>16</sup> indicate that the nZVI is one of the most

important materials for water purification and environmental remediation. nZVI particles have a core-shell structure, which enables them to behave as an electron source (core) and a site for surface complexation (shell). Precipitation and adsorption on the surface is the most common sequestration mechanism of metal ion removal by nZVI.<sup>17</sup>

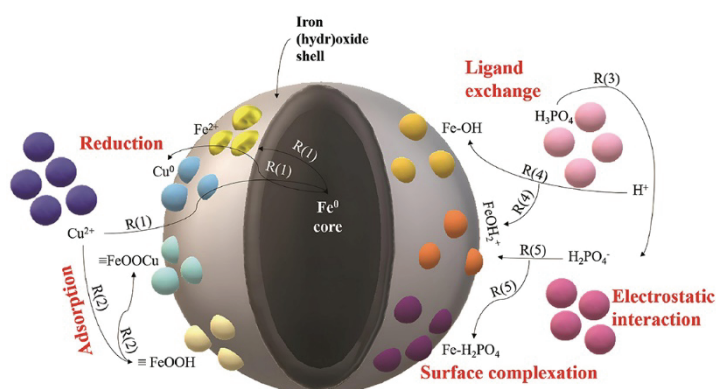


Fig. 6. Schematic diagram of possible mechanisms removal for copper and phosphate.

The green synthesis of nZVI makes this research favorable from both economic and environmental points of view. Cheap and green starting materials and the use of water as a green reaction medium is a promising option for large-scale synthesis.

Obtained high removal efficiencies of investigated pollutants (>99 % for Cu, and >92 % for PO<sub>4</sub><sup>3-</sup>) makes this material a promising candidate for implementation of a new generation of adsorbent used in a full-scale system.

Nanotechnology in environmental applications is experiencing significant growth, reflecting the real need for progress in both practice and research. However, since its initial use, nZVI has primarily been employed for remediating contaminated groundwater and soil, with its application in real wastewater, has yet to be extensively documented. Treating industrial effluents poses unique challenges due to their often high concentrations of pollutants in the presence of complex mixtures of different chemicals and impurities.

Key questions regarding nZVI technology relate to recirculation and reuse in treatment processes, enhancing material efficiency, reducing nZVI dosage and overall treatment cost. Green synthesis emerges as a cost-effective method for large-scale nZVI production, utilizing waste and further reducing treatment costs. The construction of this process requires minimal investment, with short reaction times. Additionally, nanoparticle regeneration, becomes crucial for economic reasons. Investigation into regeneration and the potential reuse of nZVI after Cu<sup>2+</sup> adsorption shows promise for cost reduction and increased sustainability.<sup>18</sup>

Researchers have focused on regenerating waste from a solution used in fixing radiological and photographic films. The achieved results highlight success in extracting silver and directly synthesizing nanoparticles from this waste, contributing to a circular economy and reducing overall waste. The end product carries a high concentration of precious metals, which can contribute to offsetting treatment costs.<sup>19</sup>

Addressing limitations in nZVI application, issues such as agglomeration and sludge production stand out. However, these challenges can be directed towards the production of biochar and reuse in wastewater treatment.<sup>20</sup> Another avenue is the application of solidification and stabilization after wastewater treatment, producing construction materials. Applications include road construction, embankments, and other infrastructure projects, where these materials can serve as alternatives to traditional ones.

This integrated approach to nanotechnology in remediation demonstrates significant potential for achieving sustainability and meeting the growing demand for clean water.

#### CONCLUSION

In this study, there were two removal efficiencies (copper and phosphates), and based on the obtained efficiency values, DSD proposed two models. The first model monitored the efficiency of copper removal in the presence of phosphate, while the second model monitored the efficiency of phosphate removal in the presence of copper. Since the entire study was promoted as “green”, in terms of the application of nanomaterial synthesized from oak leaves, as well as in terms of the application of the DSD model itself which, in addition to accuracy and precision, reduced the number of experiments, we can make our experiment even more economical. According to the Decree on emission limit values for pollutants in water and deadlines for their achievement (Official Gazette of RS, No. 67/2011, 48/2012 and 1/2016), the emission limit values for phosphate wastewater are 2 mg L<sup>-1</sup>. While the verified model for phosphates suggested a higher efficiency of ≈95 %, considering other parameters, the most important being the pH value (proposed value 2), the process is unfavorable in terms of the need for additional neutralization treatment which requires additional operating costs and chemicals. During the verification of the model for removing copper in the presence of phosphate, in addition to the analyzed copper residue, it also monitored the phosphate residue. Based on the analysis, a removal efficiency of ≈74 % was obtained, *i.e.*, the phosphate concentration was ≈0.85 mg L<sup>-1</sup>, which satisfies the legal regulations. Since we have already mentioned that at pH 2 and 6 the pollutants of interest are in the same form, it can be concluded that at pH 6, phosphate would have the same removal mechanism as at pH 2. Copper on the nZVI surface changes from Cu<sup>2+</sup> to Cu<sup>0</sup> covers the surface of the nZVI, which acceler-

ates the removal of phosphate because the copper in this case is attributed to the properties of the catalyst. From this study, several conclusions can be drawn, first nano adsorbents such as nZVI significantly affect the improvement of pollutant removal, which is responsible for their large specific surface area, associated with sorption sites and surface chemistry. And the other main conclusion is that in the examined process there was a simultaneous removal of copper and phosphate on the so-called green adsorbent. The “green” adsorbent was used, we removed two pollutants in one process, no additional tertiary treatment is needed to remove phosphate and it is not necessary to neutralize the effluent, because according to the previously mentioned regulation, the pH value should be 6–9 before discharge into the recipient. There are many publications on the application of nZVI, their modification, removal of various pollutants from all environmental media, but it must be taken into account that everything is still at the level of laboratory research. To achieve practical application, it is necessary to focus on the following challenges:

- 1) The use of large-scale with a guarantee of efficiency, safety and economy.
- 2) Monitoring terrain data due to the presence of numerous environmental influences.
- 3) Long-term effects on biological cycles and their fate in the environment.

#### SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/12592>, or from the corresponding author on request.

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ИЗВОД  
ЕКОНОМИЧНА МЕТОДА ИСТОВРЕМЕНОГ УКЛАЊАЊА БАКРА И ФОСФАТА НА  
ЕКОЛОШКИ ПРИХВАТЉИВОМ НАНОМАТЕРИЈАЛУ

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Еколошки одрживе и економски оправдане методе су неопходне при одабиру материјала и техника за синтезу нано-нултовалентног гвожђа. Биљке, са својим високим садржајем полифенола и антиоксидативним капацитетом, пронашле су примену у еколошки прихватљивим процесима синтезе. Definitive screening design (DSD) надгледао је четири кључна процесна параметра за истовремено уклањање бакра и фосфата: концентрацију бакра (у распону од 1 до 9 mg L<sup>-1</sup>), концентрацију фосфата (у распону од 1 до 9 mg L<sup>-1</sup>), почетне рН вредности (у распону од 2 до 10) и дозу нано-нултовалентног гвожђа (у распону од 2 до 16 mL). Резултати анализе пружају драгоцене увиде у значајне појединачне факторе који утичу на процес, као и потенцијал за њихове међусобне интеракције. Модел такође предлаже оптимизацију процеса ради постизања максималне ефикасности уклањања, а накнадна верификација потврдила је његову супериорност у односу на алтернативне методе. Механички процеси као што су сорпција, редукција, комплексација, електростатичка привлачност и размена лиганда играју кључну улогу у ефикасном уклањању бакра и фосфата применом нано-нултовалентног гвожђа. Укратко, ово истраживање доноси низ користи: употребу еколошки одрживих материјала, значајно смањење експерименталне сложености, уз истовремено високу ефикасност уклањања бакра и фосфата, повољне рН вредности и, посебно, непотребност додатних третмана.

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