

## THE CATALYTIC REDUCTION OF NITRATES BY BI- AND TRIMETALLIC NANOPARTICLES FOR SOIL PURIFICATION

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**Abstract.** In this work, bi- and trimetallic nanoparticles (FeNi, FeCu, FePd, FeNiCu, FeCuPd) were synthesized in the presence of a surfactant by the reduction of sodium borohydride. Stable and well-dispersed nanoparticles were obtained in the presence of sodium oleate surfactant. The main purpose of this study was to study the effectiveness of bi- and trimetallic nanoparticles in the catalytic purification of nitrates from the natural objects of soil. The experiments were carried out in soil from potatoes and cotton fields, where nitrogen fertilizer was used. The studied parameters were the effect of bi- and trimetallic nanoparticles on other ions that were in these soil samples ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{HCO}_3^-$ ). The morphology characterization of nanoparticles before and after soil treatment was investigated by TEM.

**Keywords:** bimetallic, trimetallic, nitrates, contamination, nanoparticle.

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### 1. Introduction

Small amounts of nitrogen are essential for crop growth; however, its excessive use leads to nitrates migration into the surface runoff, leaching (Bai *et al.*, 2010). Nitrogen fertilization often increases acidity through oxidation by converting  $\text{NH}_4^+$  to  $\text{NO}_3^-$ . Nitrates are the most dangerous form of N available in soil, which can be transported from the soil system to nearby water bodies (Lucas *et al.*, 2011). The oxidation of nitrogen fertilizers in the soil is carried out by microorganisms that release ions, which cause acidity. Thus, nitrogen fertilizers, being converted into ammonia and nitrate forms, significantly increase the amount of protons in the soil, thereby reducing pH. Due to nitrification of ammonia and ammonium, microorganisms responsible for soil acidification release  $1\text{H}^+$  and  $2\text{H}^+$  ions into the soil (Khan *et al.*, 2018). When nitrogen fertilizers are absorbed by agricultural crops in the form of nitrates,  $\text{H}^+$  ions are reduced, which leads to soil alkalinity. There are a number of studies illustrating the effect of nitrogen fertilizers on soil acidity (Chien *et al.*, 2009). A lower pH increases the solubility of aluminum in the soil, which becomes toxic to crop growth at  $\text{pH} < 5.5$ .

During irrigation, nitrates are washed out with water into groundwater and soil (Schroder *et al.*, 2011). When the soil dries up, nitrates rise to the upper dry layers of soil. Because of this the using of nitrogen by plants is limited. All this leads to significant losses of nitrogen from the soil as a result of washing off nitrates, as well as due to denitrification. According to the US Environmental Protection Agency and public health organizations,  $\text{NO}_3\text{-N}$  levels in drinking water should be less than  $10 \text{ mg l}^{-1}$  (EPAR 2001). However, a high concentration of  $\text{NO}_3\text{-N}$  in groundwater in Japan was noted due to the use of nitrogen fertilizers (Kumazawa *et al.*, 2002; Kang *et al.*,

2012). The concentration of  $\text{NO}_3\text{-N}$  in some wells reached  $100 \text{ mg L}^{-1}$ , which posed an increased danger to human health. There are studies illustrating spatial and temporal variations in nitrogen loss from fertilizers. In a study (Chen *et al.*, 2016), a significant linear correlation between total nitrogen (TN) and  $\text{NO}_3\text{-N}$  was observed in surface runoff.

The experimental results of this study showed that  $\text{NO}_3^-$  can be reduced by bi- and trimetallic nanoparticles to  $\text{N}_2$  and ammonia ( $\text{NH}_4^+$ ) as a minor by-product. They also proved to be stable and suitable for reuse in the process of catalytic reduction of nitrates. This method can meet the demand for a cost-effective, environmentally friendly, highly efficient, stable and selective environmental technology to solve the problem of  $\text{NO}_3^-$  pollution in natural and industrial water supply systems (Westerhoff *et al.*, 2003).

For this purpose, several soil samples were taken in the Gadabay area to test by nanoparticles. Potato and cotton fields were selected for soil analysis, where nitrogen fertilizer was used. Soil samples were collected in the spring in mid-April, when certain seeds were sown. Before sowing, 1/3 of the total nitrogen norm was added, further nitrogen fertilization was carried out partially in several stages. The number of stages is determined due to the amount of nitrogen applied during sowing and the general condition of the plants. Samples were taken from two points in each site. Water after irrigation accumulated in 2-3 places near the field, from which samples were taken and treated with nanoparticles.

## 2. Materials and methods

### 2.1. Chemicals

All reagents used for the experiment are chemically pure: iron (III) chloride hexahydrate (PLC 141358 - chemically pure 99%), sodium borohydride (PLC 143314 - chemically pure 99%), nickel (II) sulfate heptahydrate (PLC 141445, chemically pure 98 %), copper sulfate pentahydrate (PLC 175639), Pd solution 99.999%, sodium oleate (PLC 113655) were used for the synthesis of bi- and trimetallic particles. Sodium nitrate (LC24650) was used to prepare the nitrate solution.

### 2.2. Production of bi- and trimetallic nanoparticles

Bi- and trimetallic nanoparticles were synthesized in a round bottom flask with three necks, as shown in Fig. 1. To avoid agglomeration, surfactants were used during the synthesis. Several stabilizing agents were evaluated in this work, including sodium oleate, sodium carboxymethylcellulose, cetyltrimethylammonium bromide, polyethylene glycol. It has been found that in the presence of sodium oleate, the nanoparticles are better stabilized and become more resistant to oxidation and agglomeration.

All used nanoparticles were prepared by mixing a  $0.1 \text{ M Fe}_3^+$  solution with 30 ml of a 0.5% sodium oleate solution. Then it was mixed well on a magnetic stirrer at 500 rpm. After 15 minutes, various amounts of the second and third metal (Ni, Cu, Pd) were added to the solution to determine the best mass ratio. In parallel, 100 ml of a 0.3 M sodium borohydride solution was prepared and added to the iron solution drop by drop with continuously stirring. All reactions were carried out at room temperature and under nitrogen gas. The mixture was left for another 10 minutes on a magnetic stirrer after adding the sodium borohydride solution to complete the reaction.

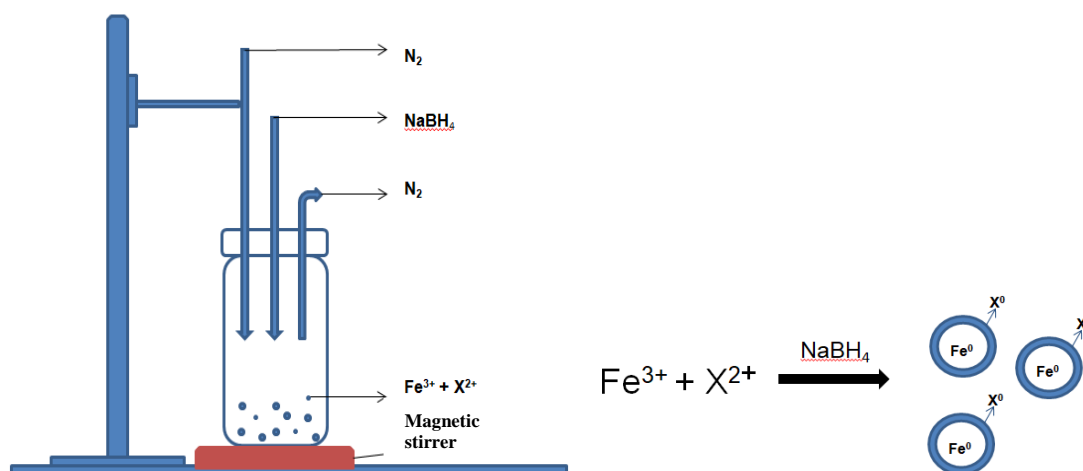


Fig. 1. Schematic illustration of bi- and trimetallic nanoparticles synthesis

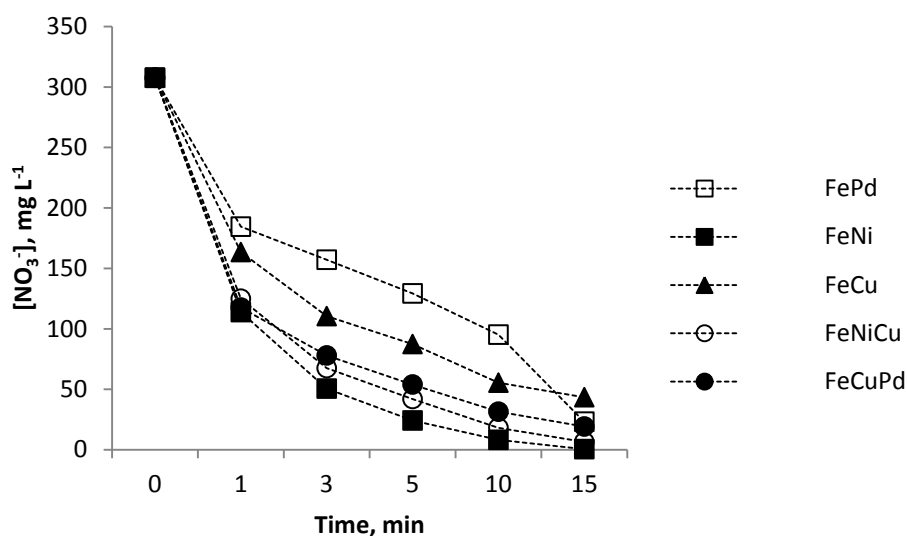
To completely remove of nonreactive ions, the synthesized nanoparticles were washed three times with absolute ethanol. An analytical centrifuge CR4000 was used to wash the nanoparticles. The freshly synthesized nanoparticles were then tested for nitrate purification.

### 2.3. Nitrate and other anions reduction experiments

The initial solution of nitrates was prepared by dissolving 0.17 g of  $\text{NaNO}_3$  in 400 ml of distilled water ( $300 \text{ mg L}^{-1}$ ). The experiments were carried out by using bi- and trimetallic nanoparticles in different weight ratios ( $0.05, 0.1, 0.2, 0.3, 0.4 \text{ g L}^{-1}$ ). All reactions were carried out in a three-necked round-bottom flask at room temperature and under nitrogen gas. Freshly prepared nanoparticles were added to a sodium nitrate solution ( $300 \text{ mg L}^{-1}$ ) and stirred for 15 minutes at 500 rpm. The optimal dose of particles was  $0.2 \text{ g L}^{-1}$  for FeNi,  $0.4 \text{ g L}^{-1}$  for FeCu, FePd, and  $0.3 \text{ g L}^{-1}$  for FeNiCu, FeCuPd trimetallic nanoparticles. The amount of  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^-$  ions was measured every 1, 3, 5, 10 and 15 min using ion chromatography (Dionex ICS - 5000), and  $\text{HCO}_3^-$  ions - by titrametric method. Prior to injection into ion chromatography, samples were centrifuged on a CR4000 centrifuge and filtered through syringe filters ( $0.45 \mu\text{m}$  pore size) to obtain pure, clear water without nanoparticles.

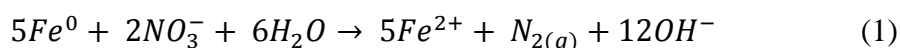
## 3. Results

As shown in Fig. 2, the influence of the identified optimal doses of nanoparticles on the reduction of nitrates after 15 min of reaction was studied. The optimal dose for each nanoparticle was chosen differently, based on previous studies, and was  $0.4 \text{ g L}^{-1}$  for FePd, FeCu,  $0.2 \text{ g L}^{-1}$  for FeNi, and  $0.3 \text{ g L}^{-1}$  for FeNiCu, FeCuPd. It was found that when using bimetallic FeNi nanoparticles at a concentration of more than  $0.2 \text{ g L}^{-1}$ , it is possible to achieve complete purification (99.8%) of nitrate after 15 min of treatment. Since the maximum purification of nitrates was observed when using nickel-based nanoparticles, further reactions in soil samples were carried out with these nanoparticles.



**Fig. 2.** The effect of optimal concentrations of bi- and trimetallic nanoparticles on time for the reduction of nitrates with an initial concentration  $[\text{NO}_3^-] = 306.74 \text{ mg L}^{-1}$

The inefficiency of purification of nitrates by nanoparticles is due to the fact that after 10 minutes of the reaction the solution had an alkaline pH (according to equation 1), which prevents the continuation of the reduction of nitrates.



In previous studies, the effect of zero-valent iron nanoparticles on the reduction of nitrates was also investigated (Muradova *et al.*, 2016). Despite small doses of nitrates, it was not fully restored even after 150 minutes.

For the application of bimetallic nanoparticles on soil samples, the optimal concentration of nanoparticles was used, which was revealed in laboratory conditions. And since bimetallic nanoparticles based on FeNi showed the best result compared to other bi- and trimetallic nanoparticles, they were used in further applications on objects. Soil samples were taken from 2 points in each field. The experimental results of anions before and after nanoparticles application are shown in Tables 1 and 2.

**Table 1.** Determination of anions in soil samples of potatoes field in the Gadabay region

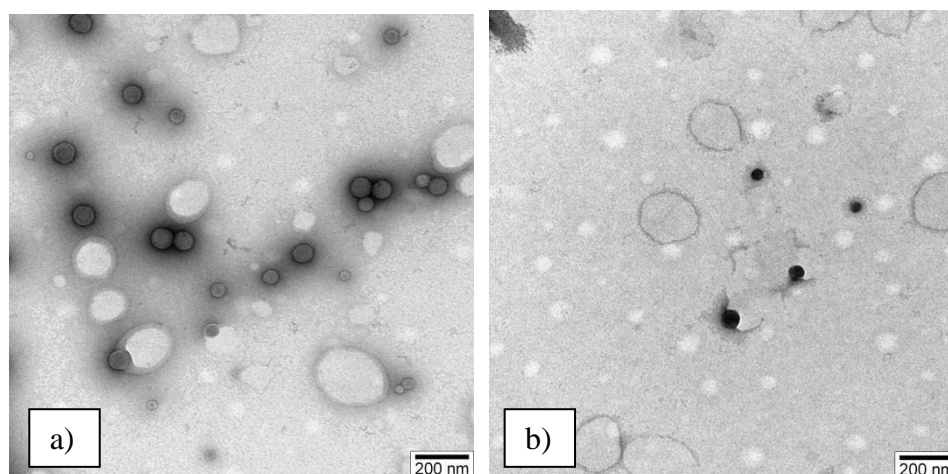
Anions	1		2	
	Initial concentration, $\text{mg L}^{-1}$	After remediation with nanoparticles, $\text{mg L}^{-1}$	Initial concentration, $\text{mg L}^{-1}$	After remediation with nanoparticles, $\text{mg L}^{-1}$
$\text{Cl}^-$	17.1	23.3	14.5	20.7
$\text{NO}_3^-$	17	<0.016	22	<0.016
$\text{SO}_4^-$	8	7	12	12
$\text{HCO}_3^-$	1038	1024	887	861

**Table 2.** Determination of anions in soil samples of cotton field in the Gadabay region

Anions	1		2	
	Initial concentration, mg L <sup>-1</sup>	After remediation with nanoparticles, mg L <sup>-1</sup>	Initial concentration, mg L <sup>-1</sup>	After remediation with nanoparticles, mg L <sup>-1</sup>
Cl <sup>-</sup>	20.3	26.2	18.6	24.1
NO <sub>3</sub> <sup>-</sup>	6	<0.016	12	<0.016
SO <sub>4</sub> <sup>-</sup>	10	10	16	16
HCO <sub>3</sub> <sup>-</sup>	749	733	801	787

It can be seen from the tables that the content of nitrates in the soil was not high, which may be due to the possible rapid dissolution of nitrates in water and merging with water into the underground layers. Nevertheless, after the introduction of bimetallic nanoparticles, nitrates were completely reduced, which cannot be said about other ions. The presence of bimetallic nanoparticles did not significantly affect the amount of other ions. There was a slight increase in chlorides, the amount of sulfates remained unchanged, and the concentration of bicarbonates decreased. The reason for the increase in chlorides is the insufficient washing of the used bimetallic nanoparticles after their synthesis, that is, there were chloride ion residues in the nanoparticles. And the decrease in the amount of bicarbonates is due to the competitive property of this ion with NO<sub>3</sub><sup>-</sup> ions, which may be due to their identical structure. Since the concentration of nitrates was not significantly high, the inhibitory effect of other ions did not affect the reduction of NO<sub>3</sub><sup>-</sup>.

The morphologies of nickel contained bimetallic nanoparticles were studied by TEM after synthesis. Fig.3 shows the transmission electron microscopy images of synthesized bimetallic nanoparticles FeNi before (a) and after (b) nitrates treatment.

**Fig. 3.** TEM images of bimetallic FeNi nanoparticles before (a) and after (b) nitrates reemediation

As shown from images, bimetallic nanoparticles were like iron nanospheres, which were covered with nickel before reduction (a). But after reduction bimetallic nanoparticles morphology has changed sufficiently due oxide layer over the nanoparticles.

#### 4. Conclusion

Bi- and trimetallic nanoparticles were synthesized and used in various concentrations ( $0.05 \text{ g L}^{-1}$ ,  $0.1 \text{ g L}^{-1}$ ,  $0.2 \text{ g L}^{-1}$ ,  $0.3 \text{ g L}^{-1}$ ,  $0.4 \text{ g L}^{-1}$ ) to reduce nitrates in water. Over 90% of nitrates were recovered within 15 minutes. The results showed that the synthesized nanosized particles can efficiently reduce nitrates. The main recovery products are dissolved ammonium, ammonia and nitrogen gas. Despite the high amount of nitrates (over 300 ppm), the results showed that complete (over 90%) purification was observed after 15 minutes and the optimal concentration was  $0.4 \text{ g L}^{-1}$  for FePd, FeCu,  $0.2 \text{ g L}^{-1}$  for FeNi and  $0.3 \text{ g L}^{-1}$  for FeNiCu, FeCuPd. The best removal effect was obtained using FeNi (optimum concentration for complete nitrate reduction was  $0.2 \text{ g L}^{-1}$ ). For this reason, nickel contained nanoparticles were used in further experiments. It was found that while using FeNi nanoparticles in the soil, it is possible to achieve complete purification of nitrates. No significant effect on the quantitative content of chlorides, sulfates and bicarbonates was observed. The use of nanoparticles is an environmentally and economically viable solution for the treatment of high concentrations of nitrates from water using a small amount of nanoparticles in a very short time.

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