

COMPARISON OF ECOTOXICITY OF NICKEL AND IRON OXIDES AND THEIR NANOFORMS

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ABSTRACT

In the model experiment, the ecotoxicity of nanoparticles (10-20 nm) and conventional (non-nano) powders (100 nm and above) of Ni and Fe oxides was compared. Their effect on microorganisms, plants and enzymatic activity of the soil was investigated as well.

It was found that the microbiological indicators (the total number of bacteria and the abundance of *Azotobacter*) were most strongly affected by the nanoforms of Ni and Fe oxides. The enzymatic activity of the soil (the activity of catalase and dehydrogenase) was largely dependent on Ni and Fe oxides and not on their nanoparticles. The indicators of phytotoxicity (germination and length of the radish root) were influenced both by Ni and Fe oxides and their nanoforms in equal measure.

Thus, nanoparticles of Ni and Fe oxides (10-20 nm) are more toxic for bacteria than particles of Ni and Fe oxides of usual sizes (100 nm and above), and vice versa for soil enzymes. A hypothesis was also tested, according to which the toxicity of metal nanoparticles does not depend on their chemical nature. For this, the effect of nanoparticles of nickel, highly toxic for biota, and low-toxic iron was compared. The addition of equal amounts of nickel and iron (from 100 to 10,000 mg/kg) had approximately the same comparable negative effect, whereas nickel is considered a significantly more toxic heavy metal than iron.

Keywords: Nanoparticles, Ecotoxicity, Pollution, Nickel, Iron, Ordinary Chernozem, Total Bacterial Count, Catalase Activity, Dehydrogenase Activity, Cellulolytic Activity, *Azotobacter* Abundance, Soil Phytotoxicity.

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INTRODUCTION

At present the hazard of environmental pollution with nanoparticles of heavy metals increases due to the intensive development of nanotechnologies and increased production of nanomaterials, including those containing metals. According to estimations by Lux Research advisory company, the share of only three market segments of nanomaterials (power engineering, catalysts, and structural materials) amounts to \$364.9 million. Global cumulative consumption of nanomaterials exceeded \$13 billion. Nanopowder industry is one of the most developed commercial segments of nanomaterial market. Its average annual growth is 15%. In natural terms of production, the market of nanopowders of pure metals is comprised of 16.5% of Ni and Cu powders. The top positions are also occupied by Fe, Al, Zn, and Ti. In Russia, as in the rest of the world, the production of oxide nanopowders is the most developed branch. In great demand are nanopowders of copper and nickel (annual production of at least 1500 t), aluminum and titanium (1350 t each), iron (1250 t) and other metals.^{1, 2}

Since nanomaterials are a new product type, characterization of their potential hazard for human health and environmental conditions is highly urgent.

Numerous researches are devoted to estimation of nanoparticle environmental impact. The influence of nanopowders on animals³⁻⁷, plants⁸⁻¹⁶, bacteria¹⁷⁻²⁵, ferment activity²⁶⁻²⁹ has been studied. The environmental impact of nanopowders, including the impact on soil, should be studied in more details due to the inconsistency of estimations: some authors evidence safety of environmental pollution with

nanoparticles, and the others point to significant risks. However, the common agreement is that it is necessary to investigate into ecotoxicity of nanomaterials due to increased hazard on environmental pollution with technogenic nanoparticles as a consequence of the development of nanotechnologies and increased production of nanomaterials. The most urgent issues are the selection and/or development of evaluation methods of ecotoxicity of nanoparticles and determination of mechanisms of their toxicity. This work is aimed at comparison of ecotoxicity of nickel and iron oxides and their nanoforms with regard to microorganisms, plants and chernozem fermentative activity in the model experiment.

EXPERIMENTAL

Soil pollution was simulated on a laboratory scale. Ordinary chernozem of southern European facie (North Azov area) was used. Chernozem is the most fertile soil in the world, it plays a significant role in foodstuff production. Soils were sampled in Botanic garden of the Southern Federal University, Rostov-on-Don. Ni and Fe oxides (Ni_2O_3 and Fe_2O_3) were used as toxicants.

Aiming at verification of the existing hypothesis that toxicity of metal nanoparticles actually does not depend on their chemical essence but only on the nanoparticle size, it has been interesting to compare the toxic impact of Ni and Fe, since Ni is characterized by high toxicity with regard to biota^{30, 31}, and the Fe content in soil is higher and its toxicity is insignificant.

Conventional (not nano-) powders of nickel and iron oxides were used as references. Particle sizes of nickel and iron oxides in nanopowders were 10-20 nm, and higher than 100 nm in conventional powders. The impact of various concentrations of metal oxides was tested: 100; 1,000; 10,000 mg/kg. Maximum allowable concentration (MAC) of Ni in soil is 100 mg/kg³⁰. Fe content in soil is not regulated due to its high level. In order to compare the toxicity degree of these two elements, Fe was added to soil in the same amount as Ni.

The soil was incubated in vegetation vessels at ambient temperature (20-22°C) and optimum moisture content (60% of water field capacity) with three replications. Samples for laboratory analysis were taken in ten days after pollution.

Laboratory analyses were performed according to methods commonly applied in biology, soil science, and ecology^{32, 33}. Total bacterial count in soil was measured by direct luminescence microscopy, *Azotobacter* abundance – by mud balls fouling on Ashby medium, catalase activity was determined by decomposition rate of hydrogen peroxide, dehydrogenase activity – by oxidation rate of triphenyl tetrazolium chloride, soil phytotoxicity – by seed germination and intensity of early sprout growth (root length).

RESULTS AND DISCUSSION

In the experiments, it was established that pollution of ordinary chernozem with Ni, Fe oxides and their nanopowders resulted in deterioration of its biological condition (Table-1). As a rule, a significant decrease in all considered biological performances was observed. The decrease extent depended on the essence of pollutant and its concentration in soil. In most cases, the direct interrelation between pollutant concentration and the extent of deterioration of the considered soil properties was observed.

Influence on Microbiological Performances

Microbiological properties of soil state, such as total bacterial count and *Azotobacter* abundance, responded more significantly to nanoforms of nickel and iron oxides. Herewith, nickel nanoparticles exerted a higher toxic impact on microorganisms than iron nanoparticles.

Thus, when introducing iron and nickel oxides to the soil at a concentration of 100 mg/kg, the total number of bacteria decreased to 92% and 80% of the control, respectively. A significantly greater decrease in this indicator is observed when introducing the same amount of nanoparticles of iron (76% of the control) and nickel oxides (63% of the control) to the soil. Nickel nanoparticles had a greater toxic effect on microorganisms than iron nanoparticles. Bacteria of the genus *Azotobacter* were more significantly affected by high concentrations (10,000 mg/kg) of nanoparticles of iron (66% of the control) and nickel oxides (75% of the control) than ordinary iron (81% of the control) and nickel oxides (78% of the control). The high toxicity of nanoparticles with respect to bacteria was recorded by researchers for other metals as well²¹⁻²⁷.

Influence on Soil Fermentative Activity

Ni and Fe oxides and their nanoforms exerted higher influence on the fermentative activity of ordinary chernozem in comparison with their nanoparticles. For example, with the addition of 10,000 mg/kg of iron and nickel oxides, catalase activity decreases to 62% and 57% of the control, respectively, while iron nanoparticles decrease this indicator to 86% of the control and nickel nanoparticles- to 72% of the control. Ni oxide and its nanoform decreased catalase activity more significantly than Fe oxide and its nanoparticles. Catalase activity decreased with the increase in the pollutant concentration. In terms of influence on catalase activity in ordinary chernozem, the metal oxides ranked as follows: Ni>Fe>Ni (nano form) \geq Fe (nano form). The negative effect of heavy metal nanoparticles on the enzymatic activity of soils was also observed by other researchers.²⁷⁻²⁹

Influence on Phytotoxic Performances

The length of radish roots at a concentration of 100 mg/kg and 1,000 mg/kg was more significantly affected by the nanoforms of iron and nickel oxides. At the maximum studied concentration (10,000 mg/kg), on the contrary, they turned out to be less toxic than ordinary oxides. Ni and Fe oxides and their nanoforms influenced the germination of radish in different ways depending on the concentration of the substance. Iron oxide and its nanoform at a concentration of 100 mg/kg reduced this indicator about similarly: up to 83% and 87% of the control, respectively. Nickel nanoparticles at the same concentration were more toxic (77% of the control) than nickel oxide (98% of the control). With a further increase in the concentration, iron oxide and its nanoform have an approximately equal effect on the germination of radish (72% and 71% of the control), and nickel oxide (67%) is more toxic than its nanoform (83%). At maximum concentration (10,000 mg/kg), iron oxide is more toxic than its nanoform (germination of radish is 65% and 74% of the control, respectively), and nickel oxide and its nanoform had an approximately equal effect (62% and 63% of the control).

Minimum phytotoxicity (if any) of nanomaterials in soil was observed by other researchers.^{15,16,34,35} The considered biological performances such as activities of catalase and dehydrogenase, *Azotobacter* abundance, total bacterial count, radish root length were highly sensitive to soil pollution with nanoparticles of heavy metals. These performances should be reasonably applied with the aim of monitoring, diagnostics and standardization of chemical soil pollution with nanoparticles of heavy metals.

Table-1: Comparison of Ecotoxicity of Oxides of Nickel and Iron and their Nanoforms with regard to Microorganisms, Radish and Fermentative Activity of Chernozem

Element	Amount of Pollutant				
	Reference	100 mg/kg	1,000 mg/ kg	10,000 mg/ kg	LSD05
Total Bacterial Count, %					
Fe	100	92	69	57	9
Ni	100	80	59	50	8
Fe(nano)	100	76	60	51	8
Ni(nano)	100	63	54	44	7
LSD (Lowest Significant Difference) 0.05		7	8	9	
Azotobacter Abundance, % Mud Balls Fouling					
Fe	100	98	91	81	11
Ni	100	89	86	78	10
Fe(nano)	100	99	88	66	11
Ni(nano)	100	91	79	75	12
LSD 0.05		9	11	10	
Catalase Activity, %					
Fe	100	73	71	62	7
Ni	100	72	64	57	6
Fe(nano)	100	90	89	86	8
Ni(nano)	100	83	78	72	7

LSD 0.05		5	5	5	
Dehydrogenase Activity, %					
Fe	100	81	80	74	7
Ni	100	82	78	48	7
Fe(nano)	100	85	76	75	7
Ni(nano)	100	86	83	63	9
LSD 0.05		5	6	6	
Radish Root Length, %					
Fe	100	77	75	46	8
Ni	100	79	74	49	9
Fe(nano)	100	67	66	55	8
Ni(nano)	100	71	62	61	8
LSD 0.05		10	9	7	
Radish Germination, %					
Fe	100	83	72	65	12
Ni	100	98	67	62	15
Fe(nano)	100	87	71	74	15
Ni(nano)	100	77	83	63	12
LSD 0.05		9	10	8	

CONCLUSION

Pollution of ordinary chernozem with Ni, Fe oxides and their nanoparticles caused deterioration of its biological state. It has been established that microbiological performances (total bacterial count and *Azotobacter* abundance) are most influenced by nanoforms of Ni and Fe oxides. Soil fermentative activity (the activity of catalase and dehydrogenase) was more influenced by Ni and Fe oxides, not by their nanoparticles. Phytotoxicity performances (germination and radish root length) were influenced almost equally by Ni and Fe oxides and their nanoforms.

It has not been established that nanoparticles of Ni and Fe oxides (10-20 nm) are characterized by higher ecotoxicity than particles of Ni and Fe oxides of conventional sizes (100 nm and above).

Addition of equal amounts of nickel and iron (100-10,000 mg/kg) exerts approximately similar and comparable negative impact, whereas nickel is considered a significantly more toxic heavy metal than iron.

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