# EFFECT OF PESTICIDE AND IRON OXIDE NANOMATERIALS IN SOIL ON THE DEVELOPMENT OF VETIVER (*Vetiveria zizanioides)*

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## SUMMARY

The explosion of nanotechnology in recent years has resulted in the emergence of nanomaterials in many applications in life. However, this also comes with new environmental and ecological challenges due to the accumulation of these materials in the environment when being discharged. Among metal nanomaterials, iron oxide nanomaterials are quite commonly used in different fields from health, food to environmental engineering. In this study, the impact of iron oxide nanomaterials and pesticide in soil on the development of vetiver (*Vetiveria zizanioides*) was initially measured. While the Ofatox pesticide alone in the soil at the concentration of 200 μg/kg of soil induced a significant reduction in the growth of the plant, the iron nanoparticles at the concentration of 100 mg/kg of soil showed a positive effect on the development of vetiver, expressing through the increase in the number of new shoots and the average length of the new shoots over time. On the other hands, when combining the pesticide at 200 μg/kg and iron nanomaterials at 25 mg/kg concentrations in soil, the nanomaterials showed a possible reversing effect on the negative impact of pesticide contaminants on the plant.

*Keywords*: Iron oxide nanomaterial, $Fe_3O_4$, pesticide, soil, vetiver.

## INTRODUCTION

Iron oxide has long been considered non-toxic (Dissanayake *et al*., 2015). These particles have been studied and appeared in a large number of applications over the past twenty years. According to Vance and colleagues, in the field of consumer products, iron and iron oxide nanoparticles along with other metal nanoparticles such as magnesium, aluminium oxide, copper, platinum, etc. account for about 10% of total consumer products... (Vance *et al*., 2015). Among them, iron, iron oxide and magnesium nanomaterials are often marketed as usable for medical applications, such as supplements in food and beverages. The medical field could be a traditional market for applications of iron oxide nanoparticles, where the particles can be found in imaging techniques, gene therapy, drug delivery agents and cancer treatments, especially in clinical diagnosis as diagnostic agents (Arami *et al*., 2015; Baetke *et al*., 2015; Kornberg *et al*., 2017).

The explosion in applications of nanotechnology, as a matter of course, will incorporate new risks. The number of reviews and reports addressing the toxicity and effects of metal nanomaterials on human and animal health at both cellular and organ levels is increasing in recent years. One of the key concerns is the possibility that nanomaterials can end transport chains in different types of environments, contaminating drinking water, leading to adverse health effects for humans and animals. as well as impacts on ecosystems. Among nanomaterials, iron nanoparticles of various forms can be found primarily in various applications from medicine (Vance *et al*., 2015; Kornberg *et al*., 2017; Baetke *et al*., 2015, Arami *et al*., 2015) to environmental industry (Patil *et al*., 2016; Park *et al*., 2016), in which environmental applications are considered the most common for the use of iron oxide nanoparticles. As a result, there are more chances these nanomaterials could end up in the environments such as aquatic environments, where they can subsequently find their way into living bodies like cells, animal and plant organs before entering human and animal bodies through the food chain.

An approach, called Phyto-Fenton, was developed recently which combines the use of iron oxide nanomaterials and vetiver for the remediation of soils contaminated with pesticides and/or other persistent organic compounds (Reis *et al*., 2013; Kurihara *et al*., 2017). The objective of this study is to explore the effects of iron nanomaterials on the development of vetiver in the phyto-Fenton approach to eliminate residues of plant protection chemicals in contaminated soil. In this study, the effects of iron oxide nanomaterials on the development of vetiver on different soil conditions were evaluated to demonstrate the potential of using phyto-Fenton approach for soil remediation, as well as provide a preliminary assessment on the effects of iron nanomaterial, in particular, and nanotechnology, in general, on plant ecosystems.

## MATERIALS AND METHODS

### Materials

The iron oxide nanomaterial used in this study was ferrite ($Fe_3O_4$), a commercial magnetite nanomaterial, (Sigma-Aldrich, CAS 1317-61-9) provided by Sakakibara Lab., Waseda Unievrsity. Vetiver grasses (*Vetiveria zizanioides*) were precultured and provided by National Academy of Agriculture. The soil was GT-05 organic soil (Soil and Fertilizers Research Institute, Hanoi, Vietnam) that contains already necessary nutrition and minerals for plant growth was purchased in bags of 10 kg from a local distributor. Pesticide was Ofatox 400 EC containing Fenitrothion 200 g/l and Trichlorfon 200 g/l in 100 ml bottle (No. 1 Central Plant Protection Company, Hanoi, Vietnam) was purchased from a local distributor.

**Figure 1. Pre-selection of vetivers with 15 - 20 cm of root length and 3 branches each**

**Experimental setup**

Experiments were conducted in 5 plastic pots (28 × 30 × 22 cm of pottery mouth diameter × height × bottom diameter) each contains 5 kg of soil. Experiments were repeated 3 times during the time between September to Nevember 2017. The soil was pre-mixed with either pesticide or iron oxide nanomaterial or both to the following conditions before being distributed in pots.

- Pot 0 (Control): original soil without addition of pesticide and iron oxide nanomaterials.
- Pot 1: the soil was mixed with Ofatox pesticide at the concentration of 200 μg/kg of soil.
- Pot 2: the soil was mixed with Ofatox pesticide at the concentration of 200 μg/kg of soil and iron oxide nanomaterials at the concentration of 25 mg/kg of soil.
- Pot 3: the soil was mixed with iron oxide nanomaterials at the concentration of 25 mg/kg of soil.
- Pot 4: the soil was mixed with iron oxide nanomaterials at the concentration of 100 mg/kg of soil.

After the preparation of pots containing soils of different conditions, 3 young vetivers were planted in each pot. Vetivers were pre-selected carefully with 3 branches and 15 - 20 cm of root length each (Figure 1). Leaves were cut to a height of 20 cm from the soil.

**Experimental conditions**

The original moisture was 28% and the initial pH was 7. After the plantation, the soil moisture and pH were periodically measured with a soil tester (MS04, Sonkir, Hanoi, Vietnam) and kept maintaining at > 80 % moisture and pH 7 in all pots. The temperature during the time of the experiment was ranged from 19 to 22°C at night and 27 to 29°C during the day; relative humidity was 80 - 90%. Luminance was from natural sunlight at 1500 - 1600 lux average daytime recorded during the time of conducting the experiment.

**Observation and plant growth measurement**

Periodically, the number and length of new stretches shooting out from the ground and the cut were measured and photoshoot providing information on the growth of the plants. Data and images are processed and analysed on Microsoft Excel.

## RESULTS AND DISCUSSION

In this experiment, vetivers in each pot were observed periodically, and the numbers of leaves shooting out from the ground and the cut were counted, the lengths of those leaves were measured. Figure 2 shows the vetivers in different pots at 1, 2 and 3 weeks after planting. At 1-week time point, all vetivers showed new stretches shooting out from the cut. In the two cases where plants were treated with pesticide (pots no. 1 and 2), plants seemed to grow in lower rates in comparison to plants in the control case (pot no. 0). It suggested a growth inhibitory effect of pesticide on the plants. However, in the case where the soil was mixed with both the pesticide and the iron material (pot no. 2), the plants grew better than the plants in the case where the soil was mixed with only the pesticide (pot no. 1). This indicated a possible reversing effect of the iron oxide nanomaterial to the inhibitory effect of the pesticide in soil. This hypothesis was further supported with data on the plants in the two other cases where the soil was mixed with the iron material only at two different concentrations (pot no. 3 and 4). In these cases, the plants showed well-growing capacity that was compatible with those of the plants in the control case. There was no inhibitory effect observed in these two cases. In the pot containing iron material at the concentration of 100 mg/kg of soil, the plants showed a better growth rate than that of the control plants. It once again indicated a supportive effect of the iron material to the growth of plants.

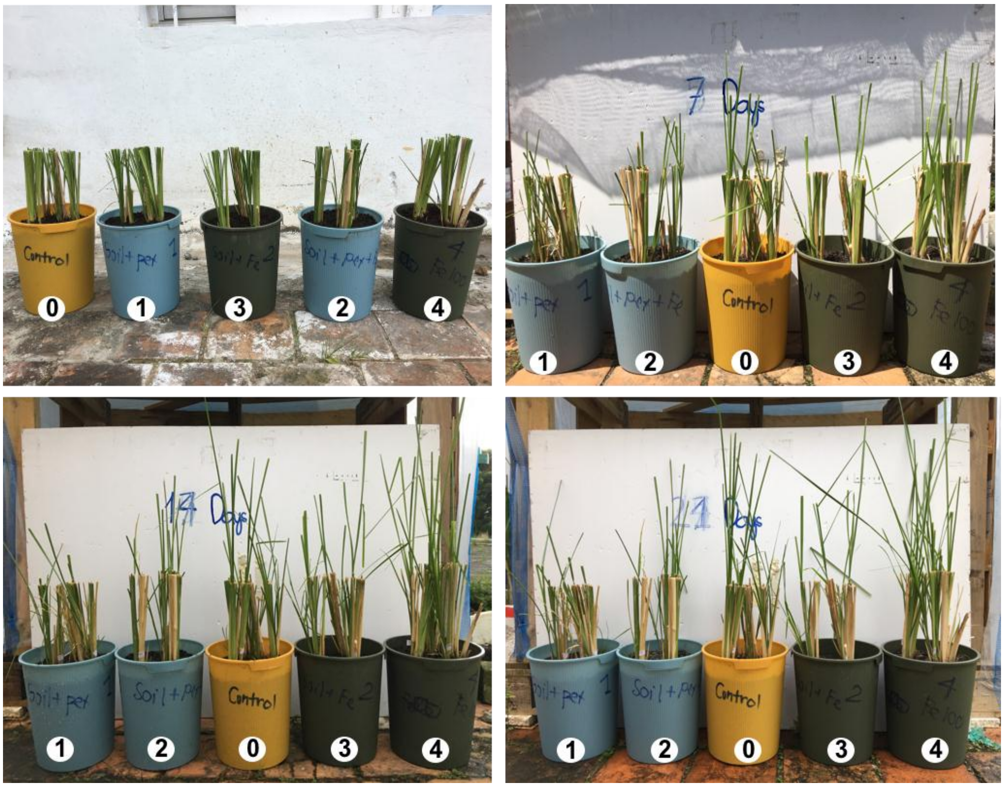


**Figure 2. The growth of vetiver by days**

*(0) control – soil containing neither pesticide nor nanoparticles, (1) soil containing pesticide at 200 $\mu$g/kg of soil, (2) soil containing pesticide at 200 $\mu$g/kg of soil and iron oxide nanoparticles at 25 mg/kg of soil, (3) soil containing iron oxide nanoparticles at 25 mg/kg of soil, and (4) soil containing iron oxide nanoparticles at 100 mg/kg of soil*

Figure 3 provides supportive evidence on the effect of pesticide and iron oxide nanomaterial on the plant growth through the two developmental parameters: the number of new stretches shoots out from the ground and the cut, and the average lengths of the new stretches. It clearly indicated that pesticide in soil induces retardation on the development of the plants, while the iron oxide nanomaterial in soil induces amendment effect to the development of plants growing on contaminated soil. The nanomaterial alone in soil somehow boots up the plant development at high concentration. To explain to this phenomenon, several hypotheses can be raised: 1) the iron nanomaterials could place impact on the soil microbial community and change its activity toward a supportive way of contribution to the plant growth, 2) the iron nanomaterials directly put an impact on the growth of the plants by changing the metabolism, uptake and circulation processes in the plants, 3) the iron nanomaterials could turn the natural organic matters of soil into the forms that could be easier to be uptaken by the plants.

A study recently on the effects of several metal oxide nanoparticles has shown no effect of $Fe_3O_4$ nanoparticles on the germination of two crop plants, maize (*Zea mays* L.) and rice (*Oryza sativa* L.) (Yang *et al*., 2015). Another study on the effects of positive charged (PAA coated) and negatively charged (PEI coated) $Fe_2O_3$ nanoparticles on the plant *Arabidopsis thaliana* has shown that there was no effect on seedling and root length of the plants at the low treatment concentration of 3 mg/L, but the high treatment concentration of 25 mg/L with a reduction in seedling and length (Bombin *et al*., 2015). The study also pointed out the negative effect of both types of nanoparticles on pollen viability and seed production, but no observable phenotypic changes in overall size and general plant structure. Recent work of Siddiqi and Husen has reviewed the response of the plant to different engineered nanoparticles including iron oxide nanoparticles (Siddiqi and Husen, 2017). In general, the toxicity of iron oxide nanoparticles greatly depends on the size, shape and concentration of the nanoparticles in the environment. The smaller in size, the easier the particles could pass the cell membrane and exert their toxic effects on cells. The metal oxide nanoparticles are more toxic to microorganisms than the bulk materials of the same metal. In most cases of detrimental effects of the iron oxide nanoparticles mentioned in the review, the exposed concentrations normally very high from a few hundreds to thousands mg/L, which might not be really environmentally relevant.

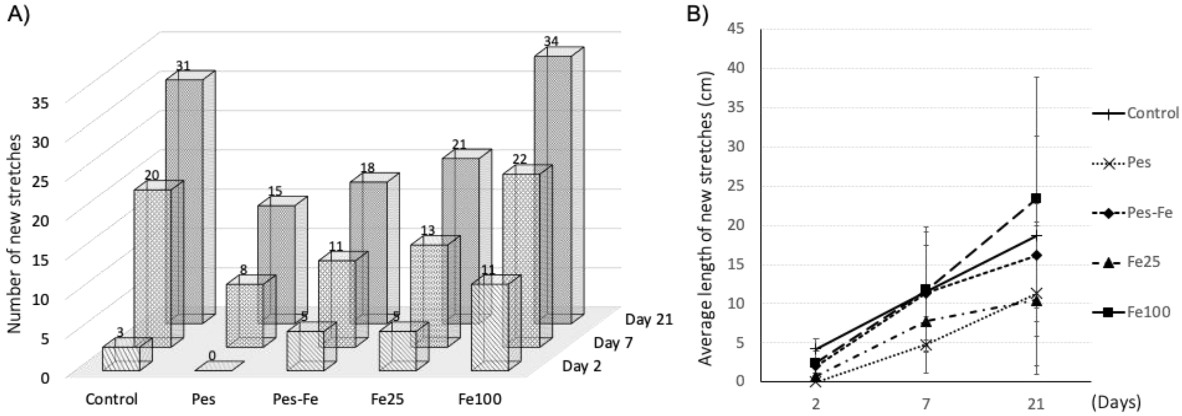


**Figure 3. Effect of iron oxide nanomaterial in soil on vetiver growth**

*A) Effect of iron nanomaterial on the number of new stretches shouting out from the ground and the cut, B) Effect of iron nanomaterial on the average lengths of the new stretches. Control - soil containing neither pesticide nor iron nanomaterial, Pes - soil containing pesticide at 200 μg/kg of soil, Pes-Fe - soil containing pesticide at 200 μg/kg of soil and iron oxide nanoparticles at 25 mg/kg of soil, Fe25 - soil containing iron oxide nanoparticles at 25 mg/kg of soil, and Fe100 - soil containing iron oxide nanoparticles at 100 mg/kg of soil*

A number of reports has proven the translocation of metal nanoparticles including iron oxide nanoparticles to roots and shoots of plants (Siddiqi and Husen, 2017; Amde *et al*., 2017). Plant roots when exposed to γ-$Fe_2O_3$ nanoparticles at relatively high concentrations 50 - 100 mg/L could show root length reduction and the reduction of the root hydraulic conductivity thus reducing the uptake of nutrients and minerals (Ruttkay-Nedecky *et al*., 2017). However, another study with the plant *Citrus maxima* suggested no changes of chlorophyll content and root activity upon exposure to 20 - 100 mg/L γ-$Fe_2O_3$ nanoparticles and $Fe^{3+}$ (Hu *et al*., 2017). The authors also pointed out the accumulation of the nanoparticles in shoots and roots. Another paper suggested using the iron oxide ($Fe_2O_3$) nanoparticles as a potential fertilizer for peanut *Arachis hypogaea* since the particles showed a promotive effect on phytohormone content and antioxidant enzyme activity, thus increasing root length, plant height, biomass, and SPAD values (related to chlorophyll contents) of peanut plants (Rui *et al*., 2016).

## CONCLUSION

To conclude, this study initially measured the effect of the Ofatox pesticide and iron oxide nanoparticles in soil on the development of vetiver (*Vetiveria zizanioides*). It showed that while the pesticide at the concentration of 200 μg/kg of soil induces retardation on the development of the vetiver, iron nanomaterials at the concentration of 100 mg/kg of soil shows a positive effect. When added the nanoparticles at 25 mg/kg concentration to the soil containing the pesticide, it showed a possible reversing effect of the nanoparticles to the negative effect of the pesticide on plant development. The phytotoxicity of the iron oxide nanoparticles, perhaps, is still a controversial issue which needs more elaborated studies to elucidate. Studies so far focused only on the direct impacts of the nanoparticles on cellular and plant organ systems, but not the surround environments, which also affect the development of plants. In our study, we used bulk iron materials, the mechanism of the impacts thus might not just limit to cellular or plant organ levels. We should also consider its impacts in a context of a whole system where there are interactions between plant and microbes, plant and the nanoparticles, plant and soil structure/composition, soil and the nanoparticles, etc.

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## REFERENCES

Amde M, Liu J, Tan Z-Q, Bekana D (2017). Transformation and bioavailability of metal oxide nanoparticles in aquatic and terrestrial environments. A review. *Environ Pol* 230: 250-267.

Arami H, Khandhar A, Liggitt D, Krishnan KM (2015). In vivo delivery, pharmacokinetics, biodistribution and toxicity of iron oxide nanoparticles. *Chem Soc Rev* 44(33): 8576-8607.

Baetke SC, Lammers T, Kiessling F (2015). Applications of nanoparticles for diagnosis and therapy of cancer. *Br J Radiol* 88: 20150207. doi: 10.1259/bjr.20150207.

Bombin S, LeFebvre M, Sherwood J, Xu Y, Bao Y, Ramonel KM (2015). Developmental and reproductive effects of iron oxide nanoparticles in *Arabidopsis thaliana*. *Int J Mol Sci* 16: 24174-24193.

Dissanayake NM, Current KM, Obare SO (2015). Mutagenic Effects of Iron Oxide Nanoparticles on Biological Cells. *Int J Mol Sci* 16: 23482-23516.

Hu J, Guo H, Li J, Wang Y, Xiao L, Xing B (2017). Interaction of γ-Fe2O3 nanoparticles with *Citrus maxima* leaves and the corresponding physiological effects via foliar application. *J Nanobiotechnol* 15: 51. DOI 10.1186/s12951-017-0286-1

Kornberg TG, Stueckle TA, Antonini JM, Rojanasakul Y, Castranova V, Yang Y, Rojanasakul LW (2017). Potential Toxicity and Underlying Mechanisms Associated with Pulmonary Exposure to Iron Oxide Nanoparticles: Conflicting Literature and Unclear Risk. *Nanomaterials* 7: 307. doi:10.3390/nano7100307.

Kurihara T, Inagaki Y, Dang MH, Vo HC, Sakakibara Y (2017). Phyto-Fenton process – Fenton reaction with vegetation systems. In Proceedings of the 5th International Conference on Water, Energy & Environment. UAE, Feb 28–Mar 2.

Park CM, Chu KH, Heo J, Her N, Jang M, Son A, Yoon Y (2016). Environmental behavior of engineered nanomaterials in porous media: a review. *J Hazardous Materials* 309: 133-150.

Patil SS, Shedbalkar UU, Truskewycz A, Chopade BA, Ball AS (2016). Nanoparticles for environmental clean-up: A review of potential risks and emerging solutions. *Environ Technol Innov* 5: 10–21.

Reis AD, Kyuma Y, Sakakibara Y (2013). Biological Fenton's Oxidation of Pentachlorophenol by Aquatic Plants. *Bull Environ Contam Toxicol* 91:718-723.

Rui M, Ma C, Hao Y, Guo J, Rui Y, Tang X, Zhao Q, Fan X, Zhang Z, Hou T, Zhu S (2016). Iron oxide nanoparticles as a potential iron fertilizer for peanut (*Arachis hypogaea*). *Front Plant Sci* 7: 815. Doi: 10.3389/fpls.2016.00815

Ruttkay-Nedecky B, Krystofova O, Nejdl L, Adam V (2017). Nanoparticles based on essential metals and their phytotoxicity. *J Nanobiotechnol* 15: 33. DOI 10.1186/s12951-017-0268-3

Siddiqi K and Husen A (2017). Plant response to engineered metal oxide nanoparticles. *Nanoscale Res Lett* 12: 92.

Vance ME, Kuiken T, Vejerano EP, McGinnis SP, Hochella Jr. MF, Rejeski D, Hull MS (2015). Nanotechnology in the real world: Redeveloping the nanomaterial consumer products inventory. *Beilstein J Nanotechnol* 6: 1769-1780.

Yang Z, Chen J, Dou R, Gao X, Mao C, Wang L (2015). Assessment of the phytotoxicity of metal oxide nanoparticles on two crop plants, maize (*Zea mays* L.) and rice (*Oryza sativa* L.). *Int J Environ Res Public Health* 12: 15100–15109.

# TÁC ĐỘNG CỦA THUỐC TRỪ SÂU VÀ VẬT LIỆU NANO SẮT ÔXIT TRONG ĐẤT LÊN SỰ PHÁT TRIỂN CỦA CỎ VETIVER (*Vetiveria zizanioides*)

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## TÓM TẮT

Sự bùng nổ của công nghệ nano trong những năm gần đây đã đưa đến kết quả là sự xuất hiện ngày càng nhiều của các loại vật liệu nano trong các ứng dụng trong đời sống. Tuy nhiên, điều này cũng đi kèm với những thách thức mới về môi trường và sinh thái do sự tích lũy của những vật liệu này trong môi trường khi được thải ra. Trong số các vật liệu nano kim loại, vật liệu nano sắt ôxit được ứng dụng khá phổ biến trong nhiều lĩnh vực từ y tế, thực phẩm tới môi trường. Trong nghiên cứu này, tác động của vật liệu nano sắt oxit và thuốc trừ sâu trong đất lên sự phát triển của cỏ vetiver (*Vetiveria zizanioides*) đã ban đầu được khảo sát. Trong khi thuốc trừ sâu Ofatox trong đất ở nồng độ 200 μg/kg đất đã làm giảm đáng kể sự phát triển của cây, thì các hạt nano sắt ở nồng độ 100 mg/kg đất cho thấy tác động tích cực đến sự phát triển của cỏ vetiver, thể hiện qua sự gia tăng số lượng chồi mới và chiều dài trung bình của chồi mới theo thời gian. Mặt khác, khi kết hợp thuốc trừ sâu ở nồng độ 200 μg/kg và vật liệu nano sắt ở nồng độ 25 mg/kg trong đất, vật liệu nano cho thấy có thể có tác động đảo ngược đối với tác động tiêu cực của chất gây ô nhiễm thuốc trừ sâu đối với cây trồng.

*Từ khóa*: Vật liệu nano sắt ôxit, $Fe_3O_4$, thuốc trừ sâu, đất, cỏ vetiver.

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