

# Reduction of the Mercury Concentration Present in Forest Soil using Iron Nanoparticles

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The mercury contamination in forest soils at the Madre de Dios region has been a longstanding issue, stemming from mining activities. Various elements, including climate, microorganisms and water resources, have facilitated the spread of mercury through the trophic chain impacting the area's ecosystem and nearby communities. This study proposes employing iron nanoparticles to diminish mercury presence in forest soils. Soil samples extracted from mining camps located in the district of Huepetuhe, Peru; which were subjected to three concentrations from mining sites in Huepetuhe, Peru were exposed to iron nanoparticles concentrations of 2.5 mg/kg, 5 mg/kg and 7.5 mg/kg. Each sample underwent analysis after 24 hours, 48 hours and 72 hours, to reliably assess the reduction in mercury levels. The results revealed a maximum mercury reduction efficiency of 95.33 %, with the 5 mg/kg dose, which yielded the most favorable results.

## 1. Introduction

The contamination of soil due to human activities has emerged as an international concern, largely because of its detrimental effects on health and environmental conditions. Key pollutants include fats and metallic minerals, with mercury being a notable contaminant due to its harmfulness to both ecosystems and human health.

As reported by MINSA (2010), there have been incidents of mercury poisoning in Huepetuhe district, which have resulted in symptoms like limb paralysis, memory lost, vomiting, dizziness, among others. These symptoms untreated due to a lack of medical facilities and equipment specifically for mercury poisoning.

The artisanal methods used in gold reburning and amalgamation, which heavily rely on mercury as a primary input, cause mercury to spill onto the ground due to ignorance, lack of experience, routine practices, or inadequate gold recovery equipment. This has adverse effects on the water, air and soil. Additionally, research by the Canadian NGO Artisanal Gold Council found that 181 tons of mercury are annually released into the ground in the province of Madre de Dios due to mining activities, a figure that could rise as more individuals engage in this activity.

Constant rainfall has further spread mercury contamination in the region, allowing it to be absorbed by certain microorganisms, plants and fish, transforming into methylmercury or organic mercury. In 2015, MINSA prohibited consuming the spotted speck fish after finding that residents of the Maizal community were being poisoned by their primary food source, with mercury levels in hair samples reaching 27 ppm, significantly exceeding the 1 ppm safe limit set by the World Health Organization (Gaona, 2004). Mercury usage has led to its dispersion in the air, water and soil, producing methylmercury with water being a key medium for its spread (Martinez et al., 2018). The bioaccumulation of mercury in fish and subsequent impact on other organisms, due to mercury methylation, affects populations whose diets are primary fish-based (Feingold et al., 2020). Concerning the informal and illegal mining in Madre de Dios and the resultant mercury pollution, it is estimated that around 400 tons of mercury have been released in recent years, contaminating the soil in mining areas (Osores et al., 2012). Mercury concentrations are predominantly found in mining activities and camps, while adjacent areas show lesser concentrations due to factors like proximity to rivers and soil characteristics (Mandros, 2019). Excessive mercury use as an amalgamating agent is mainly responsible for its presence in areas of mining activity and supply stores, where mercury vapor concentrations are high but unnoticed by workers (Brown et al., 2020). In the Madre de Dios region, particularly in Santa Rita, San Jacinto and Kotzimba,

two mining activity types have been identified; minimally mechanized mining (MMM) and highly mechanized mining (HMM), with findings indicating lower Hg loads than those allowed by national ECA soil legislation (Velásquez et al. 2021). Various techniques exist for treating mercury contaminated soils, including phytoextraction (Petruzzelli et al., 2012), phytoremediation using Guarumo (*Cecropia Peltata*) (Vidal et al., 2010), chili pepper (*Capsicum annuum*) as a natural mercury accumulator (Pérez et al., 2014), and using Musa Cultivar AAB banana for determining mercury concentrations in soil in Iberia, Punkiro chico and Sarayacu-Madre de Dios sectors (Arostegui, 2017). Bioremediation using *Escherichia coli* also offers a promising alternative, utilizing its mercury bioadsorption capacity to reduce soil mercury levels (Espinoza and Manziny, 2019). The application of biological barriers, through artificial wetlands inoculated with heavy metal tolerant strains, has been shown to decrease mercury concentrations (Amabilis et al., 2016). Soil washing and the application of iron nanoparticles are other methods used to address contamination from elements like Hg, Cu, As, Pb, and Zn (Boente et al., 2018). Mercury contaminated soils require long-term and costly treatments, making nanotechnology a beneficial environmental remediation tool. For employing nanoparticles in soil treatment, studies must characterize the study area, considering factors like location, soil type, porosity, and depth, as well as physicochemical soils properties (Carrillo and Gonzales, 2019). Nanoparticles vary by composition, including carbon NPs composed of fullerenes, nanotubes, graphene, metallic NPs including gold and silver NPs, titanium oxides, cadmium sulfide, and cadmium selenide, dendrimers and nanocomposites; each with diverse applications in water, soil and air (Negrete et al., 2017). Iron nanoparticles are noted for their reducing nature against pollutants, serving as catalysts or absorbers (Gayo, 2018).

Different types of iron nanoparticles such as Reactive Nanoscale Iron Product (RNIP) and nanoscale zero valent iron (nZVI), vary in effectiveness for immobilizing As and Hg in soils (Boente et al., 2017). The synthesis of iron nanoparticles for environmental applications has been shown to efficiently reduce water and soil contaminants at lower costs and shorter treatment times. However, the impacts of using modified iron nanoparticles must be assessed to prevent altering water and soil quality; thus, prior laboratory studies are essential to understand the effects of these nanoparticles in contact with organic and inorganic contaminants (Stefaniuk et al., 2016).

The research aimed to determine the effectiveness of iron nanoparticles in reducing mercury concentrations in forest soil of Huepetuhe, Madre de Dios, Peru.

## **2. Materials and methods**

### **2.1 Iron nanoparticles**

In the experimental procedure, iron nanoparticles were synthesized by dispersing 11 g of  $\text{FeCl}_3$  in one liter of deionized water. The mixture was then sonicated for 30 minutes at a frequency of 40 kHz and a temperature of 30 °C. The peak absorbance was measured using spectrophotometry, showing a wavelength of 341 nm; with the iron nanoparticles having an average diameter of 60 nanometers. After sonication, the iron nanoparticles were filtered and left to dry at room temperature. Once dry, the nanoparticles were weighed into quantities of 5 mg, 10 mg and 15 mg for use in samples labeled M2, M3 and M4 respectively.

### **2.2 Soil Samples**

A total of 16 soil samples were collected from decommissioned sites within the jurisdiction of the Huepetuhe district. In accordance with Supreme Decree No. 002-2013-MINAM, a small pit ranging from 15 to 20 cm in deep was dug to collect the soil samples, which were then sealed in Ziploc bags and labeled. It is noted that the sampling areas are devoid of vegetation due to previous deforestation activities. The collected samples predominantly come from locations where mining camps are set up and where artisanal amalgamation processes are conducted. Additionally, the sampling points are situated near the Huepetuhe river.

### **2.3 Conditioning of the experimental area**

A designated area measuring 1x1.50 x 1.50 m was established, with included a table for conducting the experiments. All openings were sealed to prevent any potential leaks, and after three hours, an average temperature of 12 °C was maintained for the sample handling process.

### **2.4 Preparation for experimentation**

The initial dry soil sample was first assessed for its pH and moisture content. For this purpose, 10 g of soil was extracted and mixed with 20 mL of deionized water, after which the electrical conductivity was measured. The soil samples were categorized into a control sample (M1) and three additional samples (M2, M3 and M4), each containing 2 kg of soil. Additionally, the distribution of iron nanoparticles was calculated based on the samples's weight.

Table 1. Relationship between iron nanoparticles and soil sample

No. Sample	Weight of Iron nanoparticles (mg)	Sample weight (kg)	Weight of iron nanoparticles in soil sample (mg/kg)
M2	5	2	2.5
M3	10	2	5
M4	15	2	7.5

A table detailing the percentage distribution of deionized water and iron nanoparticles for each sample was subsequently prepared as follows:

Table 2. Correspondence of iron nanoparticles with water.

No. Sample	Weight of nanoparticles (mg)	Ratio Volume of water: NP Iron (mL/mg) of iron nanoparticles	Total volume of water (mL)
M2	5	5 mL for every 2.5 mg	10
M3	10		20
M4	15		30

After dissolving the iron nanoparticles in deionized water, the resulting mixture was sprayed onto each sample according to the specified proportions. It was then stirred until the soil samples achieved uniformity. Following this, the soil samples were packaged and labeled with their corresponding sample numbers (M2, M3 and M4). After intervals of 24, 48 and 72 h, soil samples were collected and transported to the laboratory to analyze the concentrations of mercury and iron within the soil.

### 3. Results

#### 3.1 Soil texture analysis

The soil texture analysis, conducted using the Bouyoucos method, revealed that sand was the predominant component at 94.48 % in the samples. This finding classifies the soil type in Huepetuhe as primarily sandy.

Table 3. Soil texture control

Texture	Percentage	Result
Sand	%	94.84
Clay	%	5.12
Silt	%	0.04

#### 3.2 Initial and Post-Treatment soil physical parameters with iron nanoparticles

The pH, temperature and moisture levels were assessed using the 4in1 Soil survey instrument pH meter. The assessment of the electrical conductivity of the soil samples was performed with the multi-parameter Water Quality test meter C-100, revealing a conductivity of 14 uS/cm, which is equivalent to 0.014 dS/m. For the control soil, the results indicated a pH of 7.0, electrical conductivity of 0.014 dS/m and moisture content at 7.0 %. Upon applying various concentrations of iron nanoparticles and measuring after 24, 48 and 72 h, across three replicates, the pH of the soil samples remained unaffected, consistently showing a pH of 7.0.

Table 4. Physical parameters of soil samples Pre- and Post- iron nanoparticles treatment.

Dose (mg NP Fe/kg soil)	Sample code	Time (h)	pH	CE (dS/m)	% humidity
M1 (control sample)	M1	0	7	0.014	7.0
M2 (2.5 mg/kg)	M2R1	24	7	0.014	11.3
	M2R2	48	7	0.014	11.3
	M2R3	72	7	0.014	11.3
	M3R1	24	7	0.013	17.1
M3 (5 mg/kg)	M3R2	48	7	0.013	17.1
	M3R3	72	7	0.013	17.1
	M4R1	24	7	0.014	23.4
M4 (7.5 mg/kg)	M4R2	48	7	0.014	23.4
	M4R3	72	7	0.014	23.4

### 3.3 Initial and final mercury concentration in the forest soil of Huepetuhe-Madre de Dios.

The soil samples underwent analysis for mercury content following EPA 7471B standards, utilizing atomic absorption spectrometry.

The measurements of mercury for sample M2, treated with 2.5 mg/kg of iron nanoparticles per kg of soil, for sample M3 treated with 5 mg/kg of iron nanoparticles per kg of soil and for sample M4 treated with 7.5 mg/kg of iron nanoparticles per kg of soil were conducted after 24, 48 and 72 h. In the M2 sample, 18.44 mg of mercury per kg of soil was detected after 24 h, 19.22 mg of mercury per kg of soil after 48 h, and, 17.35 mg of mercury per kg after 72 h, resulting in a mercury reduction efficiency of 74.27 %. For the M3 sample, mercury levels were 58.56 mg per kg of soil after 24 h, 40.11 mg after 48 h, and 3.15 mg after 72 h, indicating a reduction efficiency of 95.33 %. Lastly, the M4 sample showed mercury concentrations of 21.31 mg per kg of soil after 24 h, 17.65 mg after 48 h, and 7.63 mg after 72 h leading to a reduction efficiency of 88.68 %.

Table 5. Efficiency results of sample

Dose (mg NP Fe/kg soil)	Sample code	Time (h)	Mercury concentration (mg/kg)	Efficiency (%)
M1 (control sample)	M1	0	67.42	100.00
M2 (2.5 mg/kg)	M2R1	24	18.44	72.65
	M2R2	48	19.22	71.49
	M2R3	72	17.35	74.27
M3 (5 mg/kg)	M3R1	24	58.56	13.14
	M3R2	48	40.11	40.51
	M3R3	72	3.15	95.33
M4 (7.5 mg/kg)	M4R1	24	21.31	68.39
	M4R2	48	17.65	73.82
	M4R3	72	7.63	88.68

Figure 1 shows a comparison of the mercury concentrations observed before and after the application of iron nanoparticles in soils over time.

Based on the data acquired, the application of nanoparticles in proportions of 2.5, 5 and 7.5 mg/kg led to mercury reduction in the soil achieving reductions of 72.3 %, 49.6 % and 77 % respectively after 72 h among the three groups studied. When compared to Vidal et al. (2010), who observed a 33.1 % reduction of mercury in the soil over four months using Guanuro, and Espinoza and Manziny (2019), who achieved an 83.2 % reduction using *Escherichia coli* in just 120 minutes; it is apparent that iron nanoparticles can rapidly decrease high mercury concentrations in a short duration.

Regarding the optimal concentration of iron nanoparticles for mercury reduction in forest soils, Boente et al. (2017) demonstrated a decrease in mercury and arsenic concentrations through the application of iron nanoparticles at a 2.5 % by weight concentration. After 72 h, mercury reduction ranged from 39 to 54 %

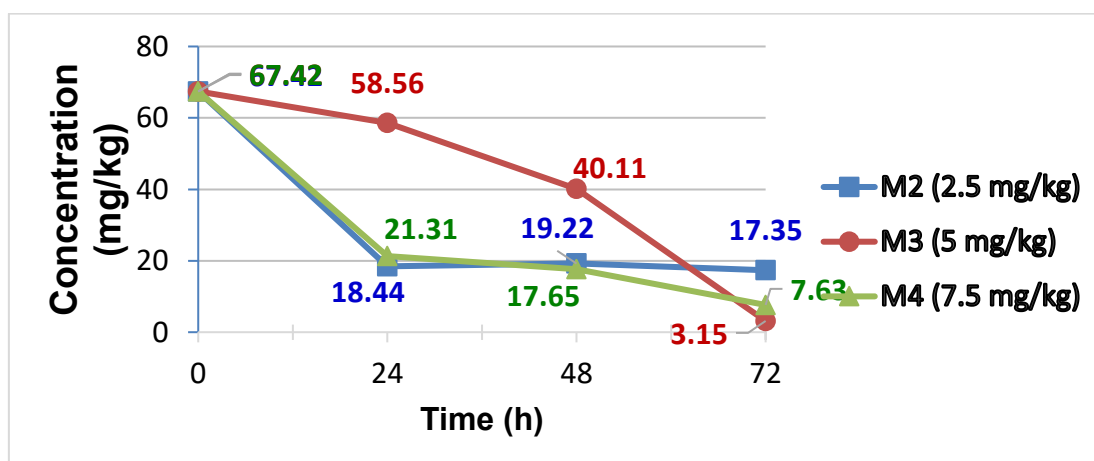


Figure 1. Concentration of Mercury vs time

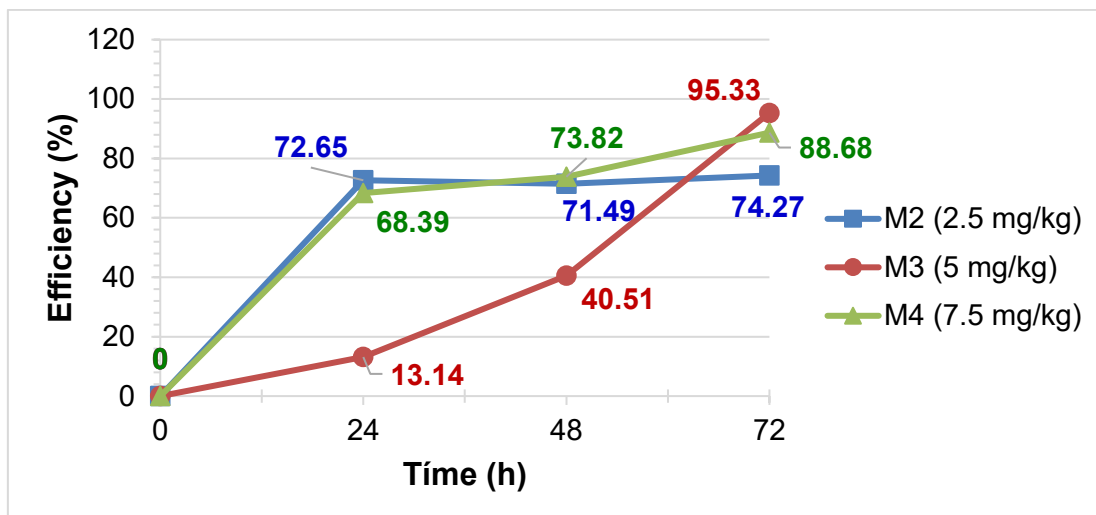


Figure 2. Mercury removal efficiency vs time

#### 4. Conclusions

The soil characteristics, specifically sandy texture, neutral pH and low organic matter have influenced the efficiency of iron nanoparticles in reducing mercury concentrations. Iron nanoparticles have proven effective at lowering mercury levels in forest soils, without causing significant alterations, as the soil's pH and electrical conductivity remained stable and there was only a slight increase in soil iron content. The effectiveness of iron nanoparticles in the presence of mercury is contingent on the dosage and treatment duration. In this case, doses of 2.5, 5 and 7.5 mg NP Fe/kg were employed, resulting in reductions of 74.27 %, 95.33 % and 88.68 % respectively after 72 h.

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