

Green Nanotechnology: Efficacy of Iron Nanoparticles in the Remediation of Soils Contaminated with Lead

Eliana Mullisaca Contreras ^a, Benito Hugo Fernandez Ochoa ^b, Máximo Cisneros Tejeira ^{c,*}, Delicias E. Natividad Huasupoma ^c, Fiorella Vanessa Guere Salazar ^d, Willam C. Santos Tello ^e, Raul Minaya Human ^c, Nestor O. Mercado Ayamamani ^b

a Universidad Nacional de Juliaca, Puno Perú.

b Universidad Nacional del Altiplano, Puno, Perú

c Universidad Nacional José Faustino Sánchez Carrión, Huacho, Perú.

d Universidad Nacional Mayor de San Marcos, Facultad de Ingeniería Industrial, Lima Perú

e Universidad Continental, Av. Alfredo Mendiola 5210 Los Olivos, Lima, Perú

f Universidad César Vallejo, AV. Alfredo Mendiola 6232, Los Olivos, Lima, Perú

mcisneros@unjfsc.edu.pe

Soil contamination by heavy metals, particularly lead (Pb), represents a critical environmental challenge that affects the quality of soils and agricultural ecosystems worldwide. This problem, caused mainly by human activities such as mining, the metallurgical industry, and inadequate waste management, has led to the accumulation of lead in the soil, reaching toxic levels that threaten human health and biodiversity. In response to this problem, nanotechnology has emerged as an innovative solution, highlighting the use of iron nanoparticles. The objective of the research was to evaluate the adsorption of Pb from soil (contaminated at a concentration of 10 mg/kg) using Fe nanoparticles obtained through green chemistry, analyzing the influence of pH (3, 4, and 6) and temperature (15, 30, and 45 °C) on the process. Fe nanoparticles were used according to a 3k factorial design. In this research, a 99.8% adsorption rate of Pb was achieved at a pH of 4 and temperatures between 15 and 45°C. Finally, it is established that the use of iron nanoparticles, obtained through green chemistry, is an alternative for the remediation of lead-contaminated soils, as it is an efficient, rapid, and environmentally friendly solution, representing a significant advance in the remediation of contaminated soils. Furthermore, nanoparticles have the advantage of being easily integrated with other bioremediation techniques.

1. Introduction

Soils contaminated with heavy metals, such as lead, cadmium, and arsenic, represent a global challenge due to their significant toxicity, persistence, and bioaccumulation in organisms. Therefore, various soil remediation methods have been established, each with operational, economic, and environmental advantages and disadvantages. Given this, nanotechnology is emerging as an innovative technology with highly efficient and environmentally friendly approaches for the remediation of contaminated soils (Dhanapal et al., 2024).

Nanoremediation has been demonstrated to be effective in the adsorption of metal compounds, with an efficiency of up to 82% in chromium-contaminated soils. Furthermore, this methodology has been found to increase phytoremediation efficiency by 30% to 40% when enzyme stimulation is used (Mathur et al., 2022). This technology, used alongside other traditional technologies, offers a sustainable approach to restoring contaminated soils, especially agricultural soils, but research is still needed to optimize dosages and assess the potential long-term effects of nanomaterials on ecosystems (Gong et al., 2018).

In the case of lead-contaminated soils, the use of Fe nanoparticles to reduce lead in soil and modify its toxicity in the environment has already been investigated (Arancibia-Miranda et al., 2014), but nanoparticles synthesized from plant extracts have other special characteristics. However, the production method and applications have not yet been studied or optimized; for example, the critical aspects requiring optimization are efficacy and stability, as bionanoparticles can be unstable under certain environmental conditions, rendering

them ineffective in the long term. It is also necessary to optimize the distribution and uniform penetration of nanoparticles into the soil, which is important, considering the soil structure that can limit their mobility, as well as the presence of other contaminants that can hinder access to more contaminated areas (Mathur et al., 2022), without forgetting that bionanoparticles can react with clays and organic matter, decreasing their efficiency or generating unwanted products (Medina-Pérez et al., 2018; Medina M et al., 2015).

Studies on the remediation of lead-contaminated soils have yielded promising results, such as: through the use of hydroxyapatite nanoparticles, Pb was immobilized in the soil, reducing its availability and mobility to promote plant growth and prevent its entry into the food chain (Lago-Vila et al., 2019); With iron nanoparticles, such as magnetite (Fe_3O_4) and hematite, soils and water containing lead were remediated with high removal efficiency at acidic pH (Singh et al., 2021); Furthermore, with iron nanoparticles synthesized through green chemistry, lead toxicity in rice and corn plants was mitigated, improving their growth and reducing oxidative stress (Maryam et al., 2024); Using zero-valent iron nanoparticles, good results were obtained in reducing Pb bioavailability in the soil, facilitating the planting of Persian maple and *Tagetes erecta* species, improving their growth and efficiency in Pb uptake (Arora et al., 2023). Studies have also shown that nanoparticles synergize with cellulosic waste in reducing the bioavailability of heavy metals such as lead and cadmium (Tafazoli et al., 2017). The mechanism of action of Fe nanoparticles in this bioremediation process is based on the adsorption of Pb ions. Furthermore, antioxidant activity in plants can be enhanced by reducing the oxidative damage caused by Pb, which improves plant growth under Pb stress conditions (Salmen and Alharbi, 2024). The advantages of using nanoparticles to achieve high efficiency in soil and water treatment lie in their high surface area-to-volume ratio, which improves the adsorption capacity and removal efficiency of heavy metals such as Pb from the soil (Castañeda-Olivera et al., 2023; Ali et al., 2024). Another advantage is that, since the nanoparticles obtained are environmentally friendly, the treatment is sustainable and environmentally friendly, as no harmful chemicals are introduced into the soil (Thilakan et al., 2022). Soil remediation with bionanoparticles also offers a certain advantage in terms of cost-effectiveness, which in the long term translates into an effective reduction in lead toxicity and improved soil health (Ali et al., 2024). In this context, given the environmental problems of many soils used for agricultural activities, currently contaminated by the use of chemicals containing heavy metals, including lead (Pb), the research aimed to determine the percentage of lead adsorption efficiency in agricultural soil samples using bionanoparticles obtained through synthesis with plant extract (quinoa). This process included tests at three different pH levels and temperatures.

2. Methodology

The biosynthesis of Fe nanoparticles was carried out with quinoa leaf extract. 100 mL of FeCl_3 (0.1 M) was added to a 250 mL Erlenmeyer flask, followed by the addition of quinoa leaf extract dropwise in a 1:1 ratio until a color change from yellow to black was observed. The resulting solution was pH-corrected to 4 with NaOH solution (0.1 M). The formation of a black precipitate was indicative of the formation of Fe nanoparticles. The solution was centrifuged at 10,000 rpm for 10 minutes and washed with an acetone-alcohol mixture (50% v/v). The solid obtained was dried at 50°C for 24 hours, yielding shiny black nanoparticles. The Fe bionanoparticles were characterized in size by Transmission Electron Microscopy (TEM) and the functional groups present were evaluated by Fourier Transform Infrared (FTIR) spectra.

3. Treatment Process

The treatment followed the process indicated in Figure 1.

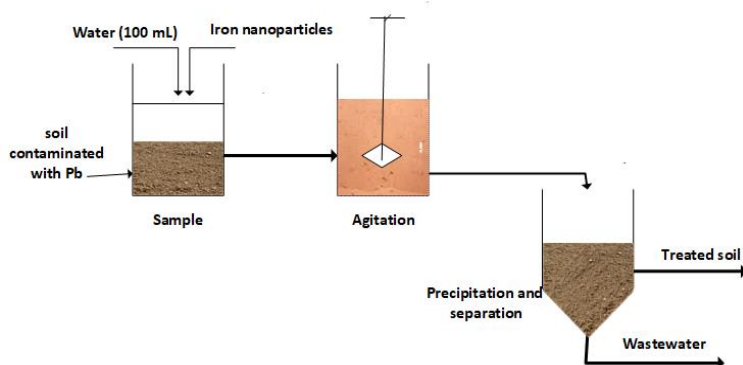


Figure 1: Treatment process

The laboratory procedure consisted of taking nine 2-g samples of lead-contaminated soil (at a Pb concentration of 10 ppm), which were placed in nine beakers. Nanoparticles were then added to each sample at a dose of 0.2 g and 100 mL of distilled water. For the study, the pH of the solution was adjusted to 2 in three beakers, to 4 in three others, and to 6 in the remaining three by adding nitric acid solution (0.1 M) and sodium hydroxide (0.1 M). In the same system, the temperature of each group of three beakers was controlled, maintaining it at 15, 30, and 45°C, respectively. Each sample was treated with stirring at 170 rpm for 30 minutes. It is worth noting that the research aimed to evaluate the optimal pH conditions (2, 4, 6) under which Fe nanoparticles could exhibit adsorption, since it is at acidic pH that greater mobility and bioavailability of lead in the soil is observed. Finally, the nine treated solutions were subjected to filtration to separate the treated soil from the solution water. The treated soil was subsequently analyzed for lead. The treated soil was subjected to inductively coupled plasma mass spectrometry (ICP-MS) analysis to quantify lead concentrations (in triplicate).

4. Results and Discussion

After sample evaluation, the following were determined:

2.2. Initial lead concentration and concentration after treatment with Fe bionanoparticles

Before and after treatments (T1, T2, T3, T4, T5, T6, T7, T8, and T9) of the lead-contaminated soil with iron nanoparticles, the soil had the lead concentration shown in Table 1. It was determined that, at pH 4, the percentage of lead adsorption is higher at temperatures of 15, 30, and 45°C.

This result establishes that the biosynthesized iron nanoparticles present significant advantages due to their high reactivity thanks to their large surface area (1 nm to 50 nm) determined by TEM, their ability to act as reducing and adsorbent agents, and their improved biocompatibility thanks to their coating with natural phenolic compounds identified by FTIR which demonstrated the presence of hydroxyl radicals (OH⁻) due to the stretching band of 3227.46 nm⁻¹. Given these results, Vasquez Guerrero, et al., (2021) states that the presence of OH⁻ ions on the surface of the nanoparticles allows the adsorption of metals, which occurs due to weak Van der Waals interactions (physisorption) or the formation of chemical bonds (chemisorption) between two compounds present (adsorbate and adsorbent) (Méndez, et al., 2019).

Table 1: Initial and final Pb concentration of the treated soil

Treatment	pH	Temperature (°C)	Initial Pb concentration (ppm)	Final Pb concentration (ppm)
T1	2	15	10	0.45
T2	4	15	10	0.02
T3	6	15	10	0.03
T4	2	30	10	0.47
T5	4	30	10	0.26
T6	6	30	10	0.04
T7	2	45	10	0.24
T8	4	45	10	0.02
T9	6	45	10	0.03

2.3. Percentage of Pb adsorption by NpFe

The values shown in Table 2 indicate a reduction range of 95.3 to 99.8% maximum in lead concentration in contaminated soils when using Fe bionanoparticles. This leads to a lead adsorption mechanism by iron nanoparticles (FeNPs) due to the presence of electrostatic charges between these nanoparticles and the lead, resulting in a reduction in the concentration of this metal in the contaminated soil.

Research indicates that the nanoparticles achieved a lead removal efficiency greater than 80% and are the most studied for the remediation of soils contaminated with heavy metals, such as cadmium (Cd), which was 100% removed (Andrade-Zavaleta et al., 2022). Wang et al. (2014) also confirm that the adsorption capacity is due to the presence of organic functional groups on the plant extract nanoparticles. The other important feature is the surface area of the nanoparticles, which increases the reaction rate (Mazarji et al., 2021), as well as the adsorption efficiency of the nanoparticles (Essien et al., 2021).

Table 2: Percentage of Fe adsorption by NpFe

Treatment	pH	Temperature (°C)	% adsorption at equilibrium
T1	2	15	95.5
T2	4	15	99.8
T3	6	15	99.7
T4	2	30	95.3
T5	4	30	97.4
T6	6	30	99.6
T7	2	45	97.6
T8	4	45	99.8
T9	6	45	99.7

When analyzing the pH of the treatments, it is observed that the highest Pb removal rate, up to 99.8%, was obtained at pH = 4 (Figure 2), therefore Shahwan et al. (2011) stated that pH is one of the most important factors in the adsorption processes, since it promotes the solubility of the metal and generates the formation of hydroxyl radicals in the nanoparticles. Both processes allow the metal to bind to the surface of the nanoparticle through electrostatic interaction (Yang et al., 2019).

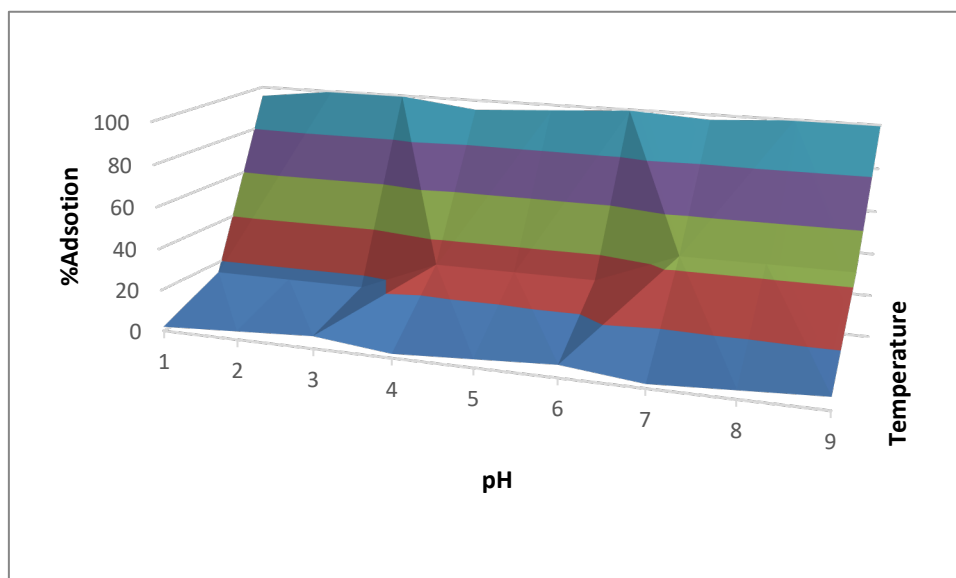


Figure 2: Graphs adsorption trends as a function of pH and temperature

Statistical analysis of variance (ANOVA) showed that pH is a significant factor (p -value of $0.0138 < 0.05$), see Table 3. The adsorption mechanisms of lead on the surface of Fe nanoparticles biosynthesized with quinoa leaf extract are due to the presence of carboxyl (-COOH) and hydroxyl (-OH) functional groups from the phenolic compounds of quinoa (identified by FTIR). The functional groups present on the surface of the nanoparticles are negatively charged in acidic media, while lead undergoes protonation (Dobrosz-Gómez et al., 2018), causing a union between them by means of electrostatic interactions (Arshadi et al., 2014), leading to the formation of chelating agents. This result is similar to that obtained by Pavan Kumar et al. (2020), in whose study he used nanoparticles biosynthesized with *M. olifeira* at pH = 5 and was able to reduce the Pb concentration through adsorption processes.

Table 3: Analysis of variance of pH and temperature of the Pb adsorption process

Source of variation	Degrees of Freedom	Sum of Squares	Mean Square	Value-F	p-value (PR(>F))
p H	1	4.797204	4.797204	27.06694	0.0138
Temperature	1	0.165668	0.16566	0.93473	0.404951
pH ²	1	0.64942	0.64942	3.664179	0.151498
Temperature ²	1	0.796743	0.796743	4.495408	0.124154
pH: temperature	1	0.25	0.25	1.410558	0.320428
Residual	3	0.531704	0.177235	---	---

Regarding temperature, variable results were obtained at the three controlled values (15, 30, and 45 °C), indicating that its influence was relative and without significant effects (see the statistical result in Table 3). This result is consistent with the research by Al-Senani and Al-Fawzan (2018), who found adsorption percentages between 25 and 60 °C, and indicate that adsorption is due to the nature of the adsorbent molecules and not to temperature. This indicates that temperature is likely to produce an increase in active sites with greater interaction strength between the adsorbent and the adsorbate, but that it may favor the diffusion of the adsorbate into the solution and decrease adsorption (Eduardo-Román, 2021). In an investigation on mercury adsorption with copper nanoparticles, it was reported that increasing the temperature resulted in lower adsorption, which infers that mercury diffusion for adsorption occurred at low temperature, the optimum temperature in this case being 20 °C (Fakhri, 2015).

5. Conclusions

Calculations show that nanoparticles synthesized from plant extract increase the percentage of lead adsorption by up to 99.8% in agricultural soil contaminated with this heavy metal. This result was obtained at a pH of 4 and temperatures ranging from 15 to 45°C. pH is determined to be a fundamental and significant parameter in the lead adsorption process in soils. Furthermore, it was developed that the special characteristics of iron bionanoparticles, which present organic functional groups, promote greater lead adsorption efficiency. Therefore, from an environmental perspective, bionanoparticles stand out for their low residual toxicity and ecological compatibility, unlike other chemical polluting methods. However, further research is required to determine whether they significantly alter some soil properties such as pH, as well as whether they promote plant growth. It was primarily determined that their use immobilizes metals in the soil matrix, limiting the side effects on ecosystems.

Acknowledgments

We express our gratitude to the University of Juliaca for the facilities provided for the use of laboratory equipment.

References

- Al-Senani G. M., and Al-Fawzan F. F., 2018, Adsorption study of heavy metal ions from aqueous solution by nanoparticle of wild herbs, *Egyptian Journal of Aquatic Research*, 44(3), 187–194. <doi.org/10.1016/j.ejar.2018.07.006>
- Andrade-Zavaleta K., Chacon-Laiza Y., Asmat-Campos D., and Raquel-Checca N., 2022, Green Synthesis of Superparamagnetic Iron Oxide Nanoparticles with Eucalyptus globulus Extract and Their Application in the Removal of Heavy Metals from Agricultural Soil, *Molecules*, 27(4), 1–25. <doi.org/10.3390/molecules27041367>
- Arancibia-Miranda N., Baltazar S. E., García A., Romero A. H., Rubio M. A. and Altbir D., 2014, Lead removal by nano-scale zero valent iron: Surface analysis and pH effect, *Materials Research Bulletin*, 59, 341–348. <doi.org/10.1016/j.materresbull.2014.07.045>
- Ali S., Naseer S., Rehman M., Wei Z., 2024, Recent trends and sources of lead toxicity: a review of state-of-the-art nano-remediation strategies, *Journal of Nanoparticle Research* 26,
- Arora D., Arora A., Bala R., Panghal V., Kumar S., 2023, Enhancement in Phytoremediation Efficiency of *Tagetes erecta* with the Application of Nano-scale Zero Valent Iron (nZVI) for the Restoration of Lead Contaminated Soil: An Approach Toward Sustainability, *Water, Air, and Soil Pollution*, 234. <doi.org/10.1007/s11270-023-06540-0>

- Castañeda-Olivera C.A., Guadalupe Sandoval G.K., Cabello Torres R.J., Acosta Suasnabar E.H., Lzarzaburu Aguinaga D.A., Merma, A.G., 2023, Systematic Review and Meta-analysis on the Use of Metal Nanoparticles in the Remediation of As and Pb Contaminated Soils, *Chemical Engineering Transactions* 101, 91–96, <doi.org/10.3303/CET23101016>
- Dhanapal A.R., Thiruvengadam M., Vairavanathan J., Venkidasam B., Easwaran M., Ghorbanpour M., 2024, Nanotechnology Approaches for the Remediation of Agricultural Polluted Soils, *ACS Omega* 9, 13522–13533. <doi.org/10.1021/acsomega.3c09776>
- Eduardo Román G., 2021, Estudio computacional de la estructura y reactividad de materiales porosos y su interacción con moléculas de interés farmacéutico.
- Essien E. A., Kavaz D., and Solomon M. M., 2018, Olive leaves extract mediated zero-valent iron nanoparticles: synthesis, characterization, and assessment as adsorbent for nickel (II) ions in aqueous medium, *Chemical Engineering Communications*, 205(11), 1568–1582, <doi.org/10.1080/00986445.2018.1461089>
- Fakhri A., 2015, Investigation of mercury (II) adsorption from aqueous solution onto copper oxide nanoparticles: Optimization using response surface methodology, *Process Safety and Environmental Protection*, 93(Ii), 1–8, <doi.org/10.1016/j.psep.2014.06.003>
- Gong X., Huang D., Liu Y., Peng Z., Zeng G., Xu P., Cheng M., Wang R., Wan J., 2018, Remediation of contaminated soils by biotechnology with nanomaterials: bio-behavior, applications, and perspectives, *Crit Rev Biotechnol* 38, 455–468, <doi.org/10.1080/07388551.2017.1368446>
- Lago-Vila M., Rodríguez-Seijo A., Vega F.A., Arenas-Lago D., 2019, Phytotoxicity assays with hydroxyapatite nanoparticles lead the way to recover firing range soils, *Science of the Total Environment* 690, 1151–1161. <doi.org/10.1016/j.scitotenv.2019.06.496>
- Maryam H., Rizwan M., Masood N., Waseem M., Ahmed T., Qayyum M.F., Zia-ur-Rehman M., Aziz H., 2024. Mitigating lead (Pb) toxicity in Zea mays (L.) plants using green synthesized iron oxide nanoparticles, *South African Journal of Botany* 175, 657–668, <doi.org/10.1016/j.sajb.2024.10.047>
- Mathur S., Singh, D., Ranjan, R., 2022. Remediation of heavy metal(loid) contaminated soil through green nanotechnology. *Front. Sustain. Food Syst.* 6, <doi.org/10.3389/fsufs.2022.932424>
- Medina M, M.E., Galván R, L.E., Reyes G, R.E., 2015, Las nanopartículas y el medio ambiente, *Universidad, Ciencia y Tecnología*, 19, 49–58.
- Medina-Pérez G., Fernández-Luqueño F., Medina-Pérez G., Fernández-Luqueño F., 2018. Nanotoxicidad: retos y oportunidades. *Mundo nano, Revista interdisciplinaria en nanociencias y nanotecnología* 11, 7–16,
- Salmen S.H., Alharbi S.A., 2024, Mitigating Pb-induced oxidative stress in rice plants by cerium oxide and iron oxide nanoparticles. *South African Journal of Botany* 172, 544–555, <doi.org/10.1016/j.sajb.2024.07.039>
- Singh A., Chaudhary S., Dehiya B.S., 2021, Fast removal of heavy metals from water and soil samples using magnetic Fe₃O₄ nanoparticles, *Environmental Science and Pollution Research* 28, 3942–3952.
- Tafazoli M., Hojjati S.M., Biparva P., Kooch Y., Lamersdorf N., 2017, Reduction of soil heavy metal bioavailability by nanoparticles and cellulosic wastes improved the biomass of tree seedlings, *Journal of Plant Nutrition and Soil Science* 180, 683–693, <doi.org/10.1002/jpln.201700204>
- Thilakan D., Patankar J., Khadtare S., Wagh N.S., Lakkakula J., El-Hady K.M., Islam S., Islam M.R., Khan M.S., Alafaleq N.O., Tarique M., 2022, Plant-Derived Iron Nanoparticles for Removal of Heavy Metals. *International Journal of Chemical Engineering* 2022, <doi.org/10.1155/2022/1517849>
- Mazarji M., Minkina, T., Sushkova S., Mandzhieva S., Bidhendi G. N., Barakhov A., & Bhatnagar A. (2021), Effect of nanomaterials on remediation of polycyclic aromatic hydrocarbons-contaminated soils: A review. *Journal of Environmental Management*, 284(January), <doi.org/10.1016/j.jenvman.2021.112023>.
- Pavan Kumar G., Shivalkar S., and Banerjee S., 2020, Synthesis of M. oleifera leaf extract capped magnetic nanoparticles for effective lead [Pb (II)] removal from solution: Kinetics, isotherm and reusability study, *Journal of Molecular Liquids*, 305, <doi.org/10.1016/j.molliq.2020.112811>
- Shahwan T., Abu Sirriah S., Nairat M., Boyaci E., Eroğlu A. E., Scott T. B., and Hallam K. R., 2011, Green synthesis of iron nanoparticles and their application as a Fenton-like catalyst for the degradation of aqueous cationic and anionic dyes. *Chemical Engineering Journal*, 172(1), 258–266,
- Vázquez-Guerrero A., Cortés-Martínez R., Alfaro-Cuevas-villanueva R., Rivera-Muñoz E. M., and Huirache-Acuña R., 2021, CD(II) and PB(II) adsorption using a composite obtained from moringa oleifera lam. cellulose nanofibrils impregnated with iron nanoparticles, *Water (Switzerland)*, 13(1).
- Yan W., Herzing A. A., Kiely C. J., and Zhang W. X., 2010, Nanoscale zero-valent iron (nZVI): Aspects of the core-shell structure and reactions with inorganic species in water, *Journal of Contaminant Hydrology*, 118(3–4), 96–104, <doi.org/10.1016/j.jconhyd.2010.09.003>
- Wang T., Jin X., Chen Z., Megharaj M., and Naidu R., 2014, Green synthesis of Fe nanoparticles using eucalyptus leaf extracts for treatment of eutrophic wastewater, *Science of the Total Environment*, 466–467, 210–213, <doi.org/10.1016/j.scitotenv.2013.07.022>.