Synthesis of Novel Iron-based Nanomaterials for the Removal of the Antibiotic Ciprofloxacin from Water

オマル エイ エム ファリオウナ

https://hdl.handle.net/2324/6787659

出版情報：Kyushu University, 2022, 博士（学術）, 課程博士
バージョン：

（様式３）Form 3

氏　　名　：OMAR A. M. FALYOUNA

Name

論 文 名　：Synthesis of Novel Iron-based Nanomaterials for the Removal of the Antibiotic Ciprofloxacin from Water （水から抗生物質シプロフロキサシンを除去するための新しい鉄ナノ材料の合成）

Title

区　　分　：甲

Category

論 文 内 容 の 要 旨

Thesis Summary

The persisting occurrence of ciprofloxacin (CIP) and other antibiotics in our limited water resources has fatal health and environmental consequences. This research adopts zerovalent iron nanoparticles (Fe^0) as an excellent remedial agent to propose novel iron-based nanomaterials with unique properties to efficiently remove CIP from water.

<u>The first project</u> focused on coating Fe^0 nanoparticles with a shell of magnesium hydroxide [$Mg(OH)_2$] to overcome the shortcomings of Fe^0 nanoparticles and promote the remediation of CIP from aquatic environments. The outcomes of the batch experiments demonstrated that encapsulating Fe^0 nanoparticles by $Mg(OH)_2$ layer with a [$Mg(OH)_2/Fe^0$] mass ratio of 5% boosted the removal efficiency of CIP from 41.76% to 96.31%. Moreover, the optimization process for the treatment parameters revealed that CIP-polluted water was optimally treated by Mg/Fe^0 nanoparticles under the following conditions: [Mg/Fe^0] = 0.5 g L^{-1}, [CIP] = 100 mg L^{-1}, initial pH = 3 – 11, temperature = 25 ℃, and treatment time = 60 min. Also, the desorption experiments confirmed that the removal of CIP by Mg/Fe^0 nanoparticles was completely governed by chemical and physical adsorption. Furthermore, the proposed regeneration protocol succeeded in recycling Mg/Fe^0 nanoparticles for five consecutive treatment cycles with removal efficiencies higher than 95%.

<u>The second project</u> aimed to enhance the reactivity of Fe^0 nanoparticles in eliminating CIP from aqueous solutions by adding the organic ligand oxalate. The outcomes of the batch experiments showed that adding 0.3 mM of oxalate to Fe^0 nanoparticles increased the adsorption of CIP from 45.05% to 95.74%. Moreover, the optimal removal of CIP by (Fe^0/oxalate) nanoparticles was attained under the following circumstances: [Fe^0] = 0.3 g L^{-1}, [Oxalate] = 0.3 mM, initial pH = 7, temperature = 25 ℃, and treatment time = 30 min. Similar to Mg/Fe^0 nanoparticles, the desorption experiments emphasized that the remediation of CIP by (Fe^0/oxalate) nanoparticles was fully controlled by adsorption instead of oxidation. In addition, the results proved that adding oxalate is a cost-effective approach to improve the reactivity of Fe^0 nanoparticles as the treatment cost of 1 L of CIP-polluted water notably declined from ¥65.716 (Fe^0 alone) to ¥29.124 (Fe^0/oxalate). It is important to highlight that the performance of Mg/Fe^0 and (Fe^0/oxalate) nanoparticles in remediating CIP-polluted water are reported for the first time in this study. Also, their outstanding competence is promising and has great potential in tackling CIP contamination in actual polluted waters.

The framework of the Ph.D. thesis consists of five main chapters as follows:

Chapter 1 provides background information about water pollution by antibiotics, particularly the recalcitrant ciprofloxacin. In addition, it discusses the occurrence and fate of ciprofloxacin in the environment and its health threats and ecotoxicity. Moreover, chapter 1 covers the state-of-the-art treatment technologies

for CIP pollution. Also, it includes an overview about zerovalent iron nanoparticles, their features and defects, their modification techniques, and their applications in CIP remediation from polluted waters. Finally, chapter 1 summarizes the aim and objectives of the Ph.D. research projects.

Chapter 2 summarizes the list of chemicals utilized in all experiments. Moreover, it describes the procedures to synthesize various kinds of iron-based nanomaterials in detail. Also, it explains the concepts of the characterization techniques employed to reveal the physicochemical properties of the iron-based nanomaterials. In addition, chapter 2 clarifies the specifications of each component of the prototype lab-scale treatment system. Furthermore, it epitomizes the experimental plan for the research work, the procedures for conducting the batch experiments, and the analytical instruments used in the laboratory. In addition, it clarifies the concept of kinetics, isotherm, and thermodynamic modeling for the adsorption of CIP by iron-based nanomaterials.

Chapter 3 covers the outcomes of remediating CIP-polluted water by Mg/Fe^0 nanoparticles. In detail, chapter 3 reveals the physicochemical properties of Mg/Fe^0 nanoparticles, such as external morphology, surface elemental composition, crystallinity, etc. It also discusses the effectiveness of Mg/Fe^0 nanoparticles in eliminating CIP from water under different treatment conditions, for example, Mg/Fe^0 dosage (g L^{-1}), initial pH of the polluted solution, reaction temperature (℃), and initial CIP concentration (mg L^{-1}). Moreover, the removal mechanism of CIP by Mg/Fe^0 nanoparticles was illustrated in this chapter. In addition, chapter 3 provides a regeneration and recycling protocol for Mg/Fe^0 nanoparticles. Moreover, chapter 3 demonstrates the adequacy of utilizing Mg/Fe^0 nanoparticles in a prototype treatment system to remediate large volumes of CIP-polluted water. Also, chapter 3 illustrates the appropriate storage option for Mg/Fe^0 nanoparticles for one month. Finally, chapter 3 includes an economic assessment of using Mg/Fe^0 nanoparticles for environmental and remediation applications.

Chapter 4 presents the results of removing CIP from aqueous solutions by (Fe^0/oxalate) nanoparticles. In detail, it elucidates physiochemical changes of Fe^0 nanoparticles before and after the reaction with different concentrations of oxalate in water. Also, it explains the impact of various parameters, for instance, oxalate concentration (mM), Fe^0 nanoparticle's dosage (g L^{-1}), initial pH of polluted water, reaction temperature (℃), and initial concentration of CIP in water (mg L^{-1}), on the competence of (Fe^0/oxalate) nanoparticles to clean up CIP-polluted solutions. Moreover, it discloses the enhancement mechanism of adding oxalate to Fe^0 nanoparticles toward removing CIP from water. Furthermore, chapter 4 investigates the influence of water matrix, such as ionic strength, dissolved organic matters, and coexisting ions (e.g., cations and anions), on the remediation efficiency of (Fe^0/oxalate) nanoparticles. Similar to Mg/Fe^0 nanoparticles, chapter 4 suggests regeneration and recycling procedures for reusing (Fe^0/oxalate) nanoparticles for multiple treatment processes. Finally, chapter 4 provides a cost estimation for the treatment of CIP-polluted water by (Fe^0/oxalate) nanoparticles.

Finally, **Chapter 5** highlights each research project's significant findings and conclusions. In addition, it summarizes the recommendations for prospective researchers. Finally, chapter 5 includes possible research ideas for future work.