frontiers | Frontiers in Environmental Science

ORIGINAL RESEARCH
published: 13 June 2022
doi: 10.3389/fenvs.2022.915465

Cu/Fe Bimetallic Treatment Performance on Organophosphorus Pesticides

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Typical organophosphorus pesticides, such as glyphosate, trichlorfon, and ethephon, are widely used nowadays, and the treatment of their production wastewater is difficult to achieve by conventional water treatment methods. A Cu/Fe bimetallic system has been proposed as a viable technology to treat toxic and refractory pollutants. The performance of the system with different pH, Cu/Fe molar ratios, Cu/Fe dosages, and initial glyphosate concentrations was analyzed to investigate the operational factors affecting glyphosate removal by the Cu/Fe bimetallic system. Acidic pH (2.0), 250 g/L Cu/Fe dosage, 0.25% Cu/Fe, and 60 mg/L initial glyphosate concentration were the appropriate conditions for glyphosate removal, in which the efficiency of the system was in accordance with the pseudo–second-order kinetic model. Under this condition, the removal efficiencies of total phosphorus and total organic carbon reached 99 and 65%, respectively. The Fe/Cu bimetal surface was characterized by scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The optimal conditions for glyphosate decomposition were applied to the treatment of trichlorfon and ethephon. The removal efficiency of the system was poor, but its toxicity to luminescent bacteria Q67 was remarkably reduced.

Keywords: organophosphorus pesticides, Cu/Fe bimetallic, glyphosate, reduction, operational factors, toxicity

Edited by:
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Specialty section:
This article was submitted to Water and Wastewater Management, a section of the journal Frontiers in Environmental Science

Received: *08 April 2022*
Accepted: *19 May 2022*
Published: *13 June 2022*

Citation:
Wu X, Wang Y, Xu J and Wang H (2022) Cu/Fe Bimetallic Treatment Performance on Organophosphorus Pesticides. Front. Environ. Sci. 10:915465. doi: 10.3389/fenvs.2022.915465

1 INTRODUCTION

Organophosphorus pesticides are widely used in agricultural production (Fu et al., 2022) due to low toxicity and high efficiency. According to the roles, they are categorized into herbicides, insecticides, plant growth regulators, and others. Commonly used glyphosate, trichlorfon and ethephon, are broad-spectrum and non-selective typical organophosphorus pesticides (Tian et al., 2016; Dubois et al., 2018), which are widely used in agriculture, forestry, orchards, and gardens. For example, glyphosate can effectively control 76 of the world's 78 harmful weeds (Wang et al., 2006; Hansen and Roslev, 2016). However, due to the excessive use of organophosphorus pesticides in the environment, some harmful effects have been reported for plants, animals and agricultural production. Besides, they can be transferred into water environment through runoff resulting their frequent detection in the aqueous environment (Ajiboye et al., 2022). The concentration of glyphosate in natural water bodies were reported to range from 0.01 to 0.7 mg/L, and it may reach 1.7–5.2 mg/L in worst-case scenarios such as direct application or accidental spills (Peruzzo et al., 2008; Annett et al., 2014). The applied concentration of trichlorfon in ponds to eradicate ectoparasites range between 0.1 and

1.0 mg/L (Ma et al., 2018). Ethephon concentrations in the aqueous environment are rarely reported, but the residual level in plant origin samples reached as high as 4.5 mg/kg (Gormez et al., 2021).

Methods for treating wastewater from organophosphorus pesticide production include physicochemical treatment, chemical oxidation and biological treatment. For example, porous materials such as activated carbon (Mailler et al., 2016) and clay-biochar composite (Rallet et al., 2022) are used in the adsorption treatment of glyphosate. Besides, glyphosate and its degradation products, including aminomethylphosphonic acid, were reported to be adsorbed to mineral surface through coordination of both the carboxyl and phosphonic group (Khoury et al., 2010). Degradation of glyphosate is driven by primarily oxidation using minerals (Paudel et al., 2015), mineral-activated carbon composite (Cui et al., 2012), UV–photo-oxidation (Jaisi et al., 2016) or electrochemical degradation (Aquino Neto and de Andrade, 2009). The degradation pathways include the C–N bond cleavage pathway with aminomethylphosphonic acid as the main product, and the C–P bond cleavage pathway with the formation of sarcosine and glycine accompanied by phosphoric acid formation (Grandcoin et al., 2017; la Cecilia and Maggi, 2018).

However, existing methods are limited due to the complex composition of organophosphorus pesticide production wastewater, which contains organophosphorus by-products and metal ions (Saleh et al., 2020). Biochemical treatment is ineffective because of the presence of toxic and non-biodegradable components in the wastewater (Badawy et al., 2006). Physicochemical treatment, such as adsorption method, requires an acidic environment, and existing adsorbents have no selectivity for pesticides. The treatment effect is likely affected by the competitive effect with metal ions and anions, such as PO_4^{3-} and NO_3^- (Feng et al., 2020; Mostafa et al., 2021). The coagulation sedimentation method has high operating cost, produces a large amount of sludge for disposal, and is only used in the pretreatment process of organophosphorus pesticide wastewater. Advanced oxidation technology, such as Fenton method, has high degradation rate and simple operation, but its use is limited by acidic conditions, which increases the cost of water treatment. Moreover, Fenton method produces a large amount of iron-containing sludge (Ameta et al., 2018).

The Cu/Fe bimetallic system is constructed using copper as the inert electrode and plated on the surface of zero-value iron to form a galvanic battery (Xiong et al., 2017). This system is a cost-effective technology (Shahmahdi et al., 2020) with adaptability to a wider pH range (Lai et al., 2014). The Cu/Fe bimetallic system has been used to treat toxic and refractory pollutants (Xiong et al., 2015), including azo dye (Trujillo–Reyes et al., 2012), organochlorine compound (Ghauch and Tuqan, 2008; Chen et al., 2018), nitrobenzene and aromatic compounds (Lai et al., 2014), and nitrate (Shubair et al., 2018). The influencing factors of the system's operation, including Fe^0 dosage, initial pH, initial pollutant concentration, temperature, and the Cu/Fe molar ratio have been studied and reported by previous researches (Lai et al., 2016; Huong et al., 2021). The mechanism of removal by the Cu/Fe bimetallic system is complex and includes the direct reduction by Fe^0; the indirect reduction by •H generated from H^+ at the cathode surface (Xiong et al., 2017); and the adsorption, flocculation, and precipitation of iron hydroxides (Huong et al., 2021).

The feasibility of removing organophosphorus pesticides remains a challenge for Cu/Fe bimetallic system. In this work, a Cu/Fe bimetallic system with optimum operating parameters was established to realize efficient removal of glyphosate. Treatment performance and toxicity reduction were evaluated by treating trichlorfon and ethephon in the same system.

2 MATERIALS AND METHODS

2.1 Reagents

Glyphosate (analytical grade, J&K Scientific), ethephon (40%; Shanghai HuaYi Group HuaYuan Chemical Industry Co., Ltd.), and trichlorfon (30%, Shuyang Guoxiang Seedling and Gardening Farm) were separately dissolved and diluted into different concentrations to serve as the artificial pesticide wastewater. All the chemical reagents used were analytical grade or above. Ultrapure water (18.2 MΩ cm) was used for dissolution and dilution in the experiments.

2.2 Cu/Fe Bimetallic Material Preparation and Characterization

Waste iron shavings are usually selected as zero-value iron materials owing to its good economic benefit (Shahmahdi et al., 2020). In this study, iron shavings were obtained from 20CrMoTi steel of a metal machinery plant. It was been pretreated to remove the oil and other impurities on the surface according to Li (Li et al., 2018). The modified iron shavings were added into $CuSO_4$ solution according to desired Cu/Fe molar ratios. Then the iron shavings after pretreatment were added into CuSO4 solution according to the desired Cu/Fe molar ratios to form the Cu/Fe bimetallic. Then it was freeze-dried under vacuum to use.

The Cu/Fe bimetal was freeze-dried under vacuum. Scanning electron microscopy (SEM) images were obtained using a field-emission scanning electron microscope (Jeol JSM-6360LV, Japan) to visually observe the changes in surface morphology. Electron-dispersive X-ray spectroscopy (EDS) images made by an energy-dispersive spectrometer (EDAX, Falcon, United States) was used to analyze the main element composition of the surface of the iron fillers. X-ray diffraction (XRD) images made by a powder diffractometer (Bruker, D8 Advance, Germany) was used to analyze the changes in the crystallinity of the surface of the iron fillers. Fourier transform infrared spectrometry (FTIR; Thermo Electron, Nicolet 5700, United States) was used to analyze the bonding state of the groups when glyphosate or its degradation products were complexed with the metal.

2.3 Experimental Procedures

2.3.1 Optimization of the Cu/Fe Bimetallic System

Different dosages of Cu/Fe (62.5, 125, 187.5, and 250 g/L) bimetallic material with the desired Cu/Fe molar ratio (0.1,

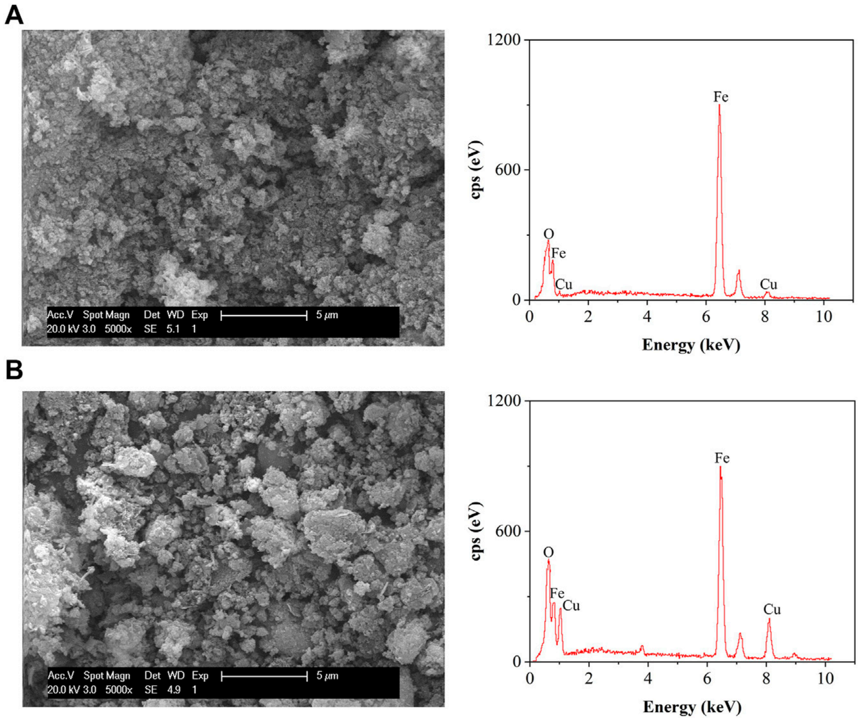


FIGURE 1 | SEM and EDS images of the Cu/Fe bimetallic system **(A)** before and **(B)** after reaction.

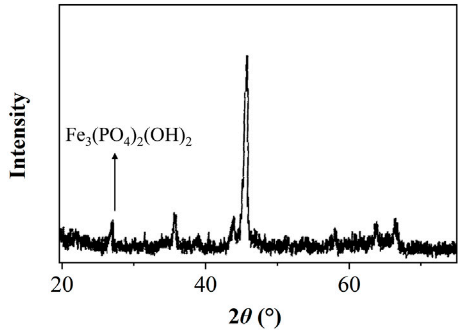


FIGURE 2 | XRD results of the Cu/Fe bimetallic surface after reaction.

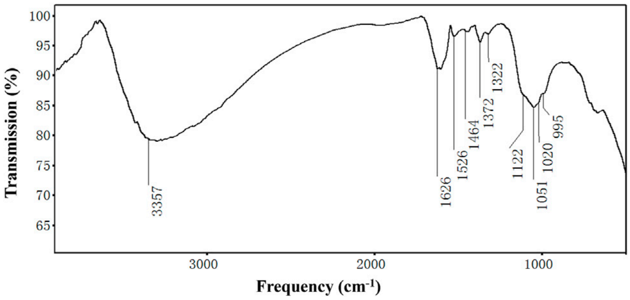


FIGURE 3 | FTIR image of the precipitate in the Cu/Fe bimetallic system.

0.25, and 0.5%) were added to the glyphosate solution (initial concentrations of 30, 60, 90, and 120 mg/L). The initial solution pH was adjusted to 2.0, 7.0, and 12.0 using H_2SO_4 (1.0 mol/L) and NaOH (1.0 mol/L). Experiments were conducted in a 500 ml conical flask at 120 rpm and 25°C for 240 min. Three replicates of samples were collected at 0, 15, 30, 60, 120, 180, and 240 min and filtered by 0.45 μm polyethersulfone syringe filter for analysis.

2.3.2 Treatment of Other Pesticides by the Cu/Fe Bimetallic System

Based on the study of the operational factors, the pH, Cu/Fe dosage, and Cu/Fe molar ratio with the best treatment performance were selected to treat ethephon solution with a mass fraction of 2% and trichlorfon solution with a mass fraction of 3%. The shaking conditions and duration were the same as those for glyphosate treatment.

2.4 Analytical Methods

Total phosphorus (TP) was determined by alkaline potassium persulfate digestion and molybdenum antimony anti-spectrophotometry. Total iron and ferrous iron ions were determined by o-phenanthroline spectrophotometry. Total organic carbon (TOC) was determined by a TOC analyzer (Tsushima, TOC-L CPH CN200, Japan).

Glyphosate was mostly measured by high-performance liquid chromatography (HPLC) with a derivatization protocol (Pimenta et al., 2020), which used phosphate or borate buffer solution (Nedelkoska and Low, 2004; Kim

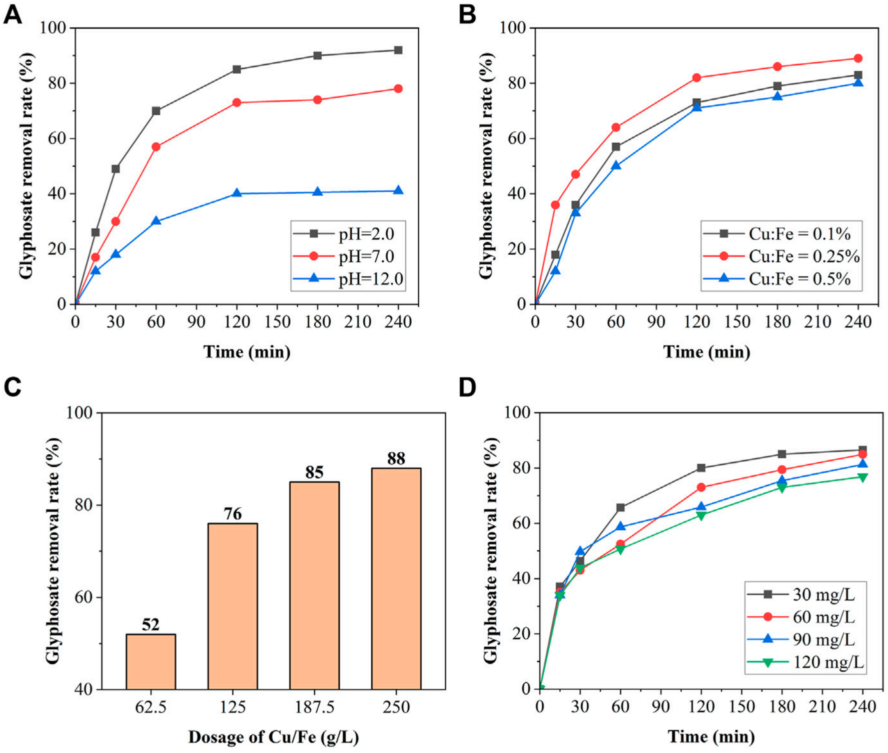


FIGURE 4 | Glyphosate removal efficiency of the Cu/Fe bimetallic system with different **(A)** initial pH, **(B)** Cu/Fe molar ratios, **(C)** Cu/Fe dosages, and **(D)** initial glyphosate concentrations.

et al., 2007). However, in this study, Cu/Fe bimetallic was used to treat glyphosate, and a large amount of dissolved iron ions would be generated during the experiment. Phosphate forms precipitation with iron ions, which will block the column if not pretreated. Therefore, ion chromatography (Zhu et al., 1999) was selected for glyphosate determination in this study using the following chromatography conditions: column, Dionex ICS-900; inhibition current, 84 mA; mobile phase, 28 mmol/L NaOH; flow rate, 1.0 ml/min.

2.5 Toxicity Test

Luminescent bacteria can serve as good indicators for toxic substrates and have been widely used in detecting pesticide residues (Jian et al., 2017). Luminescence inhibition assays were conducted using *Vibrio qinghaiensis* sp. Q67 as the luminescent bacteria to investigate whether the biodegradability of pesticide wastewater improved after treatment. Twelve concentration gradients were designed as geometric series with a dilution factor of 0.7 (Liu et al., 2009). The relative light units of various concentrations of pesticide and controls to Q67 were determined on a Veritas™ luminometer (Turner BioSystems, Inc., United States). The toxicity of a treatment to Q67 was expressed as an inhibition ratio of bioluminescence, which is calculated as follows:

$$\textbf{Inhibition ratio} = \frac{I_0 - I}{I_0} \times 100\% \tag{1}$$

where I_0 is an average of the relative light units of the controls (distilled water) and I is an average of the relative light units of the treatments with an identical concentration of pesticide.

3 RESULTS AND DISCUSSION

3.1 Characterization of Cu/Fe Bimetal

The SEM image (**Figure 1**) shows that the surface of the Cu/Fe bimetal before the reaction was relatively smooth with smaller protruding particles, more uniform particle size, and fewer pores and cracks. Similar results were observed in other studies (Bransfield et al., 2007; Lai et al., 2014). The content of metallic iron was 83.2%, and the content of oxygen was very little. After the reaction, many protrusions were formed on the surface of the Cu/Fe bimetal, and the small particles aggregated into clumps of different sizes, making the surface rough and uneven. The content of metallic iron was 73.02%, and the content of oxygen rose up to 22.02%. Therefore, a large amount of iron oxides/hydroxides were produced during the reaction and covered the metal iron surface.

The XRD results of the Cu/Fe bimetallic surface after the reaction are shown in **Figure 2**. The crystal phases of oxides on the surface of the Cu/Fe bimetal include the crystal structures of magnetite, hematite, goethite, and leucoside. The formation of $Fe_3(PO_4)_2(OH)_2$ was detected, which proved that glyphosate degradation underwent the C–P bond cleavage pathway as

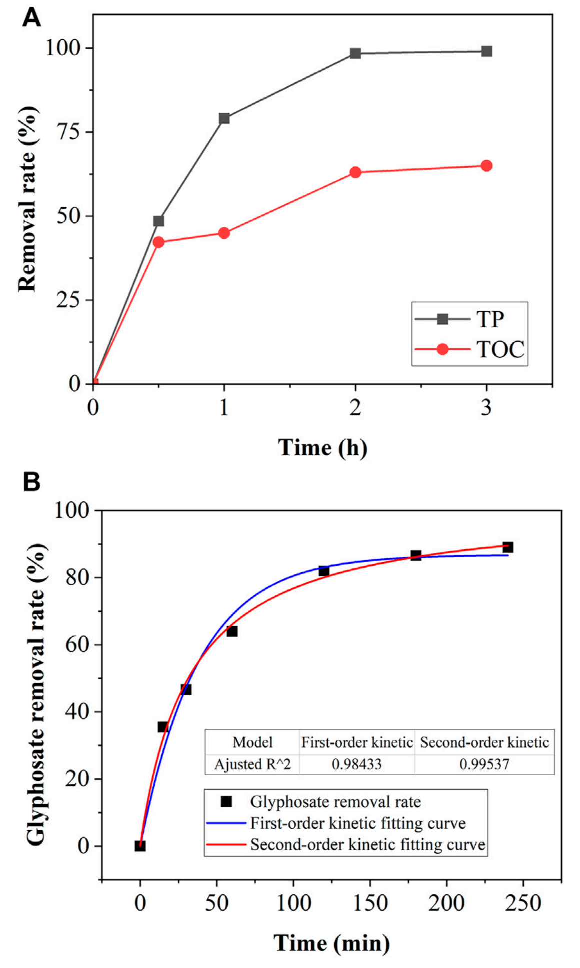


FIGURE 5 | (A) TOC and TP changes **(B)** Reaction kinetic curve fitting in Cu/Fe bimetallic system treating glyphosate.

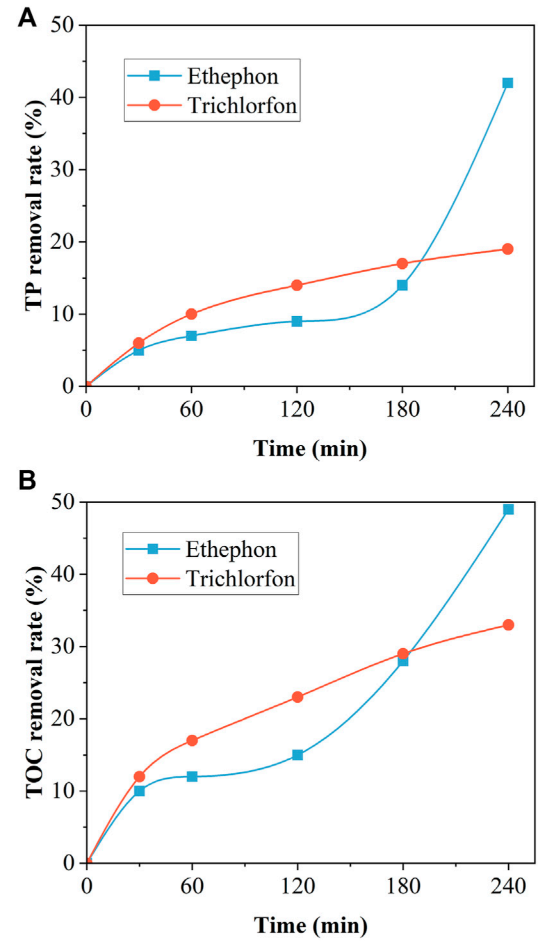


FIGURE 7 | (A) TP and **(B)** TOC removal from two organophosphorus pesticides by the Cu/Fe bimetallic system.

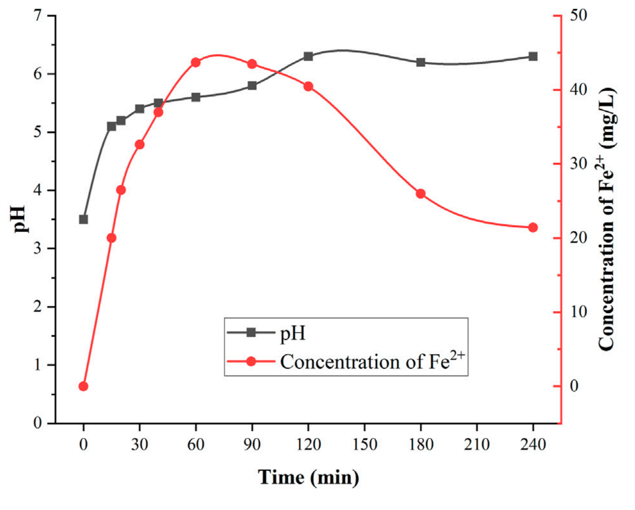
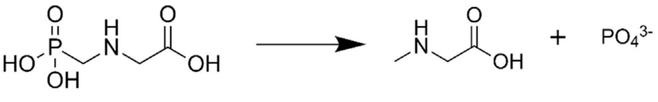


FIGURE 6 | Changes in pH and Fe^{2+} concentration during the reaction.

shown in Equation 2, and the reaction was made go forwards due to the formation of precipitation of Fe(II, III) and PO_4^{3-}(Priambodo et al., 2017).

Equation 2 Degradation of glyphosate by C–P bond cleavage



(2)

$$Fe^{2+} + PO_4^{3-} \rightarrow Fe_3(PO_4)_2, K_{sp} = 10^{-3.8} \quad (3)$$

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4, K_{sp} = 10^{-29} \quad (4)$$

Figure 3 shows the infrared spectrum of the precipitate after the reaction of the Cu/Fe bimetallic system. The high-frequency region (~3,300 cm^{-1}) is the stretching vibration absorption band of –OH or H_2O in the hydrate, and the wavenumber 1700–1,300 cm^{-1} is the carboxyl group (–COO–), amine group (–NH_2), methylene group (–CH_2), and carbon skeleton (–C–C–) vibration absorption band. The four absorption peaks at 1,200–950 cm^{-1} represent the stretching vibration of –P–O– in

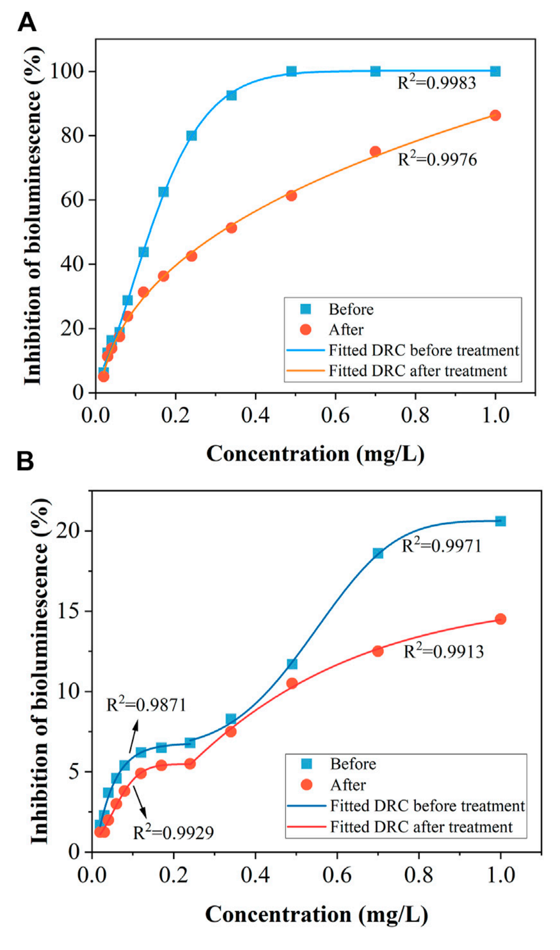


FIGURE 8 | Fitted concentration–inhibition ratio curves of **(A)** ethephon and **(B)** trichlorfon.

$-PO_2(OFe)-$. The results of the spectrogram showed the presence of iron ion–organic complexes containing crystal water and iron (hydro)oxides in the precipitate. Glyphosate molecule contains negatively charged ligands (amine group, carboxyl group, and phosphonic acid group), leading to adsorption of glyphosate on mineral surfaces through surface complexation, and even coadsorption with Cu(II) at the mineral interface (Sheals et al., 2003; Yang et al., 2018). Iron hydroxides such as goethite and ferrihydrite can also adsorb glyphosate in acidic or neutral medium (Orcelli et al., 2018; Pereira et al., 2019), although the sorption amount of glyphosate decreased because the pH increased in the Cu/Fe bimetallic system.

3.2 Operational Factors of Glyphosate Removal by Cu/Fe Bimetal System

According to **Figure 4A**, the glyphosate removal efficiency of the Cu/Fe bimetal system reached 90% after 4 h of reaction in acidic (pH 2.0) medium. Organophosphorus pesticide molecules were removed in the Cu/Fe bimetallic system as the result of the direct reduction of Fe^0 and the indirect reduction of •H, and the treatment efficiency of both gradually weakened with increasing pH (Lai et al., 2014). Besides, acidic media enhanced the surface activation rate of Fe and make the plating process more efficient (Ghauch and Tuqan, 2008). Therefore, the glyphosate removal efficiency of the Cu/Fe bimetallic system decreased to 60% (pH 7.0) and 40% (pH 11.0) after 4 h with the increase in pH. The initial pH of the solution without pH adjustment was 3.5 and the medium remained acidic or weakly acidic throughout the reaction (**Figure 6**); therefore, adjusting the solution pH for the follow-up experiments was not necessary.

Figure 4B shows that the removal efficiency rose when the Cu/Fe molar ratio increased from 0.1 to 0.25%. The reason for the improvement is that the amount of Cu attached to the surface of the iron shavings increased, forming more Cu–Fe galvanic corrosion cells on the material surface (Lai et al., 2014; Chen et al., 2018), and the reduction effect was enhanced. However, the treatment effect decreased when the Cu/Fe molar rate reached 0.5%. The contribution of Cu on the reduction benefits from facilitating the generation of surface-bond atomic hydrogen (Bransfield et al., 2006). However, when the produced Cu was excessive, the reaction sites on the Fe^0 surface of the anode in the Cu–Fe galvanic cell are excessively occupied by Cu, which reduces the direct contact between the metal iron and the glyphosate and results in a decrease in mass transfer rate and poor treatment effect. A similar phenomenon of excess ratio of Cu/Fe was observed in a previous study (Chen et al., 2018). Therefore, the molar ratio of 0.25% was selected in the follow-up experiments for subsequent study.

Figure 4C shows that the amount of Cu/Fe bimetal has a positive effect on glyphosate removal. The removal efficiency was only about 50% after 4 h of reaction when the amount of Cu/Fe was 62.5 g/L but rose up to 88.2% when the amount of Cu/Fe increased to 250 g/L. Therefore, the glyphosate removal efficiency was easily enhanced by increasing the bimetal dose, which increases the available surface area for adsorption and reaction sites (Guan et al., 2015). However, when the dose was increased from 200 to 250 g/L, the enhancement of the removal performance was not obvious because of the limitation of glyphosate. Therefore, the dosage of 250 g/L was selected for the follow-up experiment.

The removal efficiency decreased slightly with the increase in initial glyphosate concentration as shown in **Figure 4D**. The glyphosate removal efficiencies of the Cu/Fe bimetallic system at all tested initial concentrations were between 75 and 85% after 4 h of reaction. A glyphosate solution with an initial concentration of 60 mg/L was selected for the follow-up experiments. The mass fraction of glyphosate was reported to be less than 2% (Dai et al., 2013; Shen et al., 2013) in production wastewater, which further decreases after recycling, so the initial concentration selected is close to the actual concentration.

3.3 Treatment Performance and Kinetics

The removal efficiencies of TP and TOC by the Cu/Fe bimetallic system after 3 h of reaction were 99 and 65%, respectively (**Figure 5A**). The Cu/Fe bimetallic system showed reaction equilibrium at 2 h. Almost all organics containing phosphonic acid groups were removed from the solution and the removal efficiency of TP was much higher than that of TOC, which indicates that glyphosate was not completely mineralized by the Cu/Fe bimetallic system.

Based on the previous discussion on the influence factors of the Cu/Fe bimetallic system for treating glyphosate, the optimum experimental conditions (Cu/Fe dosage, 250 g/L; initial glyphosate concentration, 60 mg/L, and Cu/Fe molar ratio, 0.25%) were selected to study the kinetics of the reaction. Reaction kinetic curve fitting was realized through the "non-linear curve fit" module in Origin 2022. The correlation coefficient (R^2) of the second-order reaction kinetics was higher than that of the first-order reaction kinetics (**Figure 5B**). Therefore, the pseudo-second-order reaction model better describes the removal process of glyphosate in bimetallic systems. The reaction system was multiphase and involved various mechanism including redox reaction, precipitation, and surface adsorption.

3.4 Changes in pH and Fe^{2+} Concentration

The initial pH of the reaction system was 3.5 (**Figure 6**), which rose rapidly to 5.4 after 30 min of reaction and increase slowly from 5.4 to 6.3 in the next 90 min. The pH value was stable at about 6.3 after 4 h. Glyphosate degradation in acidic solution occurs through the direct reduction of metallic iron and electron reduction in the cathode region of the corrosion cell. The metal iron is oxidized and dissolved as a result of the reaction; therefore, the dissolved iron concentration in the solution gradually increases. This process is a reaction that consumes H^+, and a secondary electrochemical corrosion of metallic iron occurred. Therefore, the pH of the solution rose slowly.

$$\mathbf{Fe}^0 \rightarrow \mathbf{Fe}^{2+} + 2\mathbf{e}^- \tag{5}$$

$$\mathbf{H}^+ + \mathbf{e}^- \rightarrow \bullet\mathbf{H} \tag{6}$$

Another proton consumption process is the oxidation of Fe^{2+} into Fe^{3+}, which has a strong ability to bind to hydroxide ions and precipitate when the pH is 2.7. Therefore, $Fe(OH)_3$ was formed under the pH of the reaction system. This process results in a decrease in the concentration of dissolved iron in the solution. Moreover, the reaction process consumes OH^- in the solution; therefore, the pH value of the solution will not continue to rise and finally stabilize in a weak alkaline environment.

3.5 Treatment of Other Pesticides by the Cu/Fe Bimetallic System

The removal efficiencies of the TP and TOC of ethephon by the Cu/Fe bimetals was between 40 and 50% at the reaction time of 4 h, respectively (**Figure 7**), and the trend of reaction equilibrium at this time was not observed in the figure. This result indicates that a higher removal efficiency is expected for engineering applications. The treatment performance for trichlorfon was even lower with a TP removal efficiency of approximately 20%. The poor treatment effect of trichlorfon may be attributed to the difficulty of degrading trichlorfon as an ester-containing phosphorus (Bai et al., 2010; Tian et al., 2016), whereas glyphosate-containing phosphonic acid groups and its main intermediate product as phosphate are more easily adsorbed or precipitated by metals.

The dose–response relationship of several pesticides also fits the Weibull and Logit nonlinear functions (Scholze et al., 2001; Liu et al., 2009). The dose–response curves of ethephon to Q67 were also effectively described by the Weibull function using the "non-linear curve fit" module in Origin 2022 (**Figure 8**). After ethephon was treated with the Cu/Fe bimetal for 4 h, the inhibition of luminescence was weakened compared with that before the reaction, which indicates an increase in bioluminescence intensity and the decrease in solution toxicity. The concentration–luminescence inhibition relationship of trichlorfon was not consistently in accord with the Weibull model (the fitting curves of low and high concentrations with 0.24 mg/L as the boundary show different trends), but it still indicates that the inhibition rate was reduced after 4 h of treatment with the Cu/Fe bimetal.

4 CONCLUSION

The appropriate conditions of the Cu/Fe bimetallic system for treating glyphosate were as follows: acidic initial medium, 25% Cu/Fe ratio, 250 g/L Cu/Fu dosage, and 60 mg/L initial glyphosate concentration. The removal of glyphosate was in accordance with the pseudo–second-order kinetic model, and removal efficiency reached 99% because of the reduction and adsorption of the Cu/Fe bimetal. During treatment, the pH of the solution increased from 3.5 to 6.3 accompanied by the dissolution and oxidation of Fe ions. The toxicity of other organophosphorus pesticides, such as ethephon and trichlorfon, can be effectively reduced by the Cu/Fe bimetal, but the treatment efficiency needs to be improved (Bransfield et al., 2006).

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

XW: Data, Formal analysis, Writing—original draft, Writing—review and editing, Conceptualization. YW: Writing—review and editing. JX: Data, Investigation, Conceptualization. HW: Writing—review and editing, Conceptualization.

FUNDING

This work was supported by the National Natural Science Foundation of China (51778449).

REFERENCES

Ajiboye, T. O., Oladoye, P. O., Olanrewaju, C. A., and Akinsola, G. O. (2022). Organophosphorus Pesticides: Impacts, Detection and Removal Strategies. *Environ. Nanotechnol. Monit. Manag.* 17 (May), 100655. doi:10.1016/J.ENMM.2022.100655

Ameta, R., Chohadia, A. K., Jain, A., and Punjabi, P. B. (2018). "Fenton and Photo-Fenton Processes," in *Advanced Oxidation Processes for Wastewater Treatment*. Editors S. C. Ameta and R. Ameta (London, UK: Emerging Green Chemical Technology), 49–87.

Annett, R., Habibi, H. R., and Hontela, A. (2014). Impact of Glyphosate and Glyphosate-Based Herbicides on the Freshwater Environment. *J. Appl. Toxicol.* 34 (5), 458–479. doi:10.1002/jat.2997

Aquino Neto, S., and de Andrade, A. R. (2009). Electrochemical Degradation of Glyphosate Formulations at DSA Anodes in Chloride Medium: an AOX Formation Study. *J. Appl. Electrochem* 39 (10), 1863–1870. doi:10.1007/s10800-009-9890-6

Badawy, M. I., Ghaly, M. Y., and Gad-Allah, T. A. (2006). Advanced Oxidation Processes for the Removal of Organophosphorus Pesticides from Wastewater. *Desalination* 194 (1–3), 166–175. doi:10.1016/J.DESAL.2005.09.027

Bai, Y., Chen, J., Yang, Y., Guo, L., and Zhang, C. (2010). Degradation of Organophosphorus Pesticide Induced by Oxygen Plasma: Effects of Operating Parameters and Reaction Mechanisms. *Chemosphere* 81 (3), 408–414. doi:10.1016/J.CHEMOSPHERE.2010.06.071

Bransfield, S. J., Cwiertny, D. M., Roberts, A. L., and Fairbrother, D. H. (2006). Influence of Copper Loading and Surface Coverage on the Reactivity of Granular Iron toward 1,1,1-Trichloroethane. *Environ. Sci. Technol.* 40 (5), 1485–1490. doi:10.1021/es051300p

Bransfield, S. J., Cwiertny, D. M., Livi, K., and Fairbrother, D. H. (2007). Influence of Transition Metal Additives and Temperature on the Rate of Organohalide Reduction by Granular Iron: Implications for Reaction Mechanisms. *Appl. Catal. B Environ.* 76 (3–4), 348–356. doi:10.1016/J.APCATB.2007.06.003

Chen, S., Chu, W., Wei, H., Zhao, H., Xu, B., Gao, N., et al. (2018). Reductive Dechlorination of Haloacetamides in Drinking Water by Cu/Fe Bimetal. *Sep. Purif. Technol.* 203, 226–232. doi:10.1016/J.SEPPUR.2018.04.048

Cui, H., Li, Q., Qian, Y., Zhang, Q., and Zhai, J. (2012). Preparation and Adsorption Performance of MnO2/PAC Composite towards Aqueous Glyphosate. *Environ. Technol.* 33 (17), 2049–2056. doi:10.1080/09593330.2012.660641

Dai, Z. X., Li, F. H., Gong, Z., and Liao, Q. B. (2013). The Comprehensive Utilization of Waste Water Derived from the Glyphosate Production. *Adv. Mater. Res.* 781-784, 2051–2054. doi:10.4028/www.scientific.net/AMR.781-784.2051

Dubois, M., van den Broeck, L., and Inzé, D. (2018). The Pivotal Role of Ethylene in Plant Growth. *Trends Plant Sci.* 23 (4), 311–323. doi:10.1016/j.tplants.2018.01.003

Feng, D., Soric, A., and Boutin, O. (2020). Treatment Technologies and Degradation Pathways of Glyphosate: A Critical Review. *Sci. Total Environ.* 742, 140559. doi:10.1016/J.SCITOTENV.2020.140559

Fu, H., Tan, P., Wang, R., Li, S., Liu, H., Yang, Y., et al. (2022). Advances in Organophosphorus Pesticides Pollution: Current Status and Challenges in Ecotoxicological, Sustainable Agriculture, and Degradation Strategies. *J. Hazard. Mater.* 424, 127494. doi:10.1016/J.JHAZMAT.2021.127494

Ghauch, A., and Tuqan, A. (2008). Catalytic Degradation of Chlorothalonil in Water Using Bimetallic Iron-Based Systems. *Chemosphere* 73 (5), 751–759. doi:10.1016/J.CHEMOSPHERE.2008.06.035

Gormez, E., Golge, O., Dincay, O., and Kabak, B. (2021). A Potential Threat to Black Figs Intended for Export from Turkey: Ethephon. *J. Food Compos. Analysis* 102, 103989. doi:10.1016/J.JFCA.2021.103989

Grandcoin, A., Piel, S., and Baurès, E. (2017). AminoMethylPhosphonic Acid (AMPA) in Natural Waters: Its Sources, Behavior and Environmental Fate. *Water Res.* 117, 187–197. doi:10.1016/J.WATRES.2017.03.055

Guan, X., Sun, Y., Qin, H., Li, J., Lo, I. M. C., He, D., et al. (2015). The Limitations of Applying Zero-Valent Iron Technology in Contaminants Sequestration and the Corresponding Countermeasures: The Development in Zero-Valent Iron Technology in the Last Two Decades (1994-2014). *Water Res.* 75, 224–248. doi:10.1016/J.WATRES.2015.02.034

Hansen, L. R., and Roslev, P. (2016). Behavioral Responses of Juvenile Daphnia Magna after Exposure to Glyphosate and Glyphosate-Copper Complexes. *Aquat. Toxicol.* 179 (August), 36–43. doi:10.1016/j.aquatox.2016.08.010

Huong, D. T., Van Tu, N., Anh, D. T., Tien, N. A., Ngan, T. T. K., and Van Tan, L. (2021). Removal of Phenol from Aqueous Solution Using Internal Microelectrolysis with Fe-Cu: Optimization and Application on Real Coking Wastewater. *Processes* 9 (4), 720. doi:10.3390/pr9040720

Jaisi, D. P., Li, H., Wallace, A. F., Paudel, P., Sun, M., Balakrishna, A., et al. (2016). Mechanisms of Bond Cleavage during Manganese Oxide and UV Degradation of Glyphosate: Results from Phosphate Oxygen Isotopes and Molecular Simulations. *J. Agric. Food Chem.* 64 (45), 8474–8482. doi:10.1021/acs.jafc.6b02608

Jian, Q., Gong, L., Li, T., Wang, Y., Wu, Y., Chen, F., et al. (2017). Rapid Assessment of the Toxicity of Fungal Compounds Using Luminescent Vibrio Qinghaiensis Sp. Q67. *Toxins* 9, 335. doi:10.3390/toxins9100335

Khoury, G. A., Gehris, T. C., Tribe, L., Torres Sánchez, R. M., and dos Santos Afonso, M. (2010). Glyphosate Adsorption on Montmorillonite: An Experimental and Theoretical Study of Surface Complexes. *Appl. Clay Sci.* 50 (2), 167–175. doi:10.1016/J.CLAY.2010.07.018

Kim, M., Stripeikis, J., Iñón, F., and Tudino, M. (2007). A Simplified Approach to the Determination of N-Nitroso Glyphosate in Technical Glyphosate Using HPLC with Post-Derivatization and Colorimetric Detection. *Talanta* 72 (3), 1054–1058. doi:10.1016/j.talanta.2006.12.047

la Cecilia, D., and Maggi, F. (2018). Analysis of Glyphosate Degradation in a Soil Microcosm. *Environ. Pollut.* 233, 201–207. doi:10.1016/J.ENVPOL.2017.10.017

Lai, B., Zhang, Y., Chen, Z., Yang, P., Zhou, Y., and Wang, J. (2014). Removal of P-Nitrophenol (PNP) in Aqueous Solution by the Micron-Scale Iron-Copper (Fe/Cu) Bimetallic Particles. *Appl. Catal. B Environ.* 144, 816–830. doi:10.1016/J.APCATB.2013.08.020

Lai, B., Yuan, D.-H., Chen, Z.-Y., Yuan, Y., and Yang, P. (2016). Influence of Temperature on the Removal of Extremely High Concentrationp-Nitrophenol Simulated Wastewater by Fe/Cu/H2O Systems. *Clean. Soil Air Water* 44 (4), 345–355. doi:10.1002/clen.201400321

Li, X., Chen, W., Ma, L., Wang, H., and Fan, J. (2018). Industrial Wastewater Advanced Treatment via Catalytic Ozonation with an Fe-Based Catalyst. *Chemosphere* 195, 336–343. doi:10.1016/J.CHEMOSPHERE.2017.12.080

Liu, S.-S., Song, X.-Q., Liu, H.-L., Zhang, Y.-H., and Zhang, J. (2009). Combined Photobacterium Toxicity of Herbicide Mixtures Containing One Insecticide. *Chemosphere* 75 (3), 381–388. doi:10.1016/J.CHEMOSPHERE.2008.12.026

Ma, Y., Li, B., Ke, Y., Zhang, Y., and Zhang, Y. (2018). Transcriptome Analysis of Rana Chensinensis Liver under Trichlorfon Stress. *Ecotoxicol. Environ. Saf.* 147, 487–493. doi:10.1016/J.ECOENV.2017.09.016

Mailler, R., Gasperi, J., Coquet, Y., Buleté, A., Vulliet, E., Deshayes, S., et al. (2016). Removal of a Wide Range of Emerging Pollutants from Wastewater Treatment Plant Discharges by Micro-grain Activated Carbon in Fluidized Bed as Tertiary Treatment at Large Pilot Scale. *Sci. Total Environ.* 542, 983–996. doi:10.1016/J.SCITOTENV.2015.10.153

Mostafa, M., Bin Jumah, M. N., Othman, S. I., Alruhaimi, R. S., Salama, Y. F., Allam, A. A., et al. (2021). Effective Removal of Different Species of Organophosphorus Pesticides (Acephate, Omthosate, and Methyl Parathion) Using Chitosan/Zeolite-A as Multifunctional Adsorbent. *Environ. Technol. Innovation* 24, 101875. doi:10.1016/J.ETI.2021.101875

Nedelkoska, T. v., and Low, G. K.-C. (2004). High-Performance Liquid Chromatographic Determination of Glyphosate in Water and Plant Material after Pre-column Derivatisation with 9-Fluorenylmethyl Chloroformate. *Anal. Chim. Acta* 511 (1), 145–153. doi:10.1016/j.aca.2004.01.027

Orcelli, T., di Mauro, E., Urbano, A., Valezi, D. F., da Costa, A. C. S., Zaia, C. T. B. V., et al. (2018). Study of Interaction between Glyphosate and Goethite Using Several Methodologies: An Environmental Perspective. *Water Air Soil Pollut.* 229 (5). doi:10.1007/s11270-018-3806-1

Paudel, P., Negusse, A., and Jaisi, D. P. (2015). Birnessite-Catalyzed Degradation of Glyphosate: A Mechanistic Study Aided by Kinetics Batch Studies and NMR Spectroscopy. *Soil Sci. Soc. Am. J.* 79 (3), 815–825. doi:10.2136/sssaj2014.10.0394

Pereira, R. C., Anizelli, P. R., Eduardo, M., Daniel, F. V., Costa, A. C. S. D., Zaia, C. T. B. V., et al. (2019). The Effect of PH and Ionic Strength on the

Adsorption of Glyphosate onto Ferrihydrite. *Geochem Trans.* 20 (1), 1–14. doi:10.1186/s12932-019-0063-1

Peruzzo, P. J., Porta, A. A., and Ronco, A. E. (2008). Levels of Glyphosate in Surface Waters, Sediments and Soils Associated with Direct Sowing Soybean Cultivation in North Pampasic Region of Argentina. *Environ. Pollut.* 156 (1), 61–66. doi:10.1016/j.envpol.2008.01.015

Pimenta, E., da Silva, F., Barbosa, É., Cacique, A., Cassimiro, L., de Pinho, G., et al. (2020). Quantification of Glyphosate and AMPA by HPLC-ICP-MS/MS and HPLC-DAD: A Comparative Study. *J. Braz. Chem. Soc.* 31 (2), 298–304. doi:10.21577/0103-5053.20190175

Priambodo, R., Shih, Y.-J., and Huang, Y. (2017). Phosphorus Recovery as Ferrous Phosphate (Vivianite) from Wastewater Produced in Manufacture of Thin Film Transistor-Liquid Crystal Displays (TFT-LCD) by a Fluidized Bed Crystallizer (FBC). *RSC Adv.* 7 (65), 40819–40828. doi:10.1039/c7ra06308c

Rallet, D., Paltahe, A., Tsamo, C., and Loura, B. (2022). Synthesis of Clay-Biochar Composite for Glyphosate Removal from Aqueous Solution. *Heliyon* 8 (3), e09112. doi:10.1016/J.HELIYON.2022.E09112

Saleh, I. A., Zouari, N., and Al-Ghouti, M. A. (2020). Removal of Pesticides from Water and Wastewater: Chemical, Physical and Biological Treatment Approaches. *Environ. Technol. Innovation* 19, 101026. doi:10.1016/J.ETI.2020.101026

Scholze, M., Boedeker, W., Faust, M., Backhaus, T., Altenburger, R., and Grimme, L. H. (2001). A General Best-Fit Method for Concentration-Response Curves and the Estimation of Low-Effect Concentrations. *Environ. Toxicol. Chem.* 20, 448–457. doi:10.1002/etc.5620200228

Shahmahdi, N., Dehghanzadeh, R., Aslani, H., and Bakht Shokouhi, S. (2020). Performance Evaluation of Waste Iron Shavings (Fe0) for Catalytic Ozonation in Removal of Sulfamethoxazole from Municipal Wastewater Treatment Plant Effluent in a Batch Mode Pilot Plant. *Chem. Eng. J.* 383, 123093. doi:10.1016/J.CEJ.2019.123093

Sheals, J., Granström, M., Sjöberg, S., and Persson, P. (2003). Coadsorption of Cu(II) and Glyphosate at the Water-Goethite (α-FeOOH) Interface: Molecular Structures from FTIR and EXAFS Measurements. *J. Colloid Interface Sci.* 262 (1), 38–47. doi:10.1016/S0021-9797(03)00207-8

Shen, J., Huang, J., Liu, L., Ye, W., Lin, J., and van der Bruggen, B. (2013). The Use of BMED for Glyphosate Recovery from Glyphosate Neutralization Liquor in View of Zero Discharge. *J. Hazard. Mater.* 260, 660–667. doi:10.1016/J.JHAZMAT.2013.06.028

Shubair, T., Eljamal, O., Khalil, A. M. E., and Matsunaga, N. (2018). Multilayer System of Nanoscale Zero Valent Iron and Nano-Fe/Cu Particles for Nitrate Removal in Porous Media. *Sep. Purif. Technol.* 193, 242–254. doi:10.1016/J.SEPPUR.2017.10.069

Tian, J., Dong, Q., Yu, C., Zhao, R., Wang, J., and Chen, L. (2016). Biodegradation of the Organophosphate Trichlorfon and its Major Degradation Products by a Novel Aspergillus Sydowii PA F-2. *J. Agric. Food Chem.* 64 (21), 4280–4287. doi:10.1021/acs.jafc.6b00909

Trujillo-Reyes, J., Sánchez-Mendieta, V., José Solache-Ríos, M., and Colín-Cruz, A. (2012). Removal of Remazol Yellow from Aqueous Solution Using Fe-Cu and Fe-Ni Nanoscale Oxides and Their Carbonaceous Composites. *Environ. Technol.* 33 (5), 545–554. doi:10.1080/09593330.2011.584571

Wang, Y.-J., Zhou, D.-M., Sun, R.-J., Cang, L., and Hao, X.-Z. (2006). Cosorption of Zinc and Glyphosate on Two Soils with Different Characteristics. *J. Hazard. Mater.* 137 (1), 76–82. doi:10.1016/j.jhazmat.2006.02.032

Xiong, Z., Lai, B., Yang, P., Zhou, Y., Wang, J., and Fang, S. (2015). Comparative Study on the Reactivity of Fe/Cu Bimetallic Particles and Zero Valent Iron (ZVI) under Different Conditions of N2, Air or without Aeration. *J. Hazard. Mater.* 297, 261–268. doi:10.1016/J.JHAZMAT.2015.05.006

Xiong, Z., Yuan, D., Yang, P., and Lai, B. (2017). Cu 2+ Release and Transfer in Various Fe/Cu-Based Processes during Wastewater Treatment. *J. Taiwan Inst. Chem. Eng.* 80, 669–677. doi:10.1016/J.JTICE.2017.08.048

Yang, Y., Deng, Q., Yan, W., Jing, C., and Zhang, Y. (2018). Comparative Study of Glyphosate Removal on Goethite and Magnetite: Adsorption and Photo-Degradation. *Chem. Eng. J.* 352, 581–589. doi:10.1016/J.CEJ.2018.07.058

Zhu, Y., Zhang, F., Tong, C., and Liu, W. (1999). Determination of Glyphosate by Ion Chromatography. *J. Chromatogr. A* 850 (1–2), 297–301. doi:10.1016/S0021-9673(99)00558-0

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.