Oxidative degradation of p-chlorophenol by the persulfate-doped Fe-Mn bimetallic hydroxide, the parametrical significance, and systematical optimization

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1 **Oxidative degradation of p-chlorophenol by the persulfate-doped Fe-Mn bimetallic hydroxide,**
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**Oxidative degradation of p-chlorophenol by the persulfate-doped Fe-Mn bimetallic hydroxide,
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Abstract

Aqueous Fe(II)-catalyzed activation commonly deteriorates the oxidation performance of persulfate (PS) to the treatment of organic contaminants. In this study, a PS-doped layered bimetallic hydroxide (Fe-Mn hydroxide) was synthesized to construct a heterogeneously catalytic system to solve the issue brought by homogeneity. The molar ratio of Fe(II) to Mn(II) and the mass ratio of PS to Fe-Mn hydroxide both had a significant impact on the catalytic degradation of p-CP. Reaction temperatures engaged in the most essential role in influencing the degradation and removal of p-chlorophenol (p-CP). The optimal combination of factors for the preparation of PS-hydroxide and the treatment of p-CP was finally determined by significance analysis. The degradation process was appropriately fitted by the pseudo-first-order kinetic model. the benzene ring in p-CP was broken by PS-hydroxide during the adsorption. The surface modification of PS-hydroxide caused by the valence transition of Mn was beneficial to the adsorption and catalytic degradation of p-CP.

Capsule

A persulfate-doped layered bimetallic hydroxide was synthesized to construct a heterogeneously catalytic system to solve the drawback of homogeneity for the effective treatment of p-chlorophenol.

Keywords

Persulfate-doped Fe-Mn hydroxide; P-chlorophenol degradation; Optimization; Degradation kinetics; Systematical optimization

1. Introduction

Chlorinated phenols (Cl-phenols) are extensively used in some chemical and pharmaceutical-related industries, which are commonly considered as persistent organic pollutants (POPs) in the treatment of wastewater (Mikkonen et al. 2018, Tubic et al. 2019). As a vital member of Cl-phenols, p-chlorophenol (p-CP) can cause severe ecological harm to the surrounding environment and humans, such as carcinogenicity, acute toxicity, and recalcitrance (Pirzada et al. 2019, Sharma & Khare 2018). Therefore, it is essential to explore some effective technologies for the rapid removal of p-CP to avoid further contamination. Until now, some techniques have been proposed and applied on the remediation of wastewater containing p-CP, such as extraction, adsorption, membrane separation, electrochemical oxidation, zero-valent iron (ZVI) reduction, and biological degradation (Bao et al. 2019, Jin & Dong 2019, Kuntail et al. 2019, Wei et al. 2019). However, some shortcomings such as the large dosage of chemicals, low removal efficiency, a long-lasting disposal cycle, and the secondary pollution drawn by the secondary organic species have perplexed and dwarfed the wide application of these traditional technologies (Ababneh et al. 2019, Kim et al. 2019).

In recent years, the advanced-oxidation methods (AOP) have attracted more attention particularly in treating non-biodegradable POPs in the wastewater due to their operational convenience and effectiveness (El Fakir et al. 2019, Lv et al. 2020, Xiao et al. 2020a). Among the oxidants, the utilization of hydroxyl radical ($\bullet\text{OH}$) for the oxidation degradation of some organic compounds is most mentioned in various treatment processes (Laysandra et al. 2019, Shokoohi et al. 2019, Xiao et al. 2020b). $\bullet\text{OH}$ has a higher potential compared with other common oxidants. Furthermore, $\bullet\text{OH}$ can be easily produced by

several technologies such as Fenton, ozonation, photocatalysis, electrocatalysis, and photo-electrocatalysis(Das et al. 2019, Li et al. 2020, Wang et al. 2020, Zhou et al. 2019). Nevertheless, the redox potential of $\bullet\text{OH}$ is changeable in different pH environments (e.g., +2.7 V in acidity and +1.8 V in neutrality), which explicitly weakened its performance to some extent. Comparably, due to the distinctive solubility and operativity in the wide pH range, the sulfate radical ($\text{SO}_4^{\bullet-}$, $E_0 = 2.60 \text{ V}$)-based heterogeneous oxidation has attracted more favor in degrading POPs in different pH environments (Guerra-Rodriguez et al. 2018, Huang &Zhang 2019, Liu et al. 2018).

$\text{SO}_4^{\bullet-}$ can be generated by activating persulfate (PS) under ambient or heating conditions(Crincoli et al. 2020, Xu et al. 2020). The activation of PS is commonly conducted by some methods, such as heating, microwave, transition-metal catalysis, UV radiation, and electrolysis, etc. Generally, among these pathways, the transition-metal catalysis with the participation of aqueous Fe^{2+} is preferably adopted for the activation of PS in the application due to its lower temperature request and running cost(Dong et al. 2019, Jin &Dong 2019). However, the relatively hard control of activation rate and reaction disturbance brought by excess aqueous Fe(II) cations would severely deteriorate the oxidation performance of $\text{SO}_4^{\bullet-}$ on treating organic pollutants. An excessive loss rate of Fe(II) would further hamper the employment of the homogeneous activator when the pH in the environment is higher than 5. Recently, some heterogeneous activators such as iron oxide, iron-based minerals, nanoscale zero-valent iron, etc. have been used to substitute aqueous Fe^{2+} to potentially enhance the PS activation(Deng et al. 2019, Jin &Dong 2019, Jin et al. 2019, Park et al. 2019). However, the pre-judgment effect of the control in releasing Fe(II) ions is still poor. Mn(II) cations besides Fe(II) can also activate PS to produce $\text{SO}_4^{\bullet-}$ at a slower rate by transforming its bivalence to a higher valence state(Huang &Zhang 2019, Shah et al. 2019). Moreover,

the Mn species with a higher valence state is anticipated to vastly adsorb the excessive Fe(II) and Fe(III) to maintain the continuous degradation process(Eyvazi et al. 2019, Lin et al. 2019).

To solve the abovementioned issues, the layered bimetallic Fe-Mn hydroxide was synthesized as the heterogeneous activator of PS in this study. PS was doped to the bimetallic hydroxide using a mechanochemical method to increase the activation activities. To directly characterize the influence of the preparation parameters and the aqueous conditions on the oxidation performance of the PS-doped bimetallic hydroxide (PS-hydroxide), two orthogonal designs with seven factors in total were arranged and quantitatively analyzed based on the removal amounts of p-CP. The synthesis and treatment processes were optimized by the significance analysis and the marginal results. To specify the degradation mechanisms of p-CP by PS-hydroxide, FTIR, SEM, and EDS (i.e., Energy dispersive x-ray spectroscopy) were employed in combination for the characterization analysis of the solid and aqueous samples obtained from different conditions. This study solves the performance issue of PS drawn by the aqueous Fe(II)-activated drawback for the degradation of p-CP and clarifies the role of Mn(II) in the iron-dominated catalysis process.

2. Methods and materials

2.1 Chemicals

All chemical reagents including sodium hydroxide (NaOH), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), manganese chloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, PS), and p-chlorophenol (p-CP) were of analytical grade, purchased online from Aladdin Reagent Company (China), and stored in a vacuum environment. Deionized (DI) water used for the experiments was generated by a water

purification device (Super 10FV, HHITECH, China), boiled, and purged with nitrogen gas (95% N₂ and 5% H₂) to remove the dissolved oxygen gas.

2.2 Preparation of the PS-doped Fe(II)-Mn(II) hydroxide

All the glass containers and gadgets have been rinsed three times using DI water and dried before any use. The whole preparation process was conducted in a vacuum glove box to avoid the oxidation of Fe(II) and Mn(II) by O₂. The Fe-Mn bimetallic hydroxide was synthesized by the co-precipitation of the dissolved Fe(II) and Mn(II) species before the synthesis of the PS-doped Fe-Mn oxidative inducer. FeSO₄·7H₂O and MnCl₂·4H₂O were weighted at the molar ratios of Fe(II) to Mn(II) of 1, 3, and 5, respectively, and both dissolved in DI water. NaOH was weighted at some molar ratios of OH⁻ and Fe(II) and dissolved to obtain an alkaline solution. The dark-green flocculated precipitation was immediately generated once the alkaline solution was poured into the water containing Fe(II) and Mn(II) cations. Afterward, the mixture was mechanically stirred to make full precipitation, sequentially centrifuged using a centrifuge (KH19A, KAIDA, China) at 8000 rpm, and dried at 75 °C by a vacuum drying oven (ZK-50A, Biao Cheng Share Laboratory Co. Ltd, China). Finally, the PS-doped Fe-Mn hydroxide (PS-hydroxide) was prepared by mixing Fe-Mn hydroxide with PS at some mass ratios (i.e., the mass ratios of PS to Fe-Mn hydroxide of 1 – 5) and mechanically milling at 120 rpm over 2 hours (h). The PS-hydroxide samples were stored in the glovebox for further employment.

2.3 Experimental procedure

A certain amount of oxidative reducer (the PS-hydroxide) was weighted and added to the p-CP stock solution in the Erlenmeyer flask (250 mL). A water-bath shaker (COS-100B, Shanghai BILON

INSTRUMENTS Co. LTD, China) was employed to control the shaking time (6 h) and the temperature of the solution. The influence of the preparation parameters (including the molar ratio of Fe(II) to Mn(II) (Fe/Mn ratio), the mass ratio of PS to Fe-Mn hydroxide (PS/Fe-Mn ratio), and the molar ratio of OH⁻ to Fe(II) (OH/Fe ratio)) and the aqueous conditions (including the initial pH, concentration, PS-hydroxide, and temperature) on the degradation and removal of p-CP were comprehensively analyzed in batch experiments. Two orthogonal designs with different factors and levels were constructed, respectively, to optimize the synthesis of the PS-hydroxide and effectively arrange the degradation experiments affected by the changes in the preparation parameters and the aqueous conditions. Variance analysis (ANOVA) was used to obtain marginal means and quantitatively evaluate the significance of each factor. The factors and levels with specific labels are correspondingly listed in Table S1 and Table S2 in the supporting information (SI). The orthogonal designs with the p-CP removal results are shown in Table 1 and Table 2, respectively. To testify the removal kinetics of p-CP using PS-hydroxide, a pseudo-first-order kinetic model was adopted to describe the removal process following Eq. (1), where c_0 and c_t are the concentrations of p-CP in solutions at the initial and t times, respectively, k is the constant reaction rate bounded to the physicochemical characteristics of PS-hydroxide (h⁻¹).

$$\ln \frac{c_t}{c_0} = -kt \quad (1)$$

2.4 Calculations and analysis

Liquid samples taken off at a specific time were centrifuged at 5000 rpm and filtered through a membrane filter (0.22 μm) before being subjected to high-performance liquid chromatography (HPLC, ULTIMATE-3000, USA, equipped with a UV-vis detector at 280 nm and a C18 column) for the determination of p-CP concentration. The measurement process was conducted in duplication to minimize the manual

deviations. The samples of the P-CP solution and the PS-hydroxide before and after the degradation process were characterized by a Fourier transform infrared spectrometer (FTIR, Thermo Electron Co.-380 FTIR, USA) over a range of 400 – 4000 cm^{-1} at every step of 4 cm^{-1} and a scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS, Carl Zeiss AG, Germany).

3. Results and discussion

3.1 Characterization of Fe-Mn hydroxide and PS-hydroxide

FTIR spectra of Fe-Mn hydroxide affected by Fe/Mn ratio and the PS-hydroxide influenced by both Fe/Mn ratio and PS/Fe-Mn ratio are shown in Fig. 1. The morphologies and EDS distribution of samples are correspondingly displayed in Fig. 2 and Fig. S1 in the SI, respectively. The peaks at the wavenumbers (cm^{-1}) of 3420, 1626, 1384, 1121, 983, 612, and 465 were matched, respectively, at the Fe/Mn ratio of 1 for the Fe-Mn hydroxide (Fig. 1 a). However, the peak at 983 cm^{-1} disappeared in terms of the spectra at the Fe/Mn ratio of 3 and 5. Moreover, the peak at 465 cm^{-1} was shifted to 494 cm^{-1} for the Fe/Mn ratio of 3 and a brand peak at 571 cm^{-1} was newly formed for the Fe/Mn ratio of 5. The partial oxidation of Fe(II) and the substitution of Fe into the Mn-related hydroxide potentially analyzed the changes in the FTIR spectra of Fe-Mn hydroxide with the increase of Fe/Mn ratios(Chen et al. 2019, Lin et al. 2019). Comparably, more peaks were observed in the spectra of PS-hydroxide although the changes in the Fe/Mn ratios had an unobvious effect on the change of the spectra pattern (Fig. 1 b). The results confirmed that the PS had been mechanochemically doped into the Fe-Mn hydroxide, which covered the change of spectra caused by Fe/Mn ratios(Cao et al. 2017). Furthermore, the peaks within the bands of 592 – 690 cm^{-1} and 1060 – 1274 cm^{-1} gradually disappeared with the increase of the PS/Fe-Mn ratio (Fig.

1 c), which reconfirmed the PS loading on the Fe-Mn hydroxide. The layered precipitation was observed in the SEM image of Fe-Mn hydroxide (Fig. 2 a). The morphologies of the Fe-Mn hydroxide confirmed that the increase of Fe in the hydroxide facilitated the formation of the layered bimetallic hydroxide (Fig. 2 a). The Fe-Mn hydroxide was tightly wrapped by the amorphous (also flocculated) PS in the PS-hydroxide (Fig. 2 b). The flocculated morphology of PS indicated the partial catalysis of PS to sulfate radicals, which further induced the oxidation of Fe(II) and Mn(II) and the precipitation of Fe and Mn cations with OH⁻. The flocculation would be beneficial to the capture of p-CP in further degradation experiments. The intercalation of the layered hydroxide into PS was observed for all three PS/Fe-Mn ratios. The morphological characteristics of PS-hydroxide echoed with the analysis of FTIR spectra. The mass contents of Mn and Fe were 16.44 and 22.94, 10.94 and 34.95, and 4.74 and 24.79, respectively, which were roughly close to the corresponding Fe/Mn ratios (i.e., 1, 2, and 3) (Fig. S1, SI). Generally, the mass contents of Fe, Mn, and S semi-quantitatively reflected the reliability of Fe/Mn ratios and PS/Fe-Mn ratios.

3.2 Effect of preparation parameters and aqueous conditions

The main effect of the preparation parameters on p-CP removal (default $\alpha = 0.05$) is shown in Table S3 in the SI. The quantitative results analyzed by ANOVA were acceptable due to the R^2 value (R : regression coefficient) that was close to 1. The significance coefficients ($Sig.$) were 0.040, 0.038, and 0.318 for factor A (i.e., Fe/Mn ratio), B (i.e., PS/Fe-Mn ratio), and C (i.e., OH⁻/Fe ratio), respectively. The preparation parameters including A and B factors both had a significant effect on the removal of p-CP using PS-hydroxide. Contrarily, the influence of the OH⁻/Fe ratio on the removal of p-CP was unobvious. The significance order of the preparation parameters followed the descending pattern as Factor B > Factor

A > Factor C. The parameter of PS/Fe-Mn ratio played a most important role among the factors in strengthening the performance of PS-hydroxide towards p-CP removal. The different morphologies of PS-hydroxide (Fig. 2 a and b) caused by the Fe/Mn ratio and PS/Fe-Mn ratio explicitly impacted the reactions between PS-hydroxide and p-CP to some extent. The main effect of the aqueous conditions on p-CP removal (default $\alpha = 0.05$) is shown in Table S4 in the SI. The R^2 value of ANOVA analysis was 0.822, indicating that the quantitative results listed in Table S4 were moderately acceptable. The *Sig.* values were 0.457, 0.364, 0.799, and 0.012 for the factor D (i.e., Initial pH), E (i.e., P-CP concentration), F (i.e., PS-hydroxide dosage), and G (i.e., Temperature), respectively. Only *Sig.* value of factor F among the aqueous conditions was lower than the default α of 0.05, meaning only the temperature of the solution significantly affected the removal of p-CP achieved by PS-hydroxide. The impact of the other three factors on the removal results was insignificant while nonnegligible. Similarly, the significant order of the aqueous conditions followed the descending rank as Factor G > Factor E > Factor D > Factor F. Obviously, the variable of temperature engaged in the most essential role in alternating the degradation process of p-CP (Chao et al. 2018).

3.3 Optimization of p-CP removal

Marginal means of the preparation parameters and aqueous conditions in the orthogonal design (default $\alpha = 0.05$) are shown in Fig. 3. Although, the maximum removal amounts (mM) of 5.37 and 8.12 were obtained in the parametrical combination of $A_2B_1C_3$ (i.e., Fe/Mn ratio of 3, PS/Fe-Mn ratio of 1, and OH^- /Fe ratio of 6) and $D_5E_5F_3G_5$ (i.e., Initial pH of 11, the p-CP concentration of 10 mM, Dosage of 1.5 g/L, and Temperature of 70 °C) in the two orthogonal designs, respectively (Table 1 and Table 2). The results conflicted with the significance-analyzed ones (Table S3 and Table S4, SI), which cannot be used to

represent the data in the full experiments with 3^3 plus 4^5 runs. The marginal means of factors combining with the significance analysis should be employed for the determination of systematical optimization. As seen in Fig. 3, for the factor of Fe/Mn ratio, the level (i.e., 1, 3, and 5) of 3 (A_2) was most conducive to the removal peak of p-CP. Similarly, the factors with the specific levels including B_1 , C_1 , D_5 , E_4 , F_3 , and G_5 were assured as the most preferred values for the optimal removal means. Furthermore, the effect significances of all factors were ranked in the whole following $G > B > A > C > E > D > F$ under the significance results (Table S3 and Table S4, SI). It was clear that Dosage, Initial pH, and p-CP concentration were the three least significant factors. Therefore, the medium levels were preferred to maintain cost-effectiveness to some extent. The high temperature in the solution (e.g., 60 and 70 °C), the low PS/Fe-Mn ratios (e.g., 1), and the medium Fe/Mn ratio (e.g., 3) were selected in favor of the significant importance of the three factors. As a result of the analysis, the optimal combination of factors for the preparation of PS-hydroxide and the treatment of p-CP was finalized for $A_2B_1C_2D_3E_3F_3G_5$.

3.4 Kinetics description for p-CP removal

Removal amounts of p-CP affected by the preparation parameters and the aqueous conditions over time (360 min) are shown in Fig. 4. For the factor of Fe/Mn ratio, an increasing curve with a slower rate before a fast one over the whole running time was observed at all three levels. The PS/Fe-Mn ratio performed a similar trend in comparison with the Fe/Mn ratio. However, the OH^-/Fe ratio influenced the removal curves differently with a nearly constant rate obtained in the middle and later stages of experiments. However, the removal process of p-CP was intensely changed by the change of the initial pH in the middle-later phase (i.e., from 210 until to 360 min). A high p-CP concentration (e.g., 6, 8, and 10 mM) enhanced the removal rate of p-CP for the PS-hydroxide generally despite its inconspicuous significance

analysis (Table S4, SI). The increase in the dosage of PS-hydroxide based on the medium value (i.e., 2.0 and 2.5 g/L) had not supported the continuing elevation of p-CP removal although the reaction rate was strengthened in the initial and middle stage of the experiment (i.e., before 240 min). Notably, the temperature factor generated the largest removal difference in the level range among the seven factors. The significance of temperature was visually confirmed by the different removal curves over time. The linear fit of the pseudo-first-order kinetic model affected by the preparation parameters and aqueous conditions is shown in Fig. 5. The parametrical statistics for the kinetics fitting are correspondingly listed in Table S5 in the SI. As seen, most of the adjusted R^2 values (i.e., $Adj. R^2$) were larger than the default value of 0.95. Overall, the change of $\ln(c_t/c_0)$ vs time can be appropriately fitted by the pseudo-first-order kinetic model. The suitability of the model directly clarified that the removal of p-CP mostly endured a heterogeneous mechanism containing both physical and chemical pathways (Bao et al. 2019, Pirzada et al. 2019, Wan & Li 2017). Most p-CP was adsorbed onto the surface of hydroxide before the subsequent immediate oxidation by $SO_4^{\bullet-}$ with only a minor moiety was degraded through a homogeneous process (Brienza & Katsoyiannis 2017).

3.5 Mechanism exploration for p-CP degradation

FTIR spectra of p-CP before and after the degradation process and the PS-hydroxide after the degradation process are shown in Fig. 6. As seen, fewer peaks were matched in the spectra of the degraded p-CP compared with the raw sample (Fig. 6 a). The increase in the concentration of p-CP would increase the number of peaks. To analyze the changes in the molecular structure of p-CP before and after experiments, the FTIR spectrum of benzene was analyzed and shown in Fig. S2 in the SI. The standard peaks of benzene were observed at 3447, 2429, 1694, 1384, 1328, 1296, 936, 709 cm^{-1} , respectively. Except for

the peaks at 3447 and 1384 cm^{-1} , the spectra of the degraded p-CP were different from benzene. The benzene ring in p-CP had been broken by PS-hydroxide during the test. The peak at 3447 cm^{-1} is commonly associated with the O–H band in the water molecular. The peaks at 1634, 1429, and 1384 cm^{-1} represent C=O, C–C, and C=C bonds, respectively(He et al. 2015, Huang et al. 2017, Taherian et al. 2013). The results indicated that p-CP had experienced an incomplete mineralization process potentially with some by-products being produced. Similarly, fewer peaks were matched in the spectra of PS-hydroxide after the degradation (Fig. 6 b) in comparison with the raw counterpart (Fig. 1 b, c). The morphology of the PS-hydroxide after the degradation process is shown in Fig. 7. Some different morphological characteristics were observed for the used PS-hydroxide sample. A complicated physicochemical mechanism foreseeably participated in the degradation process. PS is activated into $\text{SO}_4^{\bullet-}$ radical mainly by heat, UV (also light-driven) radiation, transition metal ions, and electrolysis(Crincoli et al. 2020, Forouzesh et al. 2019). Generally, the reaction mechanism can be substantially surmised based on the above analysis and results. PS doped into the Fe-Mn hydroxide was dissolved into the solid-liquid interface once PS-hydroxide was added to the solution (Fig. 7), which thereupon was activated by ferrous ions to $\text{SO}_4^{\bullet-}$ (Eq. 2) that dominantly participated in the de-chlorination, loop disintegration, carbon-chain breaking, and mineralization processes (Table S3, Fig. 4, and Fig. 6)(Nguyen & Juang 2015, Taherian et al. 2013). Divalent Mn was oxidized to tetravalent species accompanying the activation of PS involving Fe(II) ions (Eq. 4, Fig. 5 and Table S5, SI), which induced more pores, cracks, and flocculation on PS-hydroxide (Fig. 7). Considering the removal of p-CP by PS-hydroxide mainly was a heterogeneous process (Fig. 5 and Table S5), the surface modification of the PS-hydroxide caused by the valence transition of Mn was beneficial to the adsorption of p-CP and subsequent removal or degradation. However, too high or too low Fe/Mn ratios (i.e., A₁ and A₃) were both

unacceptable during the preparation of PS-hydroxide (Table S1 and Table 1). A high Fe/Mn ratio inhibited the modification drawn by Mn while a low Fe/Mn ratio reduced the generation of $SO_4^{\bullet-}$ (Eq. 2). Heating or increasing the temperature of solution clearly enhanced the production of $SO_4^{\bullet-}$ and further increased the degradation of p-CP (Eq. 3, Table S4 and Fig. 4), which supported the setting of both PS/Fe-Mn ratio and aqueous temperature (Table 1 and Table 2).

4. Conclusion

PS was mechanochemically doped into the layered Fe-Mn hydroxide to solve the homogenous issue for the degradation of p-CP, which caused the amorphous and flocculation in the PS-hydroxide. The impact of the Fe/Mn ratio, the PS/Fe-Mn ratio, and the temperature on the removal of p-CP was significant among all factors. The quantitative influence of factors on the removal of p-CP ranked as $G > B > A > C > E > D > F$. The maximum removal amounts (mM) of 5.37 and 8.12 were obtained in the parametrical combination of $A_2B_1C_3$ and $D_5E_5F_3G_5$ in the two orthogonal designs, respectively. The optimal combination of $A_2B_1C_2D_3E_3F_3G_5$ was determined for the preparation of PS-hydroxide and the treatment of p-CP based on the significance analysis and the marginal means of the experimental results. The linear fit of the pseudo-first-order kinetic model was confirmed for the preparation parameters and aqueous conditions, which demonstrated that most p-CP was adsorbed onto the surface of hydroxide and then experienced the immediate oxidation by $SO_4^{\bullet-}$. The spectra of the degraded p-CP were different from the standard peaks of benzene. The benzene ring in p-CP had been broken by PS-hydroxide during the

removal process. Suitable surface modification for the PS-hydroxide caused by the valence transition of Mn was beneficial to the adsorption of p-CP and the subsequent degradation.

Declarations

Ethics approval and consent to participate-

Not applicable

Consent for publication

Not applicable

Availability of data and materials

The datasets generated and/or analyzed during the current study are available in the [NAME] repository,

[PERSISTENT WEB LINK TO DATASETS]

Competing interests

The authors declare that they have no competing interests

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Authors' contributions

Tao Huang, Jing Du, Danni Yu, Shihan Deng, Longfei Liu, and Shuwen Zhang contributed to the study

conception and design. Material preparation, data collection, and analysis were performed by Tao

Huang and Jing Du. The first draft of the manuscript was written by Tao Huang and all authors

commented on previous versions of the manuscript. Tao Huang, Jing Du, Longfei Liu, and Shuwen Zhang

read and approved the final manuscript.

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437

Figure captions

Fig. 1 FTIR spectra of Fe-Mn hydroxide affected by the molar ratios of Fe(II) to Mn(II) (a) and the PS-hydroxide influenced by the molar ratios of Fe(II) to Mn(II) (b), and PS-hydroxide influenced by the mass ratios of persulfate to Fe(II)-Mn(II) hydroxide (c)

Fig. 2 Morphologies of Fe-Mn hydroxide affected by the molar ratios of Fe(II) to Mn(II) (a) and the PS-hydroxide influenced by the mass ratios of PS to Fe-Mn hydroxide (b)

Fig. 3 Marginal means of the preparation parameters and aqueous conditions in the orthogonal design (default $\alpha = 0.05$)

Fig. 4 Removal amounts of p-CP affected by the preparation parameters and aqueous conditions over time (360 min)

Fig. 5 Linear fit of the kinetic model affected by the preparation parameters and aqueous conditions

Fig. 6 FTIR of p-CP before and after the degradation process (a) and the PS-hydroxide after the degradation process (b)

Fig. 7 Morphological characteristics of the PS-hydroxide after the degradation process

Table legends

Table 1 Orthogonal design with the removal amount of p-CP for the preparation parameters (Experimental conditions: pH of 7, the p-CP concentration of 6 mM, PS-hydroxide dosage of 1.5 g/L, and temperature of 50 °C)

Table 2 Orthogonal design with the removal amount of p-CP for the aqueous conditions (Experimental conditions: the molar ratio of Fe(II) to Mn(II) of 3, the mass ratio of PS to Fe-Mn hydroxide of 3, the molar ratio of OH⁻ to Fe(II) of 4)

Figures

Figure 1

FTIR spectra of Fe-Mn hydroxide affected by the molar ratios of Fe(II) to Mn(II) (a) and the PS-hydroxide influenced by the molar ratios of Fe(II) to Mn(II) (b), and PS-hydroxide influenced by the mass ratios of persulfate to Fe(II)-Mn(II) hydroxide (c)

Figure 2

Morphologies of Fe-Mn hydroxide affected by the molar ratios of Fe(II) to Mn(II) (a) and the PS-hydroxide influenced by the mass ratios of PS to Fe-Mn hydroxide (b)

Figure 3

Marginal means of the preparation parameters and aqueous conditions in the orthogonal design (default $\alpha = 0.05$)

Figure 4

Removal amounts of p-CP affected by the preparation parameters and aqueous conditions over time (360 min)

Figure 5

Linear fit of the kinetic model affected by the preparation parameters and aqueous conditions

Figure 6

FTIR of p-CP before and after the degradation process (a) and the PS-hydroxide after the degradation process (b)

Figure 7

Morphological characteristics of the PS-hydroxide after the degradation process

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