



Iron-Manganese Silicate Polymerization (IMSP) Catalytic Ozonation for Removal of *p*-Chloronitrobenzene in Aqueous Solution

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ABSTRACT

Iron-manganese silicate polymer (IMSP) was synthesized in the laboratory and characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), Fourier transformation infrared (FT-IR) and Brunauer-Emmett-Teller (BET). The mesopores and amorphous sample had nanorods structure, and on the surface was contained with abundant of surface hydroxyl groups. The catalytic activity of IMSP was investigated in terms of *p*-chloronitrobenzene (*p*CNB) and TOC removal. Ozonation catalysed by IMSP exhibited extraordinarily high catalytic performance over other studied processes. In the IMSP-catalytic ozonation process, 99.5 % conversion of *p*CNB and 50.7 % TOC was achieved in 15 min. Ozone dosage and catalyst dosage exert a positive influence on the removal rate of the *p*CNB. And the initial water pH of 7.0 ± 0.1 (the solution pH was close to the point of zero charge of IMSP) achieved the highest *p*CNB removal among all the tested conditions.

INTRODUCTION

In recent years, the increasing organic pollution in water sources promoted the development of water treatment technologies. Heterogeneous catalytic ozonation using metal materials as ozonation catalyst at mild experimental conditions and without any additional thermal and light energy was considered to be one of the most effective techniques for water remediation (Ikhlaq et al. 2015). Recent studies have found that many transition metals and oxides were an effective catalyst for ozone oxidation. For example, MnO_2 was used in the ozonation of 4-nitrophenol (Nawaz et al. 2017). Ferrocene was used in the ozonation of toxic contaminants in aqueous solution (Lin et al. 2017). Manganese silicate and iron silicate were used as catalysts, which were highly effective in catalysing ozone of *p*CNB in aqueous solution (Liu et al. 2011a, Liu et al. 2012). Many researchers have reported that heterogeneous catalysts with ozonation could significantly enhance the degradation efficiency of organic pollution and improvement of TOC removal by ozone decomposition and hydroxyl radicals ($\cdot\text{OH}$) generation compared with ozonation alone (Gao et al. 2017). $\cdot\text{OH}$ is a high-oxidation-potential and non-selective radical, which could effectively remove the organic pollutants in aqueous solutions (Ikhlaq et al. 2013). Moreover, heterogeneous catalysts in water treatment are limited by their easy to lead secondary pollution, hard to recycle, high cost and so on. So, it is very important for heterogeneous catalytic ozonation process to choose as a catalyst.

According to our previous work (Liu et al. 2011a, Liu et al. 2012), iron silicate and manganese silicate are effective heterogeneous catalysts. Moreover, compared with manganese silicate, iron silicate has a high catalytic activity and relatively weak recovery and utilization. So, we intend to use the advantages of iron silicate and manganese silicate to synthesize a compound silicate. With this in mind, the scope of the present paper was to fabricate a novel sample iron-manganese silicate polymerization (IMSP) and to study its catalytic performance in ozonation of organic pollution in aqueous solution.

As a typical halogenated nitro aromatic compound, *p*-chloronitrobenzene (*p*CNB) was selected as a model pollutant to test the catalytic activity of the IMSP. To the best of our knowledge, there was no reported research on the IMSP used in the ozonation process.

The primary objectives of this study were to synthesize and identify the characteristics of IMSP as an ozonation catalyst, to investigate the degradation efficiency of *p*CNB in the presence of a catalyst in an aqueous solution.

MATERIALS AND METHODS

Materials: All the solutions were prepared by using Milli-Q ultra-pure water. Catalysts were synthesized in the laboratory as follows: The catalyst crystalline phases were confirmed by X-ray diffraction (XRD). A stock solution of *p*CNB (Chem Service, USA) was prepared at 100 mg/L by dissolving 100 mg *p*CNB in 1000 mL ultra-pure water.

Methanol of HPLC grade was purchased from Sigma Aldrich (USA). Other reagents were all of analytic grade without further purification.

Catalyst synthesis: The IMSP catalyst was synthesized as follows: 150 mL 0.2 M $\text{Fe}(\text{NO}_3)_3$ and 150 mL 0.2 M $\text{Mn}(\text{NO}_3)_2$ were mixed intensively. Then 300 mL of 0.1 M Na_2SiO_3 was slowly added into the mixed liquor at room temperature under magnetic stirring. When the pH of the suspension was 7.0, the dropping of Na_2SiO_3 solution was stopped. The pH of the suspension was adjusted higher than 12 by NaOH solution, and it was incubated at 40°C for 24 h. The precipitate was then collected and washed with ultra-pure water for several times until the conductivity of the rinse water remained constant over three consecutive rinses. Finally, the precipitate was dried at 60°C for 10 h and then ground. Particles with diameters between 0.075 mm and 0.3 mm were used in the experiment.

Analysis methods: According to our previous work (Liu et al. 2011b), the concentration of pCNB was determined by a 1200 high performance liquid chromatography (HPLC, Agilent, USA) with UV detection at 265 nm. The pCNB mineralization was determined using a TOC analyser (TOC-VCPH, Shimadzu, Japan). Scanning electron microscope (SEM, Quanta 200FEG, FEI Corporation, USA) and energy dispersive X-ray spectroscopy (EDX) was used to measure the morphology and composition of the catalyst. The FTIR spectrum of the synthesized catalyst was determined using the KBr disc method and measured on a SHIMADZU (1730, Japan) spectrometer. The Brunauer-Emmet-Teller (BET) method on a surface area and porosity analyser (Micromeritics ASAP 2020, USA) with krypton adsorption at liquid nitrogen temperature was used to measure the surface area and pore volume of the catalyst. The metals leaching from the catalyst into the solution were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima 5300DV, Perkin Elmer, USA). A saturated deprotonation method was used to determine the density of surface hydroxyl groups of the catalyst (Laiti et al. 1995).

Catalytic ozonation experiments: Batch experiments were carried out with a 1.2-L flat-bottom flask reactor. 1-L ultra-pure water was first transferred into the flask reactor. The desired concentration of gaseous ozone, which was produced by CF-G-3-010g ozone generator (Qingdao Guolin, China) was bubbled into the reactor and dispersed into the solution by means of a porous fritted diffuser. Then, the ozone generator was turned off and immediately dosed with the desired amounts of catalyst and pCNB stock solution into the reactor. The solution was continuously stirred with a magnetic stirrer at 300 rpm. All the experiments were operated

at 20°C by a thermostatic water bath. The experiment of ozonation alone (without catalyst) was carried out under the same conditions. The adsorption experiments were conducted under the same experimental conditions as used in the previous tests, but with the pure oxygen been replaced with ozone gas. After the designated time intervals in the course of the experiments, 15 mL of the solution in the reactor was sampled. The residual dissolved ozone in the samples was immediately quenched by 0.1 mL $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 mol/L). The quenched samples were then analysed for pCNB quantification.

RESULTS AND DISCUSSION

Characterization of IMSP: The structure of the synthesized IMSP sample was examined by XRD, and the result is shown in Fig. 1. According to the literature, the broad peak in the range of 20° to 40° was typical of amorphous silica peak (Liu et al. 2011b, Aderson et al. 2000). However, due to the significant content of the amorphous phase in the sample, most of the crystals were covered. No obvious peaks belonging to IMSP or manganese oxide or iron oxide were seen.

The SEM micrographs of the synthesized IMSP are displayed in Fig. 2(a) and (b). Aggregates of nanorods were obtained for the ternary crystals. EDX was used to analyse the composition of the prepared IMSP (Fig. 2 c). The EDX analysis area was marked with a black cross in the SEM images (Fig. 2 a). The EDX result showed that this area was mainly composed of the four elements Fe, Mn, Si and O, and the weight percentages of the four elements were: Fe 20.56%, Mn 11.35%, Si 16.15% and O 51.94%, respectively. Combined with the results of Fig. 1, we could infer that

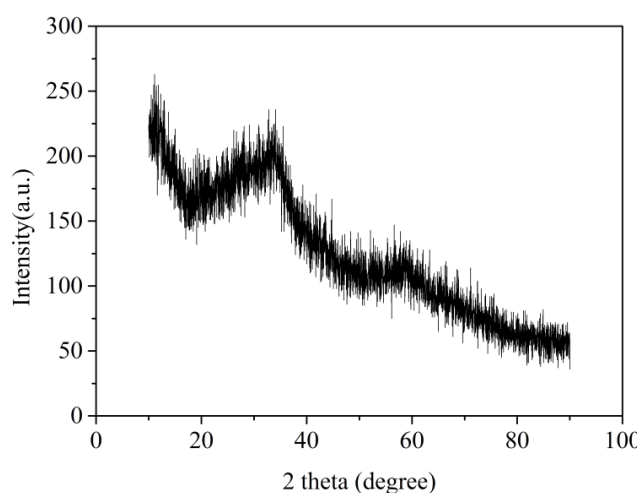


Fig. 1: XRD pattern of the catalyst.

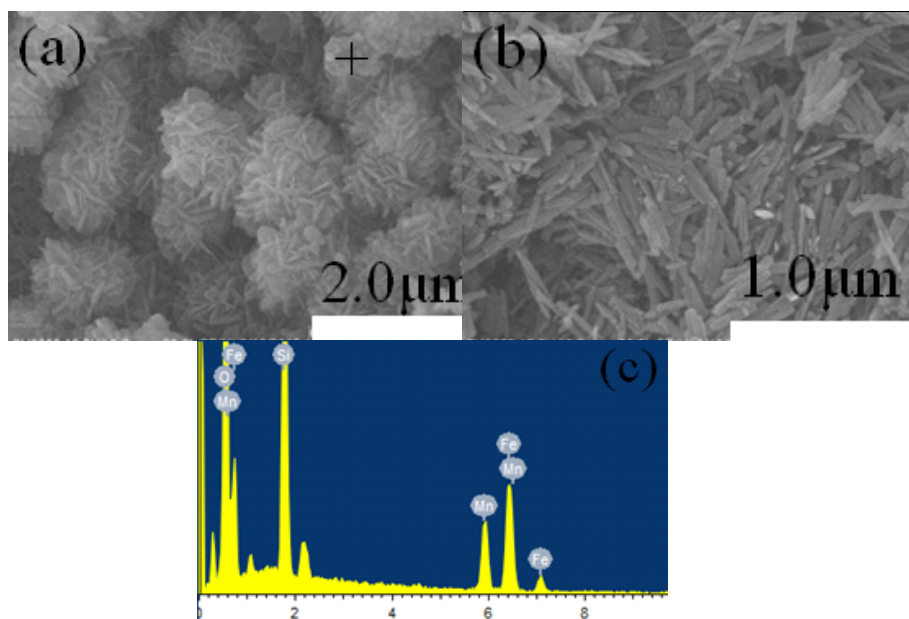


Fig. 2: SEM photographs of the IMSP catalyst (a) $\times 5000$, (b) $\times 10000$, (c) EDX analysis results of the catalyst, using a black cross to mark the structure in (a).

most of the iron oxide or manganese oxide crystals were wrapped by the amorphous silicon. The average surface area of the IMSP was found to be $312 \text{ m}^2\text{g}^{-1}$, and the pore volume of $0.37 \text{ cm}^3\text{g}^{-1}$.

The FTIR spectrum of the IMSP is depicted in Fig. 3. The band at 790 cm^{-1} is attributed the Si-O bond and the band at 1297 cm^{-1} is attributed to OH deformation vibrations of hydration of iron-manganese oxide (Abebe et al. 2017). The bands at 3452 cm^{-1} are corresponding to the O-H stretching vibrations and the peaks at 1690 cm^{-1} may be attributed to bending vibrations of adsorbed H_2O (Lu et al. 2013, Yu et al. 2015). These surface hydroxylation groups on the iron-manganese oxide surface might result in the formation of surface functional groups. Valdés et al. (2012) reported that in the heterogeneous catalytic ozonation process, the surface hydroxyl groups could accelerate the decomposition of the ozone to generate $\cdot\text{OH}$ radicals.

Catalytic activity of IMSP: Ozonation alone, IMSP-catalytic ozonation and adsorption of IMSP were conducted to investigate the catalytic activity of IMSP on the degradation of *p*CNB, and the results are shown in Fig. 4. The residual ion concentrations in aqueous solution and the TOC removal efficiency of different processes were also studied. As shown in Fig. 4, the concentration of *p*CNB decreased with the increased reaction time in all the three processes mentioned above. After 15 min reaction time, the degradation efficiency of *p*CNB in the process of ozonation alone

was 54.2%. Under the same experimental conditions, IMSP-catalytic ozonation process led to about 99.5% *p*CNB removal. And the adsorption of *p*CNB was only 7.5% in 15 min. Comparing the IMSP-catalytic ozonation process with the cumulative effect of ozonation alone and adsorption of IMSP, an increment of approximately 37.8% of *p*CNB degradation was observed.

As shown in Fig. 5, after 15 min reaction, the IMSP-catalytic ozonation and ozonation alone led to nearly 50.7% and 21.9% mineralization of TOC, respectively. And after 15 min reaction, the metal ion concentrations in the solution were far below the relevant level of international standards for drinking water.

Influence of initial pH: The initial pH of the solution exhibited a complicated effect on both ozone stability and catalyst surface properties. So it is important to examine the influence of the initial pH on IMSP-catalytic ozonation process. As shown in Fig. 6, in neutral water ($\text{pH} = 7.0 \pm 0.1$), the removal efficiency by the ozonation alone was less than 60% and with IMSP-catalysed ozonation process was 99.5%. However, under acidic conditions ($\text{pH} = 3.8$), the removal efficiency of ozonation alone and the IMSP-catalysed ozonation process were reduced to 16% and 30%, respectively. In contrast, when the pH of the solution was raised to 9.5, the degradation rate of ozonation alone increased to 89.7%, under the same experimental conditions, the degradation rate of the IMSP-catalysed ozonation process was

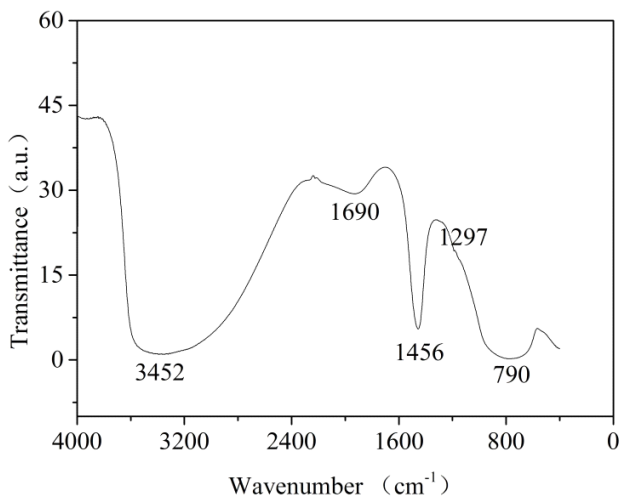


Fig. 3: FTIR spectrum of IMSP catalyst.

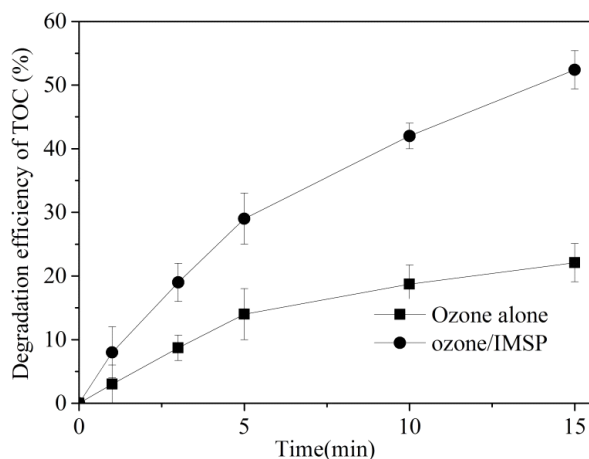


Fig. 5: TOC removal efficiency in the different process. Experiment conditions were: $[p\text{CNB}]_0 = 100 \mu\text{g/L}$, $[\text{O}_3]_0 = 1.0 \text{ mg/L}$, $[\text{IMSP}]_0 = 500 \text{ mg/L}$, $\text{pH} = 7.0 \pm 0.1$.

91.9%. For IMSP, its surface charge was affected by both, pH value of the solution and its pH_{pzc} . The pH_{pzc} of IMSP was determined to be 7.1. The results in Fig. 6 indicated that at a $\text{pH} 7.0 \pm 0.1$, IMSP had a greater influence on the catalytic ozonation of *p*CNB than at acidic and alkaline conditions. According to the characteristics of ozone, this phenomenon could be explained as follows: Under different solution pH conditions, surface hydroxyl groups of catalyst exhibited different charge properties. Under acidic ($\text{pH} < \text{pH}_{\text{pzc}}$) or alkaline conditions ($\text{pH} > \text{pH}_{\text{pzc}}$), the hydroxyl groups on the surface of the catalyst undergoes protonation or deprotonation. Moreover, when the solution is equal to the catalyst pH_{pzc} , the charge of metal oxide surface and surface hydroxyl groups was zero, which could accelerate

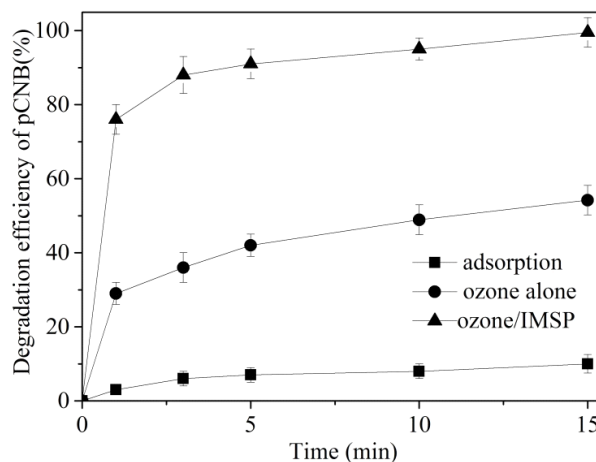


Fig. 4: Promotion of the *p*CNB degradation in different processes. Experiment conditions were: $[p\text{CNB}]_0 = 100 \mu\text{g/L}$, $[\text{O}_3]_0 = 1.0 \text{ mg/L}$, $[\text{IMSP}]_0 = 500 \text{ mg/L}$, $\text{pH} = 7.0 \pm 0.1$.

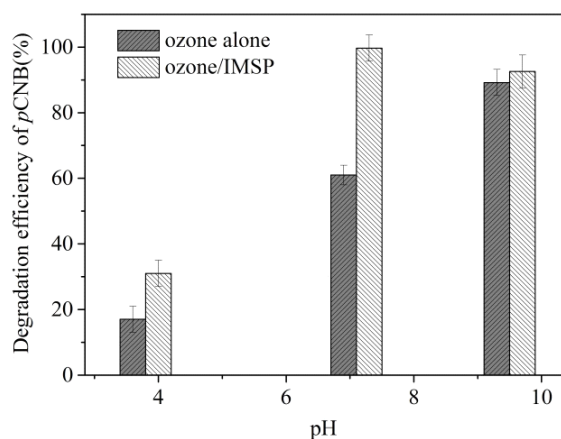


Fig. 6: Effect of initial pH on catalyzed ozonation of *p*CNB. Experiment conditions were: $[p\text{CNB}]_0 = 100 \mu\text{g/L}$, $[\text{O}_3]_0 = 1.0 \text{ mg/L}$, $[\text{IMSP}]_0 = 500 \text{ mg/L}$.

the ozone decomposition to generate high activity $\cdot\text{OH}$ radical (Qi et al. 2009). Our previous research also showed that the uncharged surface was more active than protonated or deprotonated form (Liu et al. 2012).

Influence of catalyst dosage: In the heterogeneous catalytic ozonation process, more dosage of catalyst could give more active sites for the catalytic ozonation, and the increasing of the more active sites could promote more ozone decomposition to generate more $\cdot\text{OH}$ radicals (Xu et al. 2009, Huang et al. 2015, Wang et al. 2015). The influence of catalyst dosage on the degradation of *p*CNB as a function of reaction time by IMSP-catalytic ozonation process can be observed in Fig. 6. It can be seen that the catalyst dosage exerts a positive influence on the removal rate of *p*CNB

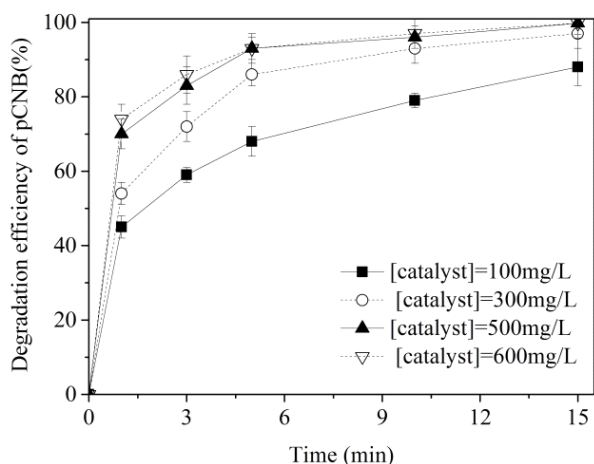


Fig. 7: Effect of catalyst dosage on catalyzed ozonation of *p*CNB. Experiment conditions were: $[pCNB]_0 = 100 \mu\text{g/L}$, $[O_3]_0 = 1.0 \text{ mg/L}$, $\text{pH} = 7.0 \pm 0.1$

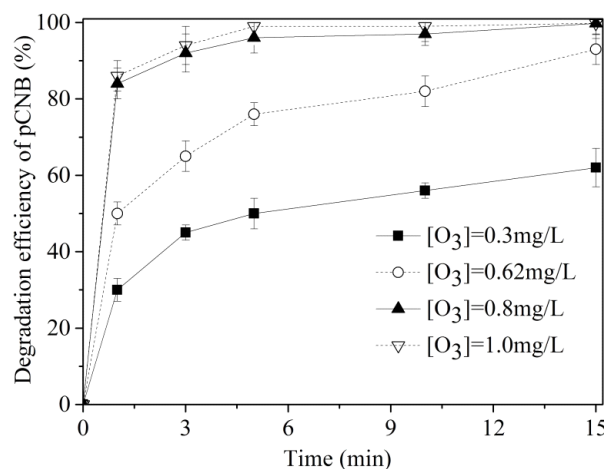


Fig. 8: Effect of ozone dosage on catalyzed ozonation of *p*CNB. Experiment conditions were: $[pCNB]_0 = 100 \mu\text{g/L}$, $[IMSP]_0 = 500 \text{ mg/L}$, $\text{pH} = 7.00.1$.

appreciably. Increasing the IMSP dosage, the removal efficiency of *p*CNB was enhanced. So the dosage of catalyst was positive in the IMSP-catalytic ozonation process for the degradation of *p*CNB. Previous research also reported that the surface hydroxyl groups of iron silicate and manganese silicate were the active sites for catalysed ozonation (Liu et al. 2011a, Liu et al. 2012). IMSP was a mixture of iron oxide, manganese oxide and so on. FTIR results showed that surface hydroxyl groups covered the surface of the IMSP. According to results of the saturated deprotonation experiment, the density of surface hydroxyl groups on iron silicate was $2.573 \times 10^{-2} \text{ mol/g}$ and IMSP was $3.169 \times 10^{-2} \text{ mol/g}$, respectively, which was much more than the efficient catalyst FeOOH (Sui et al. 2010). That was to say, more dosage of the IMSP could give more surface hydroxyl groups as active sites of catalysed ozonation reaction.

By combing the results shown in Figs. 4-7, the mechanism of IMSP catalysed ozonation of *p*CNB could be deduced as follows: In aqueous solution, surface hydroxyl groups as active sites of IMSP-catalysed ozonation reaction can accelerate the ozone decomposition to generate $\cdot\text{OH}$ radicals, which could oxidize *p*CNB efficiently.

Influence of ozone dosage: Ozone as the oxidant and treatment agent was a very important parameter in the process of heterogeneous catalytic ozonation. To determine the effect of the ozone dosage on the *p*CNB removal efficiency, a series of experiments were conducted by varying the ozone dosage from 0.3 mg/L to 1.0 mg/L, and the results are shown in Fig. 8. With an ozone concentration of 0.3 mg/L, the removal of *p*CNB in 15 min was 46%. When the ozone concentration was increased to 1.0 mg/L, its removal effi-

ciency was 99.8%. An approximately 3 times increase in ozone dosage led to about 2.5 times increase in *p*CNB removal in 15 min.

CONCLUSIONS

Based on the experimental data, the following conclusions can be drawn:

1. IMSP was synthesized in the laboratory and XRD, SEM, EDX, FTIR and BET analysis results confirmed that the amorphous IMSP contained an abundance of hydroxyl groups on the surface.
2. IMSP exhibited significant catalytic activities on the degradation of *p*CNB.
3. The degradation of *p*CNB in the IMSP-catalysed ozonation processes followed the $\cdot\text{OH}$ radicals oxidation mechanism.
4. $\text{pH} 7.0 \pm 0.1$, which nearly zero charged the surfaces of the IMSP, was found as the optimum value for the catalytic ozonation of *p*CNB. And the *p*CNB removal efficiency increased with the increased catalyst and ozone dosages.

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