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Heterogeneous Catalytic Ozonation of Phenol by a Novel Binary Catalyst of Fe-Ni/MAC

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Abstract: Iron-nickel supported on modified active carbon (Fe-Ni/MAC) was prepared and characterized by XRD, SEM, XPS and EDS, followed by evaluating the practicability of Fe-Ni/MAC in treating real wastewater with a high concentration of phenol. Results showed that the optimal conditions for catalytic ozonation obtained by response surface methodology (RSM) were catalyst 10 g/L, ozone 68 mg/L, pH 9 and reaction time 90 min. Fe-Ni alloy and NiFe$_2$O$_4$ were demonstrated to be the dominant active species involved in catalytic reaction. The Fe-Ni/MAC catalyst can be reused six times with a satisfactory performance and little leaching of metal ions. Although some radicals like ·OH and ·O$_2^-$ functioned well, singlet oxygen (1$^1$O$_2$) was regarded as the most important radical in the Fe-Ni/MAC process. Most noticeably, the fluorescence excitation emission matrices (EEMs) certified that as much as 1243 mg/L phenol in the real wastewater was completely degraded, which made Fe-Ni/MAC a fairly practical catalyst.

Keywords: catalytic ozonation; phenol degradation; binary catalyst; Fe-Ni/MAC; wastewater

1. Introduction

Phenol and phenolic compounds have been found in a variety of industrial wastewaters, such as those from petroleum refining, petrochemical, pharmaceutical, plastic and pesticide chemical industries [1]. These pollutants are not only hazardous to the environment but also harmful for human health, even at low concentrations [2], hence, they have been listed on the priority list of EPA (Environment Protection Agency) since 1976 [3]. In consideration of their strong toxicity, they must be processed prior to discharge into receiving waters. For this purpose, various related technologies have been developed. Of them, advanced oxidation processes (AOPs) are supposed to be the most suitable processes, as AOPs are characterized by low operation cost, no need for special equipment, less energy consumption and high conversion of the organic pollutants [4–6].

Despite being an effective method to degrade toxic organics in aqueous solution, homogeneous catalytic oxidation using H$_2$O$_2$ and ferrous iron as oxidizing agents would take a long time to separate catalysts. Additionally, most of the dissolved metal catalysts could exert an adverse effect on the environment. These disadvantages, however, could be overcome by using heterogeneous catalysts since they are easily recoverable and reusable [7], and thus heterogeneous catalytic ozonation has been used extensively to remove phenol and its derivatives from wastewater, including ZnAl$_2$O$_4$ as a novel high surface area ozonation catalyst [8]. Mn–Co–Fe exhibited the highest catalytic activity and stability for the mineralization of p-nitrophenol [9], magnetic carbonaceous nanocomposites were applied for the
heterogeneous ozonation of 2, 4-dinitrophenol [10], Pt/Al₂O₃ was used for the treatment of a simulated phenolic effluent [11], β-MnO₂ nanowires showed good separability and remarkable catalysis for the degradation of phenol [12], Fe–Mn–Cu/γ-Al₂O₃ was used to mineralize phenol wastewater [13] and AC/nano-Fe₃O₄ composites were capable of degrading phenol in industrial wastewater [14,15].

Transition metals and their alloys have been reported to obtain a high surface area and excellent catalytic activity with exceptional mechanical strength [16], of which Ni-based catalysts are generally employed, owing to their superior catalytic activity and low cost. Meanwhile, to further promote the catalytic activity of Ni-based catalysts, various promoters were developed, among which Fe, a VIII group metal, has been referred to as an active material and was combined with Ni to form a binary catalyst of Fe-Ni. Due to high activity, good redox properties and low cost, the Fe-Ni binary catalysts have been used widely in many fields like hydrogenation reactions [17], hydrogen production [18], pollutant degradation [19], substitute natural gas production [20], carbon nanotube synthesis [16,21] and urea electrolysis [22]. Nevertheless, to the best of our knowledge, almost no studies on the heterogeneous catalytic ozonation of phenol by Fe-Ni/MAC have been found so far.

In this work, a binary catalyst, iron-nickel supported on modified active carbon (Fe-Ni/MAC), was synthesized via the co-precipitation method. As one of the most ubiquitous industrial wastewater contaminants, phenol was selected to assess the catalytic ozonation activity of Fe-Ni/MAC. However, there are a variety of factors affecting the catalyst’s efficacy, indicative of a need to optimize related parameters. A statistical tool known as response surface methodology (RSM) was used to explore the influence of an independent variable or combination of both independent variables and dependent variables [23]. Therefore, the preparation procedure was firstly optimized by RSM to gain optimal preparation conditions, following which the structure, morphology and surface property of the catalyst were investigated through different characterization methods. Additionally, the catalyst reusability was tested and catalytic mechanisms were analyzed by using ascorbic acid, tert-butyl alcohol and L-histidine. Moreover, the catalytic ozonation capability of Fe-Ni/MAC to degrade the real phenol wastewater was evaluated.

2. Results and Discussion

2.1. Optimization of Fe-Ni/MAC Fabrication

The calcined temperature, Fe/Ni and calcined time were optimized through RSM based on a Box–Behnken design (BBD), during which the removal efficiency (RE) of phenol was chosen as the response value, and the detailed design, together with the corresponding response, are displayed in Table S3. For the purpose of depicting the relationship between phenol RE (Y) and test variables (A: calcined temperature, B: iron/nickel ratio and C: calcined time), all data went through multiple regression analysis to gain the following polynomial equation:

\[ Y = 83.91 - 3.51 \times A - 4.12 \times B - 0.9093 \times C + 1.71 \times AB + 0.345 \times AC + 1.62 \times BC - 6.23 \times A^2 - 5.04 \times B^2 - 2.91 \times C^2 \] (1)

Table 1 presents the ANOVA results of the quadratic model. The large F value indicates that most of the variation in the response can be explained by the regression model equation. The associated p-value is used to judge whether F is large enough to indicate statistical significance or not [24]. In this case, the model F-value was evaluated as 147.54, indicating that the resultant quadratic model is extremely significant. A p-value less than 0.05 shows that the model terms are significant, hence the calcined temperature, Fe/Ni ratio, calcined time and their quadratic terms had a critical effect on the RE of phenol (p < 0.05). Evidently, among all the factors, the Fe/Ni ratio was a dominating factor since its sum of squares (135.63) was higher than that of temperature (89.21) and time (5.99). The same conclusion can be also drawn from the 3D response surface and 2D contour plots (see the following section). For the mutual interaction terms, the p-value of AC was found to be 0.3659, indicative of no striking interaction between calcined temperature and time. Generally, an adequate level of precision
measures the signal to noise ratio, and a ratio greater than 4 is desirable [25]. As such, the ratio of 32.871 in the obtained quadratic model revealed a fairly adequate signal for the model that can be used to navigate the design space. Moreover, the determination coefficient $R^2$ and adjusted determination coefficient $R^2$ (adj) from the model were 0.9948 and 0.9880, respectively, further confirming a high significance of the obtained model. Additionally, an $R^2$ value higher than 0.9 could be regarded as having a high correlation. Taken together, it is quite reasonable to use the above quadratic function to analyze the trends in the response.

Table 1. ANOVA of the regression model obtained from response surface methodology (RSM).

| Source | Sum of Squares | Degrees of Freedom | Mean Square | F-Value | $p > F$ |
|--------|----------------|--------------------|-------------|---------|--------|
| Model  | 676.63         | 9                  | 75.18       | 147.54  | <0.0001|
| A      | 89.21          | 1                  | 89.21       | 175.08  | <0.0001|
| B      | 135.63         | 1                  | 135.63      | 266.17  | <0.0001|
| C      | 5.99           | 1                  | 5.99        | 11.76   | 0.0110 |
| AB     | 13.12          | 1                  | 13.12       | 25.74   | 0.0014 |
| AC     | 0.4761         | 1                  | 0.4761      | 0.9343  | 0.3659 |
| BC     | 11.68          | 1                  | 11.68       | 22.92   | 0.0002 |
| $A^2$  | 163.34         | 1                  | 163.34      | 320.56  | <0.0001|
| $B^2$  | 56.30          | 1                  | 56.30       | 110.50  | <0.0001|
| $C^2$  | 35.74          | 1                  | 35.74       | 70.14   | <0.0001|
| Residual | 3.57          | 7                  | 0.5096      |         |        |
| Lack of fit | 2.45        | 3                  | 0.8172      | 2.93    | 0.1629 |
| Pure error | 1.12        | 4                  | 0.2788      |         |        |
| Total  | 680.20         | 16                 |             |         |        |

$R^2 = 0.9948$; $R^2$(adj) = 0.988; adequate precision = 32.871.

The obtained Equation (1) was employed to visualize the effects of experimental parameters on the phenol RE, the 3D response surface and 2D contour plots, which are separately depicted in Figure 1 and Figure S2. Specifically, the relationships between A and B (Figure 1a) and between B and C (Figure 2b), as well as between A and C (Figure 1c), suggested well-defined optimum conditions, as they all showed conspicuous convexity. The 2D contour plots are graphic representations of relationships between response and experimental variables that can be used for determining the optimum conditions. Therefore, on the basis of these figures, the order of the three independent variables affecting the RE of phenol should be as follows: Fe/Ni ratio $>$ calcined temperature $>$ calcined time, since the phenol RE increased and then deceased with the Fe/Ni ratio rising at a fixed temperature, manifesting that Fe/Ni ratio and temperature play a decisive role in the catalytic ozonation of phenol. The 2D contours coupled with the $p$-value (Table 1) showed that there was an apparent interaction between the Fe/Ni ratio and temperature, as well as Fe/Ni ratio and time, whereas no obvious interaction of temperature and time was observed. According to the equation model, the optimal conditions of Fe-Ni/MAC fabrication were a calcined temperature of 431.885 $^\circ$C, an Fe/Ni ratio of 0.945 and a calcined time of 3.667 h. The corresponding predicted maximum phenol RE was 85.764%.

With the optimal parameters mentioned above, the binary catalyst was synthesized and afterwards used to degrade phenol to verify the quadratic equation. As seen in Figure S3, the RE of phenol went up gradually with time and finally reached 85.99% at 60 min, which was undoubtedly in good conformity with the predicted maximal value of 85.764% in the model. As a consequence, the optimized preparation procedure could provide a more suitable environment for the catalytic activity of Fe-Ni/MAC, thus benefiting the phenol degradation.
Figure 1. Response surface of phenol removal efficiency (RE) as a function of temperature and iron-nickel ratio (a), iron-nickel ratio and time (b) and temperature and time (c).

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Figure 2. XRD pattern (a), nitrogen adsorption–desorption isotherms (b) and pore size distribution of the fresh Fe-Ni/MAC (c).
2.2. Characterization of Fe-Ni/MAC

Figure 2a presents XRD patterns for the binary catalyst of Fe-Ni/MAC under the optimal conditions (calcined temperature: 431.8 °C; calcined time: 2h; Fe/Ni ratio: 0.946). The diffraction peaks at 2θ = 20.939, 26.667, 31.037, 35.509, 37.473, 39.509, 41.245, 43.692, 45.76 and 47.568 were attributed to the crystalline Fe-Ni alloy (JCPDS No. 18-0877), while the 2θ values at 26.603, 42.717, 43.45 and 44.669 were assigned to the carbon support (JCPDS No. 26-1076). In addition, some other peaks with the 2θ values falling into 45-50 and 65-70 also appeared, which were presumed to be NiFe$_2$O$_4$ (see XPS data). These results were almost distinct from those in a previous report, in which no distinguishable peak was observed corresponding to the crystalline Ni-Fe alloy when the catalyst was calcined at 500 °C for 2 h [17]. This phenomenon was probably due to the following two points: (1) the different catalyst support would create different crystalline structures and (2) the Ni$_x$Fe$_y$ alloy can be formed only in a certain range of Ni/Fe ratio [20]. That is to say, the Fe/Ni ratio gained by RSM in the current study was quite favorable for the formation of crystalline Fe-Ni alloy under our experimental conditions.

The nitrogen adsorption–desorption isotherms for the fresh Fe-Ni/MAC were performed and the results are displayed in Figure 2b. Evidently, with the relative pressure elevation, the catalyst adsorption volume increased and the curve of desorption was higher than that of adsorption to form a complete loop when the relative pressure varied from 0.4 to 1.0. Thereby, the N$_2$ isotherms corresponded to a type IV isotherm with the hysteresis loop being type H$_4$, in accordance with the International Union of Pure and Applied Chemistry (IUPAC) [26]. For the pore size distribution, a conspicuous peak at 4 nm could be seen (Figure 2c), which is consistent with the mesoporous range associated with the isotherm, further proving type H$_4$ as catalysts. Likewise, an average pore radius of 2.45 nm for Fe-Ni/MAC, listed in Table 2, also confirmed the above conclusion. With no doubt, ample mesoporous structures would give rise to a sufficient catalyst–pollutant contact to ensure an efficient reaction of catalytic ozonation. Apart from the mesoporous structure, a BET surface area of 502.68 m$^2$/g and an average pore volume of 0.31 cm$^3$/g were observed, which were comparable to some other relevant catalysts [15,27].

| BET Surface Area (m$^2$/g) | Langmuir Surface Area (m$^2$/g) | Average Pore Volume (cm$^3$/g) | Average Pore Radius (nm) |
|-----------------------------|---------------------------------|------------------------------|--------------------------|
| 502.68                      | 887.87                          | 0.31                         | 2.45                     |

The morphology of the developed catalysts after calcination was examined using SEM-EDS, and the corresponding results are exhibited in Figure 3. As observed in the figure, the surface of active carbon on which there were a few small holes was relatively smooth (Figure 3a), whereas the binary catalyst of Fe-Ni/MAC possessed a rougher surface coupled with a highly developed pore structure, and metal particles distributed uniformly without aggregation (Figure 3b), all of which are essential for the activity of a catalyst. A similar phenomenon could be found in a previous study where the metal particles on the catalyst support of Al$_2$O$_3$ were uniform in shape with a diameter of several tens of nanometers [20]. To further illustrate the distribution of Fe and Ni, elemental mapping was conducted to characterize the binary catalyst, as shown in Figure 3c–f. Clearly, the homogeneous distribution of both Fe and Ni was obtained, which could favor their close and effective contact to form bimetallic corrosion cells, and speed up the electron transfer of galvanic corrosion [28], thus promoting pollutant degradation.

The state of elements included in Fe-Ni/MAC was determined by XPS (Figure 4), whereby the peaks of O, C, Fe and Ni were found (Figure 4a). In Figure 4b, there are three main peaks observed at 711.0 eV, 714.0 eV and 724.2 eV that were ascribed to Fe (III) presenting in the form of NiFe$_2$O$_4$ [29], while the four peaks respectively located at the binding energy of 856.2, 861.8, 873.7 and 879.8 eV can be seen in Figure 4c, which confirmed the existence of Ni (II) [30]. In contradiction to the XRD results (Figure 2), however, both metallic Fe and Ni were not detected, the reason for which was the fact that there is an interaction between metallic Ni and Fe, leading to the binding energies of metallic Ni and Fe.
being higher than those of the standard XPS data [31], which likely suggests that the sample bulk phase is mostly an alloy phase and the surface is the oxidized species [31]. In addition, at least one regular alloy with a FeNi composition is known, and irregular bulk alloys with the compositions NiFe, Ni$_3$Fe$_2$ and Ni$_2$Fe have also been reported [27]. Thus, taking the XRD results into account, this phenomenon is consistent with a former study showing that bimetallic systems most likely contain a range of metal particles with somewhat different Fe–Ni ratios [27]. Figure 4d depicts the XPS spectra of the O 1s core level, in which the peaks with binding energy of 530.4 eV, 531.6 eV and 532.7 eV are indicative of the lattice oxygen, hydroxide oxygen and water oxygen [32,33], respectively. These results demonstrated that Fe-Ni alloy and NiFe$_2$O$_4$ were the dominant active species involved in the catalytic reaction.

**Figure 3.** SEM micrographs: active carbon (a); Fe-Ni/MAC (b) and element mapping micrographs: iron (c); nickel (d); carbon (e); oxygen (f).

**Figure 4.** X-ray photoelectron spectroscopy (XPS) spectra of full scale (a), Fe 2p (b), Ni 2p (c) and O 1s (d) for the Fe-Ni/MAC catalyst.
2.3. Catalytic Performance of Fe-Ni/MAC

2.3.1. Key Parameters Affecting the Catalytic Performance

In order to obtain optimal conditions, effects of key factors, including catalyst dosage, ozone concentration, initial pH and reaction time on the catalytic performance, were assessed through single-factor experiments (Figure 5). It is clear that the phenol RE rose dramatically from 61.94% at a catalyst dosage of 0.5 g/L to 94.25% at a catalyst dosage of 10 g/L, and then dropped to no more than 90% when the catalyst dosage was 20 g/L (Figure 5a), suggesting that (1) the increase in catalyst dosage could give a greater total number of active sites to facilitate the decomposition of ozone and produce more radical groups, (2) increasing the catalyst dosage could improve the molecule ozone transfer into the reaction solution [34] and (3) a higher catalyst dosage generated excess radical groups that may undergo recombination reactions or react with ozone to result in a decline in phenol RE [35]. Accordingly, a 10 g/L catalyst dosage was used in the following experiments.

\[ \text{HO} + \text{HO} \rightarrow \text{H}_2\text{O}_2 \]  \hspace{1cm} (2)

\[ \text{HO} + \text{O}_3 \rightarrow \text{O}_2 + \text{HO}_2 \]  \hspace{1cm} (3)

![Figure 5. Effect of catalyst dosage (a), ozone concentration (b), initial pH (c) and reaction time (d) on the phenol degradation.](image)

A gradient of different ozone concentrations (33.07, 43.82, 51.93, 64.41, 68.90 and 74.11 mg/L) exerted an obvious influence on the phenol RE (Figure 5b). For the low concentrations of 33.07 mg/L and 43.82 mg/L, phenol was hardly removed within 60 min, and subsequently the phenol RE increased to 36.39% when ozone was at 51.93 mg/L, indicating that ozone was still too low to degrade phenol effectively in a short time. When ozone was at 68.90 mg/L, the phenol RE climbed to 83.87%, yet the further increase in ozone made no remarkable contribution to the phenol degradation since the
ozone concentration in the liquid phase approached its maximum value at a fixed temperature [36]. As a consequence, the ozone concentration of 68.90 mg/L was selected as the optimal value in the following study.

Figure 5c shows the effect of initial pH on the phenol degradation. As illustrated in the figure, the range of pH could be divided into two parts: part I with a pH from 1.98 to 7.99 and part II consisting of pH between 9.96 and 12.00. In part I, the phenol RE increased from 51.99% to 67.19% within 60 min when the pH was elevated from 1.98 to 7.99, manifesting that the phenol degradation was not affected markedly in this pH range, whereas the phenol RE soared to 96.08% at pH 12.0 in part II but no significant difference was found between pH 9.96 and 12.00, revealing that a relatively high pH would contribute to the enhancement of phenol RE. A previous study reported that catalytic ozonation could be improved with the increment of initial solution pH, and the high removal efficiency was obtained under alkaline conditions [34], which was in agreement with the result observed in this study. Notwithstanding, as presented in Figure 5c, the pH beyond a certain value could not improve pollutant degradation greatly, as the catalyst is negatively charged at higher pH values, therefore creating repulsive electrostatic interactions between pollutants and the catalyst surface that may inhibit surface reactions [11].

Figure 5d exhibits the effect of reaction time on the phenol RE. As expected, the RE increased with an increase in reaction time, and the highest phenol RE was found to be 99.98% at 100 min. This phenomenon might be due to small molecular substances generated during the reaction that exerted a negative impact on the degradation of phenol. Overall, based on the results of single-factor experiments, the optimal conditions of catalytic ozonation by Fe-Ni/MAC were: catalyst 10 g/L, ozone 68 mg/L, pH 9 and reaction time 90 min, which were adopted in subsequent experiments.

2.3.2. Reusability and Stability of Fe-Ni/MAC Catalyst

From a practical point of view, durability is an extremely important property for prepared catalysts. Regarding durability, however, there are two competing conclusions. One is that the contaminant removal is improved after reuse, due to the modification of chemical functional groups on the catalyst surface by ozonation and the rise in both the pore volumes and the specific surface areas [37–39]. The other is that ozonation reduces catalytic properties of activated carbon due to a decrease in basic groups and an increase in the number of oxygenated surface functional groups, such as hydroxyl and carboxylic acid groups and nitro aromatic compounds [40]. While in the present study a slight decline could be seen in the catalytic activity of the Fe-Ni/MAC catalyst after reuse (Figure 6a), which seemed to be in accordance with the above second conclusion, the phenol RE still maintained a level of more than 86.57% after six cycles, verifying that the binary catalyst of Fe-Ni/MAC is suitable for the practical application. With respect to the catalyst stability, the leaching of Fe$^{3+}$ and Ni$^{2+}$ after recycling experiments was measured. As observed in Figure 6b, the levels of Fe$^{3+}$ and Ni$^{2+}$ leached from Fe-Ni/MAC after each cycle were below 3 mg/L and 0.5 mg/L, respectively, indicating that Fe on the catalyst surface was more prone to being dissolved than Ni during the catalytic ozonation process. However, the level of leaching of these two ions was so low that no secondary pollution could be caused. Undoubtedly, it can be concluded that the Fe-Ni/MAC process would be feasible and cost effective on the basis of both the reusability and stability results.

2.3.3. Real Phenol-Containing Wastewater Treatment by Fe-Ni/MAC

Real phenol-containing wastewater was used to investigate deeply the catalyst practicability. In this section, the characterization and analysis of wastewater were conducted by the fluorescence excitation emission matrices (EEMs), for this method is characterized by high detection sensitivity and easy operation. Figure S4 displays the 3D excitation emission matrices of the real phenol-containing wastewater before and after the treatment by Fe-Ni/MAC. It is fairly clear that a peak located at Ex/Em: 272 nm/298 nm, indicative of phenol [41], existed in the real wastewater before the reaction (Figure S4a), but it was almost totally reduced after the reaction and a new peak that might be attributed to the
intermediate of phenol degradation was observed (Figure S4b). A study reported that a more than 90% reduction of phenolic compounds in kraft pulp mill effluent was achieved when ozonation was preceded by chemical coagulation or powdered activated carbon adsorption [42]. Comparably, the binary catalyst of Fe-Ni/MAC prepared in our study would be more applicable and efficient when treating the real phenol-containing wastewater since the phenol concentration was as high as 1243 mg/L (Table S2) and no other methods were incorporated. Nevertheless, the potential intermediates produced during the phenol degradation which likely adversely affected the deep treatment of wastewater were not determined, and therefore more studies should be performed to address these problems in the future.

![Figure 6. Recycling experiments of Fe-Ni/MAC (a) and corresponding leaching of iron and nickel (b) performed under optimal conditions: catalyst 10 g/L, ozone 68 mg/L, pH 9 and reaction time 90 min.](image)

2.4. Investigation of Active Oxidative Species

As we know, the determination of active oxidative species was necessary and critical as they can enhance catalytic activity and play an indispensable part in the confirmation of reaction pathways and catalytic mechanisms in catalytic ozonation [8]. Accordingly, the catalytic mechanism of the Fe-Ni/MAC process was explored gradually through various radical scavengers, including ascorbic acid (AA), tert-butyl alcohol (TBA) and histidine (His), and the results are illustrated in Figure 7. As predicted, some radicals were generated in the catalytic ozonation process because the phenol RE fell from 91.77% to 68.41% when AA rose from 0.5 to 20 mmol (Figure 7a). AA is usually used to scavenge HO₂, OH and O₂ owing to its high reducibility [43], hence, a decrease of 28.93% for the phenol RE proved the existence of active oxidative species.

It was reported that the reaction rate constants of TBA with hydroxyl radicals and ozone were 5.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1} and 3.0 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}, respectively [44], demonstrating that TBA is a strong hydroxyl radical scavenger. Thus, TBA was utilized to assess the role hydroxyl radicals play in catalytic ozonation, and the corresponding results are presented in Figure 7b. Clearly, the addition of TBA did not remarkably suppress the degradation of phenol, implying that only a certain number of hydroxyl radicals were generated in the reaction system.

In light of the results showed in Figure 7a,b, the phenol degradation was not inhibited entirely, indicating that some other radicals should take effect apart from hydroxyl radicals. As such, His was added to the reaction system as it has been shown to scavenge both hydroxyl radicals and singlet oxygen (¹O₂) [45]. It can be seen from Figure 7c that the more His, the greater the inhibition to phenol removal. In particular, the phenol RE declined to 17.74% when His was 10 mmol, suggesting that the main reason for the degradation of phenol was due to singlet oxygen (¹O₂) rather than hydroxyl radicals (·OH). In consideration of the conversion of -O₂⁻ to ¹O₂ in a short time, it can be concluded that although some radicals like ·OH and ·O₂⁻ did function, singlet oxygen (¹O₂) was regarded as the most important radical in the Fe-Ni/MAC process.
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2.5. Possible Mechanisms Discussion

According to the above analysis and the present literature, the possible mechanisms for the removal of phenol by the Fe-Ni/MAC process was summarized as Equations (4)–(6). More specifically, after the addition of Fe-Ni/MAC, H$_2$O was strongly adsorbed on the surface of Fe-Ni/MAC and
dissociated into OH\(^{-}\) and H\(^{+}\), forming the surface hydroxyl groups. Afterwards, the adsorbed ozone on the catalyst surface interacted with surface hydroxyl groups to give rise to OH and \(\cdot O\_2\) (1O\(_2\)). Then, the resultant radicals, especially \(^1\)O\(_2\), took part in the degradation of phenol. In general, it is believed that ozone adsorbed on the surface is indispensable and subsequent transformation to active oxidative species is thought of as the main mechanism of pollutant removal by catalytic ozonation, yet various factors are involved in this process. For instance, the enhanced interfacial electron transfer resulted in the higher catalytic activity of NiFe\(_2\)O\(_4\)–H nanocatalysts \([46]\), and the textural and chemical surface properties of activated carbon might have impacts on the ozonolysis process \([47]\). As a result, more detailed studies would be needed to elucidate the heterogeneous catalytic ozonation of phenol by the binary catalyst of Fe-Ni/MAC.

\[
\begin{align*}
\text{Ni}^{2+}\text{Fe}_2\text{O}_4 + \text{OH}^- + 2\text{O}_3 & \rightarrow \text{Ni}^{3+}\text{Fe}_2\text{O}_4 + \text{OH} + \text{O}_2 + 2\text{O}_2^- (1\text{O}_2) \quad (4) \\
4\text{Ni}^{3+}\text{Fe}_2\text{O}_4 + 2\text{H}_2\text{O} & \rightarrow 4\text{Ni}^{2+}\text{Fe}_2\text{O}_4 + \text{O}_2 + 4\text{H}^+ \quad (5) \\
\text{Ni}^{2+}\text{Fe}_2\text{O}_4 + \text{H}_2\text{O} & \rightarrow \text{Ni}^{2+}\text{Fe}_2\text{O}_4 - \text{OH}^- + \text{H}^+ \quad (6)
\end{align*}
\]

3. Materials and Methods

3.1. Preparation of Fe-Ni/MAC

All chemical reagents were of analytical grade. To remove oil pollutants, the active carbon (Sinopharm, Shanghai, China) was soaked in 10% NaOH solution for 24 h and then soaked in 5% HCl solution for 4 h to eliminate metals as well as other impurities. After 2 h of water-boiling, the modified active carbon (MAC) was copiously washed with distilled water to neutral pH and dried at 105°C for further use.

Fe-Ni/MAC was synthesized by the co-precipitation method. In brief, a certain amount of MAC, ferric nitrate (Sinopharm, Shanghai, China) and nickel nitrate (Sinopharm, Shanghai, China) was mixed and oscillated for 4 h with a rotation speed of 130 rpm at 35°C. Following pH adjustment by a 5% ammonia solution, the resultant product was incubated for 4 h at 75°C and washed with distilled water until the solution was clear. Subsequently, the product was dried at 105°C for 2 h, cooled to room temperature and finally placed into a muffle furnace (LICHEN, Shanghai, China). The furnace temperature was increased gradually at a rate of 2°C/min to 400°C and was maintained for 2 h.

3.2. Characterization of Fe-Ni/MAC

For X-ray diffraction patterns, a D8 X-ray diffractometer (Bruker AXS, Karlsruhe, German) with a filtered Cu K\(\alpha\) radiation source, a voltage of 40 kV, a current of 40 mA and scanning at 2\(\theta\) from 5 to 90° was used to identify the composition and phase of the sample. To obtain specific surface area using the Brunauer–Emmett–Teller (BET) method, samples were degassed at 200°C for 6 h under vacuum conditions before measurement and then N\(_2\) adsorption–desorption was measured on an ASAP2460 instrument (Micromeritics, Norcross, GA, USA). A Zeiss HD scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) was utilized to observe the external morphology of samples. The surface oxidation states of samples were analyzed by X-ray photoelectron spectroscopy (XPS) (ThermoFisher Scientific, Waltham, MA, USA), and the high resolution spectra were calibrated by setting Cls at 284.8 eV.

3.3. Experimental Procedures

3.3.1. Optimization for Catalyst Preparation

According to our previous experimental results (data not shown), the calcined temperature, Fe/Ni ratio and calcined time were screened for the most important factors affecting the activity of catalysts. Therefore, the response surface methodology (RSM) based on a Box–Behnken design (BBD)
was employed to determine the optimal conditions of these three factors. Table S1 lists the detailed factors and levels adopted in the RSM based on a BBD. Both experimental designs and subsequent regression analysis of experimental data were conducted by Design Expert 11 (Stat-Ease, Minneapolis, MN, USA). The F-value and $p$-value were used to assess the model significance, while the quality of the polynomial model equation was judged statistically on the basis of the coefficient of determination $R^2$. All experiments were repeated at least three times.

### 3.3.2. Catalytic Activity Tests

The catalytic ozonation of phenol was performed in an experimental system exhibited in Figure S1, which consisted of ozone generating devices, a catalytic reactor and exhaust collecting devices. The ozone generating devices with air as the feed gas were composed of an ozone generator, an oxygen generator and a gas rotameter controlling ozone concentration. The catalytic reactor with a total volume of 500 mL and a height to diameter ratio of 3:1, placed on a magnetic stirrer, was continuously injected with ozone through a flexible pipe from the bottom. The exhaust collecting devices were used to destroy the gas coming out of the reactor by traps previously filled with a concentrated potassium iodide solution [48].

In a typical experiment, 0.25 g catalyst and 250 mL of 300 mg/L phenol solution were added into the reactor with the ozone concentration and flow rate being 67.03 mg/L and 100 mL/min, respectively. The suspension was magnetically stirred throughout experiments. At given time intervals, samples of no more than 5 mL were withdrawn, following which 1 mL of 0.02 mol/L sodium thiosulfate solution was added to quench the remaining ozone in the reaction solution. The effect of some factors, including pH, catalyst dosage, ozone concentration and reaction time, was investigated in light of a one-factor method. For reusability, the catalyst was recovered after each run and was subsequently dried at 80 °C for 120 min to obtain a “regenerated catalyst” that was used for the next run. This process was carried out six times under the same conditions. In the meantime, the suspension of each run was subjected to a measurement of Fe and Ni elements that might leach from the above “regenerated catalyst” because of repeated use.

In order to test the capability of degradation from engineering applications, the binary catalyst of Fe-Ni/MAC was also used to treat real phenol-containing wastewater under optimal conditions. The real wastewater came from an insulating material company (Yongchao, Dongguan, China), the quality of which is listed in Table S2.

### 3.3.3. Radical Scavenging Experiments

To identify the type of oxidation reaction, a few radical scavengers were used in the current study. As a highly reductive substance, ascorbic acid (AA) was employed to quench most kinds of reactive oxygen species (ROS) like HO$_2$, OH and O$_2^-$, while tert-butyl alcohol (TBA) and histidine (His) were utilized to scavenge OH and singlet oxygen ($^1$O$_2$), respectively. The detailed experimental procedures mentioned above can also be found in Table S4.

### 3.4. Analytical Methods

The phenol in aqueous solution was detected by UV–Vis spectrophotometry at a wavelength of 287.5 nm [49]. Briefly, a 3 mL sample was taken out periodically. After centrifugation, the sample was subjected to filtration with a pre-rinsed 0.45 µm filter and then analyzed in a spectrophotometer. The indigo method [50] was used to determine the ozone concentration in aqueous solution. COD was measured following standard methods [48]. The pH was recorded by a pH meter (FE28-Standard, Mettler Toledo, Zurich, Switzerland). Flame atomic absorption spectrometry [51] was adopted to analyze iron and nickel that leached from the catalyst. The fluorescence excitation emission matrices (EEMs) were carried out on a Hitachi spectrofluorometer F-4600 (emission wavelength: 250–550 nm; excitation wavelength: 200–500 nm; slit width: 5 nm).
4. Conclusions

A novel binary catalyst of Fe-Ni/MAC was synthesized by the co-precipitation method and the optimal preparation conditions were obtained by response surface methodology. Some conclusions can be drawn as follows:

1) The optimal conditions for catalytic ozonation obtained by response surface methodology (RSM) were catalyst 10 g/L, ozone 68 mg/L, pH 9 and reaction time 90 min.

2) Despite being reused six times, Fe-Ni/MAC catalysts were stable in the catalytic process with excellent performance and no secondary pollution.

3) The primary radical responsible for the degradation of phenol was proved to be $\cdot O_2^-$ ($^1O_2$), while other radicals played a minor role, based on radical scavenging experiments.

4) The fluorescence excitation emission matrices (EEMs) indicated that as much as 1243 mg/L phenol in the real wastewater was completely degraded.

Overall, Fe-Ni/MAC might be an efficient and practical catalyst in the degradation of phenol.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/10/1123/s1. Table S1: Factors and levels in RSM based on BBD, Table S2: Quality of the real phenol-containing wastewater, Table S3: Design and results of RSM based on BBD, Figure S1: Experimental system for the catalytic ozonation of phenol, Figure S2: Contour plots of phenol RE as a function of temperature and iron-nickel ratio (a), iron-nickel ratio and time (b) and temperature and time (c), Figure S3: Phenol removal by Fe-Ni/MAC synthesized under optimal conditions.

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