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Preparation of Ni$_x$O-Fe$_x$O/Ceramsite Catalyst and Its Application in Advanced Treatment of Pharmaceutical Wastewater

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Abstract: Using nickel oxide and ferric oxide materials, and ceramsite as carrier, the catalysts have been prepared by impregnation method including single-component and multi-component catalysts. The single-component and multi-component catalysts were used to study the COD removal performance of pharmaceutical secondary effluent respectively. First, the factors preparation parameters (i.e., calcination temperature and calcination time) of Ni$_x$O-Fe$_x$O/ceramsite and operational parameters (i.e., initial pH and the catalyst dosage) of O$_3$-Ni$_x$O-Fe$_x$O/ceramsite system were optimized, respectively. The results showed that the optimum conditions of Ni$_x$O-Fe$_x$O/ceramsite catalyst oxidation reaction were as follows: calcination temperature is 600°C, the calcination time is 5 h, the optimum catalyst dosage is 8g/L, the initial pH is in alkaline condition, which is more conducive to the reaction. The average COD removal rate of the effluent can reach about 80% under the above best conditions. then, characteristics of the Ni$_x$O-Fe$_x$O/ceramsite catalysts were studied through scanning electron microscopy (SEM), X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively. The results show that Nickel and iron oxides was uniformly deposited on the ceramsite surface when Ni$_x$O-Fe$_x$O/ceramsite was prepared. Finally, The stability of the catalyst in the system of O$_3$-Ni$_x$O-Fe$_x$O/ceramsite was studied. Collectively, these results suggest that the Ni$_x$O-Fe$_x$O/ceramsite should be proposed as a promising catalyst for the decomposition of ozone.

Keywords: Pharmaceutical Wastewater, Advanced Treatment, Heterogeneous Catalytic Oxidation, Ozone

1. Introduction

Pharmaceutical wastewater is very difficult to treat because of its complex water quality, high COD, large variation of water volume and high toxicity. The emergence of heterogeneous ozone-catalyzed oxidation technology helps to solve this problem. Ozone is extensively used as a clean and strong oxidant in wastewater treatment. Ozone heterogeneous catalytic oxidation is widely applied in pharmaceutical wastewater [1], printing and dyeing wastewater [2] and petrochemical wastewater [3], because of its simple catalytic process and no secondary pollution. Ozone can produce HO•(which oxidation potential is 2.8V, only second to F$_2$) with strong oxidation performance under the action of catalyst, which increases the mineralization degree of organic matter in wastewater [4-6].

In this paper, the ozone catalyst was prepared by impregnation with cheap ceramsite as carrier and nickel oxide and iron oxide as active components. The catalyst was used for catalytic oxidation experiments of secondary biochemical effluent from a factual pharmaceutical factory. Therefore, COD removal rate was selected as to evaluate the activity of the catalyst for the catalytic ozonation. The critical preparation parameters (calcination temperature, calcination time) were optimized to improve its catalytic performance. Also, two key operational parameters (i.e., initial pH and catalyst dosage) were investigated in Ni$_x$O-Fe$_x$O/ceramsite catalytic ozonation system, respectively. Moreover, the catalytic activities and stabilities of the Ni$_x$O-Fe$_x$O/ceramsite was investigated through scanning electron microscopy (SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD), respectively.

2. Experimental Section

2.1. Materials and Reagents

In this experiment, ceramsite, ferric nitrate (Fe (NO$_3$)$_3$·9H$_2$O), nickel nitrate (Ni (NO$_3$)$_2$·6H$_2$O), Potassium dichromate (K$_2$Cr$_2$O$_7$), Mercury (II) sulfate (HgSO$_4$), Silver sulfate (Ag$_2$SO$_4$), Ammonium ferrous sulfate ((NH$_4$)$_2$Fe (SO$_4$)$_2$·6H$_2$O) were purchased as analytical grade reagents. Meanwhile, ceramsite particles with an average particle size of approximately 3-5 mm were used in this study. Other chemical reagents used in the experiment were of analytical grade. as well, deionized water was used throughout the all experiments.

2.2. Preparation of Catalysts

The ceramsite with particle size of 3-5mm was activated by muffle furnace, and then washed and dried with deionized water. Weigh 20g of activated ceramsite carrier and immersed in 100 mL of certain concentration of nitrate solution for 24 h, filter it, dried at 120°C for 2 h and calcined at specific temperature in a muffle furnace for a certain time.

2.3. Catalytic Oxidation Experiment

The catalytic ozonation experiments were conducted in a Organic glass cylindrical reactor with an height diameter ratio is 10:1 under room temperature (20-25°C). A certain amount of catalyst was packed into the reactor. Then 500mL of pharmaceutical wastewater was added to the empty clean reactor before the experiment and the oxygen produced by the compressor compressed air entering the oxygen generator produced a mixture of ozone through the high-pressure discharge, Ozone bubbling through the microporous titanium plate at the bottom of the reactor to produces a large number of microbubbles, which reacts with the catalyst in a gas-liquid-solid three-phase reaction. The tail gas was absorbed by a 5% KI and 10% NaOH solution. Besides, To evaluate the performance of Ni$_x$O-Fe$_x$O/ceramsite, the preparation parameters (calcination temperature (from 400 to 800°C) and calcination time (from 3 to 7 h)) were investigated, respectively. The effects of operational parameters (initial pH (from 3.0 to 11.0), Ni$_x$O-Fe$_x$O/ceramsite dosage (from 2 to 10 g/L)) on the COD removal efficiency of the O$_3$-Ni$_x$O-Fe$_x$O/ceramsite system were optimized, respectively. The initial solution pH was adjusted with NaOH and H$_2$SO$_4$. Besides, five control experiments of (a) O$_3$ alone,(b) O$_3$/ceramsite,(c) O$_3$-FexO/ceramsite,(d) O$_3$-NiO$_x$/ceramsite,(e) O$_3$-Ni$_x$O-Fe$_x$O/ceramsite were setup to confirm the Catalytically active component of Ni$_x$O-Fe$_x$O/ceramsite and the best operating conditions of these control experiment. Then, characteristics of the Ni$_x$O-Fe$_x$O/ceramsite were observed by SEM, XRD and XRD, respectively. Finally, the stability of catalyst in ozonation system was studied.

2.4. Analytical Methods

The determination method of COD is potassium dichromate method. (HJ 828-2017)[7]. X-ray diffraction (XRD) measurement is carried out by X-ray diffractometer (model MAX-2500, Input Rigaku Co. Ltd., Japan) with CuKa radiation (40KV, 40 mV). Scans are taken with a 2θ range from 0.5°to 80°. The composition was determined with a Axios X-ray fluorospectrometer (XRF) (Panalytical B. V Co. Ltd, Holland). The morphology of the material was analyzed by S-4800-1 scanning electron microscope (SEM)(Hitachi Co. Ltd, Japan).

3. Results and Discussion

3.1. Effects of the Preparation Parameters

The preparation parameters were critical parameters for the catalyst performance of the Ni$_x$O-Fe$_x$O/ceramsite. To evaluate catalyst performance of the Ni$_x$O-Fe$_x$O/ceramsite for the decomposition of ozone, two experiments about preparation parameters (calcination temperature and calcination time) were carried out in impregnation-calcination system. In addition, the changes of COD removeal rate in the reaction process were analyzed to evaluate the catalytic activity of Ni$_x$O-Fe$_x$O/ceramsite. Meanwhile, the characteristics of Ni$_x$O-Fe$_x$O/ceramsite were detected by using XRD, XRF and SEM.

3.1.1. Effect of Calcination Temperature

The calcination temperature of catalyst is one of the important conditions for the preparation of catalyst. The calcination temperature has a great influence on the morphology of active components of catalyst. Under certain conditions, the nitrate supported in the carrier is calcined to lose crystalline water and decompose, which results in the decomposition of nitrate into metal oxides with catalytic activity and form crystallization and fixe catalyst structure [8-9].

The Ni$_x$O-Fe$_x$O/ceramsite was calcined by muffle furnace in the plenty of air, Nickel oxide and iron oxide compounds were formed on the surface of ceramsites substrate. Effect of calcination temperature (400, 500, 600, 700, 800°C) on the catalytic characteristics and performance of Ni$_x$O-Fe$_x$O/ceramsite was evaluated through the catalytic ozonation of organic matter in aqueous solution. As shown in Figure 1, in the high calcination temperature range, the COD removal efficiencies were better than the low calcination temperature range. The COD removal efficiency reached the uppermost value at the calcination temperature of 600°C and then declined with the increase of calcination temperature.

In short, the low or high calcination temperature would affect the catalytic activity of Ni$_x$O-Fe$_x$O/ceramsite, which could be explained at the following several points: (i) With increasing of calcination temperature, when the calcination temperature is lower than 600°C, the catalyst surface of the active center will increase. And the catalyst surface of the active sites would decrease when calcination temperature at above 600°C, which would limit the catalytic activity of Ni$_x$O-Fe$_x$O/ceramsite. (ii) The mechanical strength can be increased by increasing the calcination temperature. On the contrary, when the catalyst is calcined at a high temperature,

the catalyst channel will break, resulting in cavity collapse. And suitable mechanical strength and the catalyst channels of the catalyst surface could increase the catalytic activity of the Ni_xO-Fe_xO/ceramsite. The results show that the best calcination temperature is 600°C, the highest COD removal rate, up to 78%. Therefore, considering stability of Ni_xO-Fe_xO/ceramsite, the 600°C of the calcination temperature was selected to carry out the following experiments.
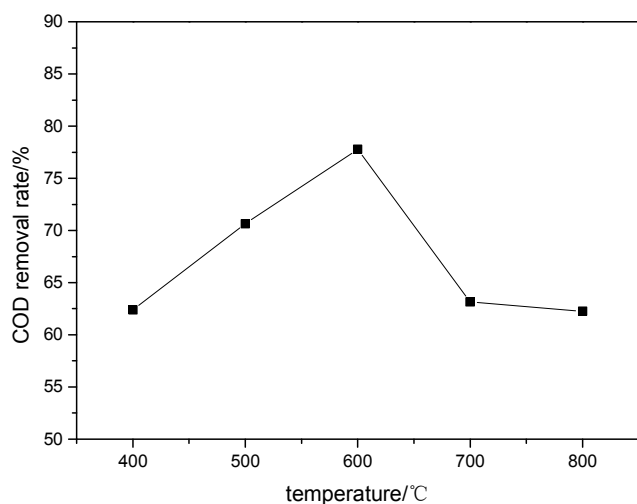

Figure 1. *Effect of calcination temperature on treatment of pharmaceutical wastewater (Ozone flow rate 1.0L/min, catalyst dosage 8g/L, pH 7, calcination time 5 h).*

3.1.2. Effect of Calcination Time

As an important step of calcination, nitrate decomposes and volatilizes to form active metal oxides during the calcination process. The experimental catalyst by impregnating in 1 mol/L nickel nitrate and iron nitrate solution for 24 hours, drying at 120°C and calcining at 600°Cfor 3, 4, 5, 6 and 7 hours respectively to prepare the catalyst for catalytic oxidation experiments. It can be seen form the figure 2 that Ni_xO-Fe_xO/ceramsite catalyst has the highest catalytic efficiency when calcined for 5h, compared with the catalyst calcined for 4 h, the removal efficiency of COD was improved by about 11%. while the COD removal rate decreases when the calcination time is 6h and the longer the calcination time is, the more obvious the COD removal rate changes. The results can be explained as follows: (i) The nickel film and iron film could not be completely oxidized to generate high active components in the surface through shorter calcination time (<5h). (ii) The Ni_xO-Fe_xO/ceramsite formed suitable catalytic surface, active sites, crystal form and crystallite size when calcination time reached up to 5h. (iii) The crystal form and crystallite size can change when the calcination time was extended from 5 h to 7h. Therefore the COD removal efficiency could reach upmost value through 5 h calcination time. Considering the cost, time and the COD removal efficiency, 5h calcination was selected as an optimal calcination time to carry out the following experience.
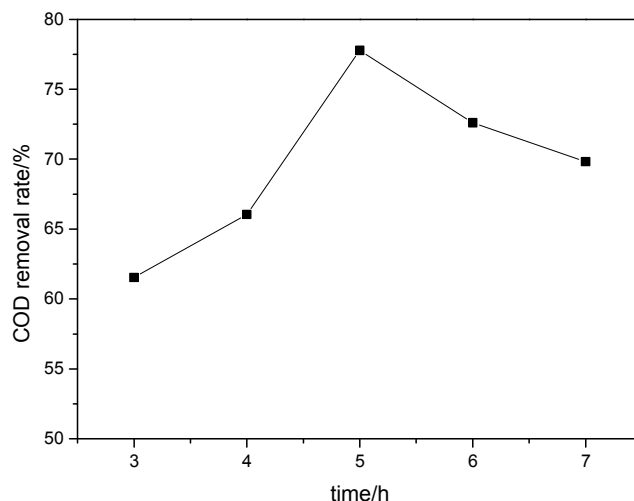

Figure 2. *Effect of calcination time on treatment of pharmaceutical wastewater (Ozone flow rate 1.0L/min, catalyst dosage 8g/L, pH 7.0, calcination temperature 600°C).*

3.2. Effects of Operational Parameters

The operating parameters are also important for the COD degradation in the O_3-Ni_xO-Fe_xO/ceramsite system. Thus, to obtain optimal conditions, two operational parameters including (a), initial pH, (b), catalyst dosage.

3.2.1. Effects of Initial pH

The pH value of solution might affect ozone decomposition and the surface properties of catalyst in the catalytic ozonation process [10]. The effect of pH on the catalytic ozonation system is shown in Figure 3. When the pH of the solution is 9.0, the removal rate of COD is the highest. When the pH of the solution increases to 11.0, the removal rate of COD slightly decreases. When the pH is less than 7.0, the removal rate of COD gradually decreases with the decrease of pH. It is known that HO• was more easily formed by ozone decomposition at alkaline condition, which react with organics in a non-selective mode [11]. However, in our study, the fastest removal of COD was achieved at pH 9.0 rather than 11.0. The results indicate that the PH is an important factor affecting the decomposition of ozone in aqueous solution. It not only affects the surface charge of organics in wastewater, but also affects the surface property of catalyst [12-13]. The pHPZC is the pH of the zero charge point of the catalyst surface [14]. On the one hand, the pH of the Ni_xO-Fe_xO/ceramsite catalyst is pHZPC=8.76. When the pH of aqueous solution is near the pHzpc of the catalyst, the catalytic oxidation system will show great advantages. On the other hand, this is consistent with the conclusion of some researchers that ozone is mainly oxidized directly in acidic conditions, while HO• is mainly oxidized indirectly in alkaline conditions. Because of the low selectivity of HO•, it has better mineralization ability for organic matter, so it is helpful for the degradation of organic matter in alkaline conditions [1, 15-16]. Therefore, Ni_xO-Fe_xO/ceramsite catalytic ozonation system shows the well efficiency for COD degradation at pH of 9.0.
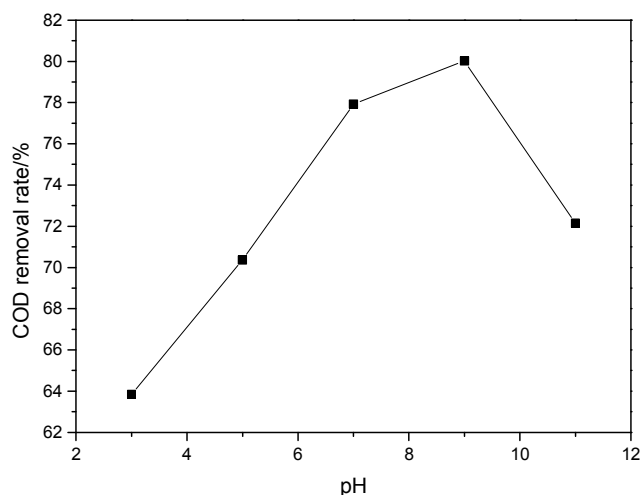
Figure 3. *Effect of initial pH on treatment of pharmaceutical wastewater (Ozone flow rate 1.0L/min, catalyst dosage 8g/L, pH 7.0, calcination temperature 600°C, calcination time 5 h).*

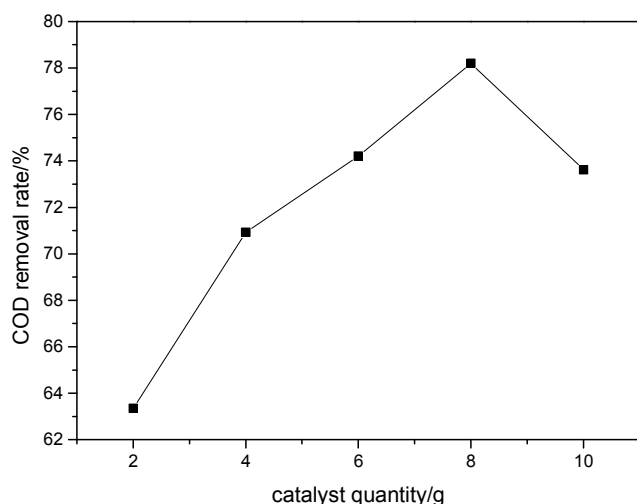### 3.2.2. Effect of Catalyst Dosage

Figure 4. *Effect of catalyst dosage on treatment of pharmaceutical wastewater (Ozone flow rate 1.0L/min, pH 9.0, calcination temperature 600°C, calcination time 5 h).*

Figure 4 shows that the influence of catalyst dosage on the COD removal by the catalytic ozonation process. The COD removal enhanced continuously from 63% to 78% with the Ni$_x$O-Fe$_x$O/ceramsite dosage increasing from 2 to 8 g/L during the catalytic oxidation. However, the COD removal dropped from 78% to 73% when the Ni$_x$O-Fe$_x$O/ceramsite dosage further increased from 8 g/L to 10 g/L during the catalytic oxidation. The result can be explained that Ni$_x$O-Fe$_x$O/ceramsite had more active sites with increasing the initial Ni$_x$O-Fe$_x$O/ceramsite dosage in a suitable range, which could heighten the reaction between the solution phase and the catalyst surfaces to promote the disintegration of ozone to generate HO• radicals [17-21]. However, the excessive amount of catalyst can not play a better catalytic effect, but has a mutual inhibition effect. At the same time, the excessive HO• radicals were produced by the excessive catalyst catalytic

ozonation, which can quench each other and reduce the COD removal rate. [22] Therefore, the phenomenon can be explained that a part of HO• radicals was quenched, which could cause the process of degradation of COD was limited. Thus, considering to the COD removal efficiency and economy, the optimal catalyst dosage of 8 g/L was selected to carry out the subsequent experiments.

3.3. Control Experiment

To evaluate the catalytic performance of Ni$_x$O-Fe$_x$O/ceramsite, five control experiments of (a) O$_3$ alone, (b) O$_3$/ceramsite, (c) O$_3$-Fe$_x$O/ceramsite, (d) O$_3$-NiO$_x$/ceramsite, (e) O$_3$-Ni$_x$O-Fe$_x$O/ceramsie, were setup to treat 500 mL pharmaceutical wastewater under the optimal conditions. As shown in Figure 5, the COD removal obtained by five control experiments (i.e., (a) 52%, (b) 63%, (c) 68%, (d) 73%, (e) 77% after 120 min treatment). The high COD removal efficiencies were obtained by the O$_3$-Ni$_x$O-Fe$_x$O/ceramsite process, while the low COD removal efficiencies were achieved by O$_3$ alone systems. For the alone ozonation system, COD molecules was degraded by direct ozonation [23]. Ni$_x$O-Fe$_x$O/ceramsite two-component catalyst can significantly improve the removal rate of COD compared with Fe$_x$O/ceramsite and NiOx/ceramsite single-active component catalysts. The results also reveal that nickel and iron oxides deposited on the ceramsite substrate can improve the catalytic activity. In other words, O$_3$ and Ni$_x$O-Fe$_x$O/ceramsite have a synergistic effect in O$_3$-Ni$_x$O-Fe$_x$O/ceramsite system. And similar literature also reported the result. [24] Therefore, the catalytic activity of Ni$_x$O-Fe$_x$O/ceramsite is better.
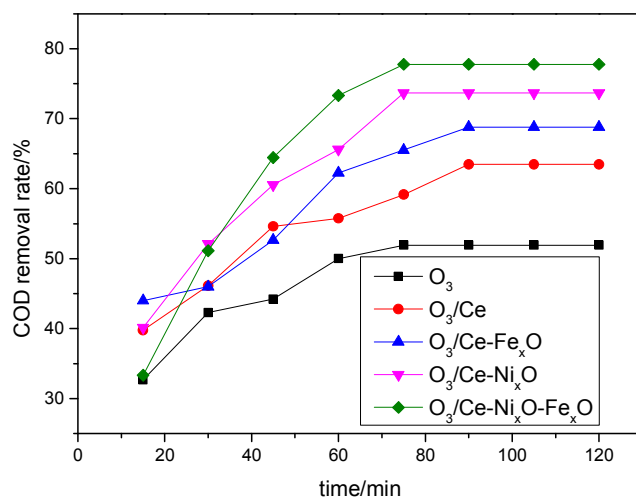

Figure 5. *Effect of active component selection on treatment of pharmaceutical wastewater (Ozone flow rate 1.0L/min, calcination temperature 600°C, calcination time 5 h, pH 9, catalyst dosage 8g/L).*

3.4. Stability of Catalyst

The stability of ozonation catalyst is an important factor in catalytic ozonation, especially for practical applications. The reusability of Ni$_x$O-Fe$_x$O/ceramsite catalyst was studied. Under the optimum preparation conditions of catalyst, the

catalyst dosage was 8g/L, and the ozone flow rate was 1.0L/min. The catalyst was recycled for 5 times and each reaction lasts for 75min. The COD removal rate of wastewater was measured, and the results are shown in Figure 6. With the increase of catalyst use times, the catalyst activity slightly decreased. From the experimental results, the average removal rate of COD of the catalyst used repeatedly remains at about 78%. The results show that the catalyst has stable activity, can meet the industrial application conditions, and has a good application prospect.
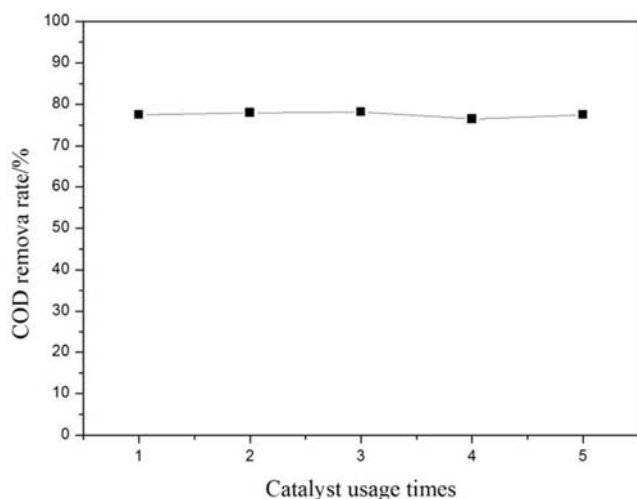

Figure 6. *Investigation of catalyst activity and stability (Ozone flow rate 1.0L/min, pH 9, catalyst dosage 8g/L).*

3.5. Characteristics of the Prepared Ni_xO-Fe_xO/ceramsite

Ni_xO-Fe_xO/ceramsite catalysts prepared under optimal preparation conditions were detected by SEM, XRF and XRD to investigate their surface morphology, elementary composition and compound structure, respectively.

Figure 7 shows the XRD patterns of ceramsite carrier and Ni_xO-Fe_xO/ceramsite catalyst. Compared with the XRD library, it is found that the distinguished peaks positioned at 37.25° and 43.28° are NiO characteristic diffraction peaks, and the 35.63° and 39.28° are Fe_2O_3 characteristic diffraction peaks. It was proved that the supported metal oxides are NiO and Fe_2O_3. In addition to the peaks related to SiO_2, the main component of ceramsite, the diffraction peaks of both NiO and Fe_2O_3 were sharp and intense, indicating their highly crystalline nature. No impurity peaks were observed, confirming the high purity of the two products.

XRF analysis of ceramsite carrier and Ni_xO-Fe_xO/ceramsite catalyst showed that the supported catalytic groups existed in the form of NiO and Fe_2O_3 from Tables 1 and 2. The Ni_xO-Fe_xO/ceramsite catalyst has higher content than the ceramsite carrier NiO and Fe_2O_3, which indicates active component is better supported on the carrier during the impregnation process, which is consistent with the XRD test results, such oxides are nickel ions and Iron oxide is a relatively stable oxide form.

The morphologies of ceramsite carrier and Ni_xO-Fe_xO/ceramsite catalyst was illustrated in Figure 8 Compared with the ceramsite carrier, the number of electron holes in Ni_xO-Fe_xO/ceramsite catalyst was increased, the oxide crystal grains can be clearly observed with good dispersion.
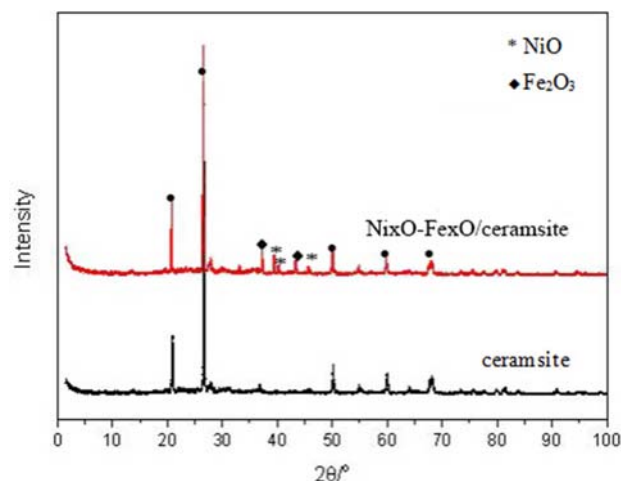

Figure 7. *XRD patterns spectra of ceramsite carrier and Ni_xO-Fe_xO/ceramsite catalyst (calcinations temperature=600°C, calcination time=5 h).*

Figure 8. *SEM imaging of (a) ceramsite carrier, (b) Ni_xO-Fe_xO/ceramsite catalyst (calcinations temperature=600°C, calcination time=5 h).*

Table 1. *The existence Form and Content of Ceramic Carrier Elements.*

elements	Si	Al	P	Ca	Fe	S
Existing form	SiO_2	Al_2O_3	P_2O_5	CaO	Fe_2O_3	SO_3
content（%）	97.506	1.134	1.021	0.206	0.060	0.073

Table 2. *The existence Form and Content of Ni$_x$O-Fe$_x$O/ceramsite catalyst Elements.*

elements	Si	Al	P	Ca	Fe	Ni
Existing form	SiO$_2$	Al$_2$O$_3$	P$_2$O$_5$	CaO	Fe$_2$O$_3$	NiO
content（%）	87.879	0.703	0.0190	1.102	4.748	5.549

4. Conclusions

The catalyst of Ni$_x$O-Fe$_x$O/ceramsite for catalytic oxidation degradation of COD in a catalytic ozone oxidation system was studied. To investigate the performance of Ni$_x$O-Fe$_x$O/ceramsite, several optimal key parameters (i.e., calcination temperature=600°C, calcination time=5 h, initial pH=9.0 and catalyst dosage=8 g/L) were obtained in this study. The Ni$_x$O-Fe$_x$O/ceramsite shows the optimal catalytic activity and stability for catalytic ozonation of COD removal under the optimal conditions. Furthermore, Ni$_x$O-Fe$_x$O/ceramsite catalysts prepared at low calcination temperatures have lower activity, while nickel and iron salts in surface of ceramsite are oxidized to require higher calcination temperature. In addition, characteristics of Ni$_x$O-Fe$_x$O/ceramsite were observed by SEM, XRF and XRD. The results indicate that Ni$_x$O-Fe$_x$O/ceramsite had formed more uniform, dense and smaller size Metal oxides and higher specific surface area to support on the surface of ceramsite substrate. In short, all results indicate that Ni$_x$O-Fe$_x$O / ceramsite has better catalytic activity and stability for ozone catalytic oxidation and Ni$_x$O-Fe$_x$O/ceramsite should be used as a promising catalyst for catalytic ozonation in the field of refractory wastewater treatment.

Acknowledgements

References

[1]   Cai, S. Q., Dai QZ, Wang JY, et al. Heterogeneous catalytic ozone oxidationfor pharmaceutical wastewater treatment. Journal of environmental science, 31 (7), 1440-1449.

[2]   Meng, G. H, Liu BH, Wan H, et al. Heterogeneous catalytic ozonation of dyeing wastewater by Cu/C-Al$_2$O$_3$. Industrial water treatment, 34 (10), 41-44.

[3]   Chen, C, Chen H, Guo X, Guo S and Yan, G. (2014). Advanced ozone treatment of heavy oil refining wastewater by activated carbon supported iron oxide. Journal of Industrial and Engineering Chemistry, 20 (5), 2782–2791.

[4]   Jans, U, Hoign J. Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals. Ozone Science & Engineering, 1998, 20 (1), 67-90.

[5]   Zhao, L, Ma J, Sun Z and Liu H. (2009). Mechanism of heterogeneous catalytic ozonation of nitrobenzene in aqueous solution with modified ceramic honeycomb. Applied Catalysis B: Environmental, 89 (3-4), 326-334.

[6]   State Environmental Protection Administration. Water and Wastewater Monitoring and Analysis Methods [M]. 4 Edition. Beijing: China Environmental Science Press, 2002: 211-213.

[7]   Wei, FS, Bi T and W Q Qi. Water and wastewater monitoring analysis methods [M]. Beijing：China Environmental Science Press, 2002.

[8]   Ye, BH., LL Jiang and KM Wei, et al. (2007) Multiple-metal (Ni-Cu-Mn-K/γ-Al$_2$O$_3$) Catalysts for High-temperature Water Gas Shift Reaction: Preparation by Equi-volumetic Impregnation and Characterization. Journal of Inorganic Chemistry, 23 (8): 1358-1364.

[9]   Yue, ZY, HF Miu and HY Ren, et al. (2012). Degradation of Medroxyprogesterone in Drinking Water by Ozone Oxidation. Environmental Science (04), 189-195.

[10]   L, N. K. V and H. Fu. pH effects on catalytic ozonation of carboxylic acids with metal on metal oxides catalysts, Top. Catal. 33 (2005) 249–256.

[11]   Ma, J, M. Sui, T. Zhang and C. Guan. Effect of pH on MnOx/GAC catalyzed ozonation for degradation of nitrobenzene, Water Res. 39 (2005) 779–786.

[12]   Huang, Y, Y Sun, Z Xu, M Luo, C Zhu and L Li. (2017). Removal of aqueous oxalic acid by heterogeneous catalytic ozonation with mnox/sewage sludge-derived activated carbon as catalysts. Science of The Total Environment, 575, 50-57.

[13]   Hu, E, X Wu, S Shang, XM Tao and L Gan. (2015). Catalytic ozonation of simulated textile dyeing wastewater using mesoporous carbon aerogel supported copper oxide catalyst. Journal of Cleaner Production, 112, 4710-4718.

[14]   Zhao, L, Z. Sun and J. Ma. Novel relationship between hydroxyl radical initiation and surface group of ceramic honeycomb supported metals for the catalytic ozonation of nitrobenzene in aqueous solution, Environ. Sci. Technol. 43 (2009) 4157.

[15]   L, N. K. V and Roshani, B. (2010). Kinetic of benzotriazole oxidation by ozone and hydroxyl radical. Water Research, 44 (6), 0-2066.

[16]   Zhou, L, D Wang, S Zhang and PP Fan. (2013). Effect of activated carbon and pH value on kinetic parameters of ozonation process. Environmental science and Technology (09), 13-16+22.

[17]   Sui, MH, Sheng L, Lu K, et al. FeOOH catalytic ozonation of oxalic acid and the effect of phosphate binding on its catalytic activity [J]. Applied Catalysis B Environmental, 2010, 96 (1-2): 94-100.

[18]   Zeng, Z, H. Zou, X. Li, B. Sun, J. Chen and L. Shao. Ozonation of acidic phenol wastewater with O$_3$/Fe (II) in a rotating packed bed reactor: optimization by response surface methodology, Chem. Eng. Process. Process Intensif. 60 (2012) 1–8.

[19]   Pillai, K. C, T. O. Kwon and I. S. Moon. Degradation of wastewater from terephthalic acid manufacturing process by ozonation catalyzed with Fe^{2+}, H$_2$O$_2$ and UV light: direct versus indirect ozonation reactions, Appl. Catal. B-Environ. 91 (2009) 319–328.

[20] Arslan, I. Treatability of a simulated disperse dye-bath by ferrous iron coagulation, ozonation, and ferrous iron-catalyzed ozonation, J. Hazard. Mater. 85 (2001) 229–241.

[21] Beltran, F. J., F. J. Rivas, R. Montero-de-Espinosa. Iron type catalysts for the ozonation of oxalic acid in water, Water Res. 39 (2005) 3553–3564.

[22] Buxton, G. V., C. L. Greenstock, W. P. Helman and A. B. Ross. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/.O− in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886.

[23] Xing, S, X. Lu, J. Liu, L. Zhu, Z. Ma and Y. Wu. Catalytic ozonation of sulfosalicylic acid over manganese oxide supported on mesoporous ceria, Chemosphere 144 (2016) 7–12.

[24] Avramescu, S. M, C. Bradu, I. Udrea, N. Mihalache and F. Ruta. Degradation of oxalic acid from aqueous solutions by ozonation in presence of Ni/Al$_2$O$_3$ catalysts, Catal. Commun. 9 (2008) 2386–2391.