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Study of Activated Carbon Supported Nickel Catalyst for Adsorption of Phenolic Wastewater

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Phenolic wastewater containing *p*-chlorophenol and *o*-chlorophenol can be adsorbed by activated carbon. This procedure reduces the COD value. In order to raise the adsorptivity of activated carbon for organic pollutants in phenolic effluent, the synthesis of activated carbon supported nickel catalyst was prepared and used in the treatment of phenolic wastewater, the affect factor and mechanism were investigated. The results showed that the adsorption capacity improved significantly because of the coordination between nickel and hydroxyl functional groups existed in the phenolic. Maintaining temperature at 25 °C, pH at 6, 2 h of reaction time and 40 mg/L of H_2O_2, the degradation rate of chlorophenol exceeded 80 %. This method incorporated adsorption and catalytic oxidation. It has important action for the practice and extension of catalytic wet oxidation.

Keywords: Activated carbon, Catalytic oxidation, Phenolic effluent, Nickel.

INTRODUCTION

Phenolic treatment is the focus of environmental research at home and abroad. Because this kind of is large amount, complex, water quality changing heavily, high concentration of organic pollutants and hard biochemical degradation, It was recognized as the most difficult to deal with the degradation [1]. At present, majority uses simple materialized-regeneration means to handle phenols, this technique can not attain the protecting environmental standard [2].

Catalytic wet oxidation (CWO) is an efficient method for treating organic that is highly concentrated, toxic and difficult to be biodegraded. Traditional wet air oxidation (CWAO) is not a good means, the effect of oxidation degradation for phenolic is low, so the catalytic oxidation technique with fixed bed loaded catalysts was utilized widely in recent years [3]. The key of this way is optimization of fixed bed, loaded catalysts and oxygenant. Wang *et al.* [4] studied the performance of catalysts supported on various fixed bed, such as Al_2O_3, SiO_2 and H molecular sieve, the results showed that activated carbon was the best carrier. Li *et al.* [5] investigated the catalytic activity of loaded different metal oxide on the fixed bed, the conclusion was that copper oxide or nickel oxide has high catalytic effect.

In this paper, the activated carbon supported nickel catalyst was used, the perhydrol was added as oxygenant. The activated carbon is a excellent and low-cost adsorption catalytic carrier due to high specific surface area. Otherwise, the perhydrol was oxidized quickly into homolytic when actived carbon was loaded by nickel compound in given conditions. This method can increase primely the removal rate of organic pollutants in phenolic because of the appearance of strong oxidative, high-active, non-selective oxhydro radical [6-8]. The experimental results indicated that this method is an proper means for phenolic treatment, which can reduce effectively the chemical oxygen demand (COD). At the same time, this technique can overcome many shortcomings of traditional wet air oxidation, such as strict reaction conditions, limited solubility and short lifetime of oxidant at constant pressure [9,10].

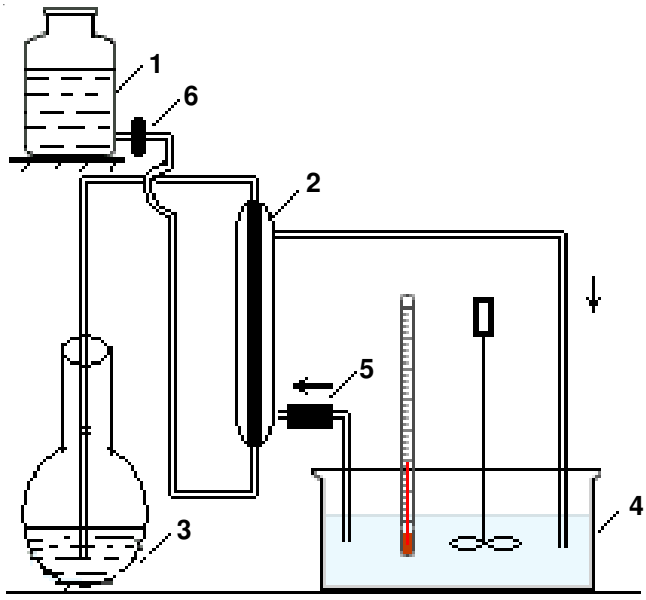
EXPERIMENTAL

Equipment and reagent: Glass column: Diameter is 25 mm, altitude is 200 mm, a constant temperature water interlayer is designed outside it; active carbon: its shape is rodlike, Diameter is 1.0 mm, height is 3 mm, Liyang Zhuxi Activated Carbon Co., Ltd); UV-265 spectrophotometer (Shimadzu company, Japan); 501 super thermostat (Shanghai experimental instrument factory); DRB200 COD determinator: The United States of America, ACAH. *p*-chlorophenol: 5.0×10^{-3} mol L^{-1}, *o*-chlorophenol: 5.0×10^{-3} mol L^{-1}; $Ni(NO_3)_2$ solution: 5.0 %; H_2O_2 solution: 75 %. The above reagents are chemically pure, the experimental water is redistilled water.

Preparation of activated carbon column supported nickel: Rod like activated carbon was dipped in 5 % NaOH

solution for 12 h, then filtrated with vacuum and washed with deionized water to neutral and that, the rod like active carbon was embathed with nitric acid solution that volume ratio is 5:1 for 12 h, filtrated with vacuum and washed with deionized water to neutral, then dried at 80 °C for 2 h. The pretreated active carbon was dipped with 5 % of $Ni(NO_3)_2$ solution for 24 h, filtered with decompress, scrubbed with water until there is no Ni(II) to be detected, then leave to dry naturally. After that the active carbon loaded nickel was dried at 80 °C, successively put in an oven at 120 °C for 2 h and chamber electric furnace at 280 °C for 3 h. In the end, the active carbon column filler supported nickel was installed evenly into constant temperature glass columns (both ends are filled with glass silk). Thus phenolic treatment column with active carbon supported nickel has been prepared.

Degradation experiment of phenolic solution: Test device of treatment of phenolic wastewater was shown in Fig. 1. Filling volume of water treatment agent was 150 mL, its height was 200 mm. A certain concentration of phenolic solution was put into the tubualted bottle (Fig. 1), connected water processing system. Keeping treatment temperature at (25 ± 5) °C, the adsorption catalysis column was filled first with phenolic, let stand for 2 h. Kept the phenolic flowing speed of 5 mL min^{-1}, the treated water sample was gathered in a volumetric flask (Fig. 1). Determined the degradation rate before and after water treatment, evaluated the effect of catalytic degradation.



1. Phenolic effluent; 2. Adsorption catalysis column; 3. Treated recovery liquid; 4. Super constant temperature batht; 5. Pump; 6. Flowmeter

Fig 1. Test device to handle phenolic effluent by adsorption-catalysis

Determination of degradation rate: Under the experimental condition, the maximum wavelength was ascertained by spectrophotometric scanning for a certain concentration of simulated phenolic, then determined the absorption of series concentration simulated phenolic at maximum wavelength, made the linear regression equation. Thus we can obtain the corresponding relationship of absorption (A) and concentration (C). Calculating formula of degradation rate (η) of the sample was shown as follow:

$$\eta = 100\ \% \times (A_0–A)/A_0$$

or

$$\eta = 100\ \% \times (C_0–C)/C_0$$

RESULTS AND DISCUSSION

Effect of aeration oxidation without catalyst: 500 mL of phenolic wastewater was transferred to the test device (Fig. 2). The oxidated degradatoin rate was investigated without catalyst. The results showed that the COD of phenolic wastewater was down slightly, its η = 15 %, the result was not satisfactory.

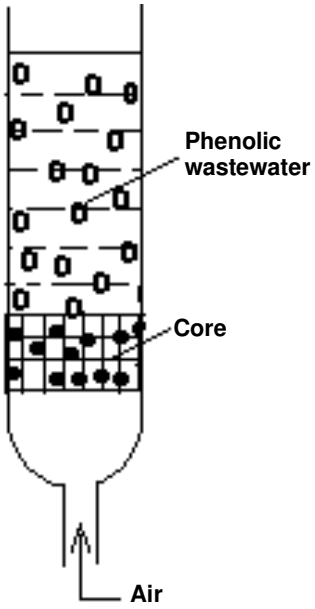


Fig. 2. Catalytic reactor for experiments

Suitable acidity of catalytic oxidation system: The active component loss and working life of catalysis was influenced by the system acidity. According to the experimental method, the removal rate of COD in phenolic wastewater was reviewed with the change of acidity and the result was showed in Fig. 3. It can be seen from Fig. 3 that the catalytic activity was higher at a pH of 5-7. The degradation rate of COD in phenolic effluent has been above 70 %. Furthermore, the degradation rate of COD was up to 86 % when the pH of reaction system was 6.0. We also found in this experiment that the catalytic activity decreased at a low acidity (pH < 4), the degradation rate was less than 50 % when the catalyst was used repeatedly 2-3 times. This is because that the active component loaded in the surface and pore of activity carbon was dissolved rapidly. So 6.0 of pH was used in the experiment.

Effect of catalyst dosage on removal rate of COD in phenolic: In order to study the effect of catalyst dosage on catalytic oxidation efficiency, the catalytic oxidation reaction was examined under different amount of active carbon supported nickel. The optimal dose of catalyst was ascertained and showed in Fig. 4. From Fig. 4, it was found that the degradation rate (η) rose slowly with the increase of catalyst dosage when the catalytic weight was less than 4 g. On the contrary, the advance of the degradation rate was not obvious when the catalytic weight exceeded 4 g. It is considered that the 8 g/L of catalyst dose was used in this work.

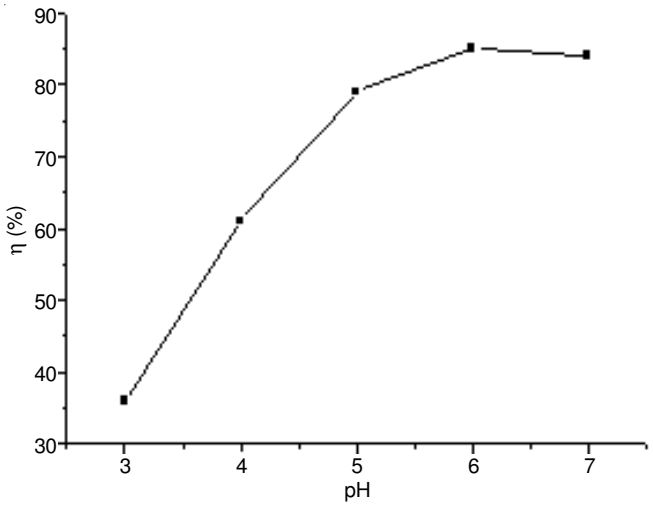


Fig. 3. Effect of pH on catalytic oxidation

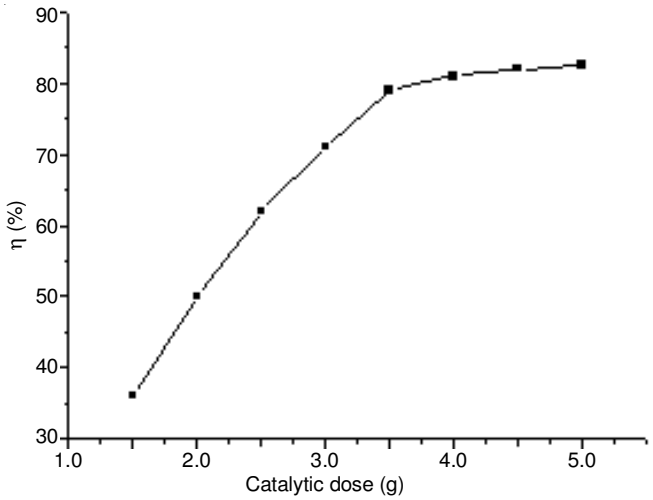


Fig. 4. Effect of catalyst dosage on catalytic oxidation

Effect of contact time of phenolic effuent and active carbon catalyst: According to test device of Fig. 1 and the experimental method, the removal rate of COD was investigated with the different residence time of phenolic wastewater in active carbon column, the result was showed in Fig. 5. It is clear from that the degradation rate increase (Fig. 5), degradation rate with the extension of reaction time and that, the degradation rate rose obviously while the reaction time was less than 120 min. The degradation rate curve became gently when the residence time of phenolic wastewater in active column was more than 120 min. All things considered, such as adding of oxidation time, power consumption and degradation time, the optimal reaction time was 120 min.

Performance comparison of activated carbon and activated carbon (AC) supported nickel: According to test device of Fig. 1 and the experimental method, the catalytic oxidation performance of activated carbon and activated carbon supported nickel was studied. The result was showed in Fig. 6. From the Fig. 6, it was found that the degradation rate was less than 33 % when activated carbon was used. Relatively, the degradation rate could exceed 80 % when activated carbon supported nickel was used. So the activated carbon supported nickel was used in this experiment.

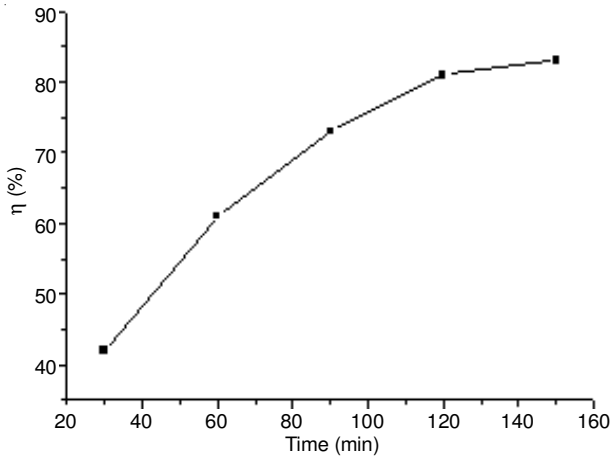


Fig. 5. Effect of contact time of phenolic effuent and active carbon catalyst

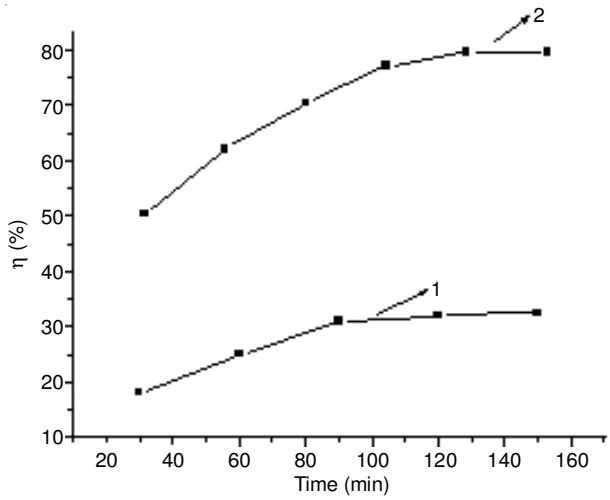


Fig. 6. Comparison of Ni/AC and AC on catalytic oxidation

Effect of adding dose of H_2O_2 on removal rate of COD: According to test device of Fig. 1 and the experimental method, the removal rate of COD was studied with the change of reaction time when different adding dose of H_2O_2 was used (Fig. 7). From the Fig. 7, it was found that adding H_2O_2 influenced significantly on the degradation rate. But the degradation rate increased indistinctively when the adding dose of H_2O_2 exceeded 40 mg/L and reaction time was more than 90 min. So 40 mg/L of H_2O_2 was used in this experiment.

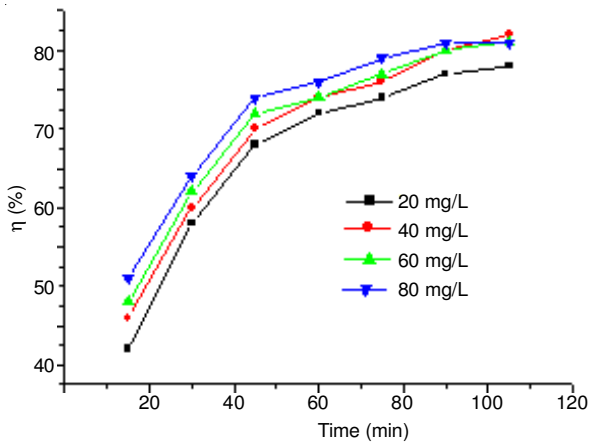


Fig. 7. Effect of the adding dose of H_2O_2 on removal rate of COD

Study of catalytic life: In order to understand the catalytic loss and the effect of repeated use, the catalyst was used in the catalytic oxidation of phenolic under the optimal conditions. The catalyst was removed from the catalytic column after each test, dried and weighed, used in the experiment again, the results was showed in Fig. 8. From Fig. 8, it was found that the removal rate of COD was more than 70 % when the repeated use of catalyst was less than six. The removal rate of COD fell rapidly when the repeated use of catalyst was more than six. So no more than six times of catalyst was used usually.

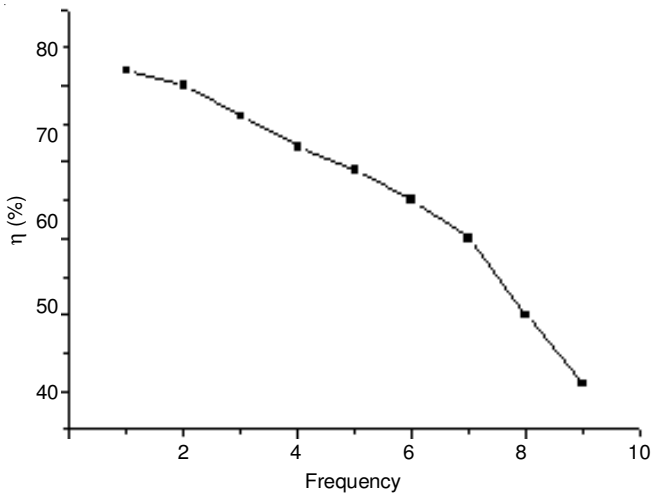


Fig. 8. Catalytic service life

Determination of phenolic wastewater taken from different sources: According to the experiment, the phenolic wastewater taken from different sources was determined under optimal conditions. The results indicated that the removal rate of all samples was more than 82.3 %.

Conclusion

The active carbon supported nickel has good catalytic oxidition ability for phenolic wastewater. Its effect was best when 6.0 of pH, 8 g/L of active carbon supported nickel, 120 min of reaction time and 40 mg/L H_2O_2 was used. On the other hand, no more than six times of catalyst was used usually, becaues the catalytic mass lost greatly due to the damage of activated carbon.This method incorporates absorption, catalytic oxidation and filtration. It is possible to put catalytic wet oxidation into practice by using fixed bed equipment.

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REFERENCES

1. F. Luck, *Catal. Today*, **53**, 81 (1999); https://doi.org/10.1016/S0920-5861(99)00112-1.
2. M. Richter, M. Fait, R. Eckelt, M. Schneider, J. Radnik, D. Heidemann and R. Fricke, *J. Catal.*, **245**, 11 (2007); https://doi.org/10.1016/j.jcat.2006.09.009.
3. X. Tang, L. Li and X. Zeng, *Fuel Chem. Technol.*, **37**, 629 (2009).
4. R.Y. Wang, Z. Li and H.Y. Zheng, *Chin. J. Catal.*, **30**, 1068 (2009).
5. W.F. Li, S.M. Zhu and T.S. Song, *J. Nanjing Univ. Technol.*, **28**, 5 (2006).
6. Q.S. Liu, T. Zheng, P. Wang, J.-P. Jiang and N. Li, *Chem. Eng. J.*, **157**, 348 (2010); https://doi.org/10.1016/j.cej.2009.11.013.
7. F. FU and Q. Wang, *J. Environ. Manage.*, **92**, 407 (2011); https://doi.org/10.1016/j.jenvman.2010.11.011.
8. M. Richter, M.J.G. Fait, R. Eckelt, E. Schreier, M. Schneider, M.M. Pohl and R. Fricke, *Appl. Catal. B*, **73**, 269 (2007); https://doi.org/10.1016/j.apcatb.2006.11.015.
9. M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv and Q. Zhang, *J. Hazard. Mater.*, **211-212**, 317 (2012); https://doi.org/10.1016/j.jhazmat.2011.10.016.
10. M.S. Han, B.G. Lee, B.S. Ahn, D.J. Moon and S.I. Hong, *Appl. Surf. Sci.*, **211**, 76 (2003); https://doi.org/10.1016/S0169-4332(03)00177-6.