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An Effective Process for Removing Acrylonitrile from Wastewater

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The aim of this paper was to study the suitability of catalytic wet air oxidation for the treatment of wastewater containing 4000 mg/L acrylonitrile. Experiments were conducted in a 0.5 L high pressure batch reactor using $Cu(NO_3)_2$ as homogeneous catalyst. Temperature, oxygen dose, catalyst concentration and residence time have been caried from 483 to 523 K, 7.67-61.32 g/L, 50 to 250 mg/L and 1-9 min, respectively. The 250 mg/L Cu^{2+} catalyst performs chemical oxygen demand, total organic carbon and acrylonitrile conversions over 97.23, 97.78 and 94.87 % after 9 min reaction at 523 K and 38.33 g/L O_2 dose. Catalyst concentration was found to have a significant impact on the oxidation of acrylonitrile wastewater. The results obtained in this work indicated that the catalytic wet air oxidation was an effective pretreatment method for the acrylonitrile wastewater.

Keywords: Catalytic wet air oxidation, Acrylonitrile wastewater, Homogeneous catalyst, Removal.

INTRODUCTION

Acrylonitrile is a kind of important organic chemical raw materials. It occupies a significant position and has a broad prospect in synthetic resin, synthetic fiber, synthetic rubber polymer material[1]. Acrylonitrile is emitted from the industrial plants in the form of vapors and aqueous effluents and is toxic and hazardous to aquatic life as well as human beings[2]. Due to its high toxicity, it is listing 4 among certain 52 kinds of priority control of toxic chemicals in China[3] and it is also the third in the EPA list among 129 priority pollutants[4]. So acrylonitrile is one of the important harmful pollutants to the environment and acrylonitrile bearing effluents cannot be discharged without detoxification into the environment. The treatment and disposal of acrylonitrile represents major challenges for petrochemical industries. Acrylonitrile wastewater treatment consumes a high portion of budget of companies' production plant and refiner. Several conventional technologies, such as landfill, biological treatment, incineration and so on, for the treatment and disposal of acrylonitrile have been implemented. However, due to the long reaction time, low removal rate and secondary pollution these methods bring to the environment, currently no technology has reached a satisfactory solution from the environmental and highly effective point of view. Consequently, there is a need for environmentally benign technologies capable to effectively neutralize the acrylonitrile wastewater and reduce its adverse impacts on the environment.

Recently, oxidation has attracted attention as a potential technique that can be employed as an alternative for the treatment of effluent containing toxic organic compounds. The wet air oxidation (WAO) process, which involves the ingredient of active oxygen species, such as hydroxyl radicals, employs severe operating conditions (temperature from 403 to 573 K and pressure from 0.5 to 20 MPa) for treatment of effluents containing high chemical oxygen demand (COD) or total organic carbon (TOC) or toxic contaminants for which other methods are unfeasible. The elevated pressure facilitates the enhancement of oxygen solubility in water, as well as keeping water in liquid state and the high temperature increases the reaction rate and generation of free radicals. The oxidation of dilute aqueous solutions of refractory organic pollutants using air or oxygen as an oxidizing agent over a catalyst, so-called catalytic wet air oxidation (CWAO), has already largely demonstrated its effectiveness in removing toxic compounds. Through the catalytic wet air oxidation method, the organic compounds are completely converted to CO_2 and H_2O or partly oxidized to less toxic intermediates[5-8]. Compare to wet air oxidation, the catalytic wet air oxidation can be carried out at much lower temperatures, leading to a significant reduction in the operating and fixed costs. A significant amount of research has been conducted on catalytic wet air oxidation and the development of catalysts for use in catalytic wet air oxidation over the last three decades[9-12].

The purpose of the present study was to investigate the performance of the catalytic wet air oxidation to acrylonitrile wastewater and to examine the feasibility of the technology as a pre-treatment for biological remediation to reduce toxic organic compound. The effect of the operating conditions on chemical oxygen demand, total organic carbon and acrylonitrile as well as removal of the acrylonitrile wastewater, including temperature, the concentration of catalyst, time of reaction and O_2 dose were studied. Based on the experimental results, optimal operating conditions will also be offered.

EXPERIMENTAL

Characteristics of the acrylonitrile wastewater: Acrylonitrile wastewater used in the experiments was obtained in a cesspit from the Sinopec Daqing Ltd., China. The wastewater contains 4000 mg acrylonitrile per liter. The other ingredient is pure water.

The catalytic wet air oxidation of the acrylonitrile wastewater was carried out in a 0.5 L high pressure batch reactor (Fig. 1). The reactor was equipped with a magnetically driven stirrer ensuring good mass transfer from the gas to the liquid phase and to a catalyst. Firstly, we injected acrylonitrile wastewater with a given mass of homogeneous catalyst into the reactor. Secondly, nitrogen flowed through the system to remove the air within the system; the valves around the reactor were closed when the air was removed entirely and began to heat. Finally, pure O_2 was introduced into the reactor until the estimated pressure was reached and the reaction started at the point called "zero time". Liquid samples (about 50 mL) were periodically withdrawn from the reactor and analyzed.

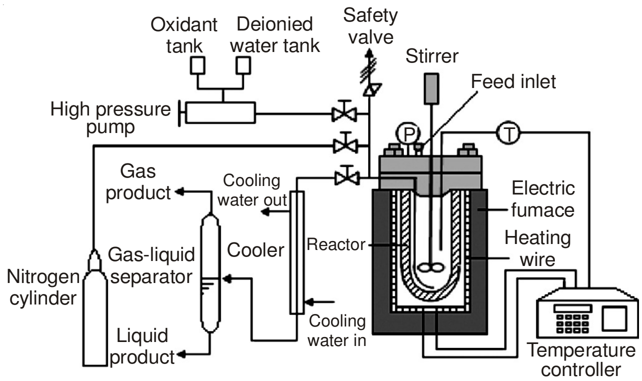

Fig. 1. Schematic diagram of the experimental setup

Analytical: The chemical oxygen demand of the collected liquid is measured by potassium dichromate method of APHA. Standard methods for the examination of water and wastewater. edn 20. Washington, 2000[13].

The total organic carbon is measured by total organic carbon determinator "SHIMADZU TOC-L CPN-CN200".

Acrylonitrile content is measured by the sodium sulfite addition method: Due to the effect of cyano electron-withdrawing, the double bond of acrylonitrile present high response performance to nucleophilic reagents. Therefore acrylonitrile can react with sodium sulfite in water solution, separate out sodium hydroxide at the same amount of substance, then titrate the generated sodium hydroxide with 0.1 mol/L vitriol standard solution and use the indicator mixed by alizarin yellow and thymolphthalein to indicate the end, carried out reagent blank experiment for correction at the same time. acrylonitrile content is defined as eqn. 1.

$$X = \frac{V_{vitriol} - V_{blank}}{V_{material}} \times c_{vitriol} \times 53000 \quad (1)$$

$V_{vitriol}$ represents the volume of vitriol standard solution during titration; V_{blank} represents the volume of vitriol standard solution used in reagent blank experiment titration; $V_{material}$ is the volume of water sample and $c_{vitriol}$ is the concentration of vitriol standard solution.

RESULTS AND DISCUSSION

Selection of homogeneous catalyst: Eight metal nitrates (include no catalyst) used as homogeneous catalyst under the same reaction condition (523 K, ion concentration 200 mg/L and O_2 dose = 0) after 9 min reaction and their chemical oxygen demand removal are shown in Table-1. It can be observed from Table-1 that Cu^{2+} has the most catalytic efficiency among 8 metal salt solutions. That is because Cu^{2+} have more catalytic activity than other metal ions.

TABLE-1
METAL ION AND CHEMICAL OXYGEN DEMAND REMOVAL (%)

Metal ion	COD removal (%)
Without catalyst	76.02
Cu^{2+}	86.07
Ni^{2+}	79.73
Fe^{3+}	82.71
Zn^{2+}	85.17
Mn^{2+}	76.06
Co^{3+}	75.67
La^{3+}	79.00
Ce^{3+}	76.10

Former transition metal ions, such as Ti(IV), Mo(VI), Fe(IV), Mn(V) take part in the Lewis acid mechanism, during which the oxidation state of the transition metal ions does not change and its role as a Lewis acid activated oxidant assist transfer of active oxygen atom. Key active intermediate of Lewis acid catalyst include hydrogen peroxide of transition metal compound (M^{n+}-OOH), alkyl peroxide compound (M^{n+}-OOR) and dioxo compound [$M^{n+}(O_2)$], where O_2 from [$M^{n+}(O_2)$] bonding side on the transition metals.

Latter transition metal ions, especially Cu(II) participate in oxygen rebound mechanism during catalytic oxidation process. The oxidation state of transition metal ions changed and involved in the transfer of active oxygen atoms directly and its key active intermediate is high-charged transition metal oxo species, such as $M^{n+} = O$.

This high-charged species have more catalytic activity than several compounds above during catalytic oxidation process, especially oxidation of double and triple bond. Since the main structures of acrylonitrile being oxidated are C=C and C=N, therefore, Cu^{2+} can be used as the homogeneous catalyst to the reaction.

Catalytic wet air oxidation of the acrylonitrile

Effect of the temperature: Temperature is an important element affecting the catalytic wet air oxidation of acrylonitrile in wastewater. The pollutant removal increased with the operating temperature. Fig. 2, respectively showed chemical oxygen demand, total organic carbon and removal of acrylonitrile from the wastewater at the same reaction time (9 min) among a series of stepped up reaction temperatures (483, 493, 503, 513, 523 and 533 K). When the temperature increased from 483 to 523 K, chemical oxygen demand removal significantly increased from 91.39 to 97.23 %, then chemical oxygen demand removal declined to 96.58 at 533 K; the range of total organic carbon removal is from 80.04 to 97.78 % when the temperature reached 523 K, then the curve remain stable until 533 K; acrylonitrile removal also present rise trend, which from 84.50 to 94.87 %. Broadly speaking, temperature had a significant impact on the oxidation of acrylonitrile in wastewater.

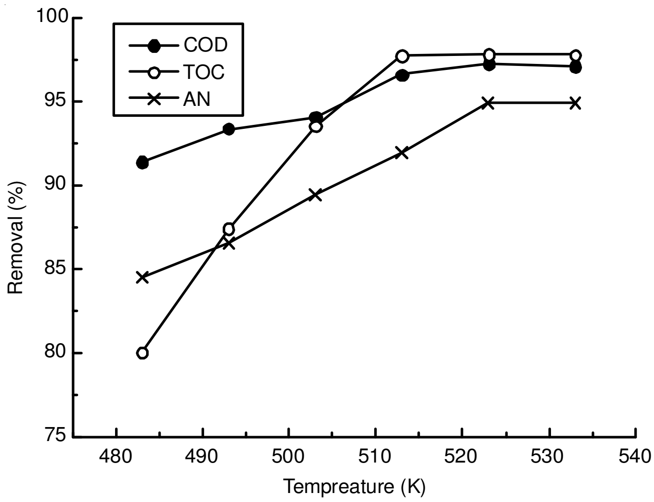

Fig. 2. Effect of the temperature (K)

This phenomenon can be explained as followings. On the one hand, oxidation of organic compounds is an irreversible process, the reaction rate equilibrium constant increases with the temperature becomes higher. Finally, it leads to increasing oxidation rates of organic compound degradation. On the other hand, the density of water declines with the increase of temperature in constant pressure, reducing the concentration of the reactants per unit volume, which can also promote the reaction rate equilibrium to the right. Although high temperature can accelerate the reaction, there is a peak which may affect the distribution of reaction rate equilibrium constant and weaken the reaction if temperature rise over it. When temperature increases over 523 K, the equilibrium of reaction will be broken and the range of the concentration reduced exceeded the increase of the rate constant and minish the oxidation rates. So, it is shown that chemical oxygen demand removal increases with increasing temperature and 523 K is the ultimate temperature that can increase oxidation rates of organic compound degradation.

Effect of reaction time: The conversion experiments were conducted at 523 K for 1-9 min. Fig. 3, respectively showed chemical oxygen demand, total organic carbon and acrylonitrile content removal of catalytic wet air oxidation at different reaction times. The result appeared that the reaction time also played an important role in conversion experiments. The three lines all present trends of increasing from 1 to 5 min and slowed down until 9 min.

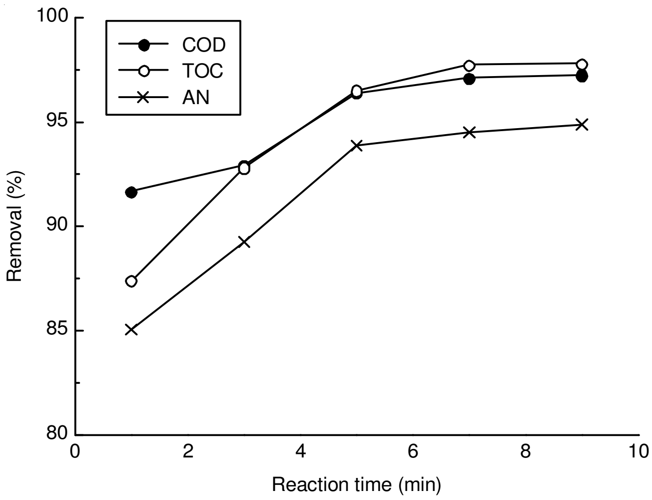

Fig. 3. Effect of reaction time (min)

This is because the reaction rate related to reactant concentration, after 5 min, the concentration of organic compound in wastewater begins to decrease rapidly with the reaction proceeding, In addition, intermediates hard to degrade are generated in the reaction system, so the reaction rate decreases.

Effect of O_2 dose: A series of experiments were conducted to determine the effect of O_2 dose on catalytic wet air oxidation of acrylonitrile wastewater. Results are presented in Fig. 4. As we can see, under the same conditions, chemical oxygen demand removal increased from 89.85 to 97.23 % when O_2 dose from 7.65 to 38.33 g/L, then remain stable when O_2 dose rise to 61.32 g/L. total organic carbon and acrylonitrile content removal got upper reaction rates at low levels of oxygen dose, then trends tend to be gently at the moment O_2 dose is 38.33 to 61.32 g/L.

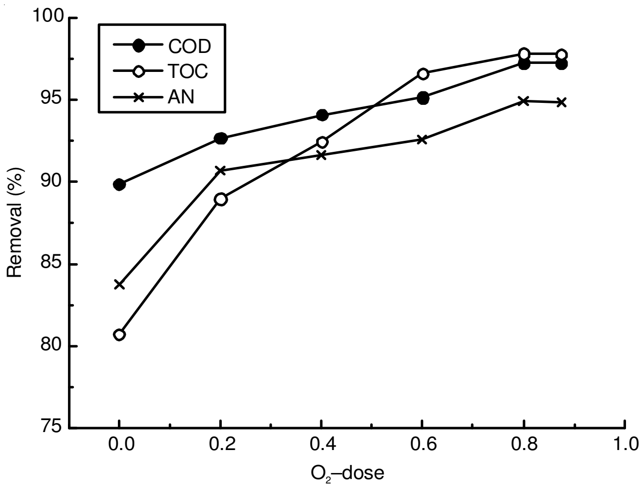

Fig. 4. Effect of O_2–dose

It is because partial pressure of oxygen has a direct impact on the oxidation rate within a certain range. When oxygen dose increases, the increasing dissolved oxygen in the solution can be helpful to the formation of oxidation species ($O_2^{\bullet-}$, $HO_2^{\bullet}$, *etc.*). Therefore, high dose of O_2 can make the oxidation of reactants in O_2 more thoroughly and speed up the oxidation rate, leading to achieving higher organic compounds conversion in catalytic wet air oxidation.

Effect of catalyst concentration: The concentration of catalyst is the last but most important factor that influences the experiment. Firstly, comparing with the experiment which don't have catalyst, the one have Cu(II) as homogeneous got much higher chemical oxygen demand removal, so catalyst is an essential factor in catalytic wet air oxidation process. Secondly, as is shown in Fig. 5, though the catalyst concentration had a little impact on the chemical oxygen demand removal, but it made a huge contribution to total organic carbon and acrylonitrile removal. Total organic carbon removal increased from 82.68 to 97.78 % when concentration of Cu^{2+} from 50 to 250 mg/L. As well as acrylonitrile removal from 80.68 to 94.87 %. This phenomenon is probably because the Cu^{2+}=O generated by catalyst can facilitates the oxidation of the substances in acrylonitrile wastewater, especially some organic radicals such as C=C and C=N, therefore total organic carbon and acrylonitrile removal had a high level.

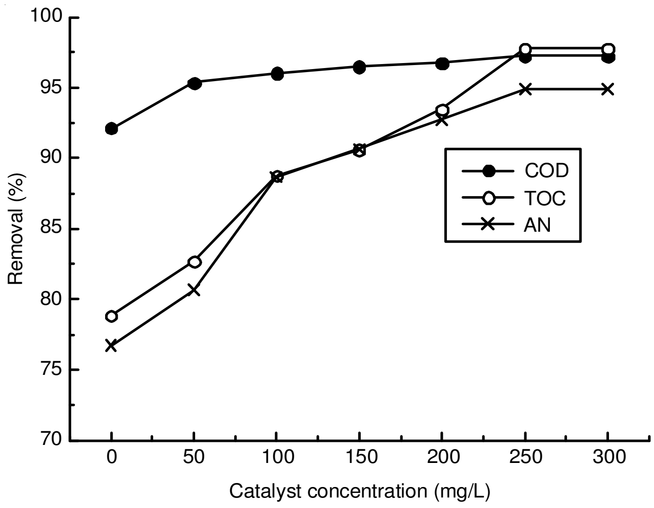

Fig. 5. Effect of the concentration of catalyst (mg/L)

Orthogonal experiments: Orthogonal experiment design is one of the methods which can study multiple factors and levels. It selects part of the typical points from the comprehensive test according to the orthogonality. These representative points are disperse symmetrical and comparable. Orthogonal test design is a main approach for the analysis of the factor design. Its advantage is that only fewer tests can find optimal collocation of points or deduce it by calculating.

In order to investigate the importance of impact of various factors on catalytic wet air oxidation, as well as the influence of various factors on the test results, the experiment makes four factors three levels orthogonal experiment design, Specific experimental scheme are shown in Tables 2 and 3. In Table-2, factors are: A: O_2 dose (mg/L); B: Reaction time (min); C: Temperature (K); D: Catalyst concentration (mg/L).

TABLE-2
FACTORS AND LEVELS

Levels	Factors			
	A	B	C	D
1	0.6	3	513	200
2	0.4	5	503	150
3	0.2	7	493	100

TABLE-3
ORTHOGONAL EXPERIMENT DESIGN

No.	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

The results of chemical oxygen demand, total organic carbon, acrylonitrile content removal are, respectively shown in Tables 4 to 6.

It can be obtained from Tables 4 to 6, the order which factors affecting reaction is: temperature > reaction time > O_2 dose > catalyst concentration in chemical oxygen demand and total organic carbon removal. Sequence in acrylonitrile removal is temperature > reaction time > catalyst concentration > O_2 dose. These phenomenons can be described as follow. The reaction rate constant rises along with the temperature, that can speed up the reaction and can be beneficial to the oxidation of organic matter decomposition. When the reaction time is short, carbonaceous compounds in acrylonitrile wastewater has not yet been fully oxidated to become intermediates, with the increase of reaction time, the intermediates are decomposed into CO_2 and H_2O. Aggrandize O_2 dose can make oxygen

TABLE-4
ORTHOGONAL EXPERIMENT OF CHEMICAL OXYGEN DEMAND REMOVAL

No.	A	B	C	D	COD Removal (%)
1	1	1	1	1	93.76
2	1	2	2	2	93.45
3	1	3	3	3	92.08
4	2	1	2	3	90.42
5	2	2	3	1	92.06
6	2	3	1	2	95.23
7	3	1	3	2	89.04
8	3	2	1	3	94.25
9	3	3	2	1	93.42
Average 1	93.097	91.073	94.413	93.080	-
Average 2	92.570	93.253	92.430	92.573	-
Average 3	92.237	93.577	91.060	92.250	-
Range	0.860	2.504	3.353	0.830	-

TABLE-5
ORTHOGONAL EXPERIMENT OF TOTAL ORGANIC CARBON REMOVAL

No.	A	B	C	D	TOC Removal (%)
1	1	1	1	1	90.22
2	1	2	2	2	89.22
3	1	3	3	3	88.11
4	2	1	2	3	84.53
5	2	2	3	1	87.18
6	2	3	1	2	94.36
7	3	1	3	2	81.9
8	3	2	1	3	89.19
9	3	3	2	1	86.49
Average 1	89.183	85.550	91.257	87.963	-
Average 2	88.690	88.530	86.530	88.493	-
Average 3	85.860	89.653	85.653	87.277	-
Range	3.323	4.103	4.103	1.216	-

TABLE-6
ORTHOGONAL EXPERIMENT OF ACRYLONITRILE REMOVAL

No.	A	B	C	D	AN Removal (%)
1	1	1	1	1	93.52
2	1	2	2	2	89.89
3	1	3	3	3	92.75
4	2	1	2	3	88.53
5	2	2	3	1	91.76
6	2	3	1	2	91.1
7	3	1	3	2	88.45
8	3	2	1	3	91.63
9	3	3	2	1	89.04
Average 1	92.053	90.167	92.083	91.440	-
Average 2	90.463	91.093	89.153	89.813	-
Average 3	89.707	90.963	90.987	90.970	-
Range	2.346	0.926	2.930	1.627	-

concentration relatively increased, which is advantageous to the oxidation reaction according to kinetics. Although the effects of catalyst concentration is the smallest according to statistics, it is the most indispensable in four factors of the experiment. High-charged transition metal oxo species makes oxidation process far more easier than reaction which don't include catalyst, but too more addition of catalyst can't add more key active intermediates. In contrast, in the case of the same content of intermediates, higher temperature and longer reaction time will accelerate oxidation reaction appropriately.

Conclusion

The Cu(II) homogeneous catalyst showed a quite high efficiency for the catalytic wet air oxidation of acrylonitrile wastewater as a pretreatment method. The impact of the operating conditions such as temperature, reaction time, O_2 dose and concentration of catalyst, is required. Experimental results indicated that in the catalytic wet air oxidation process, adding catalyst can significantly improved the chemical oxygen demand, total organic carbon and acrylonitrile removal. 97.23 % chemical oxygen demand (COD), 97.78 % total organic carbon (TOC) and 94.87 % acrylonitrile content removal were obtained after 9 min reaction at temperature of 523 K, O_2 dose of 38.33 and 250 mg/L Cu^{2+} catalyst concentration. These results indicated that compared with other methods, catalytic wet air oxidation was an efficient pretreatment method of acrylonitrile wastewater.

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