Orthogonal Design Hydrogen Peroxide Degradation of Aniline Process

Yong-Guang BI*, Min-Xia HUANG, Shi-Ting DENG, Hong YU, Xue-Wei CHEN , Xue-Mei LIU and Hai-Lan HUANG

School of Pharmacy, Guangdong Pharmaceutical University, Guangzhou 510006, Guangdong, China

*E-mail:benyg2013@163.com

Keywords: Aniline; Hydrogen peroxide; Degradation; Orthogonal test; Process optimization

Abstract: This paper aniline wastewater reaction solution using Orthogonal Design Hydrogen Peroxide Degradation of aniline process, results showed: Impact H_2O_2 Decomposing aniline five factors (aniline initial concentration, pH value, H_2O_2 dosage, reaction time, temperature), the effect of H_2O_2 dosage maximum reaction time of the minimum, the effects of aniline degradation rate of the size of the order has to: H_2O_2 dosage> initial concentration of aniline> reaction temperature (about 18 °C)> pH value> response time. Considering the economic factors, the optimum extraction parameters of each factor as follows: the initial concentration of 30mg/L, pH = 6, H_2O_2 dosage of 0.3mL, reaction time 10min, at room temperature (about 18 °C).

Introduction

Aniline is a special smell, colorless and oily liquid; after contact with air and light black; weakly basic nature of the substance. It's easy to form salts with acids, hydrogen atom on the amino group which may be substituted phthalocyanine group or a hydrocarbon group, aniline and aniline phthalate. When it is substituted aniline reactions, mainly generate ortho-substituted product. Aniline diazonium salt reacts with nitrous acid, which can be made into a series of salts of benzene derivatives, and azo compounds. Aniline can corrode copper and copper alloys. When exposed to heat, the fires are combustible [1, 2]. The oxide can react violently. Not with nitric acid, fuming sulfuric acid, nitro $^+$ glycerin, potassium peroxide, ozone, sodium peroxide and many other substances coexist.

Aniline is toxic biological effects, central nervous system, cardiovascular system and other organ damage, and aniline compounds also have carcinogenic effects. Mass production and wide application of aniline on the environment caused by pollution, but also harm to the human body [3]. It can enter the body through the skin, respiratory and digestive tract, by hydroxylation of the aromatic ring is converted to right, o-, m- amino phenol, benzene, amino acid and acetanilide, and finally excreted in the urine. Its main toxicity is to make the body's normal degeneration Hob, combined with the Hb oxidation of ferrous iron to ferric iron, and hydroxyl (OH) is firmly bonded to form Fe^{3+}Hb, loses oxygen-carrying capacity, resulting in the body of the tissue hypoxia, causing central nervous system, cardiovascular system and other organ damage. Aniline can cause red blood cells globin denatured form He Enzi body cell membranes increased brittleness, easy to damage, resulting in hemolytic anemia.

Hydrogen peroxide, commonly known as hydrogen peroxide, but refers to the aqueous solution of hydrogen peroxide is hydrogen peroxide, is not pure. An aqueous solution of hydrogen peroxide is a colorless transparent liquid, pure hydrogen peroxide as a pale blue viscous liquid. Hydrogen peroxide molecules are polar molecules, soluble in water, ethanol, and the solution showed a weak acid. Hydrogen peroxide or by exposure to light certain metals are decomposed into water and oxygen. Hydrogen peroxide oxidation method using hydrogen peroxide oxidation of cyanide under alkaline conditions can be hydrogen peroxide into cyanate CNO, and then hydrolyzed to cyanate will continue to press carbonate or ammonium bicarbonate. Since the hydrogen peroxide with the cyanide reaction rate is slow, so the metal ion catalyst is added during the reaction, such as copper, cobalt, nickel, used to speed up the reaction rate. The catalytic reactions of hydrogen peroxide become chemical oxidation. Hydrogen peroxide oxidation method technique was done by DuPont in 1974. In 1984, a Papua New Guinea gold cyanidation plant into operation means the hydrogen peroxide by the German design. At present, because the process is simple, low investment, low production costs, hydrogen peroxide oxidation treatment of wastewater containing cyanide and then there are a number of gold mines.

Hydrogen peroxide (H_2O_2) treatment of wastewater containing chemical contaminants, rely mainly on oxidative decomposition of H_2O_2 generated strong free hydroxyl (.OH). When the catalyst may increase, by means of control, pH, temperature and time parameters to achieve the purpose of destruction of some contaminants. You can also add a catalyst (such as iron, copper, etc.) in order to promote the decomposition of H_2O_2, improve the treatment effect. Especially common H_2O_2/FeSO4 system as a treatment agent, called Fenton or Fenton reagent method. H_2O_2 also with other methods (such as ozone oxidation, such as ultraviolet radiation) in combination (referred to as advanced oxidation processes the AOP), to enhance treatment effects, especially that of pollutant decomposition is difficult, more effective use of this method. Hazardous substances H_2O_2 can handle a wide range of scope is very broad, but the handling of the largest and most effective sulfide, cyanide and phenols. With H_2O_2 wastewater treatment advantages, one good effect, and second, no secondary pollution, the third is a simple process; the disadvantage compared to some of the methods, processing costs may be higher. H_2O_2 is applied more occasions wastewater treatment. It can be used independently processed until compliance; also available in other ways (such as biochemical) with its pretreatment pretreatment, or after treatment with it for polishing, and ultimately achieving emission requirements.

Aniline is an important organic chemical raw materials and chemical products, it is with alcohol, ether and benzene immiscible, can play halogenation, acetylation and diazotization, obtained by chemical products and intermediates have 300 kinds, with a wide range of applications, each aniline consumption in dyes, pharmaceuticals, pesticides, explosives, spices, rubber vulcanization promoting agent in the industry[4,5], removing a significant reduction in consumption outside the pesticide industry, MDI, rubber additives, dyes, organic chemicals intermediate consumption volume and other areas of relatively large increase, especially MDI and rubber chemicals to 42.9% and 27.6% growth respectively. China's chemical industry, dye manufacturing, production and application processes in both the medical supplies industry aniline wastewater discharge. Aniline waste water from the chemical industry in general smaller amount of water, but the concentration is high, usually around 100mg/L, and its COD value is higher; on the contrary, the amount of waste water from aniline dyes, pharmaceuticals and other industries, but larger, usually up to a day thousands of cubic meters, while its lower concentration. Due to the complexity of the production process, so the wastewater quality Yijiao complex, to purify bring some difficulties [6,7].

In this paper, thesis reaction liquid aniline wastewater, based on previous studies on single factor, optimization H_2O_2 degradation of aniline simulated wastewater by using orthogonal test method in order to provide reference for the application process.

Experimental Materials and Methods

Materials and Reagents

Aniline, potassium bisulfate, dried over anhydrous sodium carbonate, sodium nitrite, ammonium sulfamate and sulfuric acid, these reagents were of analytical reagent grade.

Instruments and equipment

V1101UV/Vis spectrophotometer (Shanghai Techcomp Instrument Co.,Ltd.); AY120 electronic analytical balance (Shimadzu Corporation, Japan); KH-400KDB type CNC high-power ultrasonic cleaner (the Kunshan Hechuang Ultrasonic Instrument Co., Ltd.).

Experimental Methods [8]

Aniline wastewater analog orthogonal to each experiment is 30mL. Aniline initial concentration, pH value, H_2O_2dosage, reaction time, reaction temperature (about 18 ^oC) as factors, each set four levels of design, examine the role of H_2O_2 degradation of aniline alone, results were as follows (see Tab.1).

Tab.1 Orthogonal head design

Factor					
Level	The initial concentration(mg/L) (A)	pH(B)	H_2O_2 Amount (C)	Time/min (D)	Temperature/^oC (E)
1	10	2	0.1	10	Room temperature
2	15	6	0.2	20	Room temperature
3	20	8	0.3	30	Room temperature
4	30	12	0.6	40	Room temperature

Results and Discussion

Tab.2 Orthogonal experiment

No.	A	B	C	D	E	Degradation rate (%)
1	1	1	1	1	1(Room temperature)	0.8
2	1	2	2	2	1(Room temperature)	46.5
3	1	3	3	3	1(Room temperature)	64.1
4	1	4	4	4	1(Room temperature)	57.4
5	2	1	2	3	4	57.9
6	2	2	1	4	3	13.8
7	2	3	4	1	2	68.2
8	2	4	3	2	1	70.8
9	3	1	3	4	2	71.6
10	3	2	4	3	1	64.6
11	3	3	1	2	4	15.7
12	3	4	2	1	3	54.6
13	4	1	4	2	3	76.7
14	4	2	3	1	4	86.4
15	4	3	2	4	1	60.6
16	4	4	1	3	2	17.7
k1	42.200	51.750	12.000	52.500	49.200	
k2	52.675	52.825	54.900	52.425	51.000	
k3	51.625	52.150	73.225	51.075	52.300	
k4	60.350	50.125	66.725	50.850	54.350	
R	18.150	2.700	61.225	1.650	5.150	

Tab.3 Orthogonal analysis of variance table

Factor	The squared deviations	DOF	F ratio	F critical value	Significance
A	664.112	3	0.337	3.290	
B	15.802	3	0.008	3.290	
C	9101.622	3	4.621	3.290	*
D	9.112	3	0.005	3.290	
E	56.487	3	0.029	3.290	

As can be seen from Table 2 and 3, the impact of the role of H_2O_2 degradation of aniline alone five factors (aniline initial concentration, pH value, H_2O_2 dosage, reaction time, temperature), the effect of H_2O_2 dosage maximum reaction tIME oF minimal, the effects of aniline degradation rate of the size of the order has to: C> a> E> B> D, namely H_2O_2 dosage> initial concentration of aniline> reaction temperature (about 18 ^oC)> pH value> response time . Considering the economic factors, the optimum extraction parameters of each factor as follows: the initial concentration of 30mg / L, pH = 6, H_2O_2 dosage of 0.3mL, reaction time 10min, at room temperature (about 18 ^oC). Statistical analysis indicated that, H_2O_2 dosage (factor C) on the degradation rate of aniline wastewater reaches a significant level; minimal impact on the degradation rate of the reaction time (factor D), no significant difference.

Experimental verification

By taking aniline wastewater 3 parts, each 30mL, set aniline initial concentration of 30mg/L, pH = 6, H_2O_2 dosage of 0.3mL, reaction time 10min, at room temperature (about 18 ^oC) conditions, the experiment was repeated three times measured aniline degradation rates were 86.4%, 87.6%, 87.2%, the average degradation rate of 87.1%, showing that the conditions can be used to determine the degradation of aniline.

Conclusion

(1)By exploring aniline initial concentration, pH value, H_2O_2 dosage, reaction time and other factors on the degradation rate of aniline, and orthogonal experiment, the optimum conditions aniline alone H_2O_2 role in the degradation of aniline initial concentration of 30mg/L, pH = 6, H_2O_2 dosage of 0.3mL, reaction time 10min, at room temperature (about 18 ^oC).(2)With respect to the conventional method, the hydrogen peroxide degradation of aniline well, can provide a theoretical basis and technological reference for large-scale application

Acknowledgements

This work is supported by Guangdong Department of Water Resources Science and Technology Innovation Project (No. 2015-20).

References:

[1]Z. Liu, H. Yang, Z. Huang, P Zhou, et al. Degradation of Aniline by Newly Isolated, Extremely Aniline-tolerant Delftia sp. AN3. Appl. Microbiol. Biotech, 2002, (58):679-682

[2]Konopka, A., Knight D., Turco R. F. Characterization of a Pseudomonas sp.Capable of Aniline Degradation in the Presence of Secondary Carbon Sources.Appl. Environ. Microbiol, 1989, (55):385-389.

[3]Wyndham,R. C. Evolved Aniline Catabolism in Acinetobacter Calcoaceticusduring Continuous Culture of River Water. Cpl. Environ. Microbiol, 1986,(51):781-789

[4]Hyung-Yeel Kahng, Jerome J. Kukor, Characterization of Strain HY99, a Novel Microorganism

Capable of Aerobic and Anaerobic Degradation of Aniline.FEMS Microbiology Letters,2000, (190):215-221
[5]McClure, N. C., VenablesW. A. PTDNl，a Catabolic Plasmid Involved in Aromatic Catabolism in Pseudomonas Putida mt-2.J.Gen.Microbiol, 1987, (133):2073-2077
[6]C. P. Saint, N. C. McClure, W .A. Venables. Physical Map of the Aromatic Amine and M-toluate Catabolic Plasmid pTDNI in Pseudomonas Putida:Location of a Unique Meta-cleavage Pathway. J. Gen. Microbiol, 1990, (136):615-625
[7]Fukumori, F, Saint, C. P. Analysis of the Aniline Degradation Pathway of Pseudomonas Putida UCC2 (pTDNI). Fifth International Symposium on Pseudomonas Putida: Biotechnology and Molecular Biology, abstract, 1995, 70
[8]Yong-guang Bi, Min-xia. Huang. Analysis degradation effect of aniline wastewater by ultrasound [J]. Advanced Materials Research, 2013, (773):923-926.