Application of copper-based heterogeneous catalysts in organic wastewater treatment

Lingfeng He[1, a], Yuan Chen[2, b], Liang Shi[3, c], Yongli Zhang[1, *]

[1]School of Environmental and Chemical Engineering, Foshan University, Foshan 528000, China
[2]School of Foreign Studies, South China Normal University, Guangzhou 510000, China
[3]Environmental Protection Engineering of Sikete, Foshan University, Foshan 528000, China

[*]Corresponding author e-mail: 670511266@qq.com, [a]331538792@qq.com, [b]891532849@qq.com, [c]402225029@qq.com

Abstract. Copper-based heterogeneous catalyst is a kind of catalyst which is created by the effect that copper, ferrum, palladium, lanthanum together with their corresponding oxides have on the carriers such asγ-Al_2O_3. With the development of related research in recent years, its applications and theories are becoming more and more abundant. The properties, structures and designs of experiments of copper-based heterogeneous catalysts are reviewed and the establishment of applied kinetics equations is briefly introduced in this paper.

1. Introduction

The copper-based catalyst has many unique properties and quite a few catalysts with different catalytic properties could be made based on their different types of metals as well as oxides and component proportions. Oxides made from the dopant of noble metals and their oxides can exert better catalytic effect than those from the single component. This catalytic method is called catalytic wet air oxidation (CWAO for short). CWAO has been extensively studied since the 1950s, and in recent years, it has attracted much international attention. Catalytic oxidation of organic wastewater by the modification of the properties of copper-based catalysts has become another research area for environmental engineering. Zhou Yan-bo et al. established the applied kinetics model according to catalytic oxidation of Cu-Fe-Pd-La catalyst's reaction with methyl orange but he didn't build any models for other factors [1]. In this paper, the kinetic model of catalytic oxidation is established according to several influential factors: the concentration of methyl orange, pH, rational speed, and the catalyst particle diameter, the reuse of catalyst, dissolved oxygen, oxygen ion concentration, turbulence and jetting.

Table 1. Original Parameter of Water Sample of Methyl Orange

Concentration of methyl orange (mg/L)	COD (mg/L)	Turbidity (NTU)	Absorbance	PH
2238.5	3775	83.76	40.8	7.04

Table 2. Catalyst preparation

Name	Copper - based heterogeneous catalyst
Preparation method	Take transitional metals Cu, Fe, Co salt, rare metals Ce, La salt and noble metals Pt, Ru, Pd salt as the source of metal and make 20 mL6 wt% nitrate solution according to a certain metal proportion. Then immerse 10 g γ-Al_2O_3 carrier particles in the prepared nitrate solution at room temperature for 12 h, and later dry it for another 12 h in an oven at 105 ° C. After that bake it in a muffle furnace (heating rate 8 ° /min) for 4 h at the setting temperature and after cooling it down at a constant rate (cooling rate 10°/min), the needed catalyst would be obtained

2. Copper - based heterogeneous catalyst

Copper is a mixture of copper, ferrum, palladium, lanthanum and their oxides. Heterogeneous refers to the liquid phase, solid phase and etc. When these mixtures are supported on the pores of γ-Al_2O_3, the catalyst and carrier are formed. The catalyst is obtained through the metal salt being immersed in γ-Al_2O_3, dried and calcined. Compared with the traditional wet air oxidation (WAO) method, this method is easier in the scale-up treatment of organic wastewater.

Copper based heterogeneous catalysts can reduce the total cost due to the advantages of less investment, higher treatment efficiency and lower operating cost.

The heterogeneous catalyst has good recyclability and high catalytic efficiency. During the reaction, it is in solid form and after that process, it becomes easier to detach from reaction solution. The components of catalyst consist of transitional metals, rare earth metals and noble metals and so on. Transitional metal, a kind of homogeneous catalysis, is easy to dissolve but it owns high catalytic activity. The limitation of rare earth metal lies in catalytic inactivity, but this kind of metal can change catalyst structure so that it can increase the possibility of contacting with oxygen, and produce more free radicals and improve the overall performance. As for noble metal, its drawbacks are high price and limited application but it possesses good catalytic effect and strong stability.

3. Research status of kinetics

The study of kinetics is helpful to clarify and reflect mechanism. Relevant scholars have already done some related researches.

Liu Shao-lei has studied the kinetics by studying Pd-Fe/Graphene catalytic cathode and electrolytic degradation of 4-Chlorphenol [2].

Table 3. Original Parameter of the Water Sample

Drug Name	Reagent Grade	Pharmaceutical Manufacturers
4-chlorophenol	Analytical Reagent	Shanghai Feixiang Chemical Factory

Table 4. Catalyst preparation

Name	Pd-Fe/Graphene multifunctional catalytic cathode
Preparation method	Step 1: Prepare graphite oxide by adopting modified Hummer method; Step 2: Restore graphite oxide by adopting photo-reduction method and complete making the metals load on the surface of the catalyst.

Guo Min analyzed the reaction kinetics by removing nitrate from Nano-FeO/Pd/Cu particles (water sample and catalyst can be seen in Table 1.5 and 1.6) and concluded that the reduction of nitrate by Nano-FeO/Pd/Cu particles was in accordance with the pseudo-first-order reaction kinetics [3]. The factors that affect the removal rate are as follows: Nano-FeO/Pd/Cu dosage, initial DO, stirring speed, coexisting oxygen anion, nitrate initial concentration, initial pH, etc. All are different affecting factors

from those studied by the aforementioned scholars. After learning from the experience and making analogy, it is found that the subject can also be studied around those several factors.

Table 5. Original Parameter of Water Sample

Drug Name	Preparation Method
Micro-polluted acid salt	As experimental request, Wahaha pure water and potassium nitrate need to prepare the solutions of different concentration gradients and simultaneously take into account the influence of other oxygen anions and organics. On such basis, add materials such as sodium nitrite, potassium chlorate, potassium bromate, potassium dihydrogen phosphate, sulfuric acid Potassium, sodium bicarbonate, humic acid (HA) into the potassium nitrate solution and then prepare expected mixed solution according to a certain proportion.

Table 6. Catalyst performance

	Nano-FeO/Pd/Cu
Color	Black
Properties	Agglomeration: slight suspense occurs in the solution; Good settle ability: generally settlement is completed within 20 min or so. It is stored in deoxidized anhydrous ethanol and it is wet added quantitatively during reduction reaction.

Li Chang-fang used nano Pd/Fe catalytic to reduce degradation BDE-47 (water sample and catalyst seen in Table 1.7 and 1.8) The reacting rate of BDE-47 increases with the increase of Pd loading rate [4].

Table 7. Original Parameter of Water Sample

Drug Name	Reagent Grade	Pharmaceutical Manufacturers
2,2',4,4'-Tetrabromodiphenyl ether	99%	American Chemical Services
2,2',4,4'-Tetrabromodiphenyl ether	Standard sample	American Accu Standard Company

Table 8. Catalyst Preparation

Name	Nano Pd/Fe
Method	NaBH4 is used as reduction agent to reduce Fe^{2+}.Nano zero valent Fe particles are obtained. Then $PdCl_2$ is used as Pd agent and the Pd is loaded on the surface of zero valent Fe.

Tang Di studied the treatment of PVA by the pure iron-carbon system under acidic conditions (water sample and catalyst are shown in Table 1.9 and 1.10) and concluded the kinetics equation V1=1.03x10-3p1.59, and the kinetics equation of the treatment with iron-carbon system by rare earth La V2=1.81x10-2P1.105M0.323[5].

Table 9. Original Parameters of Water Samples

Drug Name	Preparation Method
PVA Simulated wastewater	Calculate and weigh a certain amount of PVA that has been dried in the blast drying oven of 110 degrees Celsius; Stir and at the same time add PVA slowly into the cold water of about 25 ℃ to make it swell and disperse fully; 10 min later, put it into the water bath kettle of 90℃ below to dissolve (during this process of dissolution, stir it properly); In about 10 h when it is completely dissolved, cool it down to the room temperature; Filtering so as to remove impurities from the solution and dilute the concentration of filtered solution to about 1500 mg/L

Table 10. Parameters of Catalyst

System	Content of Iron/g	Content of Coke/g	Concentration of Lanthanum Nitrate /g/L
Rare Earth La- iron Carbon System	100	100	0.4

In the Fe/Fenton system, Wang Jing discovered that the degradation of methylene blue in 0-45 min accords with the pseudo-first-order reaction kinetics equation.(water sample and catalyst are seen in Table 1.9 and 1.10) The activation energy was 82.708KJ/mol. The study found that a new kind of methylene blue decomposes intermediate products of benzothiazole, and derived methylene blue in Fe/Fenton system degrades along three paths [6]. The previous research of this subject is two-step reaction. Therefore, we can assume that there are also intermediate products in the subject, and they also degrade along three paths.

Table 11. The Original Parameters of Water Sample

Drug Name	Reagent Grade	Pharmaceutical Manufacturers
Methylthionine Chloride	BS	Shanghai Jingchun reagent Co.,Ltd

Table 12. Catalyst preparation

Catalyst	Method
Ferric iron Hydrotalcites	Weigh a certain amount of $FeSO_4 \cdot 7H_2O$ and $Fe2(SO_4)_3$ and put them in a three-necked flask; Use the approved deionized water to prepare the solution, to achieve the equation $[Fe^{2+}]+[Fe^{3+}]=1.2$ mol•L-1; Under the protection of $[Fe^{2+}]/[Fe^{3+}]=2$:l, 1:1 and N2 and the condition of $[Fe^{2+}]/[Fe^{3+}]$=l:0 and air atmosphere, in the water-bath of 40°C, add 2 mol/L NaOH solution to the solution until the pH of the solution is constant; After the reaction is completed, locate the three-necked flask in ice-bath for 4 h, filter, washed with ice water through N2 and at last wash twice with ethanol of 0°C; Store it in the refrigerator finally in after dry it at room temperature.
Ferrocene modified resin	Weigh a certain amount of styrene cation exchange resin and put it in a conical flask; Immerse HC1: HNO_3 = 1: 1 mixed acid to remove impurities on its surface; Place the pretreated resin in 0.5 mol-L-1 ferrocene-ethanol solution and stirred for 7 h; After the reaction, filter the mixture and rinse with ethanol to remove excessive ferrocene; Dry it at the room temperature for 2 h and seal it for preservation.

Acknowledgments
This work was supported by Water Pollution Control Engineering Technology Research Center of Foshan (2016GA10159), 2016 Foshan Science and Technology Project.

References
[1] Zhou Yan-bo. Preparation of multi component supported catalysts and properties of catalytic wet air oxidation (MS., Liaoning University of Science and Technology, China 2016)
[2] Liu Shao-lei. Study on Pd-Fe/Graphene Multifunctional Catalytic Cathode and Degradation of 4-Chlorophenol by Multi-electrodes System (MS., Beijing Forestry University, China 2015)
[3] Gou Min. Study on the Removal of Nitrate by Nanometer Fe°/Pd/Cu Composite Materials in Drinking Water (MS., Zhejiang University of Technology, China 2013)
[4] Li Chang-fang. Study on Catalytic Debromination of 2, 2', 4, 4'- Tetrabromodiphenyl Ether by Nanoscale Pd/Fe Bimetallic Particles (MS., South China University of Technology, China 2012)
[5] Tang Di. Study on Rare Earthla-Iron and Coke Micro-Electrolysis Used for PVA Waste-Water

(MS., Donghua University, China 2016)
[6] Wang Jing. Mechanisms and application of heterogeneous Fenton systems catalyzed by Ferrocene and FeFe-LDH in the treatment of Methylene Blue (Ph.D., Kunming University of Science and Technology, China 2014)