Degradation and mineralization of organic pollutants by Advanced Oxidation Processes (AOPs) using Cu-based catalysts

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Introduction

Persistent pharmaceuticals residues are considered as an emerging environmental problem in the recent years due to their harmful effects, such as chronic and reproduction toxicities for human and aquatic systems. Clofibric acid (CFA) is the main pharmacologically active metabolite of the lipid lowering drug, clofibrate. Numerous studies have demonstrated the occurrence of CFA in surface, groundwater and even drinking water [1].Wastewater contaminated with phenol has drawn much more attention, as it is a basic structural unit for a variety of synthetic organic compounds. Wastewater originated from many industries contains phenol and substituted phenols [2]. Catalytic ozonation is proved as an effective technology for the removal of organics from wastewater [3]. Also, among the various approaches of generation of hydroxyl radicals, the Fenton reaction is one of the most efficient processes to eliminate toxic compounds present in the wastewater [4]. The main aim of our work is to develop new catalytic materials and effective method in the removal of organic pollutants. In this paper, we report the efficiency of different Cu-based catalysts for the degradation and mineralization of CFA and phenol by means of catalytic ozonation and Fenton-like process.

Materials and Methods

Catalysts Preparation: Three kinds of Cu catalysts were synthesized.

[I] Cu-dawsonite catalysts: Cu-dawsonite with Cu/Al mass ratios 0 (NH₄DW), 0.02 (Cu2DW) and 0.1 (Cu10DW) were synthesized by a co-precipitation method at constant pH [5]. [II] Cu-Hydrotalcite and Cu-Spinel catalysts: Mg/Al hydrotalcite (HT) catalysts containing Cu and spinel-type materials $Cu_xAl_2O_4$ and $Cu_xMg_yAl_2O_4$ were prepared by co-precipitation and finally calcined at different temperatures for 6 h. 0.1 % Pd/CuAl₂O₄ was prepared by impregnation method. [III] Cu-Al oxide catalyst: The nanostructure Cu (Cu₁:Al₁) catalyst was prepared by a co-precipitation method [6] and further calcined at 400°C for 4h.

Catalytic Tests:

Ozonation Test: The ozonation of CFA was performed in a 1.5 L glass jacketed reactor. Ozone was produced by an Anseros ozonator (GM-6000-PRO) at a rate of 1.2 g/h with oxygen flow rate of 40 L/h and applied to the solution of CFA containing 0.5 g/L catalyst, at room T.

Heterogeneous Fenton-Like Process: The degradation of phenol was carried out at ambient conditions (25 °C and atmospheric pressure) in a glass reactor with a capacity of 250 ml. 100 ml of phenol solution (100 mg/L) and 0.5g/L of H_2O_2 with 2g/L of catalyst was introduced.

Results and Discussion

Table 1 shows the % CFA conversion and mineralization during 2 h of ozonation with the different Cu catalysts tested. All catalysts along with single ozonation show 100% CFA degradation within 15 minutes of reaction. Cu dawsonite catalysts (I) show good activity, achieving 55-67% mineralization, however with 0.5-3.3 mg/L of Cu leaching. Cu hydrotalcite and Cu-spinel catalysts (II) also show good activity with a certain amount of Cu leaching; however, after pretreatment with oxalic acid, these catalysts attain better stability. Among all these tested catalysts, best results were obtained with Cu1Al1 (III) catalyst, achieving 82% mineralization in 2h of ozonation.

 Table 1. CFA (100mg/L) degradation results using different Cu-based catalysts after 2h single and catalytic ozonation

Catalysts	%TOC	Cu (mg/L)
	Removal	Leaching
O ₃	28.1	-
I-Cu2DW	55.2	0.52
I-Cu10DW	67.3	1.29
I-Cu10DW (500)	57.9	3.37
II-Mg ₃ Cu _{0.5} Al ₁ (900)	60.0	2.1
II-Cu _{0.75} Mg _{0.25} Al ₂ O ₄ (900)	55.3	1.6
$II-Cu_1Al_2O_4(900)$	50.0	2.4
II-Cu _{0.75} Mg _{0.25} Al ₂ O ₄ (2%OA, 900)	54.4	0.7
II-Cu ₁ Al ₂ O ₄ (2%OA,900)	53.3	1.1
III-Cu ₁ Al ₁	81.7	-
Cu^{2+} (3.5 mg/L)	38.3	-

Figure 1 shows the % of mineralization of 2h ozonation process with Cu₁Al₁ (III) catalyst, at different CFA initial concentrations pH It was seen that Cu₁Al₁ catalyst shows good activity, achieving 77-79% degree of mineralization in 2h of ozonation at low concentration of CFA (10 mg/L). At pH 7 and 10, there was an

enhancement in TOC removal, achieving 85 and 87% degree of mineralization, respectively. **Figure 2** shows the % of mineralization during 6 and 24h of reaction with different Cu-spinel catalysts tested in Fenton reaction. Among all the Cu spinel catalysts tested, $Cu_{0.8}Al_2O_4$ and $Cu_1Al_2O_4$ show the best activity in phenol degradation, achieving 70% and 81% mineralization in 24h of Fenton reaction. After addition of little amount of Pd, enhancement in mineralization with high H_2O_2 decomposition was observed over $0.1\%Pd/Cu_1Al_2O_4$ catalyst, with low leaching of Cu.





Figure1. Degree of mineralization in 2h ozonation with different concentration of CFA and pH using Cu-Al catalyst (III).

Figure2. Degree of mineralization in 6 and 24h with different Cu-spinel catalysts in Fenton-like Reaction of phenol (100 mg/L) solution.

Significance

The nanostructured Cu (Cu₁:Al₁) catalyst is the most stable and active catalyst for ozonation reaction of clofibric acid, achieving 82% and 96% mineralization in 2 and 6h of ozonation, respectively, without any leaching of Cu. The efficiency of this catalyst has also been demonstrated at low concentrations of CFA. Cu-spinel type catalysts have also presented good performance in the removal of phenol by heterogeneous Fenton process, achieving up to 60 and 80% mineralization after 6 and 24 h, respectively.

References

- Cruz-Morato C.; Jelic A.; Perez S.; Petrovic M.; Barcelo D.; Marco-Urrea E.; Sarra M.; Vicent T. Bio. Eng. J. 2013, 75, 79-85.
- 2. Saeed M., Ilyas M. Appl. Cat. B: Env. 2013,129, 247-254.
- 3. Guo Y, Yang L.; Cheng X.; Wang X. J. Env. Anal. Toxicol. 2012, 2.7.
- 4. Yalfani, M.S.; Contreras, S.; Medina, F.; Sueiras, J. Appl. Cat. B: Env. 2009, 89, 519–526.
- Yalfani, M.S.; Contreras, S.; Llorca J.; Medina, F. Appl. Cat. B: Env. 2011,107, 9– 17.
- Mane R.B.; Hengane A.M.; Ghalwadkar A.A.; Subramanian V.; Mohite P.H; Potdar H.S.; Rode C.V. Cat. Lett. 2010, 135, 141–147