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Treatment of Glyphosate Mother Liquor by Catalytic Wet Oxidation

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The glyphosate mother liquor wastewater can be treated to achieve degradation of wastewater COD and organic phosphorus into orthophosphate. The glyphosate mother liquor wastewater was treated by catalytic wet oxidation technology and the effects of different process conditions on the degradation of COD and the formation of phosphate were investigated. When the experiment of 88000 mg/L COD concentration, 537 K reaction temperature, 2 h residence time, 30 mL glyphosate mother liquor, 20 mL H₂O₂ and 0.15 g CuO catalyst dosage was carried out, the removal ratio of COD and phosphate production ratio could reach 94.5 and 93.4 %, respectively.

Keywords: Catalytic wet oxidation, Glyphosate mother liquor, Phosphate.

INTRODUCTION

Glyphosate is a kind of non-selective, low toxicity and high efficiency herbicide. Due to its good properties, low cost and safe use, glyphosate has become the widely used herbicide in the world. However the wastewater generated in the production process of glyphosate has been one of the problems to be solved in the field of water treatment [1]. The incineration process of glyphosate mother liquor is used in industry, yet glyphosate mother liquor that contains a large amount of salt, is easily to accumulate in the furnace wall and influences the burning effect and efficiency and consumes a lot of fuel, results to high processing cost. When the burning temperature up to 680 °C when can produce dioxins and other secondary pollutants emerge if the burning temperature does not reach required high temperature. Therefore, catalytic wet oxidation (CWO) has been paid more and more attention by environmental protection workers in recent years.

Catalytic wet oxidation is a kind of technology which can be used to treat high concentration, high toxicity and difficult biodegradable wastewater on the basis of wet oxidation technology. Catalytic wet oxidation at high temperature (423-623 K) and pressure (0.5-20 MPa) under the condition of the use of air (oxygen) or hydrogen peroxide as oxidant in the presence of catalyst for oxidation of organic wastewater in the process of decomposition of CO₂ or water and other inorganic or small

organic molecules, effectively reduces the wastewater COD and improves the biodegradability of wastewater. The use of catalytic wet oxidation treatment of glyphosate mother liquor, not only achieves the removal of COD and degradation of organic phosphorus, but also re recoveries phosphorus resources. Different process conditions [2] to treat glyphosate mother liquor are carried out to test the effect of heterogeneous catalyst, such as, TiO₂, MnO₂, Fe₂O₃, CuO and ZnO.

EXPERIMENTAL

Glyphosate mother liquor wastewater has the yellow appearance, COD up to 88000 mg/L, pH 1.29, total phosphorus 9220 mg/L, total salt 75911 mg/L and only 0.13 of BOD/COD which means low biochemical ability, is from a glyphosate production plant in Jiangsu province, China.

The steel kettle is volume of the 100 mL column reactor, whose upper part is connected with a volume of 20 mL elbow, connecting the safety valve, pressure gauge and oxygen outlet. The catalyst in the reaction process wrapped by 200 mesh filter cloth with wastewater are added into the steel kettle. Then, the kettle is heated through salt bath.

Water quality analysis method: COD, BOD₅, total phosphorus and phosphate are respectively determined in accordance with the Chinese national standard GB 11914-89, GB 7488-87, GB 11893-89 and GB/T 9727-2007.

RESULTS AND DISCUSSION

Catalytic wet oxidation of glyphosate mother liquor

Oxidant: The reaction temperature is 533 K, the amount of wastewater is 30 mL, catalyst CuO dosage is 0.15 g and the partial pressure of oxygen (oxygen) is 3.5 MPa or 20 mL with 30 % hydrogen peroxide (calculated according to the 10 % oxidizing wastewater COD), the residence time is 2 h, the effects of different oxidants on the COD removal ratio of glyphosate mother liquor and orthophosphate production ratio were shown in Table-1.

TABLE-1 EFFECT OF OXIDANT TYPE ON CWO		
Oxidant	COD removal ratio (%)	Orthophosphate production ratio (%)
O ₂	88.9	70.7
H ₂ O ₂	95.9	> 85.0

As shown in Table-1, the COD removal ratio of wastewater and the formation ratio of orthophosphate are improved obviously with H₂O₂. The main reason that H₂O₂ has good reaction effect is due to a homogeneous environment containing H₂O₂ and wastewater. While poor effect with O₂ is due to a heterogeneous environment, in addition, due to bad contact of O₂ and catalyst sinking in the wastewater. Make full use of oxygen is not conducive in this procedure. So, in order to avoid the defects of this reactor, H₂O₂ was used in this work as oxidizing agent.

pH: The COD removal ratio and phosphate production ratio were detected by adding NaOH in 30 mL glyphosate wastewater with 20 mL hydrogen peroxide and 0.15 g catalyst (CuO powder) at 533 K, the residence time of 2 h (Fig. 1).

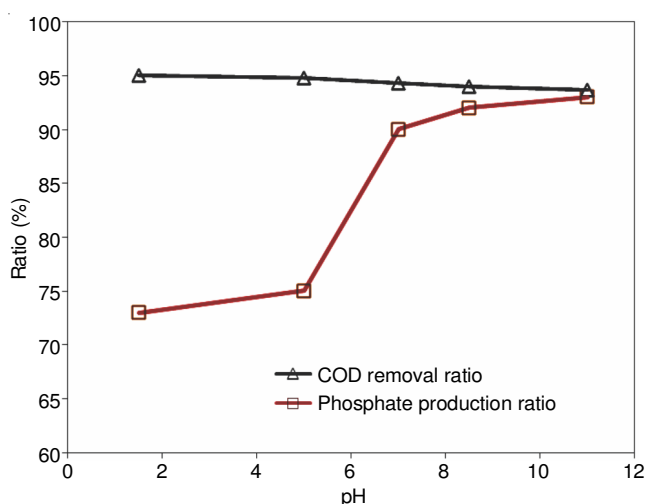


Fig. 1. Effect of pH value on COD removal ratio and phosphate production ratio

It can be seen from Fig. 1 that the pH of the reaction solution has no obvious effect on the removal rate of COD. The pH value of wastewater is adjusted by alkaline adding in acidic liquid. And COD removal ratio decreased slightly, the main reason is that iron ion as homogeneous catalyst in reactions is dissolving out from reaction kettle under acidic conditions of

corrosion, improved the conversion rate of COD. In addition, Santos [3] studies showed that the leaching of copper under acidic conditions increased, the formation of homogeneous Cu²⁺ led to an increase in COD removal. The pH value has obvious effect on phosphate production ratio. When wastewater was acidic, only 72.5 % the total phosphate in the liquid became phosphate production, part of the phosphate to formed insoluble phosphate sedimentation out during the cooling process. When wastewater was adjusted to alkaline, the yield of phosphate was 94 % and this phosphate was not easy to settle down. The solubility of HPO₄²⁻ and H₂PO₄⁻ formation in acidic liquid was bellow that of PO₄³⁻ and precipitation was easily obtained. However, HPO₄²⁻ and H₂PO₄⁻ could change into PO₄³⁻ in alkaline liquid and precipitation reduced.

Temperature: The influence of different reaction temperature on ratios of phosphate production and COD removal was investigated in 30 mL glyphosate mother liquor with 20 mL H₂O₂, 0.15 g CuO powder, 11 pH value and 2 h residence time (Fig. 2).

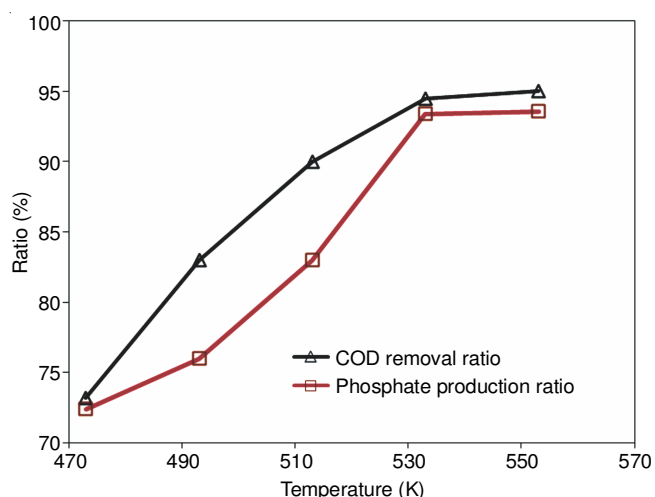


Fig. 2. Effect of temperature value on COD removal ratio and phosphate production ratio

The effect of reaction temperature on COD removal ratio and phosphate formation ratio was obvious. With the increase of the reaction temperature, the removal rate of COD increased gradually, the ratio of organic phosphorus to phosphate increased and reduced the chrominance and the pH value was neutral. When the temperature was 473 K, the COD removal ratio and phosphate formation ratio were only about 72.4 and 73.2 %, respectively, when the temperature raised to 533 K, the COD removal ratio and phosphate formation ratio were up to 93.4 % and 94.5 %, respectively. With the temperature continued to rise, the rising trend of the removal ratio of COD and that of phosphate formation was not obvious. The reason was that the higher the reaction temperature, the higher the energy absorbed by H₂O₂, the more easily to break O-O bond, the more easily production of HO• and the easier the oxidation of organics [4]. At the same time, with the increasing temperature and reducing liquid viscosity, the more easily mother liquor passes through the metal filter, accelerate organic molecules attached to the surface of the catalyst to accelerate the reaction speed. In addition, a large amount of gas is produced

in the process of catalytic wet oxidation, so that the high pressure could promote O_2 from H_2O_2 pyrolysis back into the liquid, which is favourable for the catalytic wet oxidation.

Reaction time: The influence of reaction time on ratios of phosphate production and COD removal was investigated in 30 mL glyphosate mother liquor with 20 mL H_2O_2 at 533 K, 0.15 g CuO powder, 11 pH value and 2 h reaction time (Fig. 3).

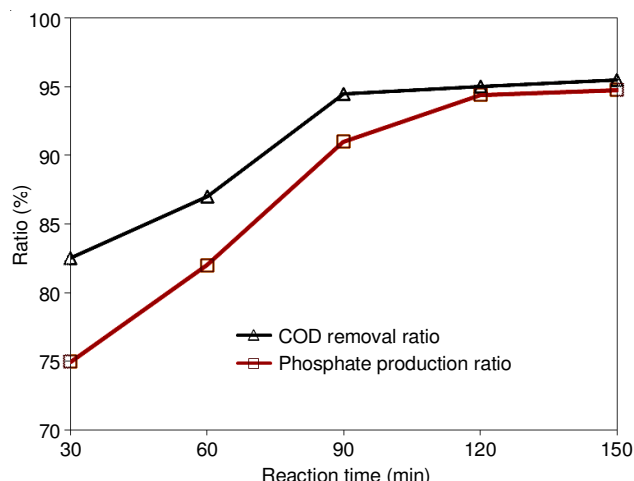


Fig. 3. Effect of reaction time on COD removal ratio and phosphate production ratio

The results showed that the COD removal ratio and the ratio of phosphate formation increased gradually with the extension of time, however the growth rate gradually slowed down. After 2 h, the removal ratio of COD and the phosphate conversion ratio beginning to stabilize.

Catalyst dosage: The influence of catalyst dosage on ratios of phosphate production and COD removal was investigated in 30 mL glyphosate mother liquid with 20 mL H_2O_2 at 533 K, 11 pH value and 2 h residence time (Fig. 4).

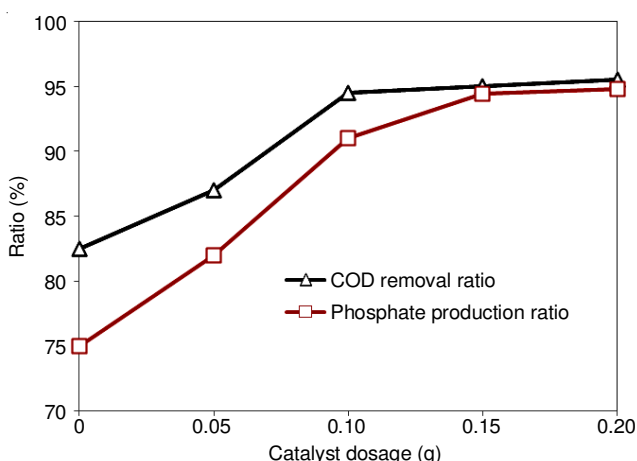


Fig. 4. Effect of catalyst dosage on COD removal ratio and phosphate production ratio

With the increasing of the dosage of catalyst, the removal ratio of COD and the ratio of phosphate formation showed a trend of increasing first and then decreasing. When the dosage of catalyst was 0.15 g, the removal ratio of COD and phosphate formation were up to the equilibrium removal rate of 95 and 93 %, respectively. If the catalyst increases continuously, the removal ratio of COD and the ratio of phosphate formation decreased slightly. The main reason is that the excessive solid catalyst could quickly cause the reaction production adhesion on the catalyst surface and the catalyst compaction took place easily [5]. The results showed that the H_2O_2 decomposition ratio increased with the increase of catalyst dosage, while, the decomposition ratio of H_2O_2 decreased when the catalyst was more than enough [6].

Kind of catalysts: The influence of kind of catalysts on ratios of phosphate production and COD removal was investigated in 30 mL glyphosate mother liquid with 20 mL H_2O_2 at 533 K, 11 pH value and 2 h residence time. The results were shown in Table-2. It can be seen that effect of CuO and TiO_2 treatment was the best, Fe_2O_3 treatment effect is the worst.

TABLE-2
EFFECT OF KINDS OF CATALYST ON COD REMOVAL RATIO AND PHOSPHATE PRODUCTION RATIO

Catalyst	COD removal ratio (%)	Phosphate production ratio (%)
CuO	94	93
MnO_2	92	88
Fe_2O_3	91	84
ZnO	93	86
TiO_2	95	94

Phosphate precipitation: Phosphate precipitation experiment was carried after 2 h reaction of 30 mL wastewater with 0.15 g CuO, 20 mL H_2O_2 at 535 K. The main purpose of this experiment was to convert the phosphate present in wastewater to calcium phosphate or magnesium phosphate under alkaline condition with 10.5 pH value that total phosphorus and phosphate removal ratios were 88.3 and 87.5 %, respectively (Table-3).

Conclusion

The catalytic wet oxidation technology in wastewater treatment of glyphosate mother liquor obtained a good result. When the experiment of 88000 mg/L COD concentration, 537 K reaction temperature, 2 h residence time, 30 mL glyphosate mother liquid, 20 mL H_2O_2 and 0.15 g CuO catalyst dosage was carried out, the removal ratio of COD and phosphate production ratio could reach 94.5 and 93.4 %, respectively. BOD/COD could increase to 0.47. After treatment, total phosphorus and phosphate removal ratios were 88.3 and 87.5 %, respectively. CuO and TiO_2 could play a good catalytic activity in glyphosate mother liquor in the process of treatment.

TABLE-3
MAIN CHANGE OF WATER QUALITY BEFORE AND AFTER PRECIPITATION

Time	Colour	pH value	Total phosphorus ($mg\ L^{-1}$)	Phosphate ($mg\ L^{-1}$)
Before precipitation	More transparent	7.74	7862.29	6665.53
After precipitation	Transparent	10.42	916.58	832.64

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REFERENCES

1. N.U. Yamaguchi, R. Bergamasco and S. Hamoudi, *Chem. Eng. J.*, **295**, 391 (2016); <https://doi.org/10.1016/j.cej.2016.03.051>.
2. C. Lousteau, M. Besson and C. Descorme, *Catal. Today*, **241**, 80 (2015); <https://doi.org/10.1016/j.cattod.2014.03.043>.
3. A. Santos, P. Yustos, A. Quintanilla and F. García-Ochoa, *Top. Catal.*, **33**, 181 (2005); <https://doi.org/10.1007/s11244-005-2524-2>.
4. Y. Yan, S. Jiang, H. Zhang and X. Zhang, *Chem. Eng. J.*, **259**, 243 (2015); <https://doi.org/10.1016/j.cej.2014.08.018>.
5. J. Sun, X. Meng, Y. Shi, R. Wang, S. Feng, D. Jiang, R. Xu and F.-S. Xiao, *J. Catal.*, **193**, 199 (2000); <https://doi.org/10.1006/jcat.2000.2901>.
6. S. Haji, M. Khalaf, M. Shukrallah, J. Abdullah and S. Ahmed, *React. Kinet. Mech. Catal.*, **114**, 795 (2015); <https://doi.org/10.1007/s11144-014-0810-3>.