ABSTRACT

Nowadays, there are increasingly stringent regulations requiring more and more treatment of industrial effluents to generate product waters which could be easily reused or disposed of to the environment without any harmful effects. Therefore, different advanced oxidation processes were investigated as suitable precursors for the biological treatment of industrial effluents containing phenol.

The promoted catalytic wet air oxidation of phenol has been investigated through the addition of hydrogen peroxide as a source of free radicals.

Keywords: Catalytic oxidation, hydrogen peroxide, promoting effect, organic aqueous wastes

INTRODUCTION

The identification of highly refractory and non-biodegradable organic pollutants in wastewater, especially coming from the chemical and petrochemical industry, has challenged the conventional wastewater treatment such as incineration, physical adsorption or biological abatement [1]. However, toxic pollutants are lethal to the microorganisms employed in bioprocesses, whereas incineration or adsorption merely transfers the pollutants from the liquid to air or to the solid leaving combustion by-products or contaminated adsorbent for further disposal. To overcome the inconveniences of conventional treatment methods various chemical oxidation techniques have emerged in the past last decades, in particular for treatment of industrial wastewaters. Wet air oxidation (WAO) is an attractive method for the treatment of waste streams which are too diluted to incinerate and too toxic to treat biologically. The use of catalysts makes the process more attractive by achieving high conversion at considerably lower temperature (353 – 473 K) and pressure (1-10 MPa). An alternative process which allows oxidation at the ambient or close-to-the-ambient conditions, thus limiting the investment costs, involves hydrogen peroxide as an oxidant in the so-called catalytic wet peroxide oxidation CWPO. The catalyst choice is the core for an efficient and cost competitive performance [2-11].

The main objective of this work is to integrate the benefits CWAO and CWPO in an intensified process, named Peroxide Promoted Catalytic Wet Air Oxidation (PP-CWAO) keeping high conversion of pollutant in wastewater and to give an effluent that could be easier biologically treated.

EXPERIMENTAL

The catalysts were prepared from the protonic forms of commercial 13X zeolite (13X-APG Molsiv™ UOP Italy, SiO$_2$/Al$_2$O$_3$ = 3.2) by ion exchange method. Ion exchange with copper acetate solution was carried out at 298 K over 24 hours after what the sample was dried overnight at room temperature. After that catalyst was calcined in air at 1023 K for 5 hours to increase its stability. Crystalline structure of prepared catalyst was checked by X-ray
diffraction analysis. The specific surface areas and the pore volumes of the sample was measured and calculated according to the BET method.

The catalytic tests were carried out in a modified stainless steel Parr reactor in batch operation mode at the different temperature (313-343 K), different hydrogen peroxide concentration (0.01 - 0.14 mol dm$^{-3}$) and constant air pressure (20 bar). The catalyst weight was 0.5 g dm$^{-3}$ and the initial concentration of phenol 0.01 mol dm$^{-3}$.

RESULTS AND DISCUSSION

The operating temperature is an important variable in the phenol oxidation. The time-dependent CWAO phenol degradation at various temperatures when reaction was performed on calcined Cu/13X catalyst is shown in Fig. 1. As can be seen at condition used in this work phenol oxidation is practically negligible because the conversion of phenol depending on temperature that was between 1 to 5 %.

![Graph](image)

Figure 1. Dependence of phenol degradation rate at various temperature: $c_{\text{Ph}} = 0.01$ mol dm$^{-3}$, $m_{\text{cat}} = 0.1$ g/200 cm$^3$, $p_{\text{air}} = 20$ bar (CWAO process)

In accordance with Henry’s law, at conditions used in this work the concentration of oxygen in the reaction mixture was only $5.73 \times 10^{-3}$ mol dm$^{-3}$. This is the reason of very low phenol conversion, because it is well known that conditions for typical CWAO process are high pressure (1-10 MPa) and temperature (353 – 473 K).

Fig. 2 shows an example of normalized concentrations of the remaining phenol and hydrogen peroxide versus time in the experiments performed at different temperatures and concentration of hydrogen peroxide of 0.14 M on calcined Cu/13X catalyst (CWPO process).

![Graph](image)

![Graph](image)

Figure 2. Dependence of phenol (A) and hydrogen peroxide (B) degradation rate at various temperature: $c_{\text{Ph}} = 0.01$ mol dm$^{-3}$, $c_{\text{HP}} = 0.14$ mol dm$^{-3}$, $m_{\text{cat}} = 0.1$ g/200 cm$^3$ (CWPO process)

As shown in Fig. 2, an elevated temperature increase the rate and degree of phenol oxidation and hydrogen peroxide decomposition but it is much lower than in the case when
powdered catalyst was used [12]. In the case of pellets of Cu/13X, there was assumed that internal mass transfer is dominant effect which means that the rate of phenol oxidation and peroxide decomposition is limited by diffusion. The external mass transfer was eliminated by high mixer’s turning.

It could be also seen a significant decrease of the efficient use of hydrogen peroxide for the mineralization of phenol. This fact must be attributed to the increase of refractory oxygenated by-products, mainly carboxylic acids into the liquid phase as the reaction proceeds, which are much less reactive with HO\textsubscript{2}, and hence leading to less efficient use of the oxidant [13].

Fig. 3 shows phenol and hydrogen peroxide concentration profile obtained from PP-CWAO test at different temperatures.

As can be seen in Fig. 3 the activity of Cat+Air+H\textsubscript{2}O\textsubscript{2} system is much higher than that of non-promoted-CWAO (Fig. 1) and CWPO system (Fig.2). Comparing phenol conversion obtained after 180 min of reaction in CWPO and PP-CWAO test it could be seen that conversion of phenol in PP-CWAO is much higher than in CWPO process. These results prove that even small concentration of oxygen used in this work also plays a role in the initiation of the reaction and that there is synergistic effect of both oxidants.

The leaching of Cu cations from Cu/13X into the solution can occur during the process, thus generating secondary pollution. In order to know the total copper content in solution, samples of phenol oxidation reaction were analysed by atomic absorption. Then the obtained leaching values were graphically presented in Fig. 4 for CWPO and PP-CWAO processes.
It can be seen that in CWPO process Cu leaching increase with increasing temperature and hydrogen peroxide concentration. The amount of copper lost from the catalyst in PP-CWAO of phenol is maximal 10 % and increase with increasing temperature and H$_2$O$_2$ concentration. The amount of leached Cu in CWAO process was negligible and is not presented.

Finally, it can be stated from the presented experimental results that the best catalytic oxidation of phenol was performed by PP-CWAO process carried out at highest temperature and H$_2$O$_2$ concentration due to the 94 % conversion and relatively low leaching. The stability measurements also showed that thermal treatment stabilizes the Cu/13X catalyst since the leaching of copper is significantly lowers [12].

**CONCLUSION**

- The PP-CWAO process leads to higher pollutant removal conversions than the CWAO and CWPO processes. The results were influenced by the temperature and the Ph: H$_2$O$_2$ molar ratio.
- A synergistic effect was found when H$_2$O$_2$ is combined with air which leads to higher mineralization of the phenol.
- Thermal treatment stabilizes the Cu/13X catalyst from leaching.

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**REFERENCES**