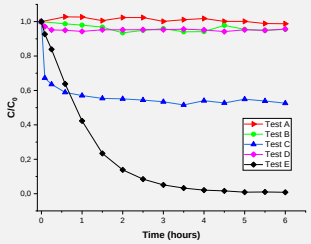
Exploring the Potential of the Advanced Oxidative Method CWPO in the Decontamination of 4-Nitrophenol in Aqueous Medium.

ORAL
Ph.D. Student: N
Journal: NONE

A. Sassaki[1], *R. Brackmann*[2], *J. L Diaz*[2]. *(1) Federal University of Technology - UTFPR, Via do Conhecimento, km 01, Fraron, CEP 85503-390, Pato Branco, Paraná, Brazil*. *(2) Rey Juan Carlos University (URJC), C.Tulipán, s/n, 28933, Móstoles, Madrid, Spain*.



The study evaluated the degradation of the emerging contaminant 4-nitrophenol (PNP) through the heterogeneous Fenton system CWPO (Catalytic Wet Peroxide Oxidation) under different experimental conditions. A high efficiency in PNP decontamination was observed, achieving approximately 99% reduction in concentration after 6 hours of treatment without the use of a catalyst. The thermal decomposition of hydrogen peroxide at 80 °C resulted in the formation of hydroxyl radicals in the solution, which acted as oxidizing agents in PNP degradation. Furthermore, the utilization of a hydrochar derived from orange peel with added iron was capable of removing approximately 50% of PNP concentration at 80°C through adsorption in just 1 hour of treatment

Introduction

The 4-Nitrophenol (PNP) is a highly toxic compound found in industrial and agricultural effluents. Its removal presents a challenge due to its high solubility in water and resistance to biological degradation. Conventional methods such as filtration and biological oxidation are ineffective due to the compound's chemical stability. Efficient removal requires advanced processes such as ozone oxidation or heterogeneous photocatalysis, which demand specific reaction conditions [1]. Additionally, the presence of other contaminants in the water can further complicate the process. Therefore, PNP removal poses a significant challenge for preserving water quality.

The CWPO (Catalytic Wet Peroxide Oxidation) comprises a heterogeneous Fenton method involving the use of hydrogen peroxide (H_2O_2) as an oxidizing agent and a catalyst. This method is effective in removing a wide range of organic pollutants, including persistent compounds like phenols, dyes, pesticides, and pharmaceuticals [2]. The process occurs under moderate temperature and pressure conditions, making it energetically viable compared to other advanced treatment methods [2,3]. In this context, the present study aims to evaluate the degradation of PNP molecules with H_2O_2 through the CWPO system employing a hydrochar prepared from orange peel with added iron as a catalyst.

Material and Methods

The decontamination tests of 4-nitrophenol from a synthetic solution with a concentration of 100 mg L^{-1} in acidified Milli-Q® ultrapure water at pH 3.0 with nitric acid were conducted in a 250 mL batch reactor with two outlets, with outlet A directed to a condenser and outlet B for aliquot withdrawals. The determination of PNP decontamination was performed using a UV-VIS spectrophotometer model Evolution 60s at a wavelength of 317 nm, where the analyte exhibits maximum radiation absorption.

To better understand the reaction variables, tests were conducted with fixed temperature at 80 °C (test A) to observe if only temperature is capable of degrading the molecule; with hydrogen peroxide at room temperature (test B); PNP adsorption on the catalyst surface at 80 °C (test C); stabilization of hydrochar adsorption (test D); temperature of 80 °C together with hydrogen peroxide (test E).

The reactor was immersed in a glycerin bath heated by a magnetic stirring hot plate to maintain reaction temperature uniformity. After reaching thermal stability, hydrogen peroxide was added. The aliquot withdrawal time for tests A and B was from 0 to 6 h with withdrawals every 30 min, and Tests C, D, and E were at intervals of 0, 5, 15, 30 min, and every 30 min up to 6 h. During this period, aliquots of approximately 2.0 mL were withdrawn from the reaction medium using a syringe. The aliquots from tests C and D were filtered through a filter with a pore size of 0.45 µm. For the other tests, the filtration step was not necessary as no solid catalyst was employed.

Results and Discussion

Figure 1 presents a normalized graph of PNP concentration over time for the different decontamination tests conducted.

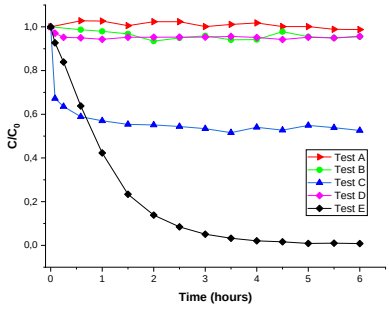


Figure 1. Concentration of PNP over time across various decontamination treatments.

Test A revealed no degradation of the molecule over time due to temperature effects, as did the test conducted solely with hydrogen peroxide at room

temperature (test B). In other words, these variables alone are not efficient for PNP decontamination. Test C, focusing on adsorption with a hydrochar concentration of 250 mg L^{-1} without H_2O_2, showed high adsorption of approximately 50% for the 100 mg L^{-1} PNP concentration. However, to better understand its catalytic effects on the reaction with H_2O_2, the catalyst concentration was decreased to 20 mg L^{-1} in test D, ensuring that contaminant removal by adsorption was less than 10%. Test E, utilizing temperature and hydrogen peroxide together, demonstrated high efficacy in PNP decontamination (around 99% efficiency over a 4-hour period without the use of a catalyst). This result stems from the thermal decomposition of hydrogen peroxide at 80 °C, generating hydroxyl radicals, which can act as oxidizing or destabilizing agents for organic molecules, thus promoting degradation.

One possible degradation pathway involves hydroxyls combining with the carbon adjacent to the nitro group NO_2 (nitrogen dioxide) in the 4-nitrophenol molecule, resulting in molecule instability. This process may lead to the formation of intermediates or further molecular degradation, resulting in progressively smaller molecules [4]. Eventually, this degradation may lead to the generation of carbon dioxide and water.

Figure 2 depicts the reduction in analyte absorbance throughout the treatment process for test E, demonstrating effective decontamination solely through the use of H_2O_2 and temperature.

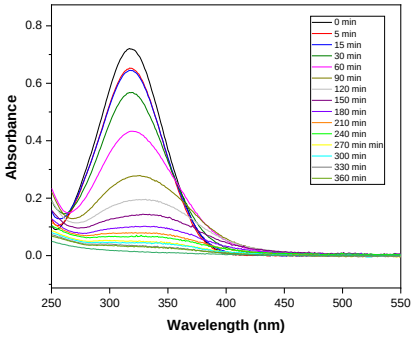


Figure 2. Graph of absorbance as a function of wavelength in UV-Vis spectrophotometry.

Conclusions

A significant reduction in the concentration of 4-nitrophenol was observed throughout the water decontamination process using the CWPO methodology, achieving 99% efficacy without the use of any catalyst, solely employing H_2O_2 and a temperature of 80 °C. The use of hydrochar at a temperature of 80 °C with a concentration of 250 mg L^{-1} was able to remove 50% of the contaminant through adsorption in just 1 hour of treatment.

Acknowledgments

The authors acknowledge UTFPR campus Pato Branco for the use of their facilities and to CNPQ for the Scientific Initiation Scholarship,

References

[1] Sistema de baixo custo para execução e monitoramento on-line de reações fotocatalíticas: aplicação em redução de nitro-fenol, Byanca S. Salvatia, Sirlon F. Blaskievicza, Patricia G. Corradinia,b e Lucia H. Mascaroa, Quim. Nova, 2021.

[2] The pH effect on the kinetics of 4-nitrophenol removal by CWPO with doped carbon black catalysts, Jose L. Diaz de Tuesta a,b, Asuncion Quintanillac , Jose A. Casasc , Sergio Morales-Torresd , Joaquim L. Fariab , Adrián M.T. Silvab, Helder T. Gomes, Madrid, Spain,Catalysis Today, 2020.

[3] Polyolefin-derived carbon nanotubes as magnetic catalysts for wet peroxide oxidation of paracetamol in aqueous solutions Jose L. Diaz de Tuesta a, Adriano S. Silva b,c,d,e , Fernanda F. Roman b,c,d,e , Lucas F. Sanches b,c,f, Fernando Alves da Silva f , Ana I. Pereira c,g , Adri´ an M.T. Silva d,e , Joaquim L. Faria d,e , Helder T. Gomes b, Madrid, Spain, Catalysis Today, 2023.

[4] High Efficient Photocatalytic Degradation of p-Nitrophenol on a Unique Cu2O/TiO2 p-n Heterojunction Network Catalyst, Lixia yang, Shenglian Luo, Yue LI, Yan Xiao, Qing Kang, Qingyun Cai, Republic of China, Meio Ambiente. Ciência. Tecnologia. 2010.