

Supplementary Material

Application of combined adsorption–ozonation process for phenolic wastewater treatment in a continuous fixed-bed reactor

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1. State of the art

Table S1. Previous studies on the treatment of wastewater through catalytic ozonation processes in the presence of activated carbon.

Pollutant	Operating conditions	Comments	Ref.
Acid blue 9, mordant black 11, reactive blue 19, reactive orange 16	Fixed-bed reactor (100×6 cm); $m_{\text{CAT}} = 200$ g; $F_G = 30$ g O_3 h^{-1} ; Neutral pH	Complete colour removal and a significant decrease in chemical oxygen demand (COD) were obtained in contrast to ozone treatment alone.	[1]
1,2-dihydroxybenzene	Fixed-bed reactor; $m_{\text{CAT}} = 2$ g; $F_G = 6$ mmol O_3 min^{-1} ; pH = 8	Ozonation combined with adsorption on activated carbon was shown effective to remove 1,2-dihydroxybenzene in 60 minutes.	[2]
Chlorophyll <i>a</i>	Fixed-bed reactor; $m_{\text{CAT}} = 2.1$ kg; $F_G = 5.0$ g O_3 h^{-1} ; pH = 8.5	Catalytic ozonation with activated carbon was able to remove more than 95% of the chlorophyll <i>a</i> and reduce 76% of the COD in only 30 min.	[3]
Natural organic matter (NOM)	Slurry-type reactor; $m_{\text{CAT}} = 0.5$ g L^{-1} ; $\text{CO}_{3,\text{G}} = 60$ mg L^{-1} ; pH = 7 / 9	The efficiency of the O_3/GAC , O_3/OH^- , and $\text{O}_3/\text{H}_2\text{O}_2$ systems for the removal of natural organic matter was compared. The same removal efficiency was obtained.	[4]
Polyphenols	Semibatch reactor; $M_{\text{CAT}} = 0.5$ g L^{-1} ; $F_G = 0.15$ L O_3 min^{-1} ; pH = 3 – 7	Ozonisation processes alone and combined (O_3/AC) were compared. It was observed that the ozonisation process with activated carbon improved significantly the primary degradation and mineralisation. The consumption of ozone was reduced via the O_3/AC process.	[5]
Carbamazepine and atrazine	Slurry-type reactor; $M_{\text{CAT}} = 0.1$ g L^{-1} ; $\text{CO}_{3,\text{G}} = 10$ mg L^{-1} ; pH = 7.3	Powdered activated carbon catalysed ozonation was more efficient for the removal of ozonation-resistant organics pollutants than ozone alone.	[6]

2. Experimental system characterisation

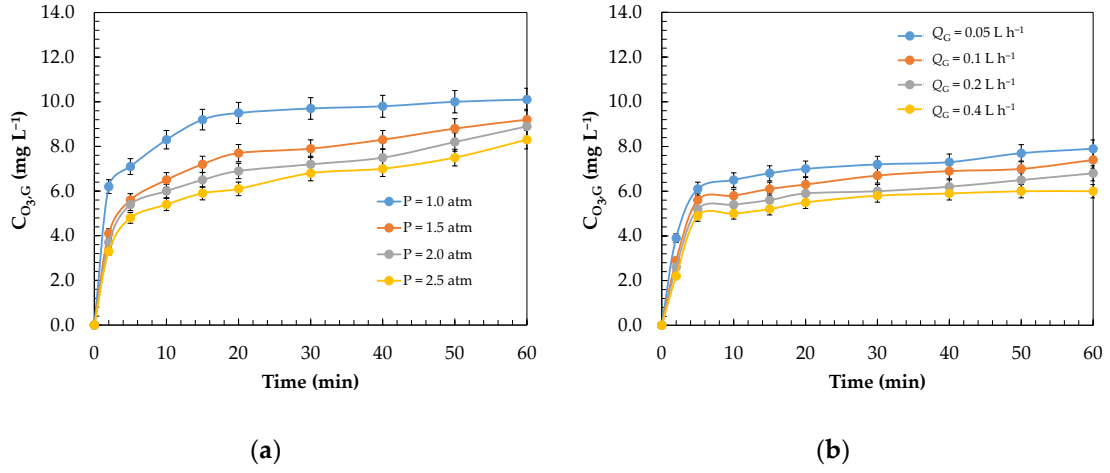


Figure S1. Evolution of ozone concentration at the reactor outlet gas stream. Effect of: (a) Pressure¹; (b) Ozone flow rate². Experimental conditions: ¹ $C_{P_0} = 250.0$ mg L⁻¹, pH = 11.0, $C_{O_3,G} = 12.0$ mg L⁻¹, $Q_L = 12$ mL min⁻¹, $Q_G = 0.05$ L h⁻¹, $V = 0.14$ L. ² $C_{P_0} = 250.0$ mg L⁻¹, $P = 2.5$ atm, pH = 11.0; $C_{O_3,G} = 19.0$ mg L⁻¹, $Q_L = 12$ mL min⁻¹, $V = 0.14$ L.

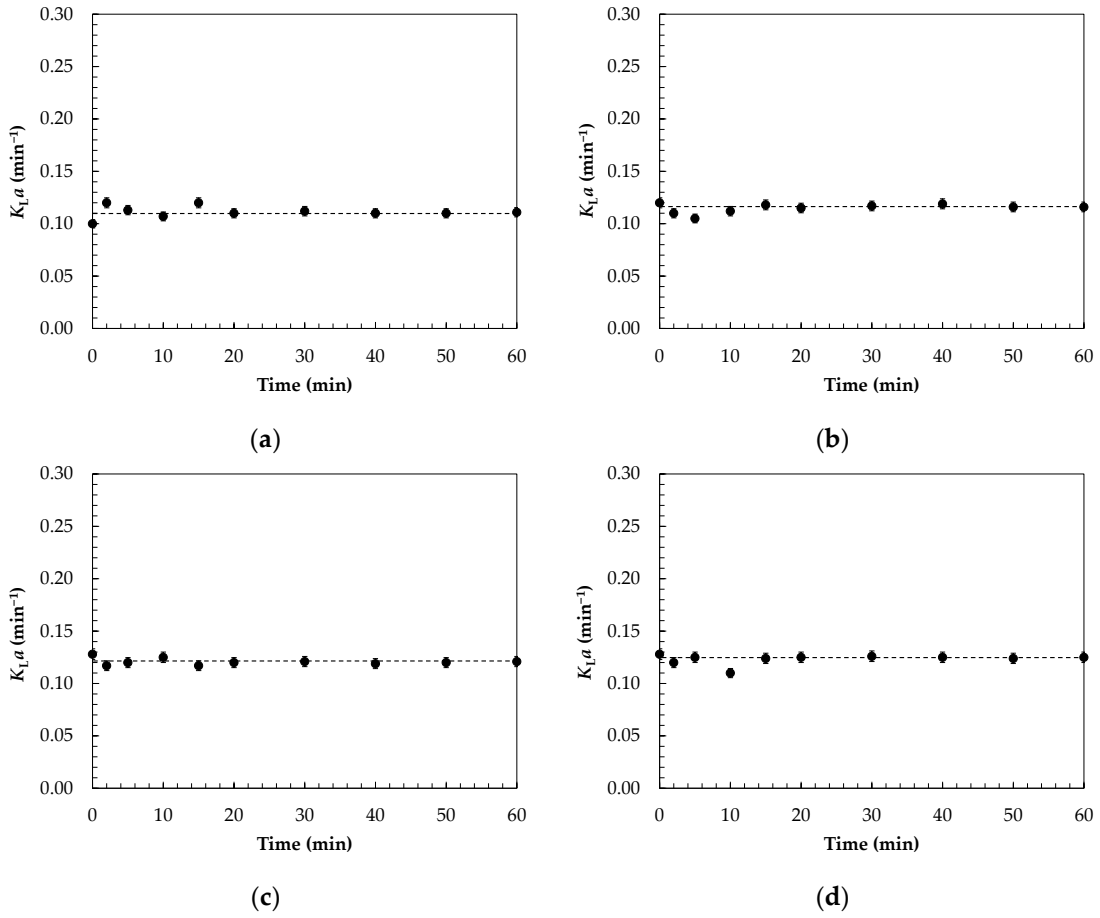


Figure S2. Determination of mass transfer coefficient of the experimental system for various pressures: (a) 1.0 atm; (b) 1.5 atm; (c) 2.0 and (d) 2.5 atm. Experimental conditions: $C_{P_0} = 250.0$ mg L⁻¹, pH = 11.0, $C_{O_3,G} = 12.0$ mg L⁻¹, $Q_L = 12$ mL min⁻¹, $Q_G = 0.05$ L h⁻¹, $V = 0.14$ L.

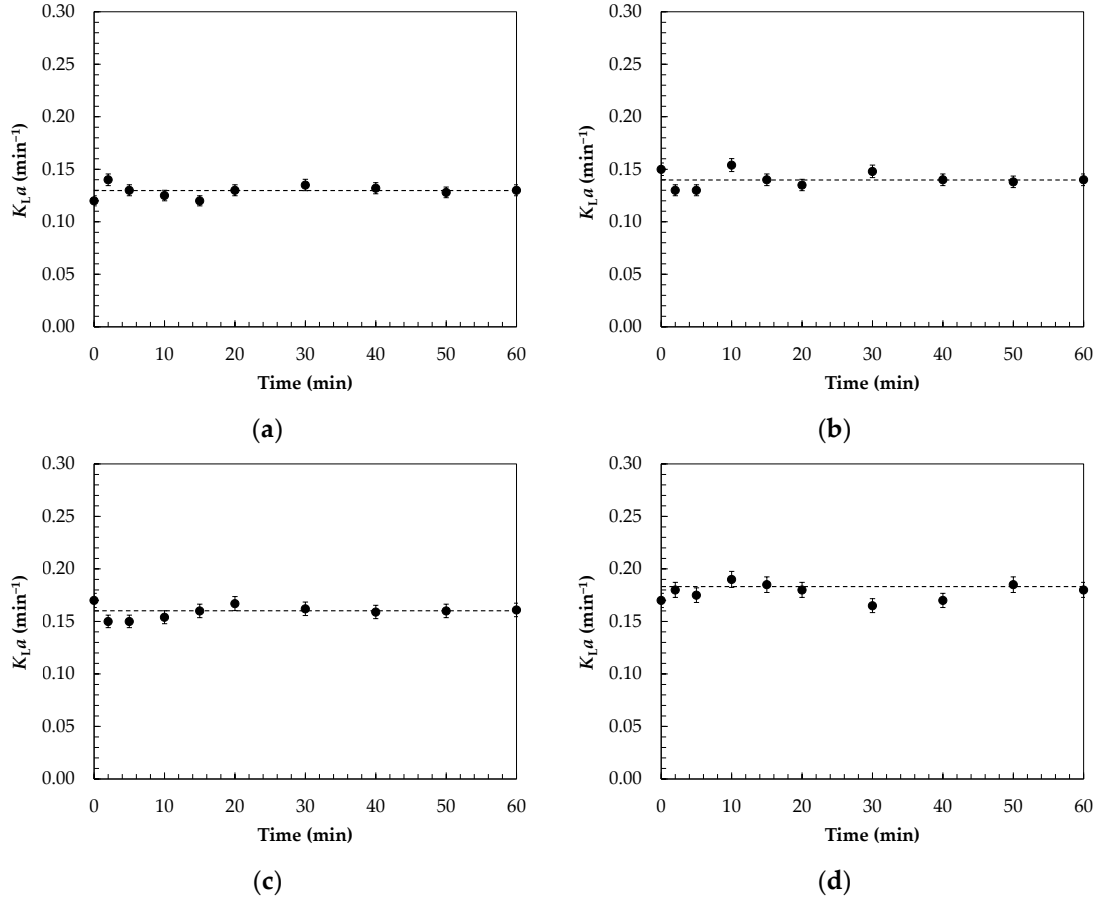


Figure S3. Determination of mass transfer coefficient of the experimental system for various ozone flow rates: (a) 0.05 L h⁻¹; (b) 0.1 L h⁻¹; (c) 0.2 L h⁻¹ and (d) 0.4 L h⁻¹. Experimental conditions: $C_{P_0} = 250.0$ mg L⁻¹; pH = 11.0, $P = 2.5$ atm; $C_{O_3,G} = 19.0$ mg L⁻¹, $Q_L = 12$ mL min⁻¹, $V = 0.14$ L.

3. Hydroxyl radical generation

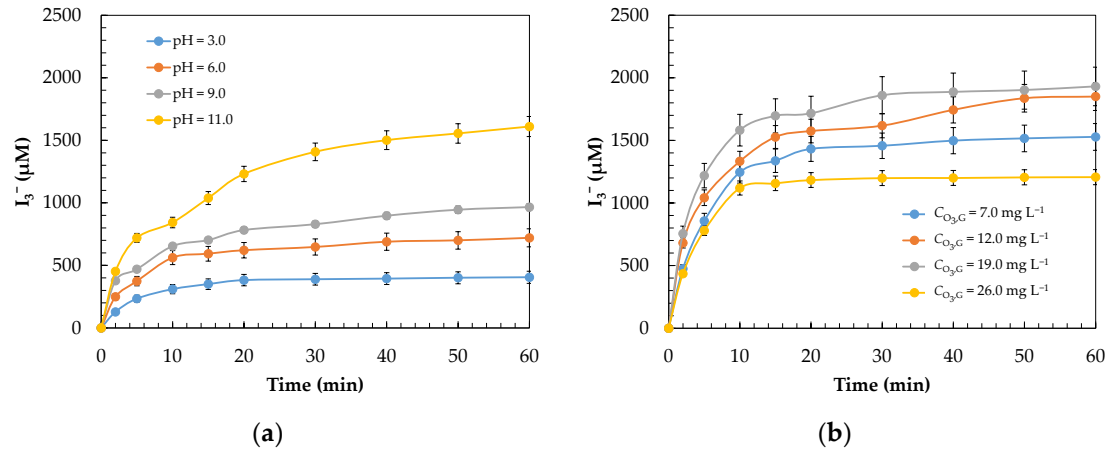


Figure S4. I_3^- concentration as a function of time for 0.1 M KI. Effect of: (a) pH¹ and (b) Ozone dose². Experimental conditions: ¹ $C_{P_0} = 250.0$ mg L⁻¹, $P = 1.0$ atm, $C_{O_3,G} = 12.0$ mg L⁻¹, $Q_L = 12$ mL min⁻¹, $Q_G = 0.05$ L h⁻¹, $V = 0.14$ L. ² $C_{P_0} = 250.0$ mg L⁻¹, $P = 2.5$ atm, pH = 11.0, $Q_L = 12$ mL min⁻¹, $Q_G = 0.05$ L h⁻¹, $V = 0.14$ L.

4. Oxidation by-products analysis

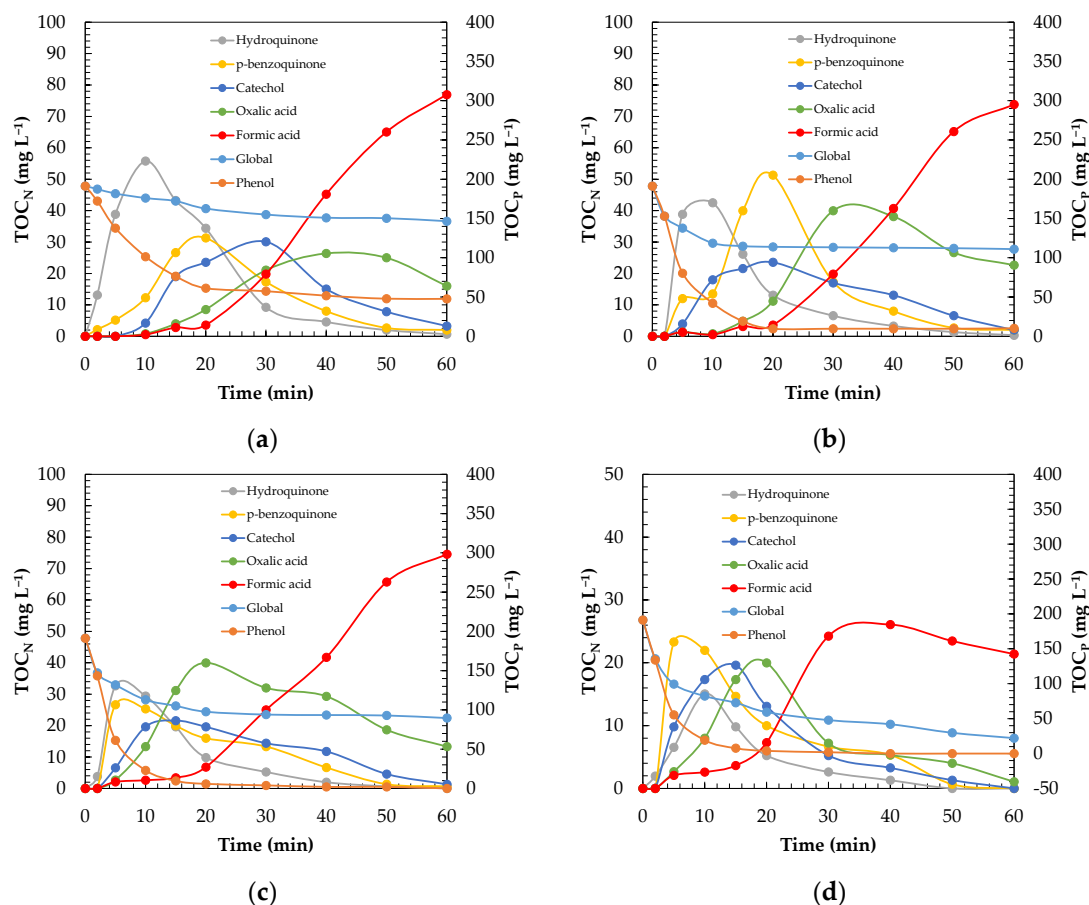


Figure S5. Analysis of the main degradation by-products during catalytic ozonation of phenol. Effect of: (a) pH = 3.0; (b) pH = 6.0; (c) pH = 9.0 and (d) pH = 11.0. Experimental conditions: $C_{P_0} = 250.0 \text{ mg L}^{-1}$, $P = 1.0 \text{ atm}$, $CO_{3,G} = 12.0 \text{ mg L}^{-1}$, $Q_L = 12 \text{ mL min}^{-1}$, $Q_G = 0.05 \text{ L h}^{-1}$, $V = 0.14 \text{ L}$.

References

1. Lin, S.H.; Lai, C.L. Kinetic Characteristics of Textile Wastewater Ozonation in Fluidized and Fixed Activated Carbon Beds. *Water Research* **2000**, *34*, 763–772, doi:10.1016/S0043-1354(99)00214-6.
2. Zaror, C.; Soto, G.; Valdés, H.; Mansilla, H. Ozonation of 1,2-Dihydroxybenzene in the Presence of Activated Carbon. *Water Science and Technology* **2001**, *44*, 125–130, doi:10.2166/wst.2001.0267.
3. Mousavi, S.M.S.; Dehghanzadeh, R.; Ebrahimi, S.M. Comparative Analysis of Ozonation (O_3) and Activated Carbon Catalyzed Ozonation (ACCO) for Destroying Chlorophyll a and Reducing Dissolved Organic Carbon from a Eutrophic Water Reservoir. *Chemical Engineering Journal* **2017**, *314*, 396–405, doi:10.1016/j.cej.2016.11.159.
4. Sánchez-Polo, M.; Salhi, E.; Rivera-Utrilla, J.; Gunten, U. von Combination of Ozone with Activated Carbon as an Alternative to Conventional Advanced Oxidation Processes. *Ozone: Science & Engineering* **2006**, *28*, 237–245, doi:10.1080/01919510600714170.
5. Giráldez, I.; García-Araya, J.F.; Beltrán, F.J. Activated Carbon Promoted Ozonation of Polyphenol Mixtures in Water: Comparison with Single Ozonation. *Ind. Eng. Chem. Res.* **2007**, *46*, 8241–8247, doi:10.1021/ie0708881.

6. Alameddine, M.; How, Z.T.; Gamal El-Din, M. Advancing the Treatment of Primary Influent and Effluent Wastewater during Wet Weather Flow by Single versus Powdered Activated Carbon-Catalyzed Ozonation for the Removal of Trace Organic Compounds. *Science of The Total Environment* **2021**, 770, 144679, doi:10.1016/j.scitotenv.2020.144679.