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Matrix influence on antibiotics photocatalytic removal from water by magnetic TiO_2–Carbon Quantum Dots composites

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INTRODUCTION & AIM

Over the years, global consumption of antibiotics has increased, as has their presence in the environment, mainly due to the discharge of ineffectively treated wastewater. Until 2045, Urban Wastewater Treatment Plants (UWWTP) with a population equivalent load of 150,000 or more must implement quaternary treatments to promote the removal of micropollutants, such as antibiotics. For such a purpose, solar-driven photocatalysis is considered promising. In this context, this study aimed to:

Synthesise a novel magnetic TiO_2/Carbon Quantum Dots (CQD) photocatalyst and assess its performance in the removal of the antibiotics: amoxicillin (AMX), sulfamethoxazole (SMX), and trimethoprim (TMP) under simulated solar irradiation, in different conditions.

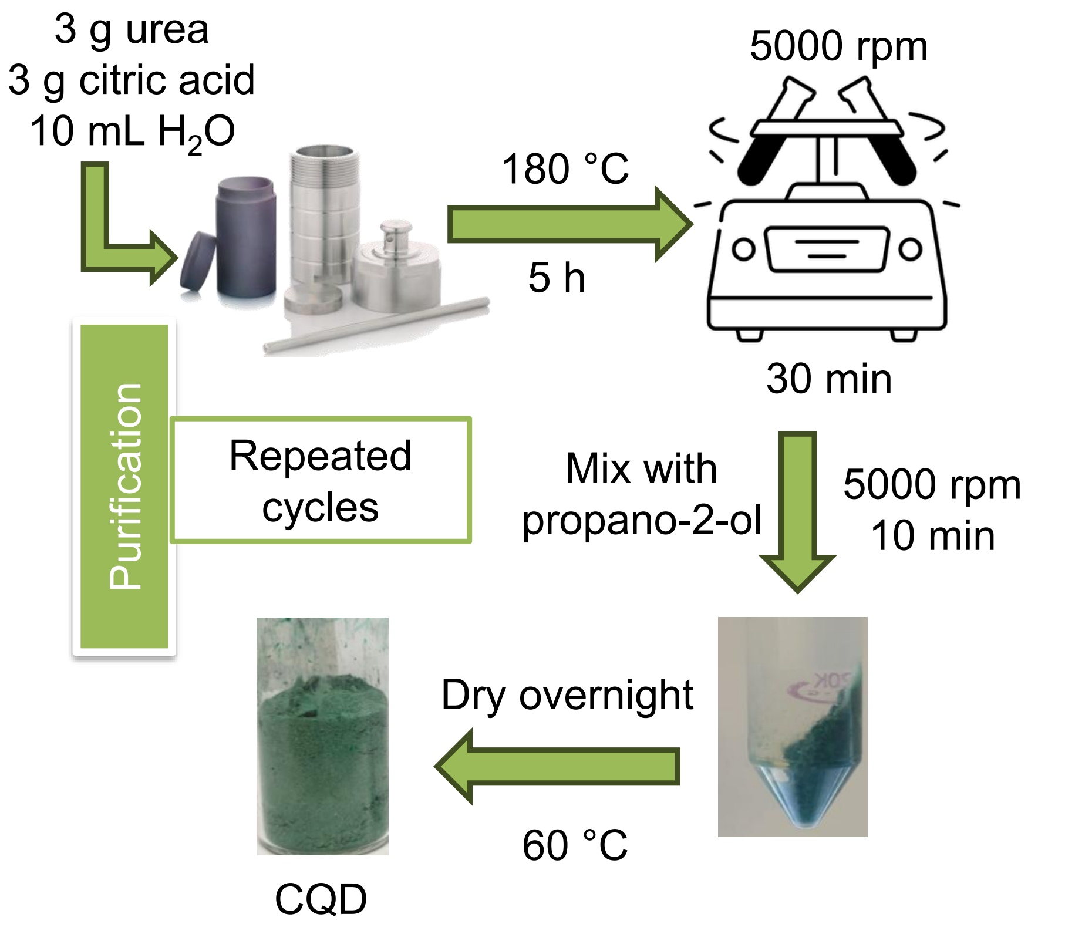
Determine the photolysis and photocatalytic kinetics of AMX, SMX, and TMP in phosphate buffer (PBS, pH 8.0) and secondary wastewater treatment plant effluent (sWWTP).

METHODOLOGY

PHOTOCATALYST PRODUCTION

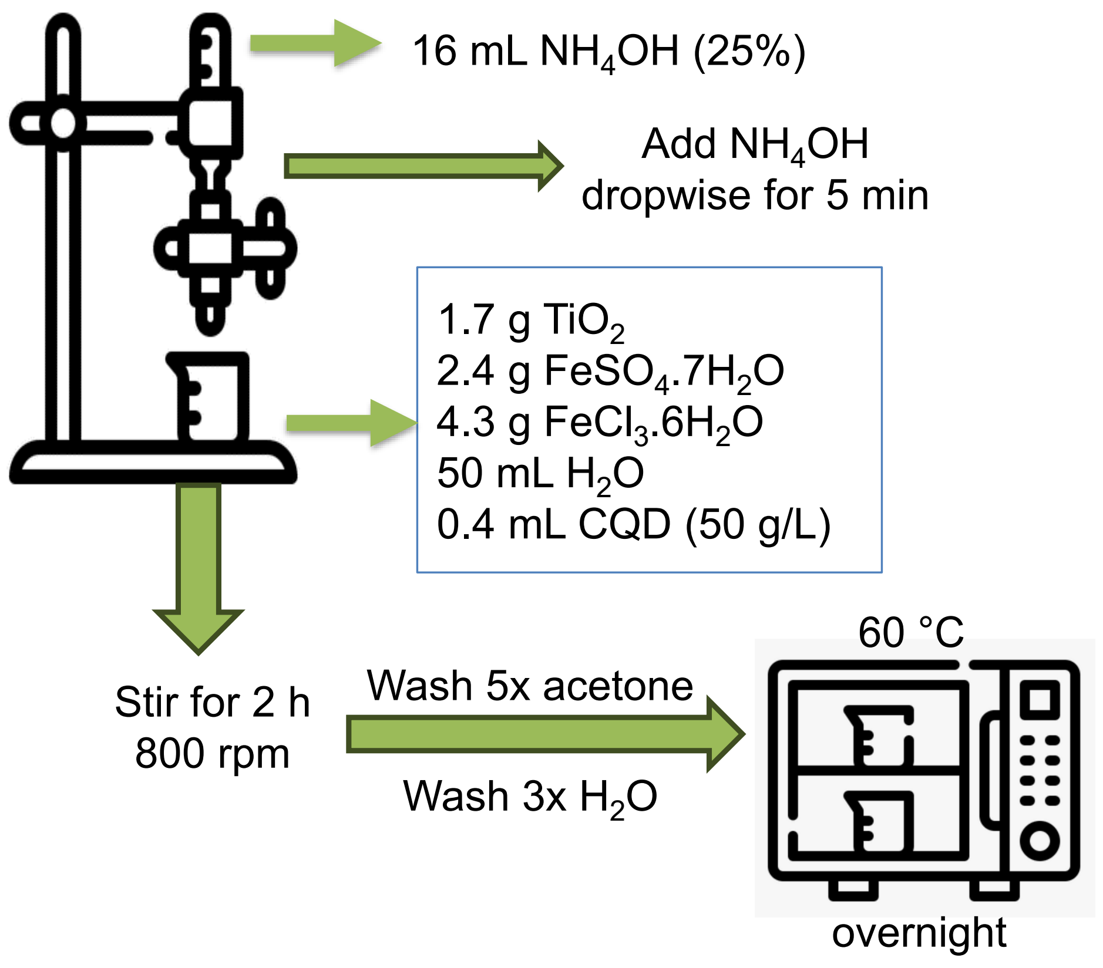
Carbon Quantum Dots Synthesis

Carbon Quantum Dots (CQD) were synthesised via a simple hydrothermal treatment using urea as N dopant.



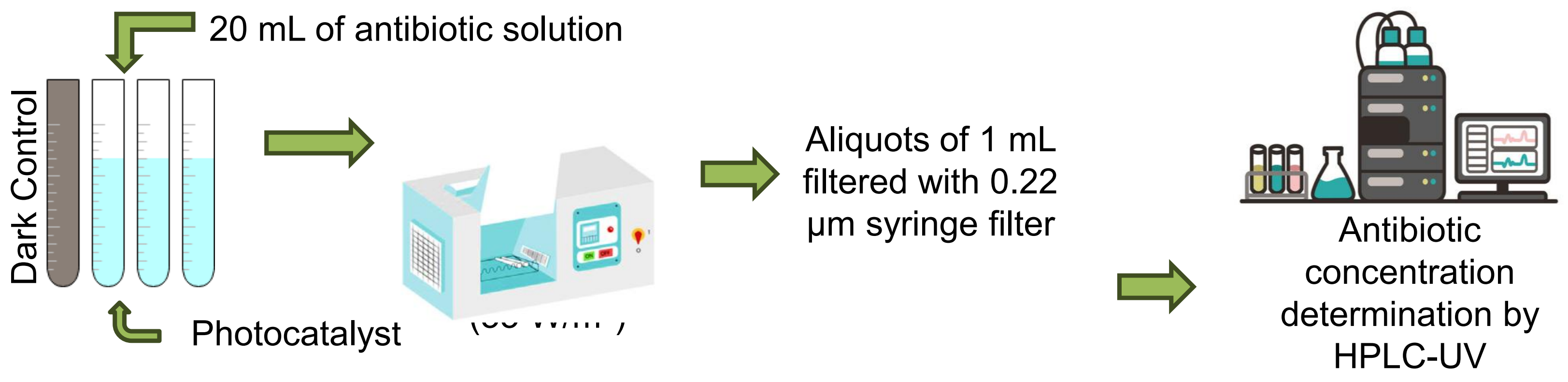
Synthesis of magnetic TiO_2/CQD

The combination of TiO_2, CQD, and magnetic nanoparticles (MNP) was achieved using an easy co-precipitation method. The final composite was named TiO_2@CQD@MNP.



PHOTOCATALYSIS EXPERIMENTS

The TiO_2@CQD@MNP (500 mg/L) was tested under different pH (6.0 – 9.0). AMX and TMP solutions were irradiated for 0.4 h in a solar radiation simulator, while SMX solutions were irradiated for 0.7 h. The effect of organic matter in the matrix was assessed using humic acids (40, 20, and 10 mg/L). Kinetic studies were performed in both PBS (pH 8.0) and sWWTP.



The removal efficiency of AMX, SMX, and TMP was assessed based on the decrease in C/C_0, where C denotes the residual antibiotic concentration after irradiation, and C_0 is the concentration in the corresponding dark control. Kinetic data were fitted to the pseudo-first-order ÷ ($C/C_0 = e^{-kt}$, where *k* is the degradation rate constant (h^{-1})) and the half-life time was determined ($t_{1/2}$ = ln(2)/*k)* for each antibiotic.

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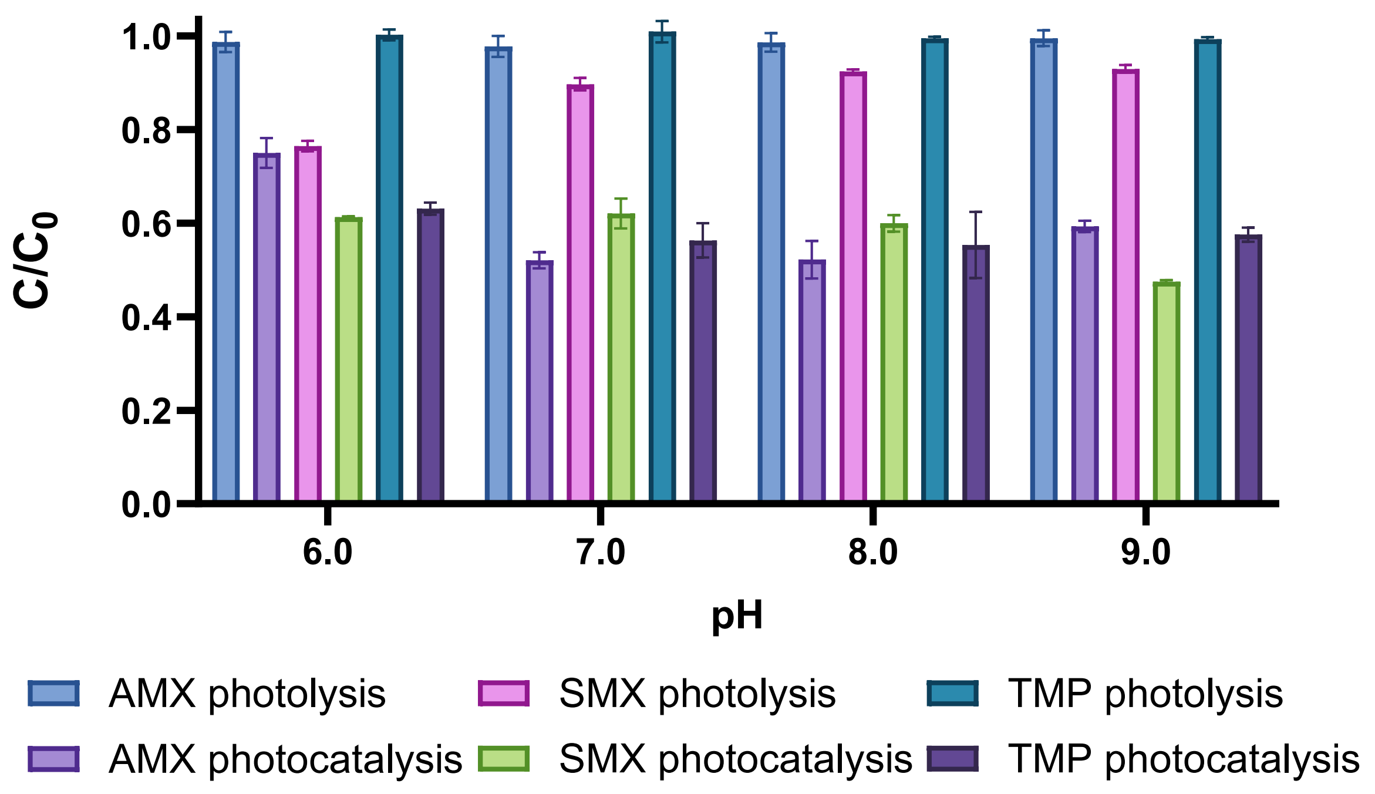
RESULTS & DISCUSSION



In general, no relevant effects of pH were observed on the photocatalytic efficiency of TiO_2@CQD@MNP, except for a decrease at pH 6 for AMX and an increase at pH 9 for SMX.

Figure 1. Effect of the pH on the photocatalytic efficiency of the TiO_2@CQD@MNP (500 mg/L) in the removal of 10 mg/L AMX and TMP (0.4 h of irradiation) and 10 mg/L SMX (0.7 h of irradiation) under stirring at 700 rpm.), in PBS

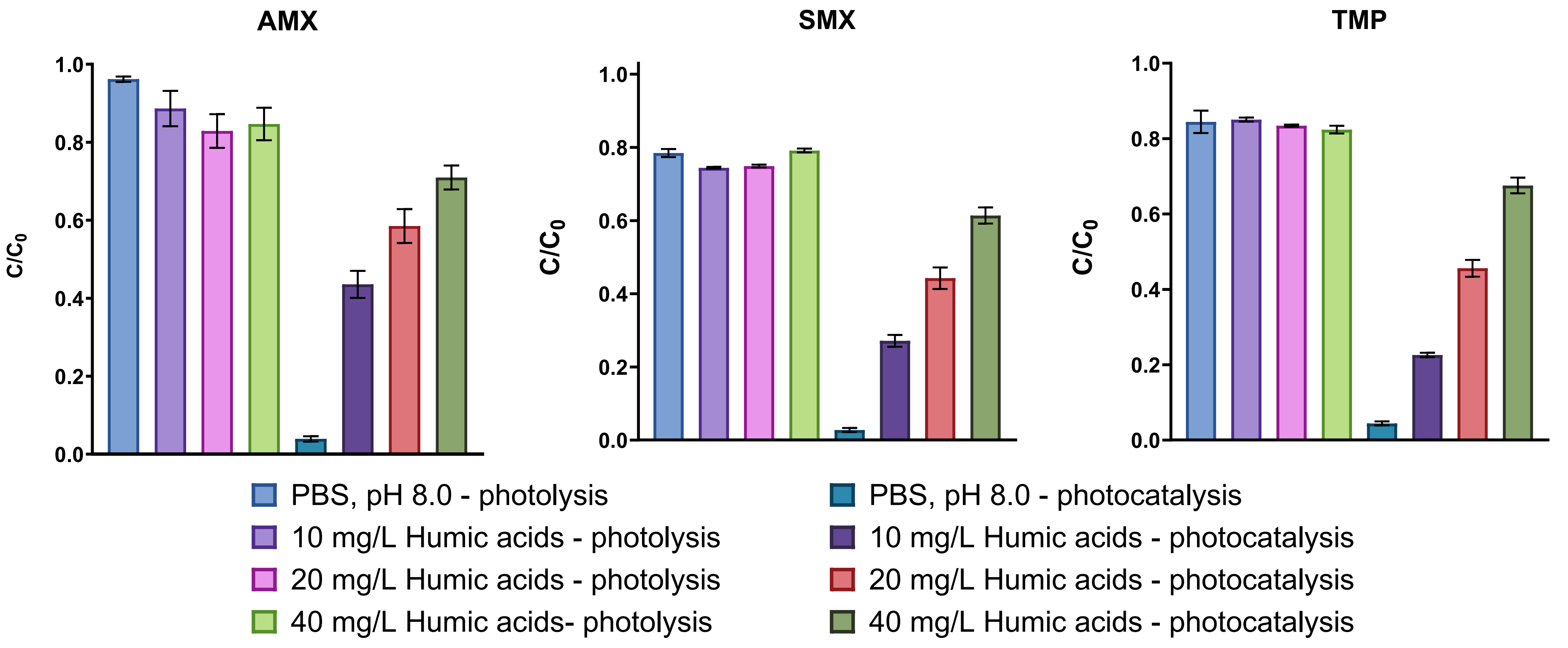


Figure 2. Results of the photolysis and TiO_2@CQD@MNP efficiency in matrices with different humic acids concentrations (40 – 10 mg/L) in the removal of 10 mg /L of AMX and TMP (0.4 h of irradiation) and 10 mg/L of SMX (0.7 h of irradiation) in PBS (pH 8.0) under stirring at 700 rpm.

TiO_2@CQD@MNP efficiently removed the antibiotics even in the presence of relatively high concentrations of organic matter.

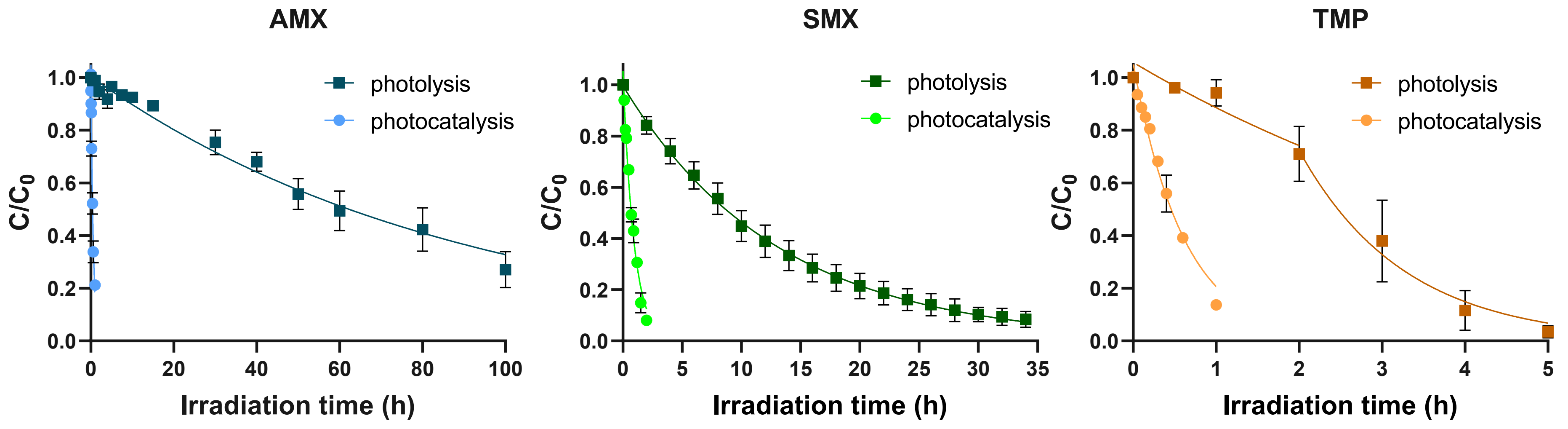


Figure 3. Kinetics of photolysis and TiO_2@CQD@MNP (500 mg/L) mediated photocatalysis of 10 mg/L of AMX, SMX and TMP, in PBS (pH 8.0) under stirring at 700 rpm.

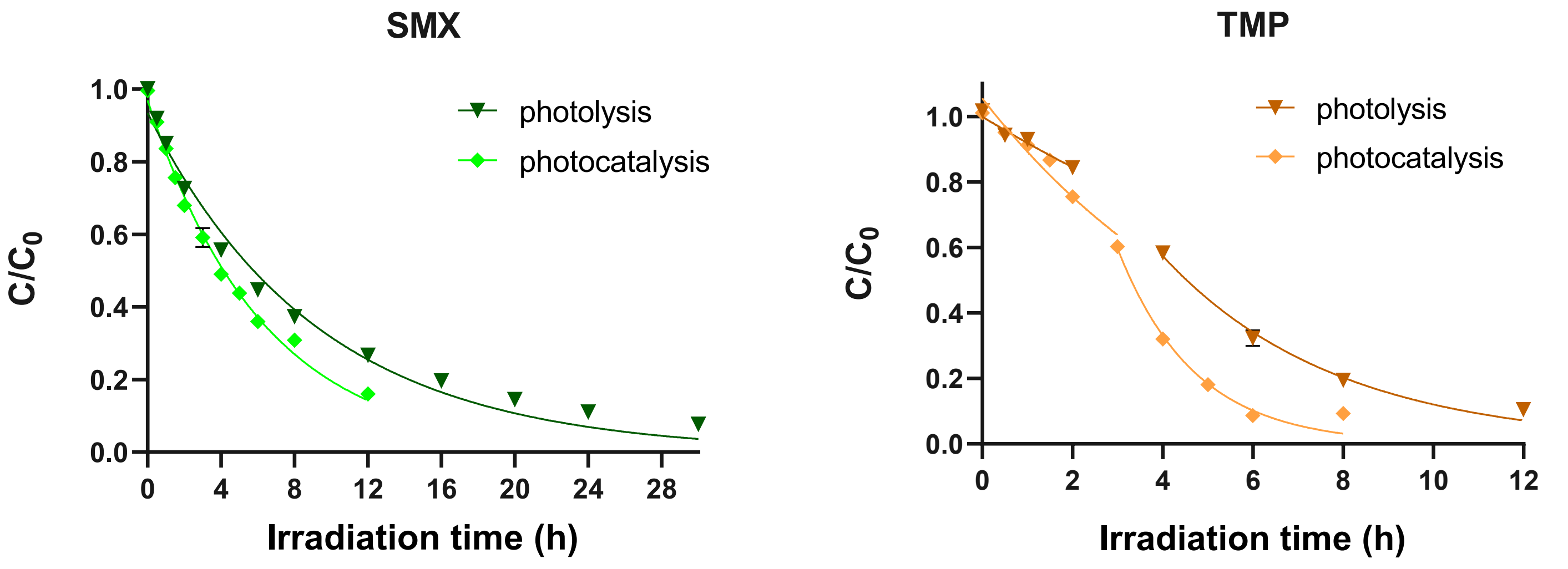


Figure 4. Kinetics of photolysis and TiO_2@CQD@MNP (500 mg/L) mediated photocatalysis of 10 mg/L of SMX and TMP, in sWWTP under stirring at 700 rpm.

CONCLUSION AND FUTURE WORK

The development of sustainable strategies for removing antibiotics from wastewater is essential to mitigate environmental and public health risks.

- The TiO_2@CQD@MNP photocatalyst showed effective antibiotic removal under different conditions. The pH had a limited influence, while dissolved organic matter had a more pronounced negative effect, as observed in humic acids and sWWTP compared to PBS.
- The kinetic model successfully described the degradation process, enabling the determination of half-life ($t_1/_2$) values. Photocatalysis significantly reduced $t_1/_2$ compared to photolysis, with a more pronounced effect in PBS than in sWWTP.

Therefore, the presented magnetic photocatalyst is a promising option for solar-driven wastewater treatment, enabling efficient antibiotic removal. This strategy aligns with green chemistry principles and material circularity, particularly through the possibility of magnetic recovery and reuse of the photocatalyst.