Photo-electrochemical oxidation flow system for stormwater herbicides removal: Operational conditions and real stormwater chemistry impact study

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Highlights

- Flow reactor system demonstrates a great potential for scaling up in future application.
- Flow rate can help with the diuron degradation process rather than light intensity.
- The real stormwater environment can support the herbicides degradation process.

Introduction

Stormwater, as an untapped water resource, can largely fulfill urban water need with proper harvesting process. However, the treatment of stormwater is still necessary since the concentration and occurrence of containing pollutants are with high variability, *e.g.* micropollutants (Page et al. 2010).

Although the conventional stormwater treatment (e.g., biofilters, constructed wetlands) can present outstanding capacity for many stormwater pollutants, *i.e.*, sediments, nutrients, heavy metal and pathogens (Spahr et al. 2020). However, their performance in removing micropollutants still has the potential to be improved. Thus, the cost-effective, low maintenance, natural-based technologies are demanded to further purify biofiltered stormwater prior to reuse. The feasibility of the advanced oxidation processes (AOP), *i.e.*, photo-electrochemical oxidation (PECO), electrochemical oxidation (ECO) and photocatalytic oxidation (PCO), had been proven before in removing stormwater herbicides (Zheng et al. 2021).

However, the previous study for PECO stormwater micropollutants was remained at the lab batch reactor status. In order to test the robustness of PECO for stormwater treatment process, it is necessary to further understand the impact of the operational conditions and stormwater chemistry on the flow reactor system performance. The flow rate has been found as the significant factor in the previous ECO flow reactor operation (Pereira et al. 2012) due to its predominant influence to the homogeneity and inner turbulence in the reactor. Thus, it is essential to investigate its impact on PECO degradation performance. In addition, the light intensity was regarded as the key factor for PCO operations. However, it varies with the time-dependent and catchment-dependent characteristics. Therefore, the light intensity needs to be considered as an influencing factor for the PECO system operation as well. The initial concentration of pollutants (with high variability properties) can pose challenging conditions for the treatment system. Consequently, it has been regarded as a factor of stormwater chemistry for the system test (Montenegro-Ayo et al. 2021). Compared with the synthetic stormwater used in the lab experiments, the real stormwater possessed more complex characteristics and compounds which may compete with the target pollutants and hinder the degradation process. Thus, the flow system needs to be tested in the real stormwater environment to understand its impact on the PECO degradation performance.

This study investigated three factors (flow rate, light intensity and initial concentration of pollutants) and the real stormwater chemistry impact with a designed recirculating flow reactor for the first time to test the scaling up potential of the PECO process for the future stormwater validation.

Methodology

Flow reactor setup design and experiment procedure

The designed reactor is in flat cartridge shape with inlet and outlet tube containing several main components: (1) quartz glass (allow the light to penetrate into the reactor); (2) metal support and metal cover (stainless steel for anode placement; conductive); (3) carbon fiber anode (8.5×8.5 cm^2); (4) stainless steel cathode (active area is 9×9 cm^2). The distance between anode and cathode is 1.35 cm. The total volume of reactor is 243 cm^2 (with 3 cm thickness). The peristaltic pump was used for recirculation. The inlet and outlet tube of reactor was placed in a bottle containing synthetic stormwater for test (675 mL). A magnetic stirrer was set as 600 rpm for stormwater mixing. The overall system setup is shown in **Figure 1**.

The experiments of PECO were applied with simulated solar light and electricity. The "standard" initial concentration (60 μg L^{-1}) of diuron and atrazine was spiked into the synthetic stormwater as the target micropollutants. The peristaltic pump transported the water from the bottle to fill up the flow reactor and back to the bottle via the connected tubes to form the recirculation cycle. The samples were analysed by high-performance liquid chromatography / tandem mass spectrometer (HPLC/MSMS) with the prepared standard curve quantification (5 ng L^{-1} as the detection limit). Triplicate tests have been conducted for each experiment to ensure the reproducibility.

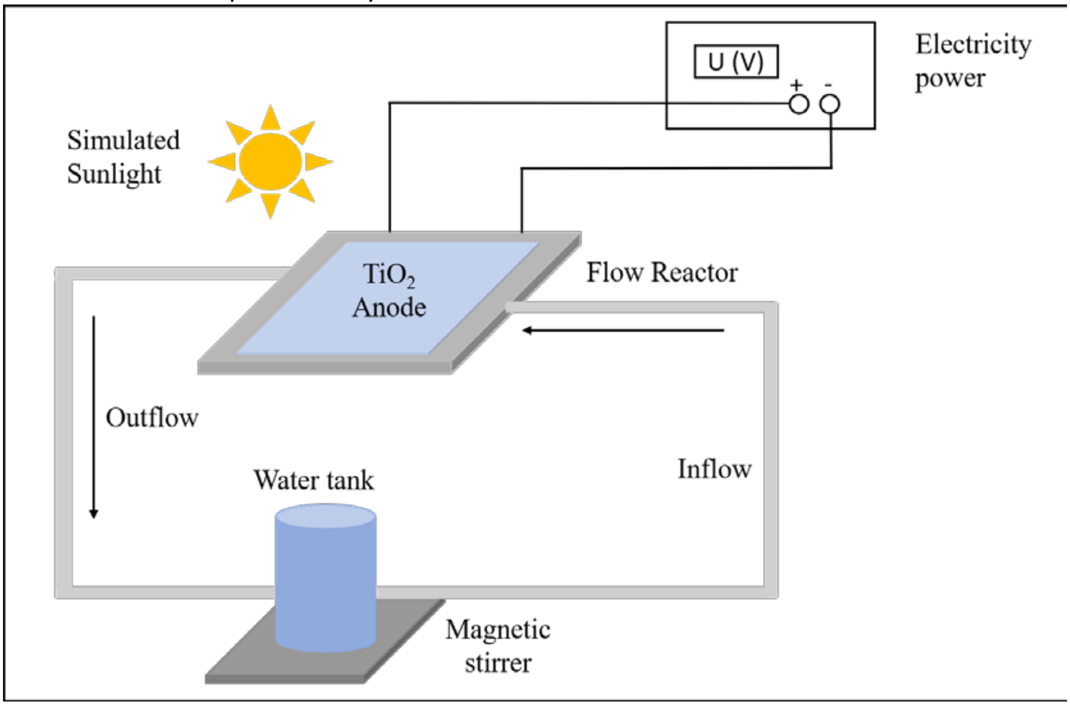

Figure 1. Schematic experiment setup diagram for flow reactor system

Operational conditions investigation

Three operational conditions were selected for investigation: (1) flow rate; (2) light intensity; and (3) initial concentration. The flow rate experiments followed the procedure described above, except the flow rate setting of peristaltic pumps: (a) 610 mL min^{-1}; (b) 280 mL min^{-1}; (c) 29 mL min^{-1}. The "standard" light intensity (100 mW cm^{-2}) and initial concentration (60 μg L^{-1}) were applied. The light intensity experiments only controlled the light intensity as the variable implemented with the highest flow rate (which was found as the optimal flow rate) and "standard" initial concentration. The light intensity was set as: (a) high intensity (144 mW cm^{-2}); (b) standard intensity- (100 mW cm^{-2}); (c) low intensity (63 mW cm^{-2}). The initial pollutants concentration experiments selected initial concentration of herbicides as the controlled parameter equipped with 610 ml min^{-1} flow rate and "standard" light intensity. The initial concentration was set as: (a) high conc (240 μg L^{-1}); (b) standard conc (60 μg L^{-1}); (c) low conc (15 μg L^{-1}). The experiment procedure, sampling method, analysis method and replication remained the same as described above.

Real stormwater chemistry impact investigation

In order to study the real stormwater impact, the collected stormwater will be applied as the supporting electrolyte for the system. The "real stormwater" was collected from the stormwater inflow in Centennial Park, Sydney (receiving stormwater runoff from the surrounding residential catchment) and the stormwater outflow at Coogee Beach, Sydney (receiving from a residential catchment). The herbicides were added into the real stormwater to form "standard" initial concentration (60 μg L^{-1}) treatment solution. The real solar light was used as the light source for PECO process. The experiment procedure, sampling method, analysis method and replication were the same as described above.

Results and discussion

For diuron degradation, 610 mL min^{-1} flow rate presented the best removal performance with around 92 % removal compared with 80 % removal of 280 mL min^{-1} flow rate and 63 % removal of 29 mL min^{-1} flow rate (shown in **Figure 2**). The enhancement for degradation process coming from the flow rate increase can be clearly noticed. From the hydrodynamic aspect, higher flow rate provides higher turbulence in the flow reactor which improves the mass transport of herbicides to the electrode surface (Pereira et al. 2012). With the contact with the oxidants generating on the electrode surface, the degradation rate of herbicides has been raised. However, the improvement effect of atrazine degradation coming from the flow rate was negligible (within the systematic error). The atrazine degradation may need higher flow rate to enhance the mass transfer rate for performance acceleration. The similar outcome has been observed for light intensity tests. The degradation performance did not present obvious difference under all three applied light intensity (high, standard and low light intensity). This suggested that the light intensity change (*i.e.*, the daily and seasonal change) would not influence the system performance. Through the initial pollutants concentration tests, 90% diuron can be degraded for all the tested concentrations (15 µg L^{-1}, 60 µg L^{-1}, 120 µg L^{-1}). While atrazine can only around 25% removal for all the concentrations. This implied that the system could present excellent diuron removal outcome. However, the atrazine removal performance still needs to be improved.

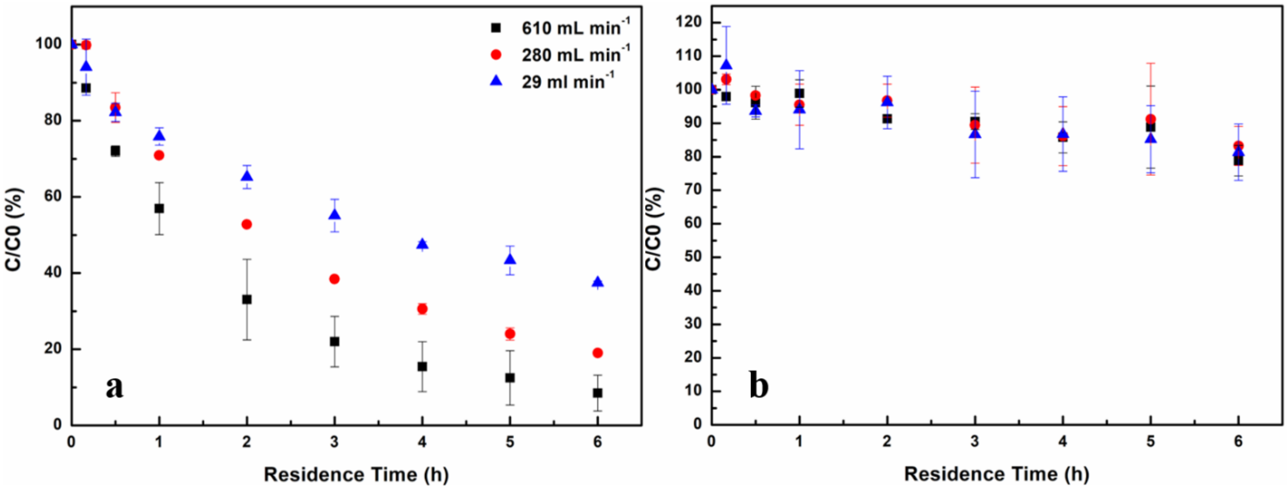

Figure 2. Degradation performance of diuron (a) and atrazine (b) under different flow rate operations: (1) 610 mL min^{-1}; (2) 280 mL min^{-1}; (3) 29 mL min^{-1}

Conclusions and future work

The recirculating flow reactor has demonstrated an effective removal performance for stormwater herbicides removal. The flow rate has been found as a supporting operational condition for the system running. The light intensity cannot present significant effect for the performance which allows the system to have the potential to deliver the stable outcome even under low light intensity circumstance. Through the initial pollutants concentration tests, diuron has been regarded as the suitable micropollutants for the system removal. The atrazine degradation process still needs to be optimized for the system design in the future studies. The real stormwater environment needs to be tested to support the PECO flow reactor system for herbicides removal operation.

References

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