Romanian Journal of Ecology & Environmental Chemistry, 5(1), 2023

https://doi.org/10.21698/rjeec.2023.101

Article

Trials on ciprofloxacin removal from wastewater using a photocatalytic membrane reactor

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Received:	Accepted:	Published:
07.06.2023	27.06.2023	10.07.2023

Abstract
Trials on ciprofloxacin removal from real aqueous systems were performed using a photocatalytic membrane reactor with catalyst in suspension. Four sets of four treatment cycles were carried out and experimental results were processed from the statistical point of view in order to assess results reproducibility. Global ciprofloxacin removal efficiencies of more than 99.85% were obtained for all treatment cycles. Coupling of photocatalytic degradation with membrane process allowed catalyst separation and reuse within further treatment cycles. Statistical analyse of experimental data recommend the use of photocatalytic membrane reactors as a feasible option for the advanced removal of pharmaceutical products like ciprofloxacin from real wastewater systems.

Keywords: *ciprofloxacin, photocatalytic membrane reactor, photo catalyse, membrane*

INTRODUCTION

The availability of freshwater resources per capita, at global level, is gradually diminished due to the population increase, urbanisation and modern lifestyle. Therefore, the wastewater management is of great concern. Various conventional treatment processes can treat wastewater discharges but these technologies are not adequate for the advanced removal of pollutants, especially refractory organic pollutants, which are organic compounds that are not readily biodegradable in the environment.

Pharmaceuticals are some of the most recalcitrant organic compounds that can be found in wastewater [1]. These refractory organic pollutants are presenting toxic, carcinogenic, teratogenic and mutagenic potential and are harmful to the environment and human health, asking for more advanced treatment technologies such as advanced oxidation processes (AOPs) for their degradation [2].

Nowadays, the main treatment methods for refractory organic pollutants include photochemical processes, Fenton oxidation and ozone treatment. Hybrid processes such as photocatalysis coupled with membrane processes represent a promising green technology for wastewater treatment, which limits potential risks to aquatic organisms and human health. Coupling UV-VIS light activity of photocatalyst and membrane based separation process presents the advantages of prolonging the lifetime of polymeric membranes due to their lower degradation [3]. Moreover, photocatalysis presents the advantages of good photocatalytic activity, nontoxicity, chemical inertness and low cost.

Ciprofloxacin (CIP) is a fluoroquinolone antibiotic extensively used in human and veterinary medicine, which is partly metabolised, being discharged into environment. The majority of wastewater treatment plants do not eliminate it effectively and therefore there is a need for development of new treatment processes [4].

Studied experimental model was a photocatalytic membrane reactor with photocatalyst in suspension, which includes two main steps: TiO2 based photocatalysis followed by photo catalyst separation and reuse using membrane processes. The selection of photocatalytic membrane reactor (PMR) with photo catalyst in suspension was done based on its advantages:

- ease of photo catalyst separation from treated solution and therefore the possibility to recover and reuse the photo catalyst in subsequent treatment cycles;
- the spent photo catalyst can be exchanged without membrane replacement;
- ease of photo catalyst concentration adjustment;
- better degradation efficiencies vs. PMR with photo catalyst immobilized in/on membrane.

Nowadays research works are focussing on application of hybrid-combined techniques both for wastewater reclamation and reuse and for advanced removal of refractory pollutants. This approach not only overcomes the drawbacks of each individual technique but also combines their advantages and closes the water resources loop on the road to a European circular economy [5].

On national level, there are very few studies on PMR with suspended catalyst used for advanced removal of refractory organic pollutants from aqueous systems [6].

At international level there are available some studies on coupling of photocatalysis with membrane processes for removal of refractory organic pollutants from water. Various authors are proposing the coupling of membrane filtration with photocatalysis in order to overcome membrane fouling and the need of removal from permeate water of some pollutants [7, 8]. The majority of photocatalytic membranes operates under UV irradiation:

- degradation of volatile organic compounds using modified PVDF membranes [9];
- water treatment using photocatalytic membrane by g-C3N4 quantum dots and TiO2 nanotube array [10];
- degradation of diclofenac using submerged PMR and N-doped TiO2 catalyst [11];
- methylene blue, methyl orange and phenol degradation using P-doped g-C3N4 integrated photocatalytic membrane reactor [12];
- hybrid photocatalysis – ultrafiltration (using ceramic membranes) process for reduction of synthetic dyes from water [13];
- photocatalytic degradation of RB5 reactive dye under artificial sunlight using ZnO and Fe3+@ZnO nano discs in PMR [14];
- preparation of photocatalytic membrane with antifouling and self-cleaning ability [15-18];
- development of photo catalysts combined with magnetic materials or coated on optical fibres [19, 20];
- new hollow fibre membrane for the removal of Bisphenol A from water under visible light [21].

Taking into account the above presented data, hybrid technologies based on photocatalysis and membrane separation are novel sustainable processes of high interest on both national and international level due to their obvious advantages: synergic effect; possibility to reuse the catalyst; improved selectivity; improved anti-fouling ability; lower degradation rate and longer lifetime of polymeric membranes.

EXPERIMENTAL PART

A laboratory-level photocatalytic membrane reactor was used for the advanced removal of CIP from real wastewater. Wastewater was sampled from a municipal wastewater treatment plant after the biological step and was spiked with ciprofloxacin (CIP) 99% purity provided by Sigma Aldrich (Germany). The laboratory PMR comprises two main components:

- An UV-VIS photocatalytic reactor (Heraeus, Germany) with a capacity of 400 mL equipped with a TQ150-Z3 lamp (λ = 320-550 nm) and a magnetic stirrer (Velp Scientifica, Italy).
- A membrane test cell KMS Laboratory Cell CF 2 (Koch Membrane Systems, Germany) with an effective membrane surface area of 28 cm^2 and a capacity of maximum 600 mL.

TiO_2 anatase form (Merck, Germany) as photocatalyst and Hydrosart 30 kDa membrane (Sartorius, Germany) were used in all experiments.

CIP concentration was determined by HPLC using and Agilent 1200 series equipment (Agilent Scientific, USA).

Processing and interpretation of experimental results was performed based on two categories of statistical parameters: indicators of data centering tendency (mean and median) and indicators of data dispersion tendency (amplitude, mean square deviation and variability).

The *mean* (x_m) – average value of obtained results, estimates the centering tendency of individual values

$$x_m = \frac{\sum_1^n x_i}{n} \quad (1)$$

The *median* (M_e) – value from the middle of data series, obtained by sorting experimental values from smallest to largest.

- if the series contain an odd number of data (n=2k+1), median value is the one from the middle of the series
- if the series contain an even number of data (n=2k), median value is calculate as the average of data from the middle of the series ($M_e = (x_m+x_{m+1})/2$)

The *amplitude* (A) – calculated as difference between extreme values. A small value of amplitude shows a minor dispersion of experimental data.

$$A = x_n - x_1 \quad (2)$$

The *mean square deviation* (MSD) – express the results dispersion around the mean value. It is an indicator of results precision and reproducibility.

$$\sigma = \sqrt{\frac{\sum_1^n (x_i - x_m)^2}{n-1}} \quad (3)$$

The *variability* (V) – indicates the homogeneity of data from series.

$$V = \sigma\ 100/x_m \quad (4)$$

- 0 < V < 15% - very low dispersion of data, analysed series is homogenous and the mean (xm) is representative;
- 15% < V < 30% - moderate scattering of data, analysed series is relatively homogeneousness and the mean (xm) is relatively representative;
- V > 30% - non-homogeneousness series and the mean is not representative.

RESULTS AND DISCUSSION

Four sets of experiments were performed using real wastewater samples spiked with CIP in order to assess the reproducibility of the results. The experiments involved two steps: photocatalysis assisted by TiO_2 followed by catalyst separation using membrane processes. The catalyst was recirculated for the following photocatalytic cycle. Four cycles were considered for each experimental set. All experiments were carried using the following parameters [22]:

- Catalyst dose [TiO2] = 400 mg/L
- Irradiation time = 75 minutes
- Working pressure for membrane module = 5 bars

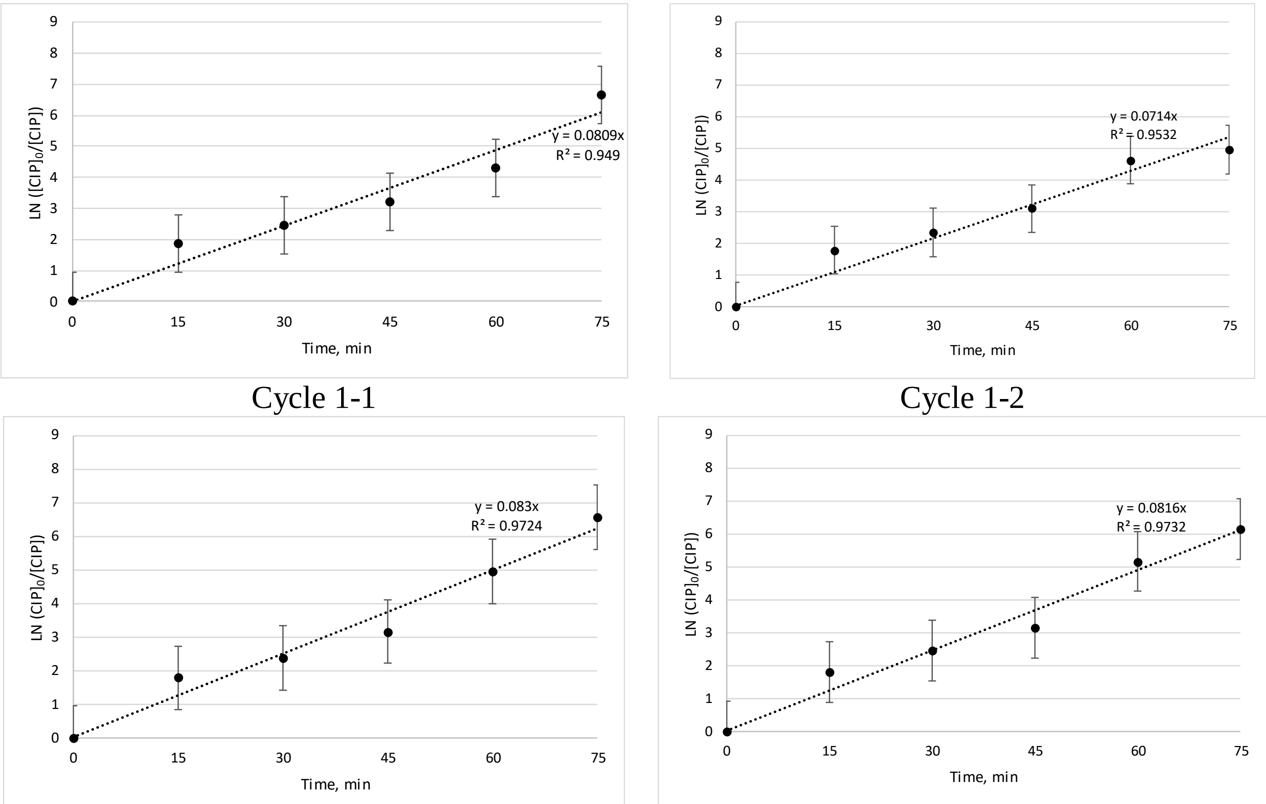
Obtained experimental results for all sets of experiments are presented within Table 1.

CIP removal efficiencies after photocatalytic step were found to be in the domain 99.29 to 99.91 with a residual CIP concentration below 0.03 mg/L. The membrane process used to separate and reuse the catalyst in further treatment cycles proved to play also a role in the advanced removal of target pollutant, the CIP removal efficiencies after membrane process step being situated within the domain 99.86 - 99.95%, with a residual CIP concentration of 0.01 – 0.02 mg/L.

Table 1. CIP removal efficiency using PMR

Set-Cycle	$[CIP]_0$, mg/L	[CIP] after UV/TiO_2, mg/L	Efficiency after UV/TiO_2, %	[CIP] after membrane, mg/L	Efficiency after membrane, %
			Experiment 1		
1-1	10.90	0.015	99.86	0.01	99.91
1-2	7.03	0.05	99.29	0.01	99.86
1-3	6.99	0.01	99.86	0.01	99.86
1-4	6.90	0.015	99.78	0.01	99.86
			Experiment 2		
2-1	20.20	0.02	99.90	0.01	99.95
2-2	14.87	0.01	99.93	0.01	99.93
2-3	14.92	0.02	99.87	0.01	99.93
2-4	14.23	0.02	99.86	0.01	99.93
			Experiment 3		
3-1	17.40	0.015	99.91	0.01	99.94
3-2	11.30	0.015	99.87	0.01	99.91
3-3	12.30	0.02	99.84	0.01	99.92
3-4	12.10	0.015	99.88	0.01	99.92
			Experiment 4		
4-1	21.60	0.03	99.86	0.02	99.91
4-2	15.60	0.02	99.87	0.01	99.94
4-3	16.70	0.03	99.82	0.02	99.88
4-4	16.30	0.03	99.82	0.02	99.88

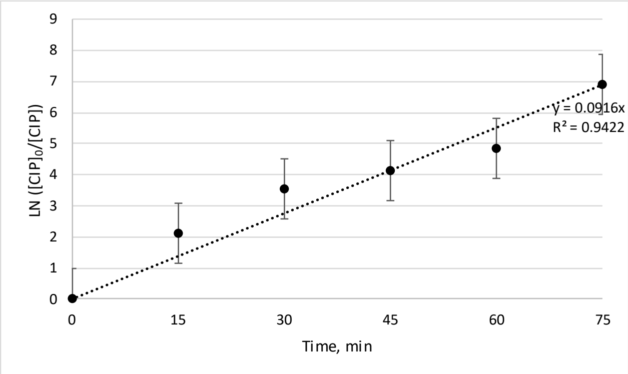
Experimental results obtained during the photocatalytic step showed that CIP degradation occurs with apparent rate constants values between 7.14 - 8.3 x 10^{-2} min^{-1} (experiment 1), 9.16 – 10.49 x 10^{-2} min^{-1} (experiment 2), 9.12 – 9.99 x 10^{-2} min^{-1} (experiment 3), 8.63 – 9.62 x 10^{-2} min^{-1} (experiment 4) (Fig 1-4).



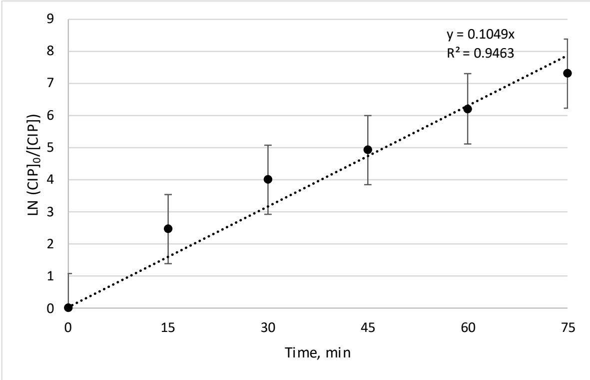
Cycle 1-1 Cycle 1-2

Cycle 1-3 Cycle 1-4

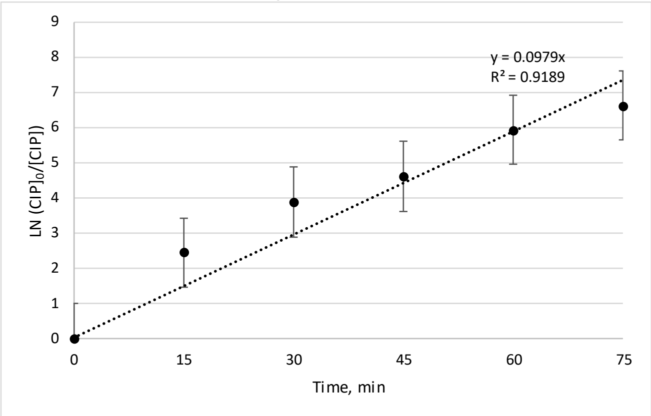
Fig. 1. Pseudo first order kinetic of CIP degradation – photocatalytic step – Experiment 1



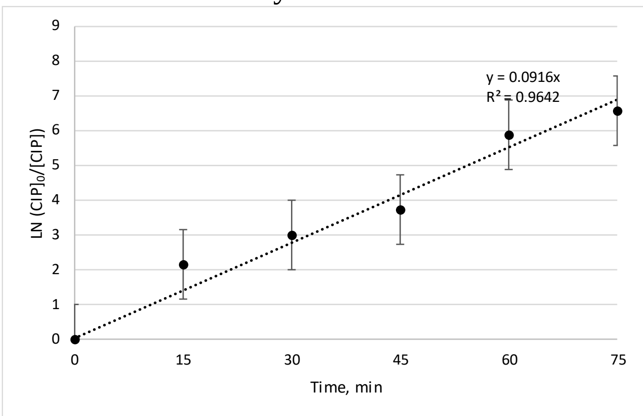
Cycle 2-1



Cycle 2-2

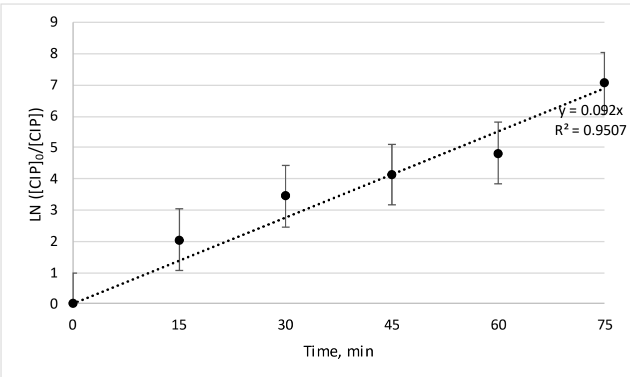


Cycle 2-3

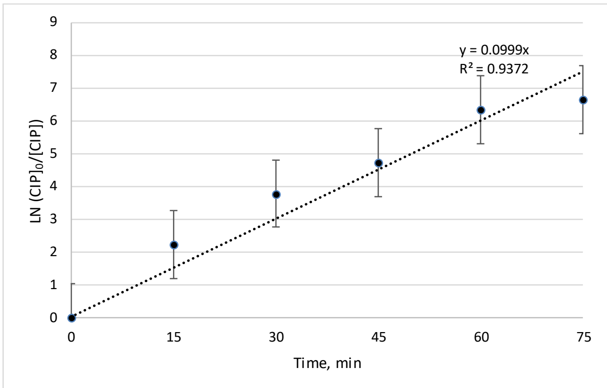


Cycle 2-4

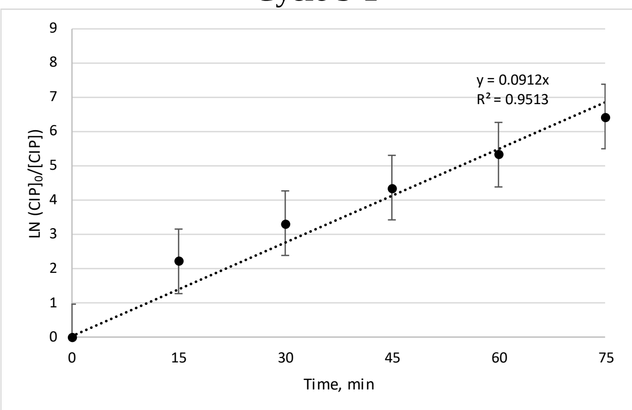
Fig. 2. Pseudo first order kinetic of CIP degradation – photocatalytic step – Experiment 2



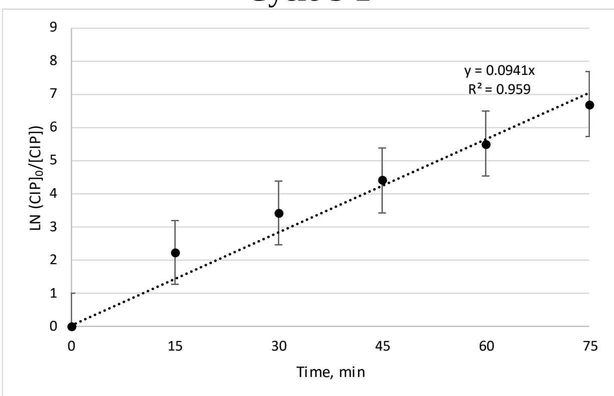
Cycle 3-1



Cycle 3-2

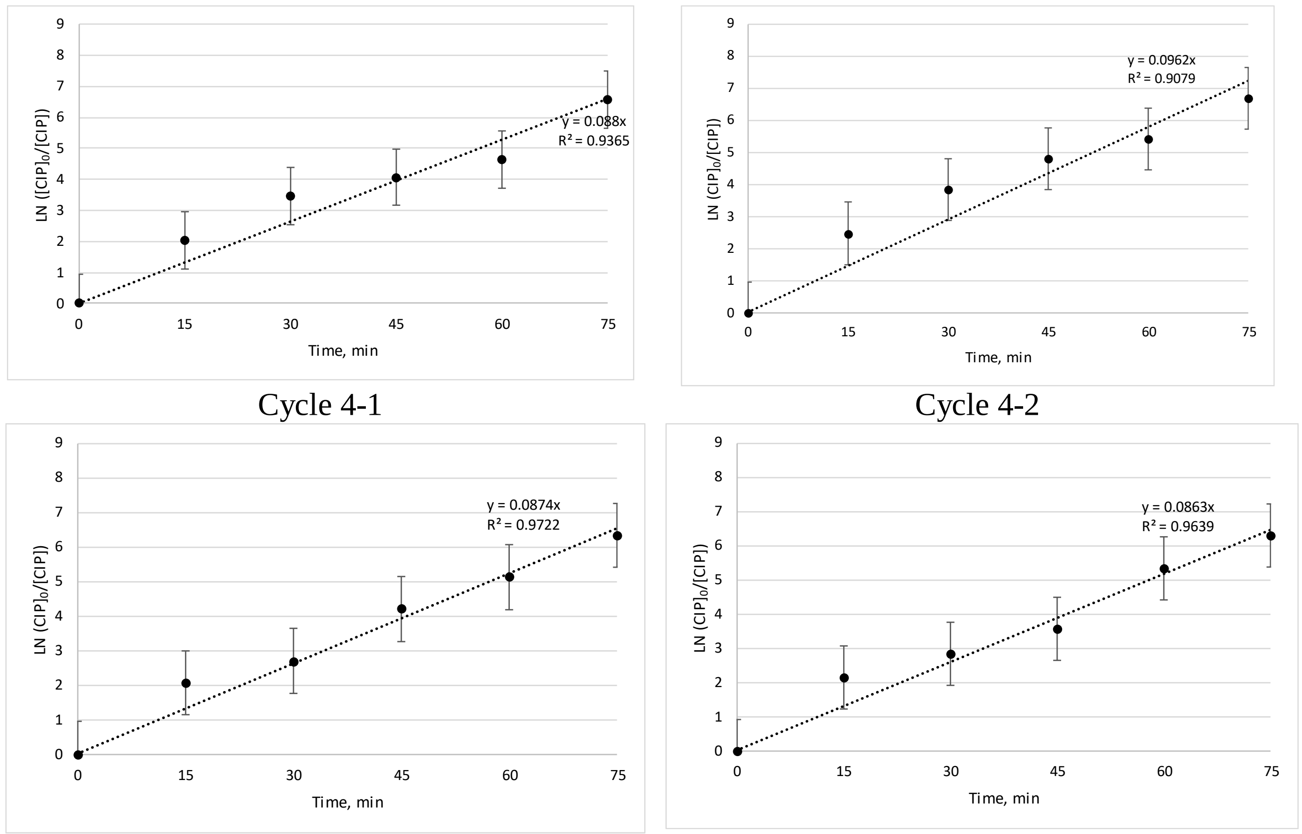


Cycle 3-3



Cycle 3-4

Fig. 3. Pseudo first order kinetic of CIP degradation – photocatalytic step – Experiment 3



Cycle 4-1 Cycle 4-2

Cycle 4-3 Cycle 4-4

Fig. 4. Pseudo first order kinetic of CIP degradation – photocatalytic step – Experiment 4

In order to assess the reliability of PMR – based experimental model for removal of CIP, four process parameters were investigated from the statistical point of view:

- Initial CIP concentration
- CIP degradation efficiency for photocatalytic step
- Pseudo-first order rate constant for photocatalytic step
- Global PMR efficiency of CIP removal

Table 2. Statistic parameters of experimental results

Parameter	x_m	M_e	A	MSD	V
$[CIP]_0$, mg/L	13.7088	14.55	14.70	4.4327	32.33
Efficiency UV-VIS TiO_2, %	99.8263	99.86	0.64	0.1475	0.15
k, min^{-1}	0.0899	0.0914	0.0335	0.0083	9.21
Efficiency PMR, %	99.9081	99.915	0.09	0.0306	0.03

In relation to the initial CIP concentration, the analyse of statistical parameters showed that the experimental data series are non-homogenous:

- The mean (xm) presented a value of 13.7088 mg/L,
- The median (Me) had a value close to the mean but the amplitude (A) of 14.70 mg/L demonstrates a large scatter of experimental data,
- The mean square deviation (MSD) of 4.4323 mg/L demonstrates a large scater of experimental data,
- The variability (V) of 32.33% demonstrates that the experimental data series are non-homogenous and the mean is not representative.

In relation to the efficiency of photo-catalytic step, the analyse of statistical parameters showed the minor scatter of experimental data, experimental data series are homogenous and experimental results are reproducible:

- The mean (xm) presented a value of 99.8263 % - very close to 100%.
- The median (Me) had a value close to the mean, and the amplitude (A) of 0.64 % demonstrates a minor scatter of experimental data,
- The mean square deviation (MSD) of 0.1475 % demonstrates a minor scatter of experimental data, the precision and reproducibility of results
- The variability (V) 0.15% demonstrates that the experimental data series are homogenous and the mean is representative.

In relation to the pseudo-first order rate constant of photo-catalytic step, the analyse of statistical parameters showed the minor scatter of experimental data, experimental data series are homogenous and experimental results are reproducible:

- The mean (xm) presented a value of 0.0899 min-1,
- The median (Me) had a value close to the mean, and the amplitude (A) of 0.0335 min-1 demonstrates a minor scatter of experimental data,
- The mean square deviation (MSD) of 0.0083 min-1 demonstrates a minor scatter of experimental data, the precision and reproducibility of results
- The variability (V) 0.03% demonstrates that the experimental data series are homogenous and the mean is representative.

In relation to the PMR global efficiency, the analyse of statistical parameters showed the minor scatter of experimental data, experimental data series are homogenous and experimental results are reproducible:

- The mean (xm) presented a value of 99.9081 % - very close to 100%.
- The median (Me) had a value (99.915 %) close to the mean, and the amplitude (A) of 0.09 % demonstrates a minor scatter of experimental data,
- The mean square deviation (MSD) of 0.0306 % demonstrates a minor scatter of experimental data, the precision and reproducibility of results
- The variability (V) 0.03% demonstrates that the experimental data series are homogenous and the mean is representative.

CONCLUSIONS

A photocatalytic membrane reactor with catalyst in suspension was used for the advanced removal of CIP from real wastewater. Experimental results proved that CIP was successfully removed with efficiencies higher than 99.85%, with catalyst recirculation and reuse in further treatment cycles.

Even if the initial CIP concentration data series were non-homogenous the obtained results: efficiency of photocatalytic step, pseudo-first order rate constant for photocatalytic step and global PMR efficiency data series proved to be homogenous and reproducible.

Performed trials are recommending the use of PMR as a viable option for the advanced removal of pharmaceuticals from wastewater.

ACKNOWLEDGEMENTS

The work was funded by the Ministry of Research, Innovation and Digitalisation of Romania through Programme Nucleu, contract no. 20N/2019, Project code PN 19 04 03 01.

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Citation: Constantin, M.A., Chiriac, F.L., Ionescu, I.A., Constantin, L.A., Trials on ciprofloxacin removal from wastewater using a photocatalytic membrane reactor, *Rom. J. Ecol. Environ. Chem.*, **2023**, 5, no.1, pp. 5-12.