Development of an intensified immobilized static mixer reactor for photocatalytic degradation of ibuprofen: Statistical modelling and optimization

S. Mosleh*, M. Hoshmandian
Department of Gas and Petroleum, Yasouj University, Gachsaran 75918-74831, Iran
Mosleh@yu.ac.ir

Abstract
A static mixer reactor was designed and fabricated to overcome the external and internal mass transfer limitations which restrict photocatalytic degradation process performance. In this regard, the application of the static mixed reactor was evaluated for degradation of ibuprofen while RGO/Ag_3PO_4 as an efficient visible-light-driven photocatalyst was immobilized on the external surface of the reactor blades. The effect of operational parameters including the initial concentration of ibuprofen, irradiation time, pH, and photocatalyst dosage on the photocatalytic degradation efficiency was studied and then optimized through the desirability function technique. Results indicated that the designed static mixer photocatalytic reactor had high efficiency (92.49%) for degradation of ibuprofen under optimized conditions, set as 20 mg/L of the initial concentration of ibuprofen, 5 of pH and 90 min of irradiation time.

Keywords: Immobilized static mixer reactor, Photocatalytic degradation, Ibuprofen, Statistical modelling, Optimization

Introduction
Photocatalytic degradation is known as an efficient technology for treatment of various types of wastewaters [1]. In general, two types of reactors including slurry reactors and immobilized reactors are applied for photocatalytic degradation processes based on the position and state of the photocatalyst. In slurry reactors, the photo catalyst particles are dispersed in the solution, while in the immobilized reactor the photocatalyst is fixed on a support [2]. Although, the slurry reactors can creates high photocatalytic surface area to reactor volume ratio, but they have some essential drawbacks, such as: (i) photocatalyst particles separation from the solution is laborious and costly, and (ii) strong light scattering/absorption can occur [3]. In this regard, an intensified immobilized reactor namely static mixer reactor was proposed in this work in order to improved removal of ibuprofen (IBP) from wastewater. The static mixer reactor as an efficient equipment in the field of photocatalytic degradation process utilizes the energy of the flow stream to produce consistent and reliable mixing, promoting the diffusion of pollutants/reactants from the bulk liquid through a boundary layer to reach the liquid-catalyst interface (external mass transfer) and also the inter-particle diffusion of pollutants/reactants within the catalyst film to the active surface sites (internal mass transfer)

[3]. Since the ibuprofen is a widely used non-steroidal anti-inflammatory drug that has been detected in the pharmaceutical wastewaters, it was chosen as the target pollutant [4, 5]. Conventional processes have no enough performance for degradation of IBP, hence photocatalytic degradation was selected as efficient treatment approach [6]. The response surface methodology (RSM) including mathematical and statistical techniques was employed to evaluate the individual and combined effects of operational parameters, while the desirability function (DF) was used to find the best optimum operational conditions.

Experimental

Designed static mixer photoreactor for photocatalytic process is shown in Fig. 1. The static mixer tubular photoreactor is composed of alternated right- and left-hand helical mixing elements that direct the fluid flow radially toward the pipe walls and back to the center. In this conditions, intense mixing is provided under both laminar and turbulent flow pattern which enhances mass transfer rate. The RGO/Ag_3PO_4 photocatalyst is coated on the surface of static mixer blades equipped with LED light source.

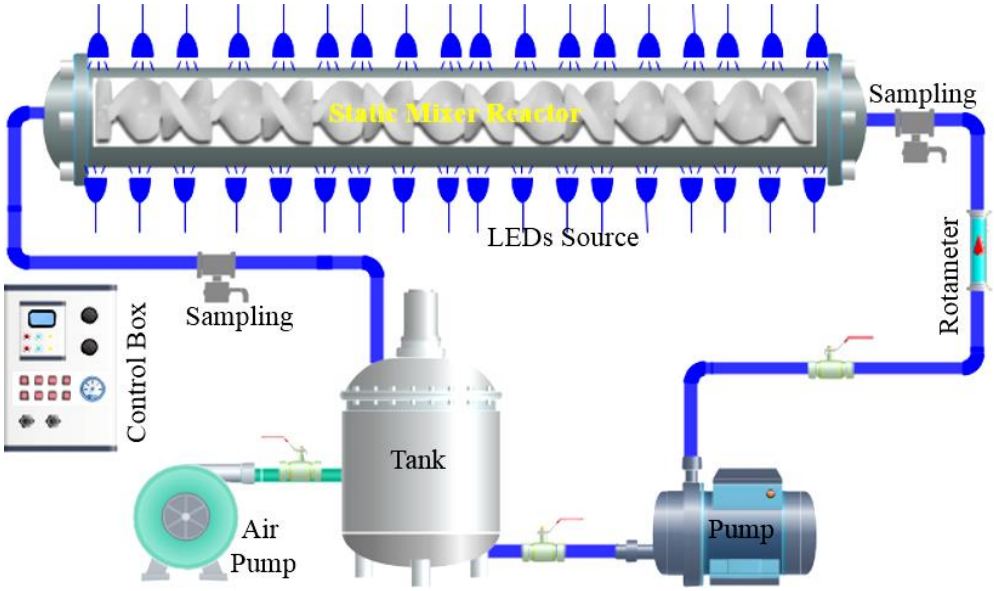

Fig. 1. The schematic of satic mixer photocatalytic reactor.

The central composite design (CCD) was used to investigate the effect of three important parameters (Table. 1) including initial IBP concentration (X_1), pH (X_2) and irradiation time (X_3) on the photocatalytic degradation efficiency with at least number of experiments.

Table 1. The operational parameters and their levels.

Parameters	Levels				
	Low (-1)	Central (0)	High (+1)	-α	+α
X_1: IBP Concentration (mg/L)	20	25	30	15	35
X_2: pH	5	7	9	3	11
X_3: Time (min)	40	60	80	20	100

Table. 2 provides the detail of the 20 experimental runs based on CCD.The response surface methodology as a comprehensive mathematical and statistical techniques was applied to evaluate the individual and combined effects operational parameters [7, 8]. According to the

experimental design, IBP with certain initial concentration stored in a tank equipped with a stirrer. The pH of IBP solution was adjusted at the desired value by 0.1 M HCl and/or NaOH solutions. The IBP solution was pumped into the static mixer reactor with a certain flow rate, while the solution passes through the blades. Based on the experiment design, at specific time, sample was withdrawn from sampling valve and then subjected to analysis using a UV-vis spectrophotometer to estimate the photocatalytic degradation efficiency.

Table 2. CCD matrix

Run	Block	X_1	X_2	X_3	R%
1	1	20	5	80	88.67
2	1	25	7	60	56.72
3	1	30	5	40	44.48
4	1	30	5	80	69.25
5	1	30	9	40	29.50
6	1	20	5	40	63.51
7	1	30	9	80	54.33
8	1	25	7	60	56.45
9	1	20	9	40	48.58
10	1	25	7	60	56.67
11	1	20	9	80	73.72
12	1	25	7	60	56.74
13	2	15	7	60	81.95
14	2	25	7	20	31.02
15	2	35	7	60	43.38
16	2	25	7	100	80.79
17	2	25	3	60	60.75
18	2	25	7	60	51.93
19	2	25	11	60	31.12
20	2	25	7	60	51.80

Results and discussion

The significance of operational parameters was evaluated based on the analysis of variance (ANOVA) using F-values and P-values tests [9 , 10]. The F-value of model is calculated from a model mean square divided by a residual mean square which compare variance of the model with residual variance [11]. The larger magnitude of F-value supports the more significant effect of each term on model response [12]. For each individual term and their binary interaction terms, the P-values less than 0.05 indicate that term has a significant effect on the response, while the ANOVA results indicated that model is significant (Table 3). Finally, the following equation was obtained based on the ANOVA for prediction of IBP photocatalytic degradation efficiency (R%) during the process:

$$R\%=54.26-9.63X_1-7.44X_2+12.47X_3-0.09X_1X_3+0.82X_2X_4+0.35X_3X_4+2.72X_1^2-1.47X_2^2+1.03X_3^2 \quad (1)$$

Three dimontional (3D) response surface plots were used to describe the relationship between operational parameters (Fig. 2). Results show that initial IBP concentration speed has a negative effect on the photocatalytic degradation efficiency (Fig. 2a). The higher concentration of IBP causes lower efficiency due to the reduction in the number of available

and activated photocatalyst sites and the enhancement in the light screening by the IBP molecules. The investigation for pH effect on photocatalytic degradation carried out at pH values in the range of 3-11 which results showed that maximum photocatalytic degradation efficiency of IBP was achieved at pH of 5.0 (Fig. 2b). Furthermore, the obtained results indicated that irradiation time has positive effect on the degradation efficiency due to more expose of IBP molecules to the light irradiation as well as more presence of free radicals (Fig. 2b).

Table 3. Analysis of variance (ANOVA) results.

Source	Sum of Squares	DF	Mean Square	F Value	p-value Prob > F
Block	81.70	1	81.70		
Model	5166.53	9	574.06	45327.08	< 0.0001
X_1	1483.40	1	1483.40	117128.06	< 0.0001
X_2	885.65	1	885.66	69930.56	< 0.0001
X_3	2486.01	1	2486.02	196293.40	< 0.0001
$X_1 X_2$	5E-05	1	5E-05	0.0039	0.9513
$X_1 X_3$	0.06	1	0.06	4.84	0.0554
$X_2 X_3$	2E-004	1	2E-004	0.016	0.9028
X_1^2	177.83	1	177.83	14041.56	< 0.0001
X_2^2	51.19	1	51.19	4041.72	< 0.0001
X_3^2	25.56	1	25.56	2018.56	< 0.0001
Residual	0.11	9	0.013		
Lack of Fit	0.05	5	0.01	0.68	0.6653
Pure Error	0.06	4	0.015		
Cor Total	5248.35	19			

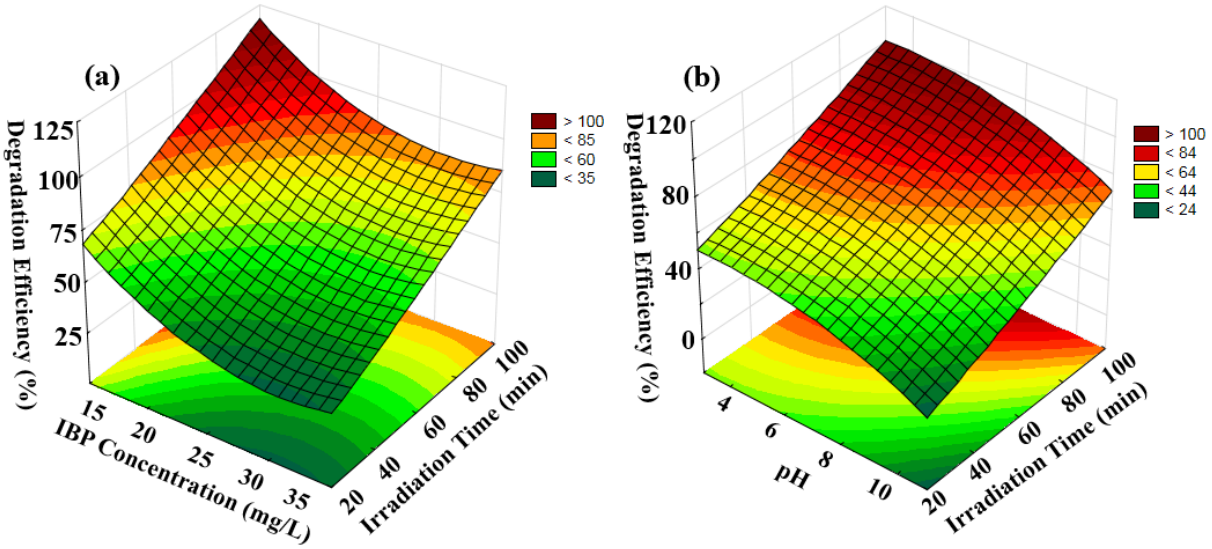

Fig. 2. 3D response surface plots

The desirability function (DF) which is a function ranging from 0 (undesirable situation) to 1.0 (ideal situation) was applied to find the best optimum values for operational parameters to

reach a maximum photocatalytic degradation efficiency. The obtained results indicated that optimum values were found to be 20 mg/L, 5 and 90 min for initial IBP concentration, pH and irradiation time, respectively. At optimum condition, the IBP photocatalytic degradation efficiency was obtained 92.49% with overall desirability of 1.0 (Fig. 3).

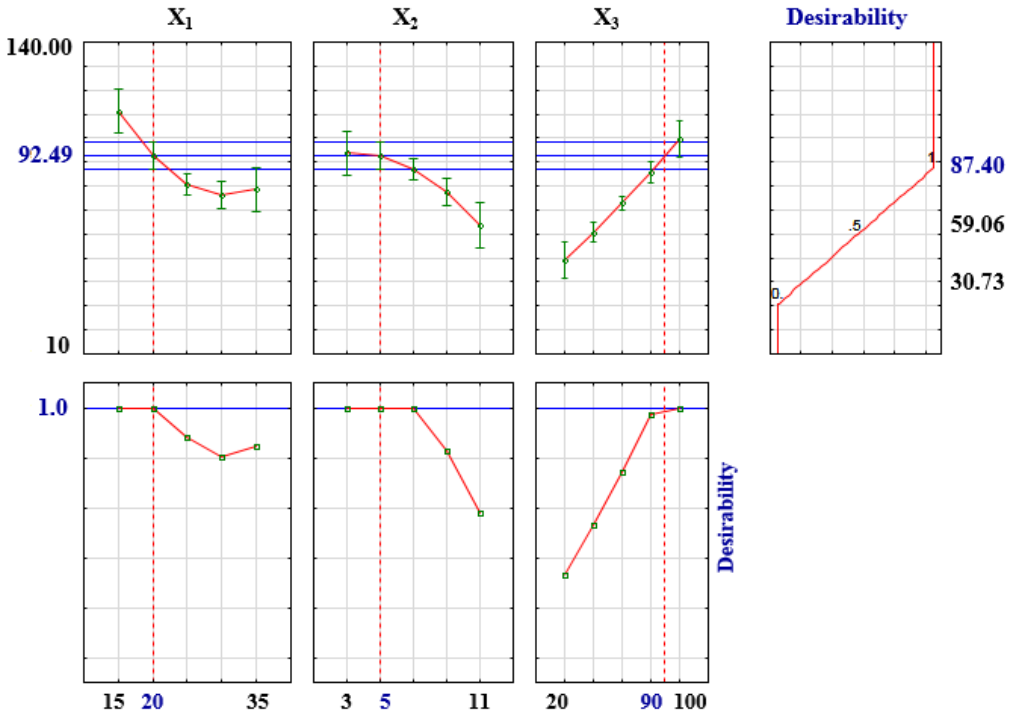

Fig. 3. Optimization profile through the desirability function.

Conclusion

The performance of an immobilized static mixer reactor was evaluated for photocatalytic degradation of ibuprofen, while central composite design based on the response surface methodology was used for statistical modelling of the process. The desirability function was applied for process optimization which result indicated that designed static mixer reactor had excellent performance for degradation of ibuprofen under optimized conditions. Results revealed that the fabricated reactor had 92.49% efficiency for degradation of ibuprofen under optimized conditions including 20 mg/L of initial concentration of ibuprofen, 5 of pH and 90 min of irradiation time.

Acknowledgements

The authors are grateful to the Research Council of the Yasouj University for providing financial support for this study.

References

[1] Mosleh, S., Dashtian, K., Ghaedi, M. and Amiri, M.," A $Bi_2WO_6/Ag_2S/ZnS$ Z-scheme heterojunction photocatalyst with enhanced visible-light photoactivity towards the degradation of multiple dye pollutants", RSC Adv., 9, 30100-30111 (2019).

[2] Visan, A., Van Ommen, J. R., Kreutzer, M. T., Lammertink R. G.," Photocatalytic reactor design: guidelines for kinetic investigation", Ind. & Eng. Chem. Res., 58, 5349-5357 (2019).

[3] Díez, A. M., Moreira, F. C., Marinho, B. A., Espíndola, J. C., Paulista, L. O., Sanromán, M., Pazos, M., Boaventura, R. A. and Vilar, V. J.," A step forward in heterogeneous photocatalysis: Process intensification by using a static mixer as catalyst support", Chem. Eng. J., 343, 597-606 (2018).

[4] Liu, N., Huang, W., Tang, M., Yin, C., Gao, B., Li, Z., Tang, L., Lei, J., Cui, L. and Zhang, X.," In-situ fabrication of needle-shaped MIL-53 (Fe) with 1T-MoS_2 and study on its enhanced photocatalytic mechanism of ibuprofen", Chem. Eng. J., 359, 254-264 (2019).

[5] Regmi, C., Kshetri, Y. K., Kim, T.-H., Dhakal, D. S. and Lee, W.," Mechanistic understanding of enhanced photocatalytic activity of N-doped $BiVO_4$ towards degradation of ibuprofen: An experimental and theoretical approach", Mol. Cat., 470, 8-18 (2019).

[6] Uheida, A., Mohamed, M., Belaqziz Nasser, W. S.," Photocatalytic degradation of Ibuprofen, Naproxen, and Cetirizine using PAN-MWCNT nanofibers crosslinked TiO_2-NH_2 nanoparticles under visible light irradiation", Sep. Pur. Tech., 212, 110-118 (2019).

[7] Jalali, S., Rahimi, M. R., Dashtian, K., Ghaedi, M. and Mosleh, S.," One step integration of plasmonic Ag_2CrO_4/Ag/AgCl into HKUST-1-MOF as novel visible-light driven photocatalyst for highly efficient degradation of mixture dyes pollutants: Its photocatalytic mechanism and modeling", Polyhed., 166, 217-225 (2019).

[8] Mosleh, S., Rahimi, M. R., Dashtian, K. and Hajati, S.," Sonochemical-assisted synthesis of CuO/Cu_2O/Cu nanoparticles as efficient photocatalyst for simultaneous degradation of pollutant dyes in rotating packed bed reactor: LED illumination and central composite design optimization", Ultra. Sono., 40, 601-610 (2018).

[9] Mosleh, S., Rahimi, M. R., Ghaedi, M., Dashtian, K., Hajati, S. and Wang, S.," Ag_3PO_4/AgBr/Ag-HKUST-1-MOF composites as novel blue LED light active photocatalyst for enhanced degradation of ternary mixture of dyes in a rotating packed bed reactor", Chem. Eng. Pro., 114, 24-38 (2017).

[10] Mosleh, S., Rahimi, M. R., Ghaedi, M. and Dashtian, K.," Sonophotocatalytic degradation of trypan blue and vesuvine dyes in the presence of blue light active photocatalyst of Ag_3PO_4/Bi_2S_3-HKUST-1-MOF: central composite optimization and synergistic effect study", Ultra. Sono. 32, 387-397 (2016).

[11] Mosleh, S., Rahimi, M. R., Ghaedi, M. and Dashtian, K.," HKUST-1-MOF–$BiVO_4$ hybrid as a new Sonophotocatalyst for simultaneous degradation of disulfine blue and rose bengal dyes: optimization and statistical modelling", RSC. Adv., 66, 61516-61527 (2016).

[12] Mosleh, S. and Rahimi, M. R.," Intensification of abamectin pesticide degradation using the combination of ultrasonic cavitation and visible-light driven photocatalytic process: Synergistic effect and optimization study", Ultra. Sono., 35, 449-457 (2017).