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Photocatalytic Degradation of Perfluorooctanoic Acid (PFOA) using Molybdenum Disulphide-Graphene Oxide Composite via Box-Behnken Design Optimization

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In this research work, molybdenum disulphide-graphene oxide (MoS_2-GO) was synthesized to be a promising photocatalyst for the degradation of perfluorooctanoic acid (PFOA) by using a photoreactor equipped with an 18-watt fluorescent lamp. Box–Behnken design (BBD) was applied to optimize parameters such as mixing ratio MoS_2 in GO (A: 0% ,7.5% ,15%), pH (B: 2, 6, 10), catalyst dose (C: 5 mg, 12.5 mg, 20 mg), and contact time (D: 10 min, 65 min, 120 min). The highest PFOA degradation efficiency of 87.5% was observed for mixing ratio MoS_2 with GO (%), pH, catalyst dose, and contact time were 15%, pH 6, 12.5 mg, 120 min, respectively. Besides, dual interactions such as AC, BD and CD were identified to be significant in this BBD model. The optimization from this study demonstrated a superior photodegradation of PFOA in fewer trials, which was time saving and cost effective. Therefore, the results of this research may pave the way for more important applications down the road, including the treatment of actual wastewater, elimination of organic pollutants, and minimization of chemical discharge.

Keywords: Molybdenum disulphide; response surface methodology; photodegradation; perfluorooctanoic acid

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Water is one of the vital nutrients needed by the living things for their sustainable life. Contamination of water from various chemicals is a major concern because countless inorganic and organic compounds pollute our groundwater and surface water [1]. Water contamination primarily occurs through the direct discharge of hazardous substances from industrial, commercial, and residential sources into water bodies, transport of pollutants in storm water runoff and leaching of contaminated soil into the water bodies [2]. Growing amount of non-conventional chemicals discharged in wastewater, surface water as well as drinking water has elevated environmental distress [3].

Perfluorinated compounds (PFCs) are a large, complex group of manufactured chemicals that are found in various everyday products. PFCs have been used for more than 60 years. PFCs are useful for some industrial applications due to their high levels of thermal, chemical, and biological inertness, however, they also result in environmental persistence and potential dangers to human health. Prior to the 1980s, scientific journals published little on PFC toxicology, presumably because it was believed that substances that were resistant to breakdown were inert. Evidence of long-lasting, bio accumulative effects has gradually surfaced, causing alarm [4].

Chemical processes employ perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$) which is also a member of perfluorinated compound (PFC) as an industrial surfactant. According to EPA Science Advisory Board (SAB) reports, PFOA resists biological breakdown and pollutes the environment. Photocatalysis is a feasible, environmentally benign, and promising method to break down PFOA. However, the photoreactor' design must consider environmentally friendly practices (choice of photocatalyst) and sustainable energy (source of light). The xenon lamp is the most typical artificial visible-light source used in photocatalytic oxidation, and the use of visible light photoreactors is currently

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the subject of extensive research. This lamp does have several disadvantages, such as high cost, short lifespan, poor light penetration, and low luminous efficiency.

Substantial research has been done on MoS_2 in a wide range of fields, including photocatalytic degradation, ion batteries, supercapacitors, and dye-sensitized solar cells. MoS_2 is receiving a lot of attention as a prospective photocatalytic material due to its excellent visible light driven photocatalytic capabilities. MoS_2 has excellent adsorption capacity and a tunable band structure. MoS_2 has received a lot of attention for its widespread use as a co-photocatalyst in the development of composites, particularly when in the removal of organic impurities. It also draws interest for its durability against photo corrosion. MoS_2 has a thin band gap whereby the number of layers makes up that band gap [5].

Graphene oxide, a material composed of atomically thick two-dimensional (2D) nanosheets of sp^2 carbon atoms, is a good charge carrier for semiconductors at room temperature. In this study, MoS_2 nanosheets were synthesized by using graphene oxide (GO). Graphene oxide not only worked well as a template for the formation of MoS_2 nanosheets, but also as an electron-acceptor or transport medium. Graphene oxide has been employed as a successful electron-acceptor or transport material in photocatalysis because it may reduce photo-generated electron-hole recombination and boost light harvesting efficiency [6].

Additionally, the production of hydrogen and presence of hydroxyl groups in the GO demonstrated photocatalytic capabilities [7]. The high negative charge and hydroxyl, epoxy, carbonyl, and carboxyl groups on the surface of GO made it incredibly active [8]. This demonstrated that to enhance its activity as a photocatalyst, the surface of GO can be manufactured with a particular functional group, such as inorganic particles, polymers, or proteins. By creating interfacial interaction with a polymer matrix, GO is a promising agent for enhancing the physicochemical properties of polymers [9]. Additionally, GO is the preferred material for visible light photocatalysis, which thrives in a carbon honeycomb structure with sp^2 hybridized carbon and delocalized π-electron clouds [10-11].

In this study, the photodegradation of PFOA via MoS_2-GO was optimized using Box-Behnken optimization design. The optimization from this study demonstrated a superior photodegradation of PFOA in fewer trials, which was time-saving and cost-effective. Therefore, the results of this research may pave the way for more important applications down the road, including the treatment of actual wastewater, elimination of organic pollutants, and minimization of chemical discharge.

EXPERIMENTAL

Chemicals and Materials

The MoS_2-GO composites were previously prepared work and well characterized as reported in literature [12]. Briefly, this work involved different pH values (pH 2, pH 6, pH 10), whereby pH value was adjusted by using 1M hydrochloric acid (HCl, 37%, R&M brand, Malaysia) and sodium hydroxide (NaOH, Bendosen, Malaysia). The detection was conducted via high performance liquid chromatography (Agilent 1100 series HPLC) equipment, whereby acetonitrile (ACN) and aqueous NaH_2PO_4 (5 mMol, adjusted to pH 7.0) (50:50, v/v) were used as the mobile phase and detected with a wavelength detector set at 210 nm.

Methodology

In this work, Box-Behnken design (BBD) in response surface methodology (RSM) was utilized to optimize and study the effects of four parameters, including mixing ratio with MoS_2 with GO (A), adsorbent dose (B), pH (C), and contact time (D), on the degradation of PFOA. The significance of each single factor, interactions and quadratic term in the optimization process was determined by using statistical analysis software [Design Expert software version 11.0 Stat ease, Minneapolis, USA]. Each factor was varied at three different levels -1, 0 and +1 signifying low, medium, and high values. Table 1 displays the levels of the utilized independent parameters, along with their coded values. The range of these independent parameters was determined on the basis of preliminary experiments.

The photocatalytic performance of MoS_2-GO-1, MoS_2-GO-5, and MoS_2-GO-15 was studied for the photocatalytic degradation experiment, which involved the degradation of PFOA under the irradiation of an 18-watt fluorescent lamp. The photocatalytic tests were conducted in a photoreactor that had multiple quartz tube reactors. In a typical photocatalytic experiment, 0.001 g of MoS_2-GO composites (different percent (percent) values of 1%, 5%, and 15%) were added to a beaker along with 10 mL of a 10 mg/L stock solution. Then, 10 mL, 50 mg/L (C) of each solution was pipetted out and placed in a UV photoreactor at the starting point (t=0), where it was constantly stirred for 30 min in the dark to monitor that adsorption/ desorption equilibrium was reached. To remove the nanocomposites, the liquids were then centrifuged and filtered. During the photocatalytic degradation reaction, the amount of PFOA was investigated by measuring the absorbance of solution samples using HPLC-UV detection. Using the measured PFOA absorption for each sample, the C/Co ratio was calculated, where Co is the concentration of PFOA at t=0 min and C is the concentration of PFOA at a specified time [12].

RESULTS AND DISCUSSION

Experimental Design

Table 1 displays the levels of the utilized independent parameters, along with their coded values. The range

of these independent parameters was determined based on preliminary experiments. Equation (1) was used to predict the degradation of PFOA and analyze the experimental data. A total of 29 experiments were employed in this work to evaluate the effects of the four main independent factors on PFOA degradation efficiency. A non-linear regression method was used to fit the second order polynomial, Equation (1) to the experimental data and to identify the relevant model terms. Considering all the linear terms, square terms and linear by linear interaction items, the quadratic response model can be described as:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \sum \beta_{ij} X_i X_j \qquad (1)$$

Where, Y is a predicted value to optimize the response, $\beta 0$ is constant coefficient, βi is linear coefficient, βii is quadratic coefficient and βij is interaction coefficient, while Xi and Xj are coded values of the independent factors.

In accordance with BBD, 29 experiments (runs) with three levels and four factors, were implemented to optimize and investigate the effects of the four input parameters (i.e., A: mixing ratio with MoS_2 with GO (0-15%), B: pH (2-10), C: catalyst dose (5-20), D: contact time (10-120 min), on the degradation of PFOA (%) by using MoS_2 composites. The range of mixing ratio MoS_2 with GO (0%, 7.5%, and 15%) was selected as 15% gave good degradation performance as compared to other photocatalyst based on the preliminary experiments. This was because there was enough MoS_2, often referred to as visible active photocatalyst. Additionally, in MoS_2-GO composites, the GO addition significantly improved the separation efficiency of photogenerated electron pairs. It is important to note that the surface-active sites of the photocatalysts were enhanced by the addition of GO [13].

The pH solution is an essential parameter for estimating the degradation performance since it will impact the quantum efficiency of oxidative/reductive species [14]. To further study the effect of pH values on the degradation of PFOA, an experiment was performed under different pH values conditions, ranging from pH 2 to pH 10. Because the free radical •OH was slowed and finally reduced at high pH value levels, it can be inferred from the results that the degradation percentage decreased with higher pH value [15]. As a result, PFOA ability to be mineralized by radicals was improved.

Different catalyst doses (5 mg, 12.5 mg, and 20 mg) were used to study the photocatalytic degradation of PFOA. According to Table 2, 12.5 mg of catalyst dosage resulted in a higher percentage of PFOA breakdown. This was because when photocatalyst concentration rose, more photocatalyst surface sites could be exposed to light [16]. As catalyst dose was increased, more active sites became accessible for photodecomposition, which improved decomposition efficiency. The percentage of degradation, however, fell when the catalyst concentration rose over 12.5 mg. This could be explained by the fact that too many catalysts may aggregate and have a smaller active site [17]. The same applied to time, to degrade PFOA efficiently, 120 minutes was selected as the maximum values. Maximum contact time required for catalyst to react with PFOA fully. The BBD matrix and the obtained response on the PFOA degradation (%) is presented in Table 1. The mixing ratio with degradation of PFOA (%) can be expressed by Equation 2 as follows:

$$D\ (\%) = \frac{(C_O - C_e)}{C_o}\ x\ 100 \qquad (2)$$

Where C_o (mg/L) and C (mg/L) represent the initial and equilibrium concentrations of adsorbates (PFOA), respectively, and D (%) represent percentage degradation of PFOA [18].

Table 1. Experimental levels of independent factors and their codes in BBD.

Factor	Description	Level 1 (-1)	Level 2 (0)	Level 3 (+1)
A	Mixing ratio with MoS_2 (%)	0	7.5	15
B	pH	2	6	10
C	Catalyst dose (mg)	5	12.5	20
D	Contact time (min)	10	65	120

Table 2. The four-factors BBD matrix and experimental results for degradation of PFOA.

Std	A Mixing ratio with MoS_2 (%)	B pH	C Catalyst dose mg	D Contact time min	Response 1 Photocatalytic Degradation (%)
1	0	2	12.5	65	42.1
2	15	2	12.5	65	76.8
3	0	10	12.5	65	16.8
4	15	10	12.5	65	59.8
5	7.5	6	5	10	28.2
6	7.5	6	20	10	51.8
7	7.5	6	5	120	57.9
8	7.5	6	20	120	39.7
9	0	6	12.5	10	40
10	15	6	12.5	10	65.8
11	0	6	12.5	120	47.2
12	15	6	12.5	120	87.5
13	7.5	2	5	65	47.6
14	7.5	10	5	65	1.6
15	7.5	2	20	65	65
16	7.5	10	20	65	15.7
17	0	6	5	65	15.5
18	15	6	5	65	70.7
19	0	6	20	65	49.2
20	15	6	20	65	64.2
21	7.5	2	12.5	10	13.5
22	7.5	10	12.5	10	53.9
23	7.5	2	12.5	120	65.2
24	7.5	10	12.5	120	7.9
25	7.5	6	12.5	65	42.7
26	7.5	6	12.5	65	36.9
27	7.5	6	12.5	65	35.2
28	7.5	6	12.5	65	28.5
29	7.5	6	12.5	65	31.5

Box-Behnken Design (BBD) Model Analysis

The solo and interactive effect of the degradation input parameters, such as mixing ratio with MoS_2 (A), pH (B), catalyst dose (C), and contact time (D), on the degradation of perfluorooctanoic acid (PFOA) were evaluated via BBD. A statistical analysis of the experimental data for PFOA degradation was is verified via analysis of variance, as shown in Table 3. According to Table 3, the F-value of the BBD model and its corresponding p-value were 10.23 and <0.0001, respectively. These results revealed that the BBD model for degradation of PFOA was statistically significant. Moreover, the coefficient of determination (R^2) was 0.9109, which indicated a high correlation between the actual and expected values of degradation of PFOA, as observed in Figure 1(e). Therefore, the terms A, B, AC, BD, and CD presented in the BBD design were considered statistically significant on the degradation of PFOA. The terms with *p*-values greater than 0.05 in the BBD model were disregarded from the quadratic polynomial equation to obtain the best fitting of the BBD model. As for the lack of fit, it was not significant (*p*-value = 0.1127) which explained that the model was fit. The relation of the quadratic polynomial equation between examined parameters and the response (degradation of PFOA) is given in Equation (3).

A positive sign in Equation 3 indicates a synergistic effect of the factors, while a negative sign indicates an antagonistic effect of the factors [19].

$$\text{Degradation (\%)} = +34.96 + 17.83A - 12.88B - 10.05AC - 24.43BD - 10.45CD + 16.82A^2 \quad (3)$$

Table 3. Analysis of variance (ANOVA) for the degradation of Perfluorooctanoic acid (PFOA).

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	12110.01	14	865.00	10.23	< 0.0001	significant
A-Mixing Ratio with MoS_2	3816.33	1	3816.33	45.13	< 0.0001	significant
B-pH	1989.19	1	1989.19	23.52	0.0003	significant
C-Catalyst dose	342.40	1	342.40	4.05	0.0639	
D-Contact time	227.07	1	227.07	2.69	0.1236	
AB	17.22	1	17.22	0.2037	0.6587	
AC	404.01	1	404.01	4.78	0.0463	significant
AD	52.56	1	52.56	0.6216	0.4436	
BC	2.72	1	2.72	0.0322	0.8602	
BD	2386.32	1	2386.32	28.22	0.0001	significant
CD	436.81	1	436.81	5.17	0.0393	significant
A^2	1835.11	1	1835.11	21.70	0.0004	
B^2	125.15	1	125.15	1.48	0.2439	
C^2	3.72	1	3.72	0.0440	0.8369	
D^2	335.79	1	335.79	3.97	0.0662	
Residual	1183.93	14	84.57			
Lack of Fit	1066.50	10	106.65	3.63	0.1127	not significant
Pure Error	117.43	4	29.36			
Cor Total	13293.94	28				

A graphical method can also be used to validate the BBD model by evaluating the nature of residual distribution and correlation between the actual and predicted degradation of PFOA values. The normal probability of the residuals in the BBD model is shown in Figure 1(a). As shown in the Figure 1(a), the points formed an almost straight line, which indicated the ideal distributions and independence of the residuals [20]. Moreover, residual vs. predicted response was plotted and presented in Figure 1(b). This plot was the residual vs. the ascending predicted response value, which tested the assumption of constant variance. The plot should be a random scatter with a constant range of residuals across the graph. Figure 1(b) shows that the residuals in the plot were distributed in a random pattern around the centre line [21].

The residuals vs. run number of degradations are shown in Figure 1(c). The points in Figure 1(c) are randomly positioned around zero, indicating that the model was reliable and accurate. Cook's distance is another statistical way that can be used for the verification of the applied models. The Cook's distance plots of degradation of PFOA are given in Figure 1(d). In Cook's distance plot, points higher than 1 in magnitude are considered outliers and question the reliability of the regression model. As a result, all the dots in Figure 1(d) were <1 and most of them were below 0.2 as well as considerable dots are seen equal to 0, suggesting the validity of applied models.

The relation between the actual and predicted values of degradation of PFOA was close to each other as shown in Figure 1(f). It was proven from Figure 1(f) that there was a significant relation between the empirical outputs (degradation of PFOA) and those that were statistically expected, revealing that the models from the statistical view were reliable. Box-Cox plot transformation was applied to test whether data transformation was necessary or not [22]. It also gave a guideline for selecting the appropriate power law transformation by generating Lambda value. It transforms the presented data to be like a normal distribution, recommended whenever this was feasible with non-normal data [23]. Figure 1(e) shows the Box-Cox plot transformation of residuals.

The model was verified with every necessary transformation and proved that no transformation was required (Figure 1e). The lambda value for residuals was 1; however, the best-suggested value of lambda was 1.43. The Box-Cox Diagnostic plot can improve to establish the most excellent lambda value to work.

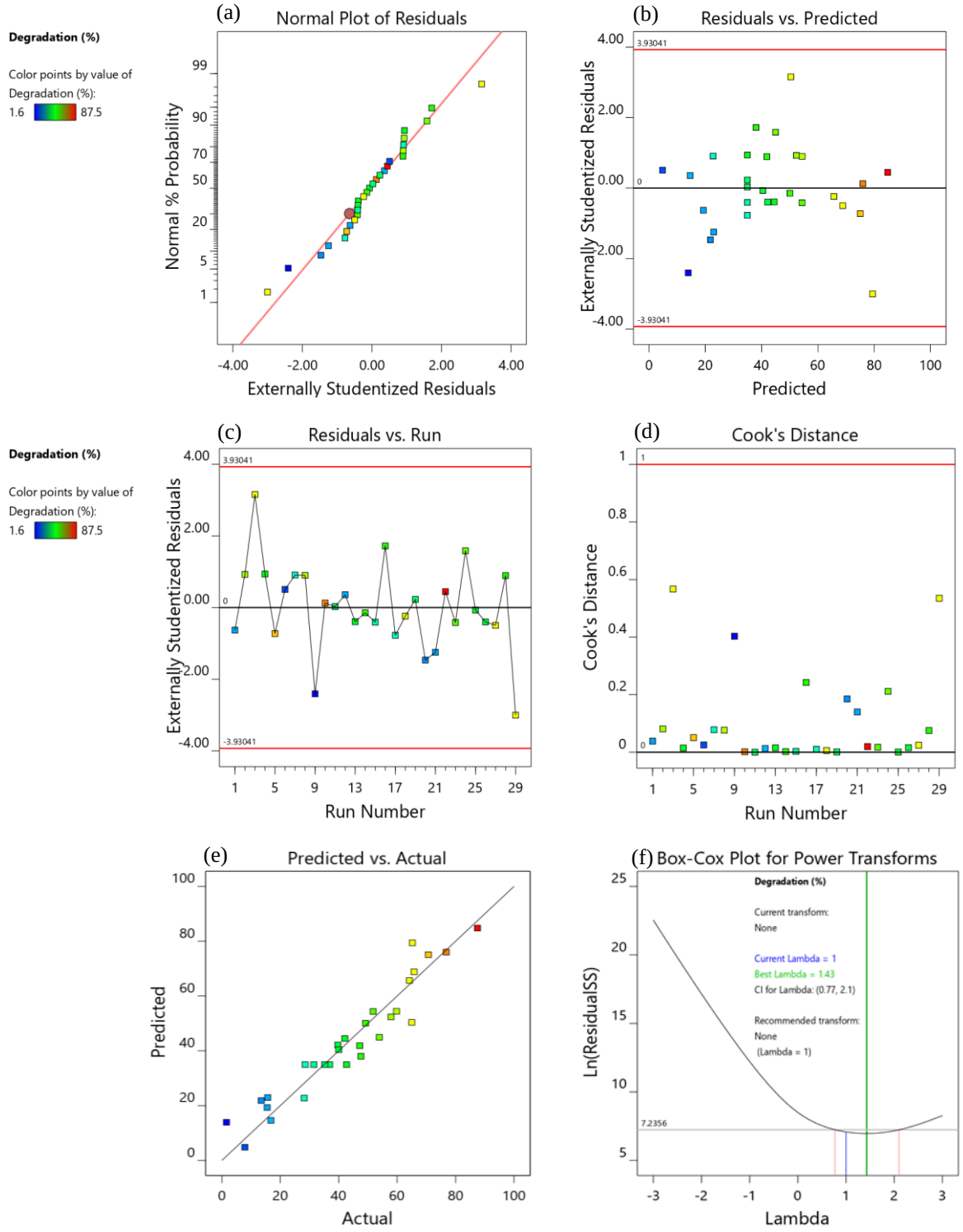

Figure 1. (a) Normal probability plot of residuals for BBD model, (b) Residual versus predicted values for degradation of PFOA, (c) Residual versus run number for degradation of PFOA, (d) The Cook's distance plots of PFOA's degradation, (e) Box-Cox plot for power transformation, (f) Plot of the relationship between the predicted and actual values of degradation of PFOA.

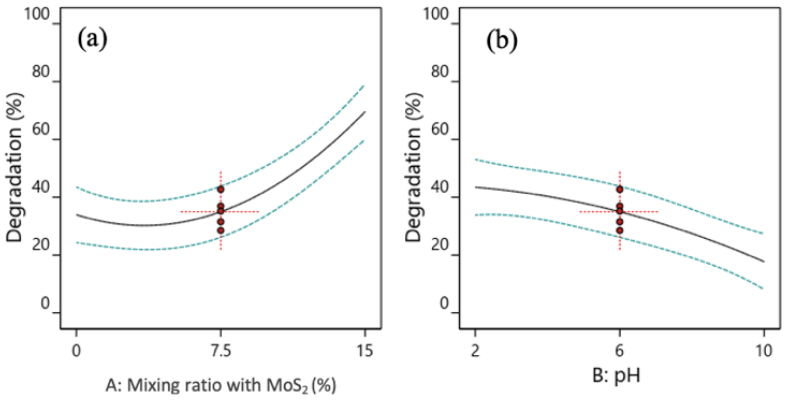

Figure 2. Plots of individual effects of (a) mixing ratio with MoS_2 (%), (b) pH.

Effect of Individual Parameters on MoS_2-GO and Degradation of Perfluorooctanoic Acid (PFOA)

The effect of the adsorption and individual key parameters on the degradation of PFOA was investigated. Figure 2 depicts the individual impacts of factors affecting the degradation of PFOA. Initially, the increase in the quantity of mixing ratio with MoS_2 from 0% to 15% resulted in a satisfactory rise in the degradation (%) of PFOA, as shown in Figure 2(a). Due to MoS_2's low energy density, poor electrical conductivity, and high recombination rate of photogenerated electron-hole pairs, MoS_2 has limitations in both its ability to store energy and function as a photocatalyst. Combining it with other graphene oxide nanostructures can help MoS_2 overcome drawbacks and boost its photocatalytic capabilities [24-25]. The transport of photogenerated electrons from the MoS_2 conduction band to the graphene can account for this [26]. The redox potential of MoS_2 will alter because of the quantum confinement effects of MoS_2, which will make photogenerated electrons more migratory [27].

As seen in Figure 2(b), the pH value variable plays a key role in the degradation of PFOA. According to Figure 2(b), the acidic environment was favourable for the degradation of PFOA due to the highly acidic content of the MoS_2-GO and the availability of cationic groups in PFOA. According to a previous study, PFOA degradation decreased as the pH value increased and efficient degradation happened when pH = 2 was optimized [12]. This was due to the formation of free radical $^{\bullet}OH$ slowed and eventually reduced the degradation performance [15]. Therefore, the capability of PFOA to be mineralized by radicals was boosted.

Significant Interactions

Three-dimensional (3D) surface and two-dimensional (2D) contour plots were used to evaluate the effect of the investigated factors and find a statistical relation between the tested parameters on the degradation of PFOA. Figure 3 depicts 3D and 2D graphs of the significant interaction between mixing ratio with MoS_2 vs. catalyst dose (mg) (AC) impacts the adsorption performance of PFOA degradation. The data reported in Figure 3(a) and (b), which related to the critical interaction between mixing ratio with MoS_2 and catalyst dose, revealed that increasing the mixing ratio with MoS_2 gradually from 0% to 15% enhanced the degradation performance of PFOA with subsequent adsorption on the MoS_2-GO surface. The raised adsorption rate of PFOA was due to a large number of binding sites on the MoS_2-GO surface.

Furthermore, as demonstrated in Figure 3(c) and (d), the increasing rise in the initial pH value from 2 to 10 lowered the adsorption efficiency of PFOA degradation and the increase in contact time, improved the degradation of PFOA (%). Two pathways could be provided to understand the impact of pH on the degradation of PFOA, i.e, pH of MoS_2-GO and the targeted form (anionic or cationic) of organic pollutant PFOA onto MoS_2-GO surface. As indicated in Figure 2(b), the best pH of MoS_2-GO for degradation of PFOA was 6.0. The MoS_2-GO surface is positively charged at acidic pH levels. As a result, the affinity of MoS_2-GO for binding positively charged PFOA molecules increased at acidic pH (pH = 6), resulting in improved PFOA degradation.

Besides, Figure 3(e) and (f) illustrates the simultaneous impact of changing the catalyst dose and contact time on the rate of PFOA degradation. From figure 3(e) and (f), the highest point observed was at the highest catalyst dose and low contact time. A high catalyst dose was applied as the cost for the material was economically low, while low contact time signified the best whereby the fast reaction was needed. From previous studies, degradation happened less than 15% under no circumstances of light and presence of catalyst [12].

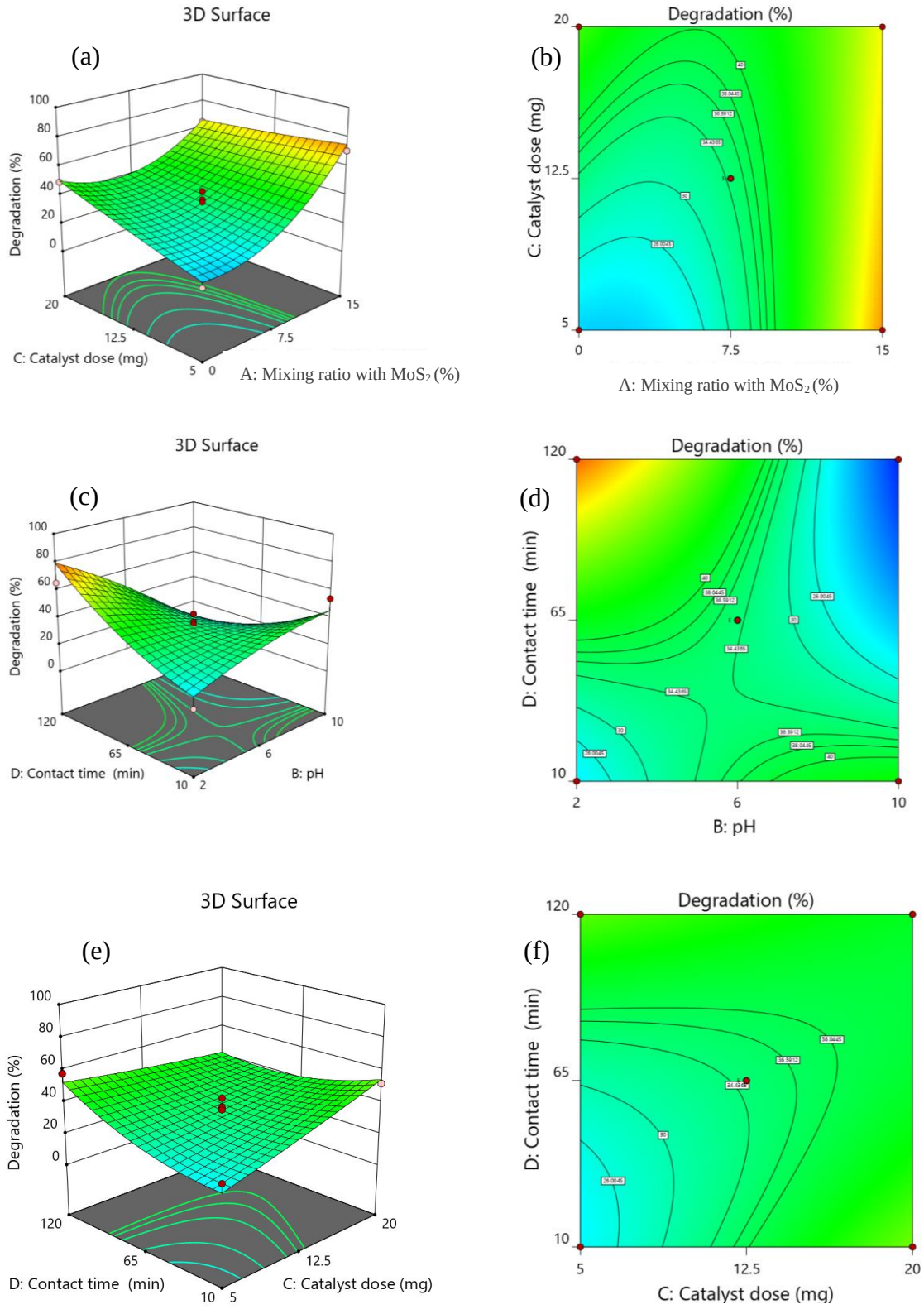

Figure 3. (a) Plots of 3D response surface showing the effect of mixing ratio with MoS_2 and catalyst dose on degradation of PFOA; (b) contour plot for the effect of mixing ratio with MoS_2 and catalyst dose on degradation of PFOA; (c) Plots of 3D response surface showing the effect of pH and contact time on degradation of PFOA; (d) contour plot for the effect of pH and contact time on degradation of PFOA; (e) Plots of 3D response surface showing the effect of catalyst dose and contact time on degradation of PFOA; (f) contour plot for the effect of catalyst dose and contact time on degradation of PFOA.

CONCLUSION

In conclusion, environmentally friendly and effective MoS_2-GO composites have been successfully used for the degradation of PFOA. Parametric optimization by Box–Behnken design was made to optimize the degradation performance of MoS_2-GO nanocomposite for degradation of PFOA. The ideal variables for the highest degradation of PFOA (87.5%) based on the desirability function were the mixing ratio with MoS_2 with GO = 15%, pH = 6, catalyst dose = 12.5 mg and the contact time = 120 min. The greatest removal of PFOA degradation was attained at BD (pH value vs contact time) interaction with *p*-value = 0.0001.

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