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Green Chemistry Advancement: Unravelling Dye Removal Potential Using Nitrogen-Doped Palm Oil Mill Effluent Sludge-Biochar as Peroxydisulfate Activator

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Abstract: Transition metal-based homogeneous or heterogeneous catalysts have been studied for activating persulfate and shown to be a good alternative for the activation of persulfate in organic pollutant recalcitrants. Nevertheless, a significant problem with these catalysts is the secondary contamination due to metal leaching during the process. Therefore, researchers have drawn their attention to nitrogen-doped biochar as a promising alternative persulfate activator due to its lower cost and being more environmentally friendly. In this study, the researchers focused on synthesising nitrogen-doped biochar from Palm Oil Mill Effluent sludge (POS). In Malaysia, POS generated an average of 2.2 million tonnes annually and was disposed of and utilised as fertiliser, indirectly creating secondary soil pollution. Various studies have reported the feasibility of Palm Oil Mill Effluent sludge biochar (POSB) in removing inorganics; however, no research has investigated the efficacy of POSB as a peroxydisulfate (PDS). Recent studies suggest that POSB sludge can be effectively transformed into biochar using low-temperature pyrolysis, resulting in substantial yields. The POS was prepared through a simple pyrolysis process and doped with Urea at temperatures of 400°C and 700°C under nitrogen conditions and used to activate peroxydisulfate (PDS). This study was conducted based on three mass ratios of the urea-doped process,

which were 25:75, 50:50, and 75:25 N-doped POSB. Based on surface morphology results, the incorporation of N-doping reagents into the raw biochar leads to the development of a more expansive porous structure and the N-doped POS biochar exhibited functional group peaks falling within the range of 1383 cm^{-1} to 1460 cm^{-1}, signifying the existence of nitro compounds. POSB at 700 °C has greater catalytic activity than POSB at 400 °C. Dye was completely degraded within 180 minutes of reaction time using 1.0 g of 50:50 Urea-doped POSB at 700 °C, 6 mM PDS, and a pH 5 initial solution as the optimum operating parameters. The pseudo-second-order kinetic model accurately described the dye degradation kinetics. This research demonstrates the efficacy of non-metallic nitrogen-doped biochar as a green catalyst in removing dye in wastewater treatment technology and simultaneously reduces the disposal of POS onto soil that leads to soil pollution.

Keywords: Nitrogen-doped biochar; Palm oil mill effluent's sludge; Peroxydisulfate; Methylene blue; Advanced oxidation processes; Sulfate radical

1.Introduction

Synthetic dyes find extensive applications across diverse industries, including rubber, plastics, textiles, printing, cosmetics, and the production of colored products. Previous research has underscored the significant concern of water pollution resulting from these dyes. Even at low concentrations, they alter the natural appearance and quality of water, impacting both human and aquatic ecosystems[1,2]. These dye-related effluents persist in the environment, resisting aerobic digestion and undergoing biodegradation at an exceptionally sluggish rate[3]. Annually, over 700,000 tonnes of dyes are manufactured, with approximately 2% of this production estimated to be released into water systems, primarily originating from the textile sector[4]. Notably, Methylene blue (MB) dye holds widespread usage in textile manufacturing, functioning as a pH indicator and a drug-enhancing agent. However, only 5% of MB dye is utilized, while the remaining 95% is discharged as effluent[5]. Various treatment methods have been explored, including enzymatic treatment, ultrasonic-assisted adsorption, and conventional adsorption. Nevertheless, these approaches face challenges related to energy costs, scalability, and continuous operation, which hinder their widespread adoption[5].

This study was centered on exploring the use of the Advanced Oxidation Process (AOP) based on sulfate radicals generated from peroxydisulfate (PDS), which is regarded as a favorable approach. During this process, sulfate radicals were generated and employed to degrade stubborn organic pollutants[6]. However, the activation of sulfate radicals in this process necessitates the use of an activator. Common activation methods for PDS include heterogeneous and homogeneous catalysts[7], external energy sources like UV and heat[8], representative transition metals[9], and electrochemical techniques[10]. Nonetheless, these methods are associated with high costs, and the use of heterogeneous/homogeneous catalysts has resulted in significant secondary contamination due to metal leaching[11]. Consequently, activated carbon has been explored as a more environmentally friendly activator option in this research. Recently, biochar has emerged as a promising type of carbon material due to its substantial surface area, high adsorption capacity, and numerous surface functional groups (SFG)[12]. It is anticipated to offer great potential for various wastewater treatment applications[12]. Biochar can act as an electron mediator, facilitating electron transfer processes during AOPs. This electron transfer is crucial for the generation of reactive species such as hydroxyl radicals (•OH) and sulfate radicals ($SO_4^{\bullet-}$), which are highly reactive and capable of breaking down a wide range of contaminants[13].

As of now, Malaysia holds the position of the leading global exporter and producer of palm oil, a development that has led to significant challenges due to the substantial generation of palm oil mill effluent sludge (POSB) by palm oil mills[14]. Recent research indicates that POSB can be efficiently converted into biochar through low-temperature pyrolysis, yielding high quantities[15]. Furthermore, studies have demonstrated that the catalytic performance of biochar can be enhanced through nitrogen-doping[16]. Nitrogen-doping has been identified as the crucial doping method for creating active sites on biochar, facilitating the activation of peroxydisulfate (PDS)[16]. Besides that, nitrogen doping serves to increase the electrical conductivity of the carbon material and improves the

wettability between the electrode and electrolyte. This improvement is achieved by incorporating functional groups, including hydroxyl, oxygen, and nitrogen functionalities, onto the carbon matrix. Consequently, this dual mechanism enhances the overall performance of the supercapacitor[17]. The primary objective of this study is to develop an environmentally friendly activator utilizing natural resources to trigger the sulfate radical activation from PDS. Additionally, the research aims to produce cost-effective nitrogen-doped biochar for catalyzing PDS activation and to determine the optimal conditions for degrading methylene blue dye.

2.Methodology

2.1 Chemicals and Materials

All chemicals and reagents used in this study are of analytical grade. MB, urea, PDS, methanol, ethanol, and tertbutyl alcohol were obtained from Sigma Aldrich. POS was collected from Felda Jengka, Pahang.

2.2 Central Composite Design (CCD)

The design of the experiment for optimization of MB removal was done using RSM by Design-Expert software. CCD was used to predict the relationship between the response and four factors, which were the initial pH of MB dye (A), concentration of PDS (B), dosage of N-doped biochar (C), and ratio of nitrogen to biochar (D). MB removal efficiency was selected as the response to the four factors.

2.3 N-doped POS Biochar Preparation

The POS was dried in the sunlight and washed with ultrapure water several times before being pyrolyzed at temperatures of 400 °C and 700 °C. The POS biochar was then doped with urea with urea mass ratios of 25:75, 50:50, and 75:25, denoted as 25U400, 50U400, 75U400, 25U700, 50U700, and 75U700, respectively. A detailed description of the N-doped biochar preparatory methods has been reported in our previous journal publication[18].

2.4 Characterization

The surface morphology of the biochar was investigated by field emission scanning electron microscopy (FESEM Quanta Fei 400f) at an acceleration voltage of 20 kV. Fourier transform infrared spectroscopy (FTIR) was performed with spectra wavelength of 400 cm^{-1} to 4000 cm^{-1}. A CHNS analyzer (Elementar) was used to examine the POS biochar's CHNS composition.

2.5 Degradation of MB by N-doped POS Biochar

In a series of batch experiments, 250 mL brown Erlenmeyer flasks were employed, each containing 25 µM MB dye solutions. Subsequently, N-doped biochar and PDS were introduced into the aqueous solution. These flasks were sealed and subjected to continuous agitation at 150 rpm using an orbital shaker for a duration of 180 minutes. At specified time intervals, 4 mL of the sample was withdrawn and then filtered through a 0.22 µm syringe filter membrane before being transferred to a cuvette. The reaction was halted by adding 20 µL of methanol. The samples were quantified using a UV-visible spectrophotometer (UV-1800 Shimadzu, Japan) at the maximum wavelength of 650 nm.

3.Results and Discussion

3.1 Characterization

As depicted in the FESEM images (**Figure 1**), it is evident that POS biochar exhibits a rugged surface with a relatively smooth and non-porous pattern. In contrast, the surface of the N-doped biochar appears smooth and displays various rod, flake, and mesoporous structures on the catalyst's surface. The introduction of N-doping reagents, namely urea into the raw biochar results in the formation of a more extensive porous structure, induced by the vaporization of these reagents[13]. This enhanced porous structure facilitates the accessibility of pyrolytic intermediates to the active functional groups within the N-doped biochar[19]. With an increasing quantity of nitrogen precursor on the biochar surface, the porosity of the biochar experiences a notable augmentation, leading to the development of larger porous structures, thereby enhancing the biochar's degradation capability[19].

Fourier transform infrared spectroscopy (FTIR) was employed to identify the functional groups and chemical bonds within both POS biochar and N-doped biochar. A notable distinction in peak patterns was observed before and after the N-doping process, as depicted in **Figure 2**. Specifically, the peaks within the 3000 cm^{-1} to 3500 cm^{-1} range were consistently present in all samples and attributed to secondary amine groups[20]. Additionally, both POS biochar and N-doped POS biochar exhibited substantial quantities of oxygen-containing functional groups, such as the O-H stretching at wavelengths between 3435 cm^{-1} and 3450 cm^{-1}[21]. This observation may be linked to the moisture content of the biochar and the presence

of hydroxyl functional groups within hemicellulose, cellulose, and lignin[22]. **Figure 2** also revealed that N-doped POS biochar displayed peaks within 1383 cm^{-1} to 1460 cm^{-1} range, indicating the presence of nitro compounds, suggesting the existence of amides on the biochar surface[20]. This finding supports the successful nitrogen-doping of the biochar.

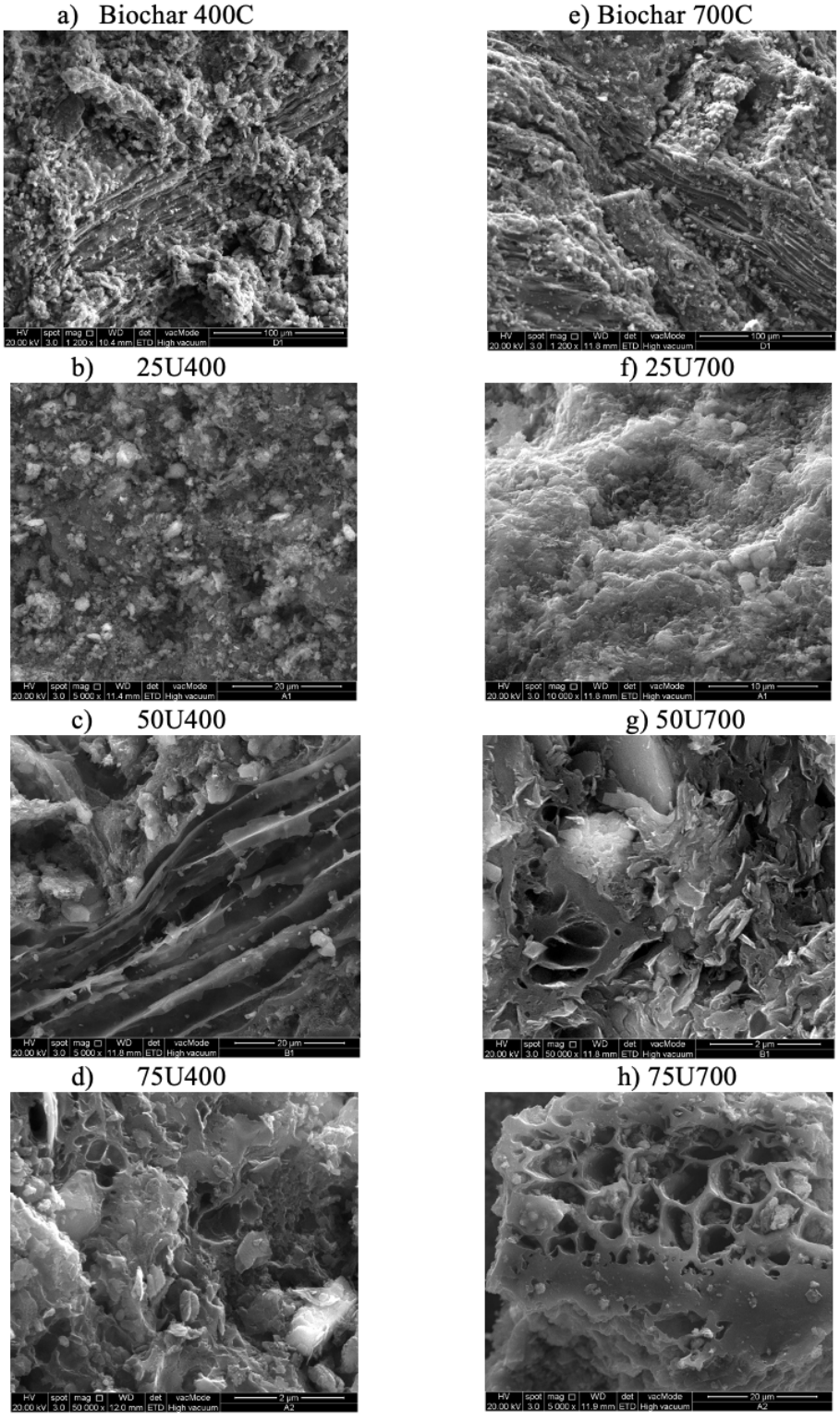


Figure 1. FESEM images for N-doped biochar

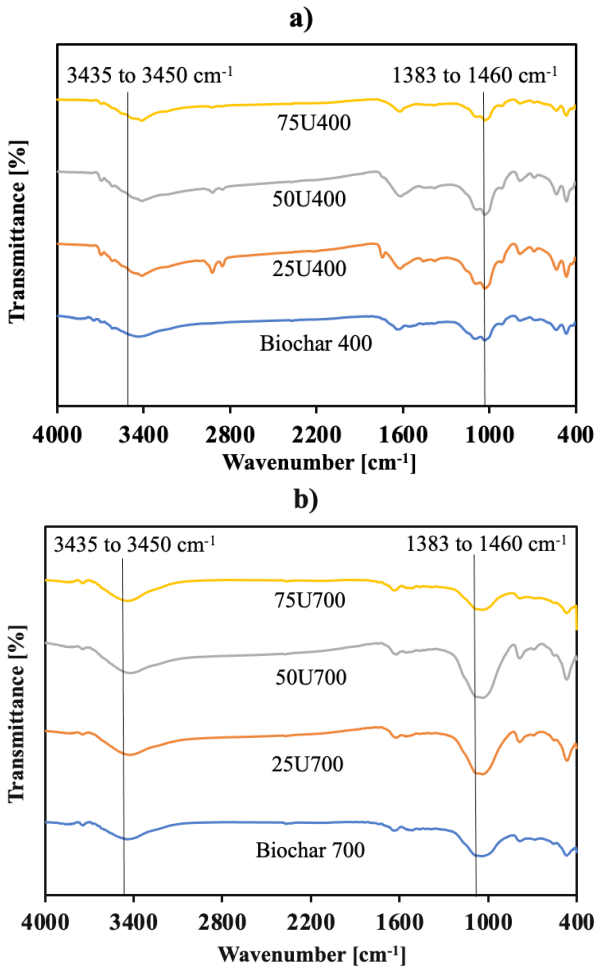


Figure 2. FTIR spectrum for N-doped biochar ratio 25:75, 50:50, 75:25, and 100:0; a) Pyrolysis temperature 400 ºC; b) Pyrolysis temperature 700 ºC

The elemental analysis of POS biochar and POS biochar with nitrogen doping was carried out by CHNS analysis, and the results are shown in **Table 1**. The atomic percentage of carbon in POS biochar is 12.00%, whereas the atomic percentage in 25U400, 50U400, and 75U400 biochar is 303.7%, 19.11%, and 20.40%, respectively. Besides that, the atomic percentage of carbon 25U700, 50U700, and 75U700 biochar is 20.33%, 19.68%, and 22.51%, respectively. The carbon content in biochar is a fundamental parameter as it contributes to the material's stability and can influence its adsorption capacity[23]. The results show that N-doped biochar pyrolysis at 700 ºC temperature showed a higher carbon content, resulting in a more stable carbonaceous structure. Besides that, with the addition of urea into the biochar, it can be observed that the nitrogen content increases with the increasing percentage of urea. The atomic percentage of nitrogen for 25U700, 50U700, and 75U700 is 3.18%, 3.41%, and 4.05% respectively. This result reveals that nitrogen is successfully doped into the carbon lattice[17].

Table 1. CHNS elemental analysis of activated N-doped carbons.

Adsorbent	Carbon	Hydrogen	Nitrogen	Sulfur	Others
Blank	12.00	0.97	1.14	5.19	80.70
25U400	30.37	0.63	1.83	5.20	71.97
50U400	19.11	0.93	1.90	5.10	72.96
75U400	20.40	0.42	1.93	5.05	72.20
25U700	20.33	0.46	3.18	5.14	70.89
50U700	19.68	0.72	3.41	5.13	71.06
75U700	22.51	0.16	4.05	5.02	68.26

3.2 Model Establishment and Analysis

Four variables (A = Initial pH of MB dye, B = Concentration of PDS, C = Dosage of N-doped biochar, D = Ratio of N-doped biochar) are influential factors on the removal of MB dye. The four Face-centered design with 30-experiment was employed by Design-Expert software to cover all possible combination are presented in **Table 2**.

Table 2. Experimental design analyzed by Design-Expert software

Initial pH of MB dye	Concentration of PDS (mM)	N-doped biochar dosage (g)	N-doped biochar ratio
5	4.5	1	50
5	4.5	0.55	50
5	4.5	0.55	50
3	6	0.1	25
7	3	1	75
5	4.5	0.55	50
5	4.5	0.55	50
5	4.5	0.1	50
3	4.5	0.55	50
7	6	1	25
5	3	0.55	50
5	6	0.55	50
5	4.5	0.55	50
5	4.5	0.55	75
7	6	0.1	75
3	3	0.1	75
5	4.5	0.55	50
7	6	0.1	25
7	3	0.1	75
3	6	1	25
7	6	1	75

Continuation Table:

Initial pH of MB dye	Concentration of PDS (mM)	N-doped biochar dosage (g)	N-doped biochar ratio
3	6	0.1	75
7	3	0.1	25
5	4.5	0.55	25
3	6	1	75
3	3	1	25
7	4.5	0.55	50
3	3	1	75
3	3	0.1	25
7	3	1	25

The significance of each factor and interaction on MB dye removal was evaluated by ANOVA, as shown in **Table 3**, and the results of ANOVA showed that the model is significant. The initial pH of MB dye showed a significant value at *P*-value < 0.0765, while the concentration of PDS and dosage of N-doped biochar were significant at *P*-value < 0.0001, respectively, and the ratio of N-doped biochar was significant at *P*-value < 0.0457. The interaction between various variables did not show vital significance. Only the interaction of the initial pH of MB and concentration of PDS and the interaction of the initial pH of MB and N-doped biochar ratio showed significant effects at *P*-value < 0.071 and < 0.089, respectively. The effect of quadratic effect for the concentration of PDS showed a significant effect at *P*-value < 0.086.

Table 3. The results of ANOVA for the removal of MB dye

Source	Sum of Squares	DF	Mean sum of Square	F-Value	P-Value
A	102.64	1	102.64	3.62	0.0765
B	531.16	1	531.16	18.73	0.0006
C	1954.24	1	1954.24	68.90	< 0.0001
D	134.72	1	134.72	4.75	0.0457
A^2	1.57	1	1.57	0.055	0.8173
B^2	0.73	1	0.73	0.026	0.8749
C^2	95.51	1	95.51	3.37	0.0864
D^2	47.10	1	47.10	1.66	0.2170
AB	106.60	1	106.60	3.76	0.0716
AC	93.44	1	93.44	3.29	0.0896
AD	36.47	1	36.47	1.29	0.2746
BC	7.28	1	7.28	0.26	0.6197
BD	3.780E-004	1	3.780E-004	1.333E-005	0.9971
CD	10.44	1	10.44	0.37	0.5532
Residual	425.44	15	28.36		
Total	4219.28	29			

The relationship equation between the removal efficiency and the four variables was obtained as follows:

$$\begin{aligned} \textit{Removal of MB dye} &= 94.11 + 2.39A + 5.43B + 10.42C + 2.74D - 0.78A^2 - 0.53B^2 \\ &- 6.07C^2 - 4.26D^2 - 2.58AB + 2.42AC - 1.51AD - 0.67BC \\ &+ 4.860E - 003BD - 0.81CD \end{aligned} \quad (1)$$

The impact of each input variable on each response was directly assessed through the regression coefficient in equation (1) of the fitted model. A positive sign in the regression coefficient signifies the factor's capacity to enhance the response, whereas a negative sign signifies its ability to diminish the response. The second-order regression model, constructed to predict the removal of MB dye, is deemed reliable due to the high coefficient of determination (R^2) value (0.899), indicating that the model effectively accounts for the majority of the variance in the dataset.

The optimization process was carried out to determine the optimum results of the maximum removal of MB dye. Using the developed second-order

model from equation (1) to set the desired goal within the selected range of selected factors (input variables), a maximum removal of 99.8% was achieved at two possible combinations, as shown in **Table 4**.

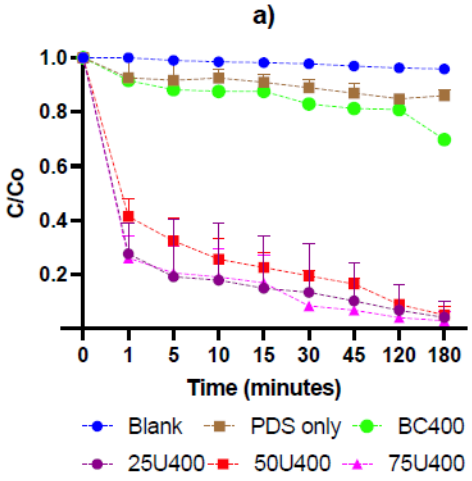
Table 4. Optimum operating conditions for the removal of MB dye

Initial pH of MB dye	PDS concentration	N-doped biochar dosage	N-doped biochar ratio	Percentage removal of MB dye (%)
4.86	5.81	0.61	53.08	99.80
6.79	3.36	0.94	53.49	99.76

As a result, the most effective conditions for removing MB dye were determined to be an initial pH of 5, a PDS concentration of 6 mM, a dosage of 1 g of N-doped biochar, and a 50:50 N-doped biochar ratio. These parameters were employed for subsequent analysis in this research.

3.3 Degradation of MB Dye by N-doped Biochar/PDS System

Based on the optimum condition achieved from response surface analysis, batch degradation of MB dye by N-doped biochar/PDS system was conducted, and the result is depicted in **Figure 3**. Based on the figure, complete degradation of MB dye was achieved when 50:50 urea-doped biochar was utilized at pyrolysis temperature of 700 oC compared to temperature of 400 ºC after 180 minutes of reaction. Raising the pyrolysis temperature can lead to higher percentages of carbon (%C) and ash (%ash) contents[24], consequently enhancing the micro surface area and pore volume of the biochar. This increase in the number of adsorbing sites available for catalytic reactions can concurrently enhance the efficiency of dye removal. This finding is consistent with the FESEM results, where it is evident that N-doped biochar pyrolyzed at 700 °C exhibits greater porosity and a higher presence of mesoporous structures, consequently boosting the biochar's degradation capacity[18].



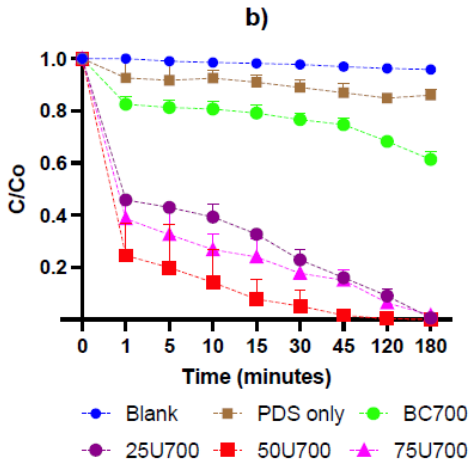


Figure 3. Removal of MB dye at different urea/biochar ratios (a) Pyrolysis temperature 400 ºC, (b) Pyrolysis temperature 700 ºC [Condition: MB initial concentration = 25 µM; Catalyst dosage = 1.0 g; PDS concentration = 6 mM]

Besides that, from response surface analysis, the high removal efficiency of MB by N-doped biochar was obtained as the initial pH ranged from acidic to neutral pH and the concentration of PDS was increased. According to Mashkoor *et al*., in an acidic environment, the surface of the adsorbent becomes more negatively charged. Therefore, it increases the electrostatic interaction between MB and negative functional groups of the biochar[25], therefore increasing the efficiency of MB degradation. Furthermore, increasing PDS concentration in a definite range could maximise active species generation efficiency. However, excessive PDS concentration would obstruct MB degradation because high PDS concentration would deplete the strong oxidizing substance and form fewer oxidizing species, therefore reducing the efficiency of MB degradation[26]. Furthermore, increasing N-doped biochar dosage also increases the efficiency of MB removal. This finding is attributed to the fact that a large amount of biochar provides more active sites for PDS activation, resulting in more generation of reactive oxygen species (ROS), simultaneously increasing MB degradation efficiency[27].

3.4 Adsorption kinetics

The adsorption kinetics of MB dye under optimal conditions were examined to further assess the efficiency of N-doped biochar in removing MB dye. As shown in **Table 5**, the adsorption of MB over time and concentration was fitted with pseudo-first-order and pseudo-second-order kinetic models, considering the optimal operating conditions. Notably, the R^2 values for the pseudo-second-order kinetics were higher than those of the pseudo-first-order kinetics. Specifically, the corresponding reaction rate constants (k values) were 1.661 min^{-1} and 2.712 M min^{-1}, respectively, for 50U700 N-doped biochar. These results strongly suggest that the adsorption kinetics align more closely with the pseudo-second-order kinetic model[23]. This model is predicated on the assumption that the rate-limiting step could involve chemical sorption or chemisorption, encompassing valence forces through the sharing or exchange of electrons between the sorbent and the sorbate[28]. Consequently, it is plausible that chemical reactions played a role in MB adsorption on the surface of biochar.

Table 5. Fitting parameter values using two models for MB dye adsorption kinetics.

Adsorbent	Pseudo-first order model		Pseudo-second order model	
	k (min^{-1})	R^2	k (M min^{-1})	R^2
25U700	1.215	0.8101	2.613	0.9270
50U700	1.661	0.9173	2.712	0.9578
75U700	1.351	0.8734	2.531	0.9777

3.5 Possible reactive species in the N-doped biochar/PDS system

The primary reactive oxygen species (ROS) commonly found in the PDS process include •OH and $SO_4^{\bullet-}$[23]. In the N-doped biochar/PDS system, an excess concentration of methanol (MeOH), ethanol (EtOH), and tertbutyl alcohol (TBA) in a ratio of 500:1 was introduced into the reaction solution to investigate potential reactive species, as depicted in **Figure 4**. According to the figure, the addition of these alcohols did not visibly affect the removal of MB dye. These findings may be attributed to the hydrophilic nature of these alcohols, suggesting that they are more efficient at quenching free radicals in an aqueous solution compared to those generated on the catalyst's surface[23]. Additionally, it has been reported that surface-bound active species can only interact with substrates adsorbed on the catalyst's surface, which could explain why the scavengers do not effectively inhibit the reaction between free radicals and substrates[29].

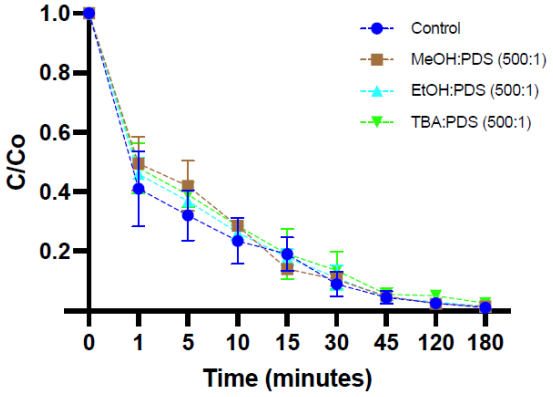


Figure 4. Influence of different concentrations MeOH, EtOH and TBA on MB dye removal in N-doped biochar/PDS system [Condition: MB initial concentration = 25 µM; Catalyst dosage = 1.0 g; PDS concentration = 6 mM, Urea/biochar ratio = 50:50]

4.Conclusions

Biochar derived from POS was prepared and subjected to nitrogen-doping using a urea precursor at ratios of 25%, 50%, and 75%. This urea-doped biochar served as a catalyst in peroxydisulfate activation to enhance the degradation of methylene blue dye, following the optimized conditions determined through response surface analysis, which included an initial pH of MB dye at pH 5, a 6 mM PDS concentration, a 50:50 urea/biochar ratio, and a 1.0 g dosage of urea-doped biochar. The experimental findings revealed that the most effective degradation of MB occurred with the use of 50:50 urea-doped biochar, pyrolyzed at 700 ºC, with a 1.0 g dosage and a 6 mM PDS concentration. Furthermore, the optimized conditions were well-matched with pseudo-second-order kinetics, characterized by a k value of 2.712 M min^{-1}. Therefore, it can be concluded that the introduction of nitrogen species onto the biochar surface enhances the generation of active sites, concurrently improving PDS activation for methylene blue degradation.

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Ethics Statement

Not applicable.

Consent for publication

Not applicable.

Availability of Supporting Data

Not applicable.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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