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Removal of cadmium from aqueous solution by optimized rice husk biochar using response surface methodology

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ABSTRACT

The removal of Cd (II) ions by rice husk biochar as adsorbent was evaluated through batch study. Activated biochar was prepared using the physicochemical activation method. Preparation was consisting of pre-impregnation of NaOH and nitrogen (N_2) pyrolysis. The Influence of preparation parameters which were chemical impregnation (NaOH: RH), pyrolysis temperature, and pyrolysis time on biochar yield, cadmium removal rate, and adsorption capacity on cadmium ions was investigated. A quadratic model for correlating biochar preparation variables with biochar production, cadmium removal rate, and adsorption capability was built according to central composite design (CCD). The experimental results revealed that pyrolysis temperature and heating time are important factors that affect the yield of biochar and positively affect Cadmium's removal rate and adsorption capacity. The impregnation ratio positively impacted Cadmium removal and adsorption capacity, and it did not affect biochar yield. The optimal biochar was obtained using 458 ◦C temperature, 120 min reaction time, and 3 NaOH impregnation ratio, resulting in 34.5% of biochar yield, 72% of cadmium removal, and 17.8 mg/g of adsorption capacity on Cadmium.

1. Introduction

With industrial development, a significant volume of metal ion-containing industrial wastewater and domestic sewage has been dumped into water bodies worldwide [1–3]. There are adverse effects on the quality of water created by these wastewaters, resulting in significant impacts on marine environments and public health [4,5]. The main feature of this impurity category is that it is unwanted and persistent in the environment, and it will create ongoing interference if it is not removed or converted [6,7]. A significant fact is that they can serve as endocrine disruptors for humans and marine animals as they are present in the population and even in absorption [8,9]. It should also be considered for volume that the trace variable is not separately contained in the expansion so that this uniqueness creates a synergistic effect that can be easier to identify, measure, and eliminate [10,11].

Recently, due to the irresponsible technological progress of urbanization, there has been a rapid development of industries, whether in developing or developed countries [9,12]. These industries often contribute indirectly to the accumulation of heavy metals released into the environment [13,14]. The industries that contribute to the accumulation of heavy metals are the manufacture of paint and dyes, batteries, paper, pesticides, and textile dyeing because they contain some derivatives of heavy metals or nitrates and sulfates of heavy metals [15,16]. Heavy metals are materials of the atomic weight of 63.5 to 200.6 and greater than five specific gravity [17,18]. Heavy metal might be essential or detrimental deadly based on their toxicity level [19]. Essential heavy metals, including zinc, copper, iron, chromium, cobalt, and

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selenium, are necessary for regular body function if they are not present in toxic amounts [20,21]. However, nonessential heavy metals such as Cadmium, mercury, lead, and arsenic are incredibly toxic at lower concentrations [22]. The toxic heavy metals can impact the human body and trigger acute or chronic effects or lead to cancer, digestive system disease, and nervous system diseases [23,24]. Cadmium is considered one of the most hazardous metals. Its danger lies in that it is used in many industries, including paint, batteries, and dyes, but municipal waste is the most complex source due to its nearness to human reach [25,26]. Cadmium can be found in the industries as a form of cadmium nitrate, cadmium sulfate and it is more likely to leach from industrial waste and is the most toxic to living organisms [27,28]. Cadmium has been included in the list of priority pollutants to control EPA priority due to the persistent Cadmium and toxicological properties. In drinking water and industrial wastewater, the permissible concentration has been set at 0.005 mg / l by US Environmental Protection Agency (USA -EPA), while the World Health Organization has set the level at 0.003 mg / l [29]. The danger of Cadmium lies not only in its irreversible toxicity characteristics but also in its abundance in many industrial sources such as batteries, alloys, coatings (electroplating), solar cells, plastic stabilizers, and pigments. Today, Cadmium is derived from zinc byproducts extracted from recycled batteries with nickel–cadmium [30]. There are many techniques for eliminating heavy metals, both uncommon and conventional. According to the removal rate, their effectiveness is evaluated, but recently adsorption is considered the best method due to its simplicity, cheapness, and potential for broader use [31,32]. Many adsorbents have been used and consumed in various industries and yet used until now such as commercial activated carbon, activated alumina, silica gel, molecular sieve carbon, molecular sieve zeolites, and polymeric adsorbents [33,34].

Although some adsorbents are effective, the use of commercially available adsorbents to adsorb heavy metals has become common, but much work has been conducted into the usage of agricultural waste adsorbents. There are many agricultural wastes in many developing countries [35,36]. For example, Malaysia produces about 408,000 tons of rice husks every year, according to the statistics of the agricultural sector in Malaysia. Due to the large amount of agricultural waste in Malaysia, these wastes can be re-developed and recycled, and made into adsorbents to treat polluted water on the one hand and clean up these wastes in a civilized way from the other end [37,38]. The husk of rice is a waste from agriculture. It comprises cellulose (32.23%), hemicellulose (21.34%), lignin (21.44%), and ash minerals (15.05%), and it has a high silica content (96.34%) in mineral ash (Table 1). The research is still ongoing in using, modifying, and improving natural resources to gain promising adsorbent. The adsorption process using natural resources and agricultural waste is economically and environmentally worthwhile. In recent years, however, numerous experiments have concentrated on the application of biochar extracted from agricultural waste to aqueous solutions for the elimination of heavy metal [39,40].

Biochar has the same properties as activated carbon, which makes it promising as an adsorbent for wastewater. The chemical and physical characteristics of biochar differ based on the quality of the raw materials, the pyrolysis method, sample size, temperature, pyrolysis time, and chemical modification of the biochar by exposure to acids or alkalis [41]. While several variables influence biochar's composition, biochar usually has an excess of functional groups on the pore system's exteriors, the large surface area, and its molecular composition (hydroxyl, carboxyl, carbonyl, and methyl). It has strong adsorption efficiency that is beneficial in terms of adsorbing wastewater [42].

Table 1
Rice husk chemical compositions.

Chemical composition	Percent (%)	Ref.
Cellulose	32.230	[67]
Hemicellulose	21.340	[68]
Lignin	21.440	[68]
Mineral Ash	15.050	[67]
High Silica	96.340	[69]

This study investigates and optimizes the adsorption of Cd (II) from synthetic aqueous solution by rice husk-activated biochar. Response surface methodology (RSM) was applied to help with the optimization of preparation parameters. The application of RSM allowed a minimal number of tests and the software is incorporated with mathematical and statistical tools, as such can be used to analyze interactions between parameters [43,44]. Some of the previous studies used RSM in the preparation of activated carbons using precursors such as olive-waste cakes [45], kenaf fiber [46], and Luscar char [47]. Monik Kasman [48] applied RSM to study cadmium removal by using raw rice husk and found that raw rice husk poorly adsorbed cadmium with 70% removal, suggesting the need for adsorbent improvement. Taimur Khan [49] found that rice husk carbon was a sufficient adsorbent for lead removal after optimization with an artificial neural network during the adsorbent development. Raphael et al also reported adsorption of Cadmium from water using Raffia Palm seed (*Raphia hookeri*) activated carbon as adsorbent [50].

To date, there has been no research on the preparation of biochar from rice husk using the RSM method by a physicochemical activation method including NaOH impregnation and N_2 Pyrolysis. This study implemented a central composite design to evaluate the effect of input parameters during the preparation of biochar. The input parameters included the pyrolysis temperature, pyrolysis time, and chemical impregnation (NaOH/RH) on the three response parameters of adsorption capacity, removal efficiency, and biochar yield.

2. Materials and methodological program

2.1. Preparation of biochar

The rice husks (RHs) were shipped from a rice mill in Perak, Malaysia. Rice husk was washed continuously with tap water 3–5 times to remove the impurities and dust, then placed in an oven for 24 h at 105° C for drying purposes. The sample was broken down to the desired mesh size (1–2 mm) by passing through the respective sieves. It is then placed in an airtight container at room temperature before characterizations and experiments. Rice husk biochar was prepared by fast and slow pyrolysis, changing preparation conditions using different response parameters (Table 2).

2.2. Design of experiments

The pyrolysis process was conducted by putting specimens in an Alumina Tube Furnace tube for different input parameters listed in Table 2. Purified nitrogen (99.995%) has been used in the process of pyrolysis, with a flow and heating rate of 100 cm^3/min and 7 °C/min, respectively. RSM is such software which usually carried out to widen screening mathematical and statistical methods for analyzing and improving products, which jointly determines regression models and optimal operational conditions through experimental quantitative data. A typical RSM scheme called CCD was introduced to optimize the production of biochar from pyrolysis. CCD may be designed for an extremely accurate second-order quadratic model with the minimum possible number of experiments [51]. In the study, activated biochar was prepared by the

Table 2
Coded and actual levels of the response parameters of biochar preparation.

Parameters	**Units**	**Code**	**Coded levels and limits**				
			− α	**−1**	**0**	**+1**	**+ α**
Pyrolysis Temperature	°C	X_1	197	300	450	600	702
Pyrolysis time	Minutes	X_2	19	60	120	180	220
Impregnation ratio	w/w	X_3	0.32	1	2	3	3.68

physicochemical method by changing the preparation parameters employing a CCD. The parameters were pyrolysis temperature (A), Pyrolysis time (B), and impregnation ratio (C) (NaOH: RRH). These three parameters were the main factors that influence the biochar adsorbent characteristics [52]. Eight-factor points, 6 axial points, and center points were scheduled for central composite design. There were five levels of selected factors (−α, −1, 0, 1, + α). As proven in Equation (1), the number of experiments was 20.

$$N = 2n + 2n + nc = 23 + 2 \times 3 + 6 = 20 \tag{1}$$

where N = No. of experiments; and n = No. of factors.

Table 2 indicates the lower and higher limits of every factor. The data analysis was performed statistically using variance analysis (ANOVA) for the model acquired. Using surface contour plots the relationship between variables was analyzed.

The central points were used to determine the experiment errors and data repeatability. The independent parameters are labeled at intervals of (-1, 1) with low and high values assigned to −1 and +1. The axial points are positioned at (±α, 0, 0), (0, ± α, 0) and (0, 0, ± α). Where α is the distance from the axial points to the central point is making the design fixed at 1.682 mm. Table 3 displays the entire design matrix and the findings generated with the experiments carried out. To eliminate unpredictable impacts, the experimental series was randomized. The responses were biochar yield (Y_1), removal efficiency (Y_2), and adsorption capacity on Cadmium (Y_3). Every response was designed to establish an empirical model that associated the response to modified biochar preparation variables with a second-degree polynomial equation provided by Equation (2) [53].

$$Y = B_0 + B_1x_1 + B_2x_2 + B_3x_3 + B_{12}x_1x_2 + B_{13}x_1x_3 + B_{23}x_2x_3 + B_{11}x_1^2 + B_{22}x_2^2 + B_{33}x_3^2 \tag{2}$$

where Y = anticipated responses, B_0 the constant coefficient,(B_1, B_2, B_3) the linear coefficients, (B12, B13, B23) the binary interaction coefficients, (B_{11}, B_{22}, B_{33}) the quadratic coefficients, and x_1, x_2, and x_3 are the coded values of the modified biochar preparation variables.

2.3. Batch study

A 1000 mg / L Cd (II) stock solution was prepared with cadmium nitrate trihydrate and then diluted to 25 mg / L for batch studies. A 25 mg / L cd$^{2\,+}$ stock solution was used for the adsorption study. The solution was treated with a fixed variable to obtain the best pyrolysis process parameters for cadmium removal. The fixed parameters were the adsorbent dose, the adsorbent's pH, the stirring speed, and time. Add each selected dose and pH of the adsorbent to 250 ml of a 25 mg / L cd^{2} stock solution. Atomic absorption spectroscopy (AAS) was utilized to establish the initial and final concentrations of the cd$^{2\,+}$ stock solution. The difference between original and equilibrium metal ion levels is the number of metal ions that the magnetic biochar has consumed. Calculate the yield, removal efficiency, and adsorption capacity of magnetic biochar according to the following equations.

$$BiocharYield\% = \frac{\mathrm{Wb}}{\mathrm{Wr}} * 100 \tag{3}$$

$$RemovalEffiecincy\% = \frac{\mathrm{Ci} - \mathrm{Ce}}{\mathrm{Ci}} * 100 \tag{4}$$

$$\mathrm{qe} = \frac{(\mathrm{Ci} - \mathrm{Ce})(\mathrm{V})}{\mathrm{m}} \tag{5}$$

İn the previous equations, W_b and W_r are the biochar weight and raw rice husk weight. C_i and C_e are initial and final concentrations (mg/l), q_e (mg/g) is the adsorption capacity, m is adsorbent dosage (g), and V solution's volume (l).

Table 3
Experimental model and the resulting consequence of the test: A central composite design.

Run	CCD Position	Biochar preparation variables x_1: Temperature(°C)	Responses x_2: Time (Min)	x_3: Impregnation ratio (w/w)	Yield%	Cd (II) Removal (%)	Adsorption capacity (mg/g)
1	Factorial	300(-1)	180(+1)	1(-1)	38.12	49.5	12.4
2	Factorial	600(+1)	60(-1)	3(+1)	32.7	78	19.5
3	Axial	450(0)	120(0)	0.32(−α)	34.6	67.1	16.8
4	Axial	197.731(−α)	120(0)	2(0)	48.6	47	11.75
5	Axial	450(0)	19.1(−α)	2(0)	35.3	65	16.25
6	Factorial	300(-1)	60(-1)	3(+1)	44.5	51.1	12.8
7	Centre	450(0)	120(0)	2(0)	34.8	69.5	17.37
8	Factorial	600(+1)	60(-1)	1(-1)	31.8	76.3	19
9	Axial	450(0)	220.91(+α)	2(0)	32.2	72	18
10	Centre	450(0)	120(0)	2(0)	34.4	69.2	17.3
11	Centre	450(0)	120(0)	2(0)	34.5	69.3	17.3
12	Factorial	300(-1)	60(-1)	1(-1)	44.2	48.5	12.13
13	Centre	450(0)	120(0)	2(0)	34.1	68.9	17.225
14	Axial	702(+α)	120(0)	2(0)	27	83.4	20.9
15	Centre	450(0)	120(0)	2(0)	34.3	70.1	17.68
16	Centre	450(0)	120(0)	2(0)	34.6	69.9	17.47
17	Axial	450(0)	120(0)	3.68(+α)	34.9	71.5	17.88
18	Factorial	600(+1)	180 (+1)	1(-1)	29.5	77.5	19.38
19	Factorial	300(-1)	180(+1)	3(+1)	39	52.5	13.125
20	Factorial	600	180(+1)	3(+1)	29.3	79.5	19.87

3. Results and discussion

3.1. Effect of the heating temperature on biochar yield and cadmium removal

The heating temperature considers as one of the extremely crucial considerations affecting the biochar preparation as whether fuel or biochar-based adsorbent. Fig. 1 demonstrates the impact of the pyrolysis temperature on biochar production. The highest percentage of biochar found at low temperatures showed that less biochar production was produced at higher temperatures. Fig. 1 shows a massive decline in biochar yield as heating temperature increases, and biochar percentage dropped from 49% to 27%. According to a literature review, many researchers prove that more solid product (biochar) of fuel is produced by pyrolysis at a low heating temperature. Nizamuddin et al. found a similar result, observed that temperature plays an essential role in biochar production, proving that the decline in product yield at a high temperature can be characterized by a low-carbon removal in a high-temperature gaseous form, which means lower biochar yields [54]. Another logical reason for decreasing the yield of biochar with increasing temperature is that the cellulose and hemicellulose of biomass decompose at higher temperatures [55]. In the other part of Fig. 1, the effect of heating temperature of biochar-based adsorbent on the removal rate of Cadmium in aqueous solution. The experiments of biochar production were implemented at a pyrolysis temperature that varies from 200 to 700 °C, while the alternative conditions of preparing biochar-based adsorbent were constant

3.2. Effect of the heating time on biochar yield and cadmium removal

To inquire about the effect of heating time on biochar-based adsorbent properties, a pyrolysis experiment was carried out using a tube furnace with heating time ranging from one to three hours at a fixed temperature to explore the optimum heating time that might give good biochar properties, whether textural or morphological properties. Fig. 2 showed that the biochar yield decreases as heating time increases; biochar yield decreases from 39% to 32%. Tangjuank et al. found the yield of carbon decrease as increase activation time where the yield reduced from 82% to 64% with the activation time's growth from 20 to 150 min [56]. The reason for the decreasing biochar's quantity when the reaction time is longer is that the further biomass decomposition leads to the volatile organic compounds removal, thereby decreasing the biochar's amount [51]. On the other hand, it found that heating time showed a vital role in the effect of cadmium removal and was found the removal rate increase from 64% to 72% with increasing heating time from 170 to 215 min. This result is similar to the result found by Runjuan Zhou et al., Runjuan found that the removal rate and adsorption capacity of Cadmium by biochar derived from Eichhornia crassipes increased from 96% to 99% and 9.63 mg/g to 9.9045 mg/g with the increase in heating time from 1 to 2 h [57]. In this study, we do not need more heating time as much as we need an appropriate time, which gives us an appropriate opportunity to restore biomass polymers that may gain biochar properties that make it capable of being an adsorbent substance.

3.3. Effect of the impregnation ratio on biochar yield and cadmium removal

Fig. 3 displays the yield of impregnated biochar at different impregnation ratios of NaOH. The biochar yield was computed by dividing the final resultant biochar by the initial mass of impregnated raw material (rice husk). The oxidation process was achieved by adding the alkali (NaOH) to the raw material then followed by the pyrolysis process using a tube furnace under a nitrogen atmosphere [58]. Fig. 3 shows that the imagination ratio does not affect the yield of biochar due to primarily solubility of NaOH with water during impregnation and due to evaporation of water during the decomposition of biomass. While there is an effect of impregnation to cadmium removal from the aqueous solution. Surface oxidation modification has been used as a beneficial method in biochar development used in heavy metals' adsorption. This primary modification might increase the functional groups of biochar such as carboxyl, phenol base, quinonoid, lactone, and fluorescein [59]. Fig. 3 shows an up and down effect on cadmium removal by adding alkali, and that effect is not going to be constant so long as the temperature is constant. From Fig. 3, it has been proven that there is a good side effect of treating biochar with NaOH but with consideration of the effect of the other essential factors such as temperature, pH, and others [60].

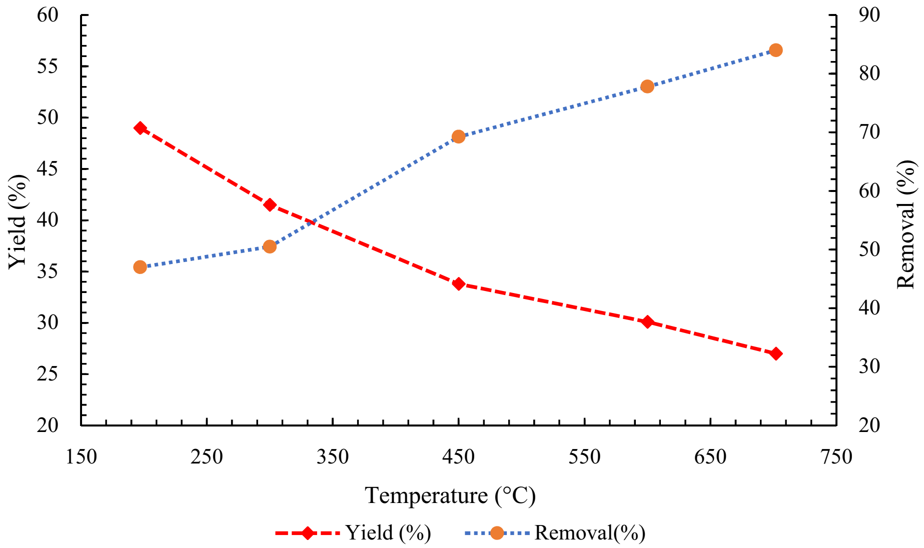

Fig. 1. Temperature effect on the yield of biochar and removal rate of Cadmium.

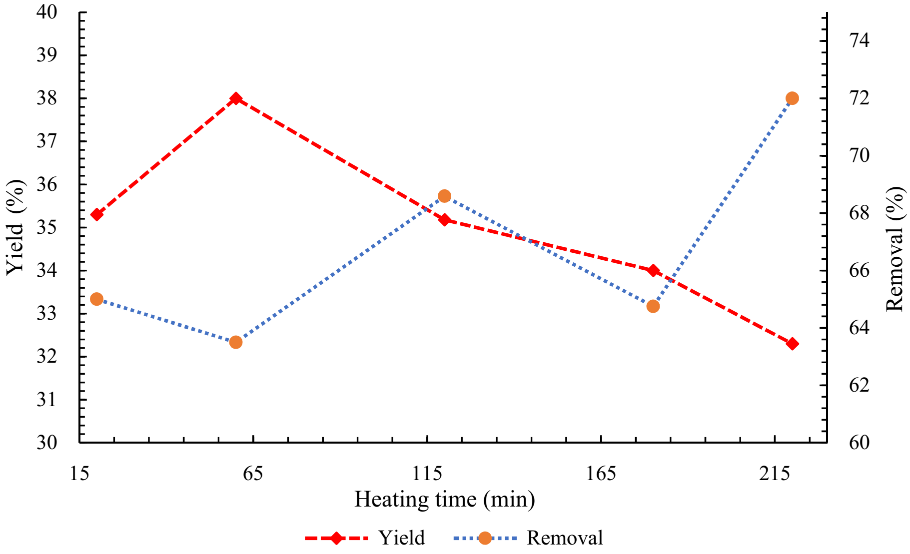

Fig. 2. Heating time effect on the yield of biochar and removal rate of Cadmium.

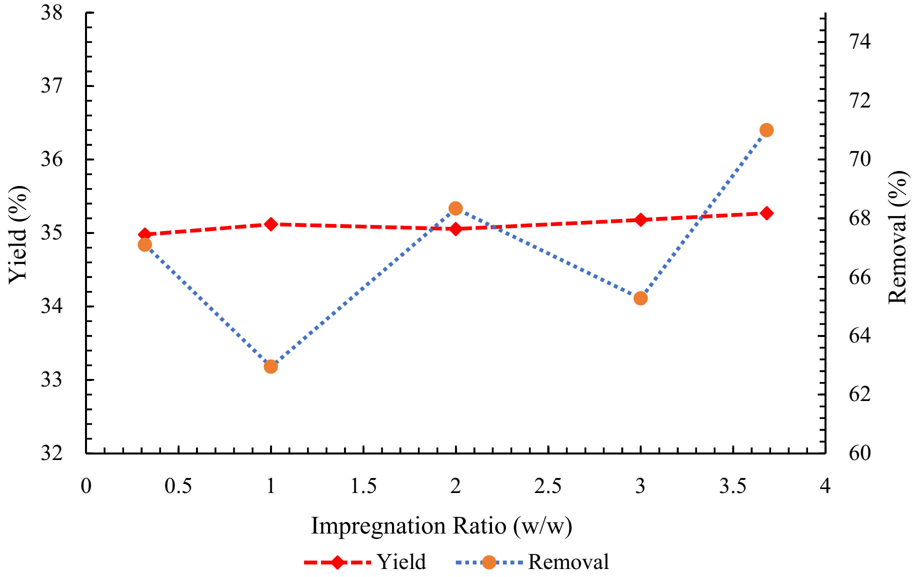

Fig. 3. Impregnation ratio effect on the yield of biochar and removal rate of Cadmium.

3.4. Analysis of statistics

In the current research, the experimental design (DOE) was performed 20 runs. The study was conducted using Design-Expert software, which uses regression analysis of experimental results consistent with the equations and statistical evaluation of the equations.

3.4.1. Regression model development

The CCD was chosen to expand and establish the correlation between biochar-based adsorbent primary preparation parameters and biochar yield, cadmium removal rate, and adsorption capacity. The main preparation parameters of the biochar studied in this research are temperature (x_1), reaction time (x_2), and impregnation rate (x_3), while the advanced preparation parameters to be considered in another study are the initial concentration of heavy metal, pH value of the solution, adsorbent quantity, and time contact. Those parameters were selected from the literature review and kept constant to select the biochar-based adsorbent's primary preparation parameters. The input parameters, together with the response parameters, are distributed in Table 3. Biochar yield obtained ranged from 27% to 48.6%. Cadmium removal rate and adsorption capacity range from 47% to 83.4% and from 11.75 mg/g to 21 mg/g, respectively.

Based on the sequential square model sum, the models were chosen solely according to the better order polynomials where extra parameters were scaled, and the models were no longer aliased. For the three response parameters, biochar yield, adsorption capacity, and cadmium removal, the quadratic model was proposed by the software.

The final empirical models in terms of coded factors after an exception the insignificant terms for Biochar yield (Y_1), cadmium removal (Y_2), and adsorption capacity(Y_3) are shown in equations (6), (7) and (8), respectively

Table 4
Responses coefficients of the models.

Coefficients	Y_1	Y_2	Y_3
B_0	34.43	69.60	17.42
B_1	−5.78	12.52	3.13
B_2	−1.65	1.24	0.31
B_3	0.175	1.22	0.31
B_{12}	0.74	0.0375	0.019
B_{13}	−0.060	−0.238	−0.051
B_{23}	−0.065	−0.0088	0.00057
B_{11}	−1.32	2.24	0.56
B_{22}	−0.11	−1.07	−0.28
B_{33}	0.25	−0.80	−0.21

$$Y_1 = 34.43 - 5.78x_1 - 1.65x_2 + 0.175x_3 + 0.74x_1x_2 - 0.060x_1x_3{}_{-}0.065x_2x_3 - 1.32x_1^2 - 0.11x_2^2 + 0.25x_3^2 \tag{6}$$

$$Y_2 = 69.60 + 12.52x_1 + 1.24x_2 + 1.22x_3 + 0.0375x_1x_2 - 0.238x_1x_3 + 0.088x_2x_3 + 2.24x_1^2 - 1.07x_2^2 - 0.79x_3^2 \tag{7}$$

$$Y_3 = 17.42 + 3.13x_1 + 0.31x_2 + 0.31x_3 + 0.019x_1x_2 - 0.051x_1x_3 + 0.00057x_2x_3 + 0.56x_1^2 - 0.28x_2^2 - 0.21x_3^2 \tag{8}$$

The regression evaluation was noticed to fit the functions' response with the experimental data. Table 4 defines the values of the correlation equation (regression coefficient). It is obtained that temperature (X_1) and time (X_2) had given adverse effects on the Biochar yield and positive effects on the cadmium removal and cadmium adsorption capacity. In contrast, the impregnation ratio(X_3) had given positive effects on the three output responses. The interaction between temperature and time showed a significant interaction with a positive impact, while the interaction of temperature and impregnation ratio showed significant interaction with a negative impact in all three output responses. The temperature interaction showed a significant effect with a positive sign (B_{11} = 2.24 for cadmium removal and B_{11} = 0.56 fir adsorption capacity).

Table 5
ANOVA findings for response surface quadratic model for biochar yield.

Source	Sum of Squares	Degree of freedom	Mean Square	F -Value	Prob > F	
Model	523.32	9	58.15	51.94	< 0.0001	significant
x_1	455.22	1	455.22	406.60	< 0.0001	
x_2	37.05	1	37.05	33.09	0.0002	
x_3	0.42	1	0.42	0.37	0.5556	
x_1 x_2	4.32	1	4.32	3.86	0.0778	
x_1 x_3	0.029	1	0.029	0.026	0.8758	
x_2 x_3	0.034	1	0.034	0.030	0.8655	
x_1^2	25.15	1	25.15	22.46	0.0008	
x_2^2	0.18	1	0.18	0.16	0.6989	
$x_3{}^2$	0.85	1	0.85	0.76	0.4045	
Residual	11.20	10	1.12			
R^2 Values	R^2 = 0.98 $R^2_{adjusted}$ = 0.960 $R^2_{Predicted}$ = 0.84					

Table 6
ANOVA findings for response surface quadratic model for cadmium removal rate.

Source	Sum of Squares	Degree of freedom	Mean Square	F-Value	Prob > F	
Model	2267.34	9	251.93	34.25	< 0.0001	significant
x_1	2139.05	1	2139.05	290.80	< 0.0001	
x_2	20.85	1	20.85	2.83	0.00621	
x_3	20.42	1	20.42	2.78	0.00652	
x_1 x_2	0.011	1	0.011	1.529E-003	0.0431	
x_1 x_3	0.45	1	0.45	0.061	0.8094	
x_2 x_3	0.061	1	0.061	8.327E-003	0.9291	
x_1^2	72.38	1	72.38	9.84	0.0106	
x_2^2	16.64	1	16.64	2.26	0.1635	
$x_3{}^2$	9.03	1	9.03	1.23	0.2938	
Residual	73.56	10	7.36			
R^2 Values	R^2 = 0.970 $R^2_{adjusted}$ = 0.94 $R^2_{Predicted}$ = 0.885					

Table 7
ANOVA findings for response surface quadratic model for adsorption capacity.

Source	Sum of Squares	Degree of freedom	Mean Square	F-Value	Prob > F	
Model	141.58	9	15.73	34.31	< 0.0001	significant
x_1	133.40	1	133.40	290.92	< 0.0001	
x_2	1.35	1	1.35	2.94	0.00543	
x_3	1.29	1	1.29	2.82	0.00432	
x_1 x_2	3.003E-003	1	3.003E-003	6.549E-003	0.0321	
x_1 x_3	0.021	1	0.021	0.045	0.8368	
x_2 x_3	2.531E-004	1	2.531E-004	5.520E-004	0.9817	
x_1^2	4.55	1	4.55	9.92	0.0103	
x_2^2	1.12	1	1.12	2.45	0.1490	
$x_3{}^2$	0.59	1	0.59	1.29	0.2818	
Residual	4.59	10	0.46			
R^2 Values	R^2 = 0.968 $R^2_{adjusted}$ = 0.940 $R^2_{Predicted}$ = 0.868					

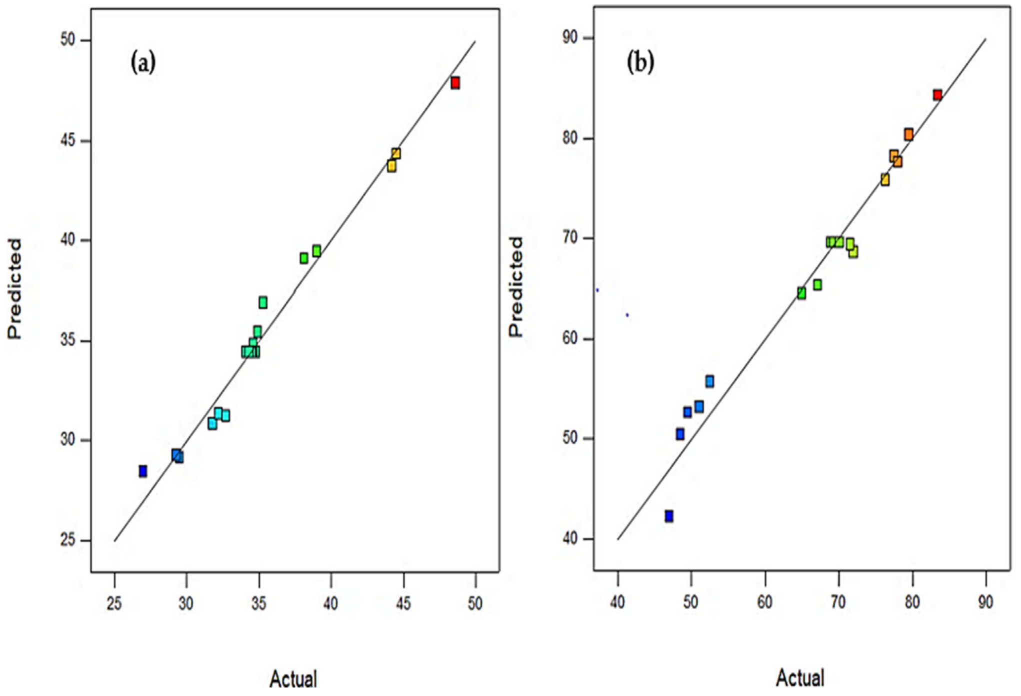

Fig.4. Correlation of experimental and predicted values a) biochar yield and b) Cadmium removal rate.

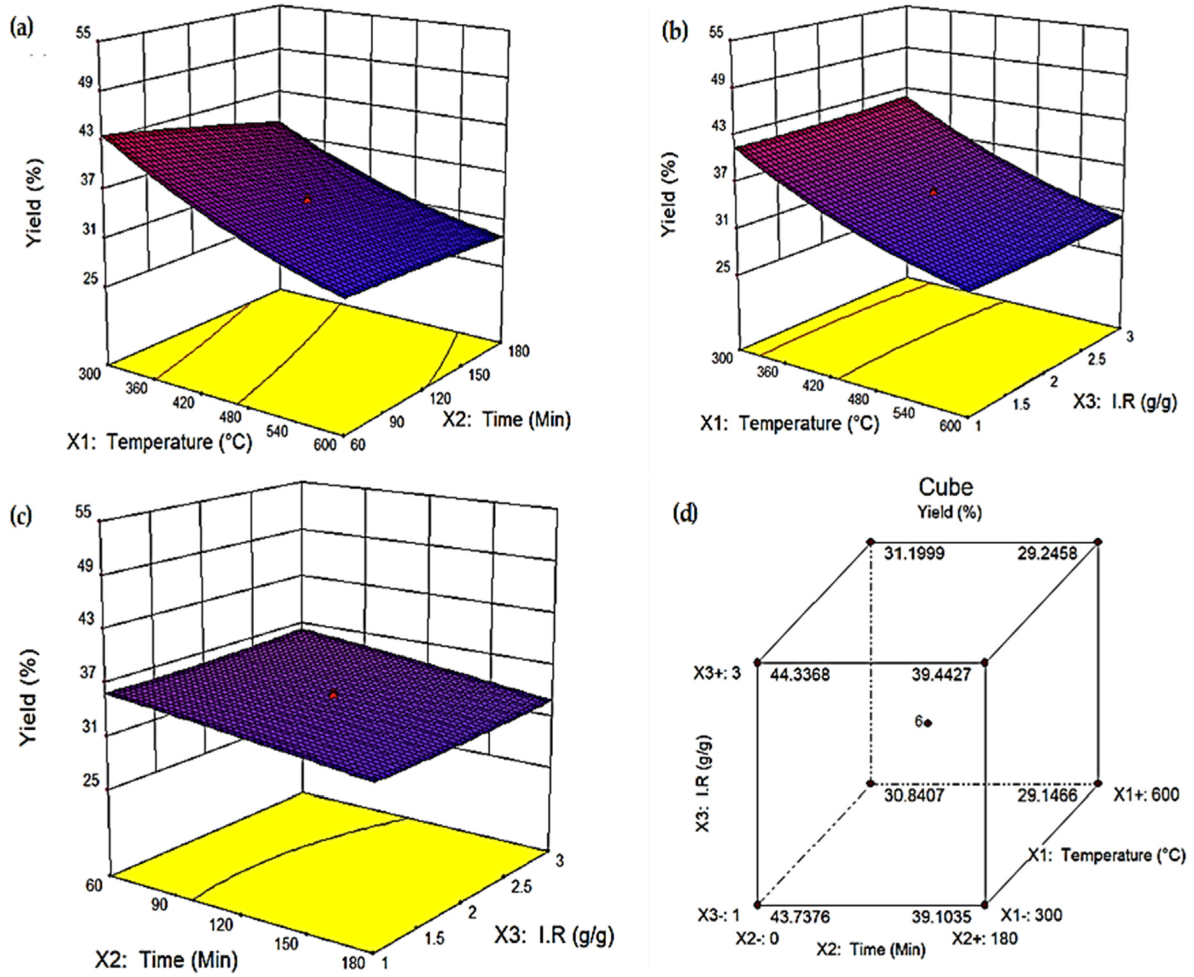

Fig. 5. The combined effect of process variables (a) temperature and time, (b) temperature and impregnation ratio(c) time and impregnation ratio on biochar yield, (d) Biochar yield at each factorial point.

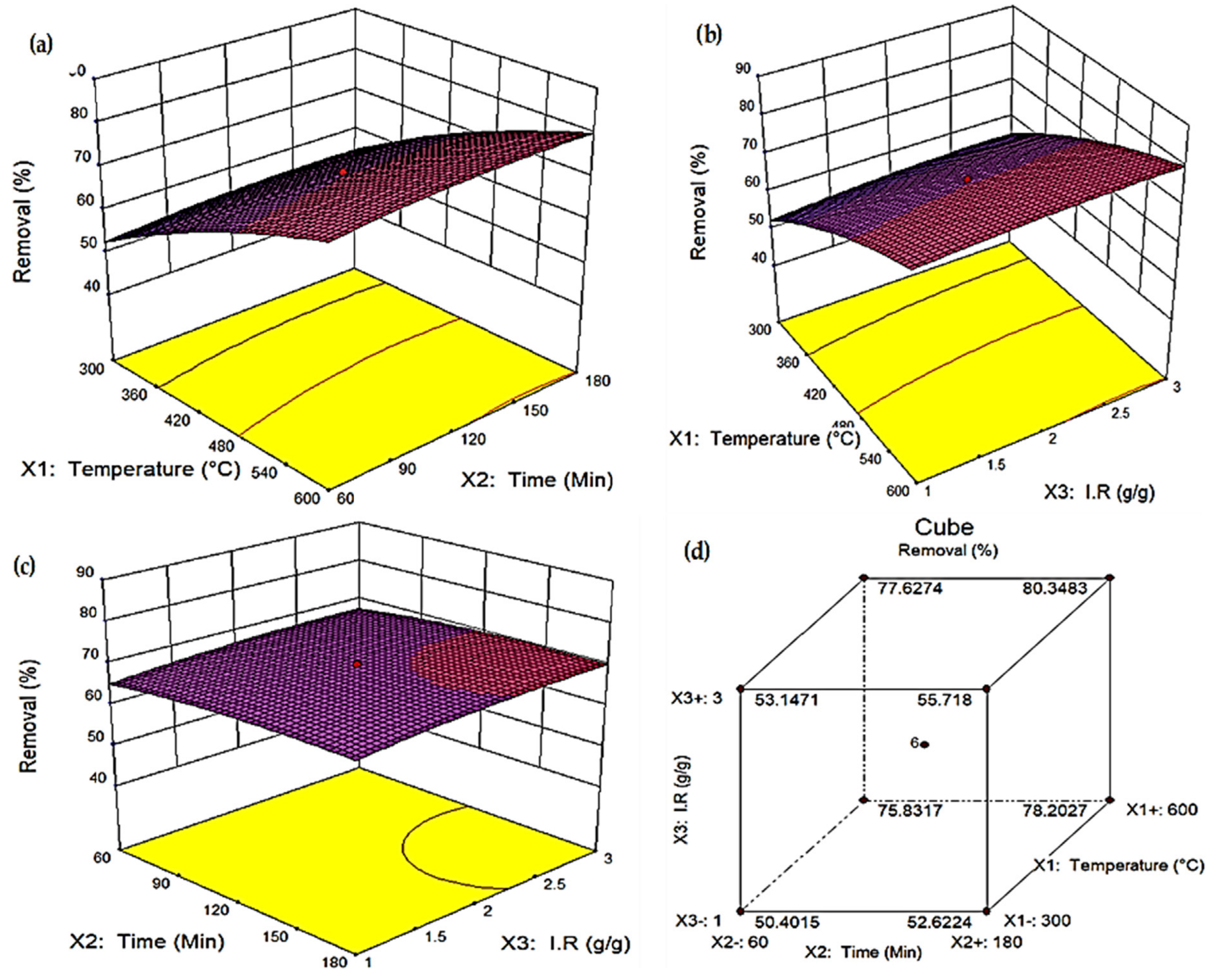

Fig. 6. The combined effect of process variables (a) temperature and time, (b) temperature and impregnation ratio, (c) time and impregnation ratio on Cd (II) removal with interaction effect of dual factors, (d) removal percentage of Cadmium at each factorial point.

3.4.2. Variance (ANOVA) analysis

Analysis of variance is such an analysis that has been utilized to describe the curvature meaning of the response at a 95% confidence interval. In other words, an analysis that helps to determine the need to reject the null hypothesis or support the alternative hypothesis. The Influence of a factor is characterized as changes in response to changes in levels factor [61]. This is often called the primary Influence considering the fundamental interest factors in the experiment. The Models and model terms are only considered necessary when the value of (Prob > F) is<0.05, and the condition is Fisher's statistical test (F test). According to these conditions, several studies have been analyzed [62]. The ANOVA evaluated the quadratic model's significance fitting for three responses biochar yield, cadmium removal, and adsorption capacity, with results indicated in Tables 5,6, and 7. ANOVA findings revealed that equations adequately expressed the actual relationship between each of the responses and relevant variables.

Table 5 shows the variance findings of the quadratic model for biochar yield. The 51.94 variable F-value revealed a significant model. Also, Prob > F values less than 0.05 demonstrated significant model terms. Therefore, temperature (x_1), heating time (x_3), and the interaction term (x_1^2) were significant model terms, while impregnation ration (x_3) and the interaction terms (x_1x_3, x_2x_3, x_2^2, x_3^2)were all insignificant to the Biochar yield. Tables 6 and 7 demonstrate ANOVA for the quadratic model for the removal and adsorption capacity of Cadmium. The Model F-values of 34.25 and 34.31 suggested that the two models were also significant. In the case of applying the products on adsorption study, it is found that temperature (x_1), time (x_2), impregnation ratio (x_3), and interaction terms (x_1x_2, x_1^2) are significant terms to the cadmium removal and cadmium adsorption capacity. The analysis of the above Tables' variance results shows that the variables analyzed are within the spectrum; the quadratic models were competent to predict the yield of biochar, the removal rate of Cadmium, and the adsorption capacity. Responses were plotted against the deviation due to the noise from the reference point selected by adjusting specific ranges to check the optimal relationship between the real and the deviation. Experimental (real) values versus predicted values for the yield of biochars and the removal rate of Cadmium are shown in Fig. 4(a) and Fig. 4(b). As shown, there is a significant correlation between the expected values and the experimental values, and this suggests that models generated successfully capture the relationship between the impregnated biochar preparation variables and the cadmium removal rate.

3.4.3. Biochar yield

It has been found that temperature negatively affects biochar production. However, in a way, it has a positive effect on the consistency of biochar in terms of chemical and physical properties (including pore size distribution and a specific surface area), making biochar rich in carbon atoms and making them able to form pores, whether mesopores or macropore [63]. The possibility of

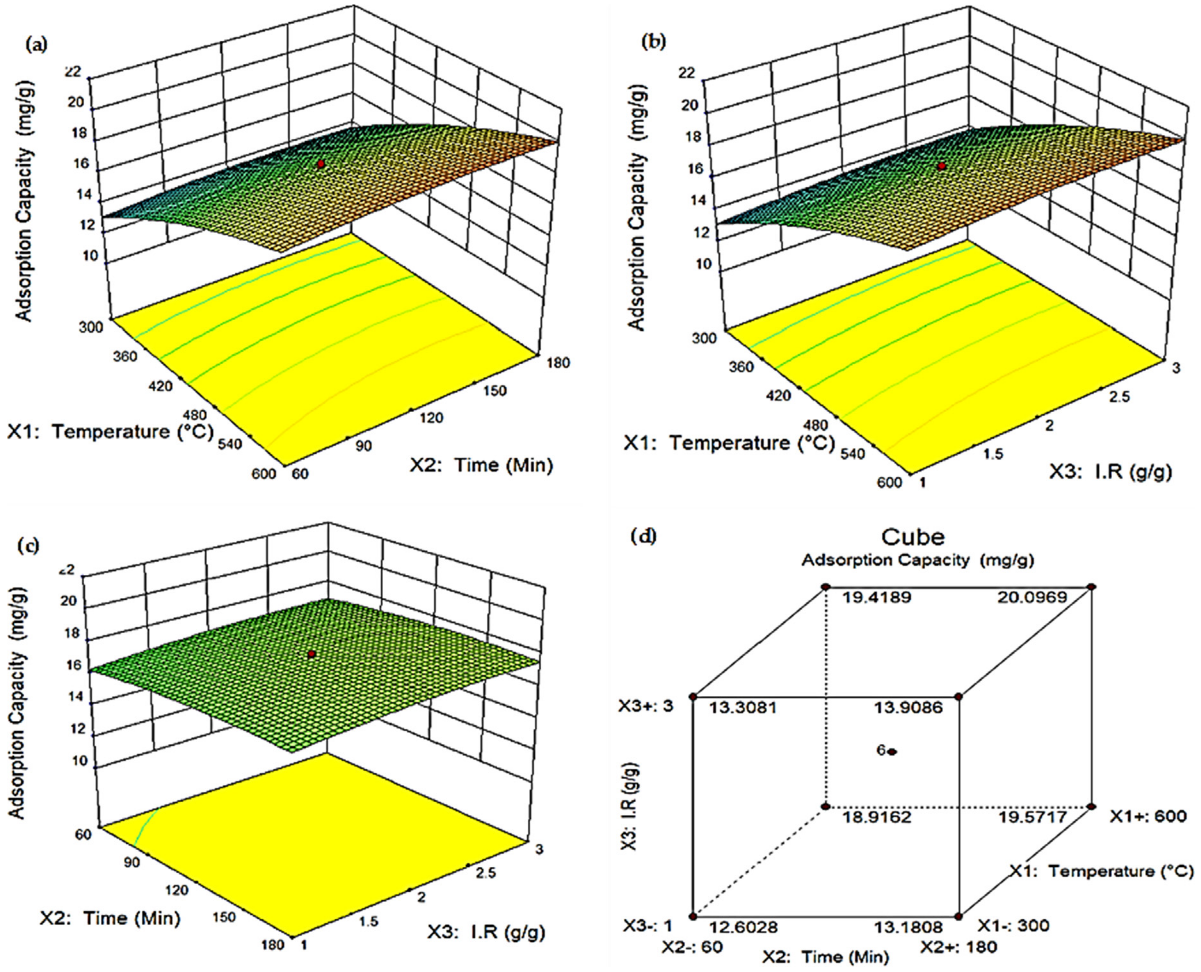

Fig. 7. The combined effect of process variables (a) temperature and time, (b) temperature and impregnation ratio, (c) time and impregnation ratio on cadmium adsorption capacity with interaction effect of dual factors, (d) Cadmium adsorption capacity at each factorial point.

including impregnated biochar characteristics in this study is not possible because the author is planning to put it in other studies, but there are promising signs in the biochar-based adsorbent found on the cadmium removal.

Table 5 found that temperature had the most significant negative impact on biochar yield, with the highest F value (406.60), while time showed a slight effect on biochar yield, with a high F value of 33. The chemical impregnation rate has little effect on the response compared to temperature and time. The quadratic effect of temperature on the yield is also significant compared to reaction time and impregnation ratio. However, the interaction between variables is less obvious. Fig. 5 shows the three-dimensional response surfaces constructed to show the effects of impregnated biochar preparation variables on the biochar yield (Y_1). Fig. 5(a) indicates the relationship between temperature and reaction time. It can be seen from the plot that low temperatures and low time produce more char, which means that both parameters play an essential role in the development of biochar. Fig. 5 (b) illustrates the interaction between temperature and chemical impregnation ratio, and the temperature is considering one of the parameters which affect the biochar qualitatively and quantitively while the chemical impregnation qualitatively affects the biochar. Since the biochar yield is considered qualitative, the interaction between temperature and chemical impregnation is small on the biochar yield compared to the interaction between temperature and reaction time [60]. Through looking at the biochar yield at each factor in Fig. 5(d), biochar yields were seen to decline with rising pyrolysis temperature, reaction time, and chemical impregnation ratio. Maximum yield was obtained when all three variables were at the minimum point within the range studied. This result was also consistent with Siddiqui et al. [42], where temperature and time have been reported as having a significant role in biochar yields derived from pomegranate peel. The explanation for this decrease in biochar yield is that as temperature increases, volatile emissions occur as a result of an increase in dehydration and elimination reactions, as well as an increase in the C-NaOH and nitrogen reaction rate during the pyrolysis, resulting in a decrease in biochar yield [64].

3.4.4. Removal rate and adsorption capacity of cadmium

The response surface three-dimensional diagrams and contour diagrams of the interaction of pyrolysis temperature (X_1), reaction time (X_2), and impregnation ratio (X_3) on the removal rate of Cadmium and adsorption capacity of Cadmium adsorbed by impregnated biochar derived from rice husk are presented in Fig. 6 and Fig. 7 respectively. It can be seen from Figures that the response surface of temperature for removal rate and adsorption capacity is greater than the time and impregnation ratio, and that is apparent on the curvature contour diagram. By looking at Tables 6 and 7, it is proven that the interaction influence between temperature and time was moderate. Although the interaction between temperature and impregnation ratio is moderate but significant effects on the removal rate and adsorption capacity comparing to the yield response.

Table 8
Complementary DOE Validation of the mathematical model (quadratic model).

Pyrolysis temperature, x_1(°C)	Reaction time, x_2(min)	NaOH impregnation ratio, x_3 (g/g)	Yield, Y_1 (%)	Cd^{2+} removal, Y_2 (%)	Adsorption capacity, Y_3(mg/g)
458	120	3	34.5	72	17.8
432	120	3	35.1	69.8	17.1

Table 9
Performance comparison of rice husk biochar with other adsorbents for Cd^{2+} removal.

Adsorbent	Adsorption Capacity (mg/g)	Ref.
Barley Husk Biomass	75.2	[70]
Canola Biomass	46.3	[71]
Azolla Filiculoides	39.46	[72]
Pinecone	92.7	[73]
Peanut Husks	26.88	[74]
Peanut Husk Biochar	28.99	[74]
Banana Peels	5.91	[75]
Walnut shell	11.6	[76]
Chicken manure	10.90	[77]
Corncob's biochar	15.40	[78]
Switchgrass	5.01	[79]
Sugarcane bagasse biochar	6.46	[80]
Rice husk biochar	17.8	This study

Figs. 6(a) and 7(a) illustrate that, when the time is set, the removal rate and the adsorption capacity change little with the temperature rise, and when the temperature is set, the removal rate and the adsorption capacity first increased and then decreased with time changes, and there was a trend of increasing and decreasing. The above figures show that the higher removal rate and adsorption capacity values are in the range of (420 °C to 430 °C) and time in the range of (100 min to 120 min).

Tan et al. [65] have done such a study, which is consistent with this work. It was confirmed that temperature and time have a considerable effect on activated carbon quality as they contribute to the carbon pores' structure. With the activation temperature and even the impregnation ratio, the pore properties have modified dramatically. Sudaryanto et al. [66] obtained that the time did not significantly impact heavy metals treated by activated carbons produced from apricot stones. After all, in this study, all three variables tested had synergistic effects on cadmium removal and adsorption capacity.

3.4.5. Process optimization

Due to the different areas of interest, it is challenging to optimize all the responses that make the product more effective and economical. There are two most essential responses which industries are focusing on them, yield and adsorption capacity. Recently, researchers are focusing more on surface modification of the products. Economic viability comes first, then specific modification based on the targeting pollutant that wanted to remove. Looking forward sustainable perspective, it is essential to recycle some of the wastes, such as agricultural waste (biomass from the second or third crops, residues of harvest, and waste collection). It is used in activated carbon production. For this reason, when adsorbents are made from waste, researchers usually use surface modification. From the above analysis, the product yield (Y_1) increases as the removal rate (Y_2) and adsorption capacity (Y_3) decrease, and vice versa. Therefore, Design-Expert Software (DOE) was then used to make a trade-off between these responses to add the desired functions. The two most suitable laboratory conditions, with 65% desirability, were chosen for verification. Biochar was developed, along with experimental yield values, removal rate, and adsorption capacity, under the experimental conditions described in Table 8. It was noted that the observed experimental values matched the values determined by the models well.

The optimal biochar was obtained using 458 °C temperature, 120 min reaction time, and 3 NaOH impregnation ratio, resulting in 34.5% of biochar yield, 72% of cadmium removal, and 17.8 mg/g of adsorption capacity on Cadmium.

3.5. Performance assessment of biochar compared to Literature-Based adsorbents

The Performance comparison of the rice husk biochar with other adsorbents is shown in Table 9. The treatment activity of rice husk biochar is better than the adsorption capacities of banana peels biochar, walnut shell, chicken manure, switchgrass biochar, and sugarcane bagasse biochar. However, the adsorption capacities of barley husk, Canola biomass, Pinecone biochar, peanut husk, and peanut husk Biochar are higher than that of rice husk biochar. The comparison results show that the rice husk biochar is competitive for application for the treatment of Cd^{2+}containing wastewater.

4. Conclusions

A CCD was performed to analyze biochar yield, cadmium removal, and adsorption capacity on Cadmium of the results of three biochar preparation variables: pyrolysis temperature, time reaction, and chemical impregnation (NaOH: RRH). The preparation variables have been established with quadratic models to align with the biochar yield, cadmium removal, and adsorption efficiency. Analysis of the response surfaces resulting from the models, temperature, time, and NaOH impregnation ratio reveals essential effects on the cadmium removal and adsorption efficiency, while the most relevant effect of the biochar yield was the temperature. The cycle's optimization was conducted, and experimental values were consistent with the expected values for adsorption efficiency and performance. Biochar-based adsorbent derived from rice husk was shown to be a promising adsorbent for the removal of Cadmium ($Cd^{2+)}$ from an aqueous solution.

Declaration of Competing 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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