



## Preparation of methacrylic acid-modified rice husk improved by an experimental design and application for paraquat adsorption

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### ABSTRACT

Methacrylic acid (MAA) grafted rice husk was synthesized using graft copolymerization with Fenton's reagent as the redox initiator and applied to the adsorption of paraquat. The highest grafting percentage of 44.3% was obtained using the traditional kinetic method. However, a maximum grafting percentage of 65.3% was calculated using the central composite design. Experimental results based on the recipes predicted from the statistical analysis are consistent with theoretical calculations. A representative poly-methacrylic acid-g-rice husk (PMAA-g-rice husk) copolymer was hydrolyzed to a salt type and applied to the adsorption of paraquat. The adsorption equilibrium data correlate more closely with the Langmuir isotherm than with the Freundlich equation. The maximum adsorption capacity of modified rice husk is 292.5 mg/g-adsorbent. This value exceeds those for Fuller's earth and activated carbon, which are the most common binding agents used for paraquat. The samples at various stages were characterized by solid-state <sup>13</sup>C NMR spectroscopy.

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### 1. Introduction

Rice husk is the main by-product of the rice milling industry, accounting for approximately 20% of all rice products [1]. The use of modified rice husk as an adsorbent for removing pollutants has attracted considerable attention in the past two decades because of its abundance in nature [2–5]. In a previous work [6], rice husk was grafted with methacrylic acid (MAA) and applied to paraquat adsorption. The results showed that modified rice husk has potential in the emergency rescue of paraquat-poisoned patients. However, the graft efficiency was low and could be further improved.

Statistical experimental design is a powerful tool for defining the effect of one or more variables on a set of responses. It provides a strict mathematical framework for changing all pertinent experimental variables simultaneously and independently of each other. It also establishes a small number of experiments in such a way that the information required is obtained in the most effective and precise way. It has been successfully applied in citric acid production [7,8], cephalosporin C production [9], the coating process

of lidocaine liposomes [10], the accumulation of FR-008/Candidin derivatives CS101 [11], the metabonomic analysis of biofluid [12], the evaluation of ash dioxins concentration from incinerators [13], and the isolation of the emulsifier concentration as a dominant factor in the copolymerization of styrene and n-butyl acrylate [14]. Central composite design (CCD) is a statistically experimental technique, which can be used to estimate the linear, quadratic, and interactive effects of the process variables using empirical models that accurately describe how responses behave at all studied values in the experimental region [15]. Unlike a one-variable-at-a-time strategy, CCD can lower the ultimate number of experiments required to resolve process optimization [16].

Paraquat, 1,1'-dimethyl-4,4'-bipyridinium dichloride, has been widely adopted as a broad-spectrum herbicide, primarily for weed and grass. Because paraquat is highly poisonous, people with a high-dose exposure to paraquat are not likely to survive. In recent years, studies have focused on the mechanism of paraquat-induced Parkinson's disease [17–20] and damage to animal organs [21–23] or plants [24,25]. There have been few studies on the emergency treatment of the paraquat in the human body. Extracorporeal removal may be the only hope for patient survival [26]. Extracorporeal removal treatment combines hemoperfusion with an activated carbon cartridge and washing the digestion system after putting Fuller's earth into the patient's stomach to capture the unabsorbed paraquat. The adsorption capacities of activated carbon and Fuller's earth are about 100 and 60 mg/g-adsorbent [27],

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respectively; there are insufficient for the clinical urgent treatment of paraquat-poisoned patients.

In this study, the graft copolymerization of MAA and rice husk with Fenton's reagent as the redox initiator was carried out. CCD was used in planning experiments to improve the graft percentage compared to that obtained using the traditional kinetic method. The graft copolymer product obtained from the optimum recipe was chosen to investigate the adsorption behavior of paraquat.

## 2. Materials and methods

### 2.1. Materials

Rice husk was obtained from a local rice mill. It was treated with a diluted NaOH aqueous solution to eliminate trace organic residues [28], and then washed several times with distilled water at a pH of 7.0. The clean rice husk was dried at 50 °C in a vacuum oven until a constant weight was achieved. Paraquat (COMLET Chemicals Co., 24% (w/w); a dose of 10 mL is potentially fatal) was diluted to an appropriate concentration before use. Methacrylic acid, ferrous ammonium sulfate, D (+)-glucose (DX), hydrogen peroxide, ammonium chloride, sodium dithionite, and acetone were analytical grade or better and used without further purification.

### 2.2. Grafting procedure

A 250 mL flask with a magnetic stirrer in a temperature-controlled water-bath was used for the graft copolymerization. A series of preliminary experiments was carried out. It was found that the graft copolymer can be obtained with a slightly higher grafting percentage when 9 g of DX is added at fixed amounts of rice husk and MAA monomer. 4 g of rice husk, 10 g of MAA, 9 g of DX, and deionized water were mixed with constant stirring and purged gently with nitrogen for about 30 min. Fe<sup>2+</sup><sub>(aq)</sub> with 0.01 M solution and H<sub>2</sub>O<sub>2(aq)</sub> with 28% (w/w) were separately added into the flask at the same time to initiate the graft copolymerization. The reaction solution, with 200.0 g total deionized water, was well mixed and kept at a constant temperature for 1 h. The copolymerization products were filtered, washed thoroughly with deionized water, and extracted with acetone in Soxhlet for 48 h to obtain the grafted copolymer freed from the polymethacrylic acid (PMAA) homopolymer. The grafting percentage and efficiency were determined gravimetrically [29,30].

### 2.3. Hydrolysis of graft copolymer

PMAA grafted rice husk was added to a conical flask that contained 0.1 M aqueous NaOH. The solution was stirred for 1 h before being filtered and washed in distilled water until it became a neutralized filter liquor. It was then dried at 50 °C under a vacuum. The hydrolyzed product was the sodium salt of PMAA grafted rice husk.

### 2.4. Adsorption of paraquat

Adsorption experiments were performed in a 1 L resin kettle with an agitation rate of 600 rpm for 2 h at 37.5 °C. The adsorption solution comprised 0.2 g of adsorbent sieved from 10 to 40 meshes. Samples (0.2 mL) were taken out using a micropipette at various times. The collected samples were then added to a sodium dithionite/saturated ammonium chloride solution and analysed using a Spectrumlab model-22PC spectrophotometer.

### 2.5. Solid-state <sup>13</sup>C NMR characterization

Solid-state <sup>13</sup>C NMR spectra were obtained from a 400 MHz BRUKER ADVANCE-400 S-S <sup>13</sup>C NMR spectrometer. 1640 scans were

**Table 1**

Central composite design for three independent variables: X<sub>1</sub>, X<sub>2</sub>, and X<sub>3</sub>.

Trials	Variables			% Grafting
	X <sub>1</sub>	X <sub>2</sub>	X <sub>3</sub>	
1	-1	-1	+1	43.88
2	+1	-1	-1	39.54
3	-1	+1	-1	36.40
4	+1	+1	+1	41.13
5	-1	-1	-1	34.49
6	+1	-1	+1	39.79
7	-1	+1	+1	50.54
8	+1	+1	-1	37.61
9	+1.5	0	0	42.85
10	-1.5	0	0	42.74
11	0	-1.5	0	35.70
12	0	+1.5	0	42.10
13	0	0	-1.5	31.14
14	0	0	+1.5	39.78
15	0	0	0	44.17
16	0	0	0	43.63

averaged for each spectrum. The experiment was performed with the sample spinning at a rate of 6.2 kHz. A 5.5 μs pulse corresponding to a 90° P1 angle was chosen. A contact time of 1 ms and a delay time of 5 s were selected. All spectra were recorded for a sample temperature of 25 °C.

### 2.6. Experimental design

The method of central composite design [8,9,31] was used to study the effect of graft copolymerization conditions on the grafting percentage. The concentration of Fe<sup>2+</sup><sub>(aq)</sub> (X<sub>1</sub>), the concentration of H<sub>2</sub>O<sub>2(aq)</sub> (X<sub>2</sub>), and the copolymerization temperature (X<sub>3</sub>) were chosen as the independent variables. The grafting percentage was chosen as the dependent output response variable. Each factor was examined at five levels, coded -1.5, -1, 0, +1 and +1.5, as shown in Table 1. In this system, some of the variables cannot be extended to 1.682 due to an insignificant response; thus, we have modified the axial points at a distance of 1.5. An equation that shows how the values of variables were transformed to the coded values is used:

$$xi' = \frac{xi - x_{cp}}{\Delta xi}$$

where xi' is the independent variable coded value, xi is the independent variable real value, x<sub>cp</sub> is the independent variable real value at the center point, and Δ<sub>xi</sub> is the step change of the real value corresponding to a variation of a unit for the dimensionless value of the variable i. Experimental ranges and levels of the three independent variables are given in Table 2. According to the applied design, twenty combinations were used. Their observations were fitted to the following second order polynomial model:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 \quad (1)$$

where Y is the dependent variable (grafting percentage); X<sub>1</sub>, X<sub>2</sub>, and X<sub>3</sub> are the independent variables; a<sub>0</sub> is the regression coefficient at the center point; a<sub>1</sub>, a<sub>2</sub>, and a<sub>3</sub> are the linear coefficients; a<sub>12</sub>, a<sub>13</sub>, and a<sub>23</sub> are the second order interaction coefficients; and a<sub>11</sub>, a<sub>22</sub>, and a<sub>33</sub> are the quadratic coefficients. The coefficients as well as the optimum concentrations were calculated using statistical Design Expert V. 7.0 software. The quality of fit of the polynomial model equation was expressed by the coefficient of determination, R<sup>2</sup>. Experiments were performed in duplicate and mean values are given.

**Table 2**

Experimental ranges and levels using central composite design of graft copolymerization of methacrylic acid and rice husk.

Independent variables	Range and level				
	−1.5	−1	0	+1	+1.5
Concentrations of Fe <sup>2+</sup> <sub>(aq)</sub> (X <sub>1</sub> ), M	3.38 × 10 <sup>−3</sup>	4.25 × 10 <sup>−3</sup>	6.00 × 10 <sup>−3</sup>	7.75 × 10 <sup>−3</sup>	8.63 × 10 <sup>−3</sup>
Concentration of H <sub>2</sub> O <sub>2(aq)</sub> (X <sub>2</sub> ), M	0.0231	0.0360	0.0618	0.0875	0.1004
Copolymerization temp. (X <sub>3</sub> ), °C	63.8	66.5	72.0	77.5	80.3

### 3. Results and discussion

#### 3.1. Evaluation of the most significant constituents affecting graft copolymerization

The effects of Fe<sup>2+</sup><sub>(aq)</sub> and H<sub>2</sub>O<sub>2(aq)</sub> concentrations ([Fe<sup>2+</sup>] and [H<sub>2</sub>O<sub>2</sub>]) and the reaction temperature (*T*) were investigated for the graft copolymerization of MAA and rice husk. Experiments were conventionally conducted by varying one factor at a time, with the remaining factors held constant. Table 3 shows the effects on the grafting percentage. A maximum value occurred at various values of [Fe<sup>2+</sup>] with [H<sub>2</sub>O<sub>2</sub>] and temperature fixed. Meanwhile, the same maximum grafting percentage was obtained by changing [H<sub>2</sub>O<sub>2</sub>] with [Fe<sup>2+</sup>] and temperature held constant. A similar trend was found when the temperature was changed with [H<sub>2</sub>O<sub>2</sub>] and [Fe<sup>2+</sup>] fixed. The maximum grafting percentage of 44.3% was obtained with 6.25 × 10<sup>−3</sup> M of [Fe<sup>2+</sup>] and 0.064 M of [H<sub>2</sub>O<sub>2</sub>] at 70 °C. This is the best result obtained using the traditional experimental technique. However, the grafting efficiency is only about 17.7% for the product obtained from the reaction conditions. Rice husk generally includes 28–6% cellulose, 21% hemicellulose, and around 21% lignin [2,3]. Therefore, the low grafting efficiency can be attributed to the low content of cellulose in rice husk, which may be the grafted location.

#### 3.2. Improvement with central composite design

In order to improve the grafting percentage and efficiency of copolymerization, the central composite design was applied to select experiments, as shown in Table 1. The grafting percentages of copolymerization products are also listed in the table. Data were analysed using multiple regression analysis. The relationship between the grafting percentage (*Y*) and the test variables in coded

**Table 3**Effects of [Fe<sup>2+</sup>], [H<sub>2</sub>O<sub>2</sub>], and temperature on the grafting percentage of graft copolymerization of methacrylic acid and rice husk factors.

Factors			% Grafting, g-PMAA/g-rice husk
[Fe <sup>2+</sup> ] (M)	[H <sub>2</sub> O <sub>2</sub> ] (M)	Temperature (°C)	
1.25 × 10 <sup>−3</sup>	0.064	70	15.9
2.50 × 10 <sup>−3</sup>	0.064	70	32.0
3.75 × 10 <sup>−3</sup>	0.064	70	38.9
5.00 × 10 <sup>−3</sup>	0.064	70	42.8
6.25 × 10 <sup>−3</sup>	0.064	70	44.3 <sup>a</sup>
7.50 × 10 <sup>−3</sup>	0.064	70	39.4
8.75 × 10 <sup>−3</sup>	0.064	70	33.2
6.25 × 10 <sup>−3</sup>	0.016	70	24.8
6.25 × 10 <sup>−3</sup>	0.032	70	41.8
6.25 × 10 <sup>−3</sup>	0.128	70	36.2
6.25 × 10 <sup>−3</sup>	0.256	70	31.4
6.25 × 10 <sup>−3</sup>	0.064	60	31.5
6.25 × 10 <sup>−3</sup>	0.064	65	37.3
6.25 × 10 <sup>−3</sup>	0.064	75	42.0
6.25 × 10 <sup>−3</sup>	0.064	80	41.3
6.25 × 10 <sup>−3</sup>	0.064	85	36.3

<sup>a</sup> The highest grafting percentage was obtained using the traditional kinetic method.

factors is

$$Y = 43.41 - 0.5859X_1 + 1.426X_2 + 3.241X_3 - 1.176X_1X_2 - 2.501X_1X_3 + 1.034X_2X_3 + 0.3949X_1^2 - 1.336X_2^2 - 2.865X_3^2 \quad (2)$$

To validate of the regression coefficient, analysis of variance was performed. The model *F*-value of 9.66 implies that the model is significant. Values of “Prob > *F*” of less than 0.0500 indicate that the model terms are significant (see Table 4). *R*<sup>2</sup> of this model is 0.8877, which is considered as having a high correlation. Therefore, it is reasonable to apply the model to analyze the trends of the responses. The cross-term of *X*<sub>1</sub>*X*<sub>3</sub> is one of the more significant terms in this model. It indicates that the traditional experiment method cannot exactly describe the behavior of the graft copolymerization.

The 2D contour plots presented in Fig. 1(a)–(d) are the graphical representations of the regression in Eq. (2), from which the grafting percentage, for various added amounts of 0.01 M Fe<sup>2+</sup><sub>(aq)</sub> and 28% (w/w) H<sub>2</sub>O<sub>2(aq)</sub> at four copolymerization temperatures can be predicted. The obtained results indicate that the increase of grafting percentage follows a lower level of Fe<sup>2+</sup><sub>(aq)</sub> and an exclusive H<sub>2</sub>O<sub>2(aq)</sub>. Copolymerization had a better response at 82 °C than it did at other temperatures. It is interesting that the maximum grafting percentage is higher than 65%, which is much larger than the 44.3% obtained from the best traditional experimental technique.

In order to verify the improved effect by statistically designed experiments, four reactions with recipes near the optimal conditions were performed. The grafting percentages of produced copolymers and calculated concentrations of Fe<sup>2+</sup><sub>(aq)</sub> and H<sub>2</sub>O<sub>2(aq)</sub> are listed in Table 5. Experimental results with reaction numbers 1–4 in Table 5 are very close to the theoretical predictions. This similarity between the predicted and observed results reflects the accuracy and applicability of the central composite design as an extremely powerful method for optimizing the copolymerization of MAA and rice husk. The grafting percentages of copolymers using statistical experimental design were over 45% higher than the best result obtained using the conventional experimental technique. The grafting efficiency increased to about 26%.

**Table 4**

Variance analysis of the form fit Eq. (2).

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> -value	Prob > <i>F</i> ( <i>p</i> -value)
Model	522.72	9	58.08	9.66	0.0005
<i>X</i> <sub>1</sub>	4.64	1	4.64	0.77	0.3987
<i>X</i> <sub>2</sub>	27.52	1	27.52	4.58	0.0557
<i>X</i> <sub>3</sub>	143.51	1	143.51	23.87	0.0005
<i>X</i> <sub>1</sub> <i>X</i> <sub>2</sub>	12.55	1	12.55	2.09	0.1764
<i>X</i> <sub>1</sub> <i>X</i> <sub>3</sub>	56.83	1	56.83	9.45	0.0106
<i>X</i> <sub>2</sub> <i>X</i> <sub>3</sub>	9.69	1	9.69	1.61	0.2305
<i>X</i> <sub>1</sub> <sup>2</sup>	1.50	1	1.50	0.25	0.6273
<i>X</i> <sub>2</sub> <sup>2</sup>	16.81	1	16.81	2.81	0.1227
<i>X</i> <sub>3</sub> <sup>2</sup>	78.29	1	78.29	13.02	0.0041
Residual	66.14	11	6.01		
Lack of fit	27.06	5	5.41	0.8310	0.5712
Pure error	39.08	5	6.51		
Cor Total	588.8651	19			

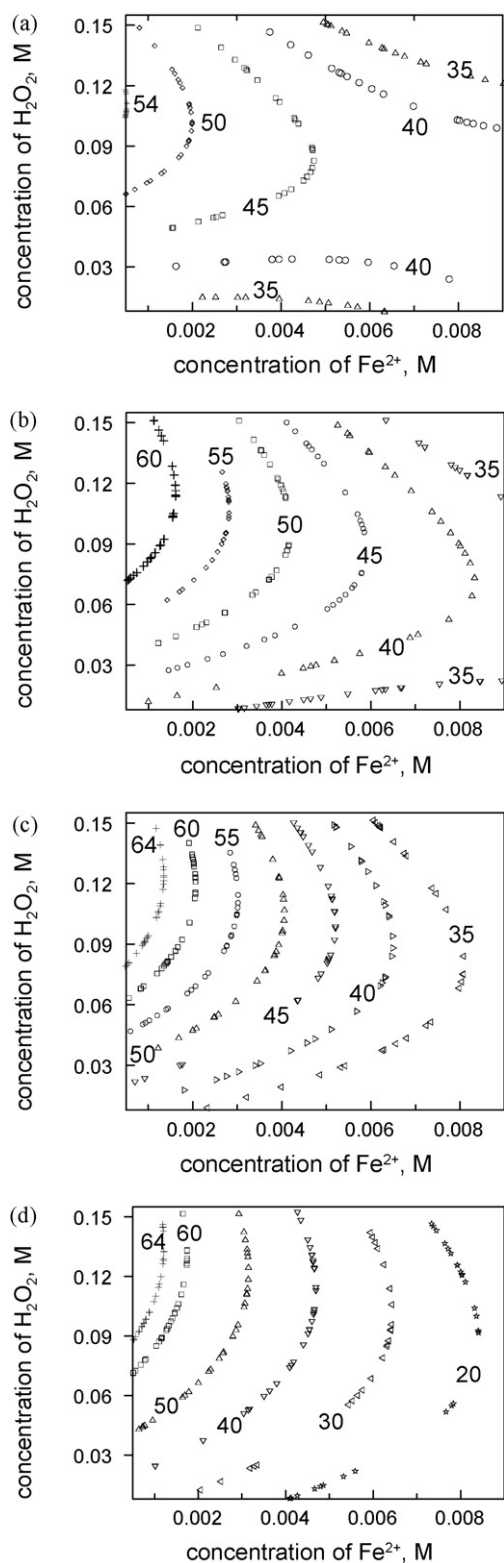


Fig. 1. Contour plot of grafting percentage (%) at copolymerization temperatures of (a) 72 °C, (b) 78 °C, (c) 82 °C, and (d) 88 °C.

For economic considerations, copolymerizations with recipes 1 and 3 in Table 5 were used without DX to check the effect of omitting DX. The % grafting of copolymers, nos. 5 and 6 in Table 5, are about 10% lower than those obtained with DX addition. This trend is consistent with the results of preliminary experiments.

Table 5

Comparison of theoretical and experimental grafting percentages of graft copolymerization of MAA and rice husk from the central composite design at 82 °C.

No.	[Fe <sup>2+</sup> ] (M)	[H <sub>2</sub> O <sub>2</sub> ] (M)	%G, theo	%G, exp
1	0.5 × 10 <sup>-3</sup>	0.14	65.34	68.7 64.7
2	1.0 × 10 <sup>-3</sup>	0.12	63.19	62.6 63.3
3	1.0 × 10 <sup>-3</sup>	0.14	62.82	61.9 63.8
4	1.5 × 10 <sup>-3</sup>	0.14	60.31	58.4
5 <sup>a</sup>	0.5 × 10 <sup>-3</sup>	0.14		61.7
6 <sup>a</sup>	1.0 × 10 <sup>-3</sup>	0.14		54.9

<sup>a</sup> Reactions with no DX added.

### 3.3. Adsorption of paraquat

The PMAA-modified rice husk of no. 1 in Table 5 was hydrolyzed with 0.1 M NaOH<sub>(aq)</sub>, and used as the model adsorbent to study in detail the adsorption behavior of paraquat at various initial concentrations. The adsorption time to reach equilibrium was around 20 min, which was shorter than those associated with other modified rice husk adsorbents, such as Cu and Pb adsorbed by the tartaric acid-modified rice husk [3,4] and Cd adsorbed by phosphate-treated rice husk [32].

Fig. 2 plots the Langmuir and Freundlich correlations of paraquat adsorbed by the adsorbent of hydrolyzed graft copolymer of rice husk and PMAA. Table 6 presents calculated results. The correlation coefficients, *r*, from the linear regression are 0.9988 and 0.9792 for the Langmuir and Freundlich equations, respectively. Therefore, the Langmuir model fitted the experiment results more closely than did the Freundlich model. The monolayer adsorption capacity, *q<sub>m</sub>*, was determined from the coefficients of the Langmuir equation to be 292.5 mg/g-adsorbent. The adsorption capacity is over three times higher than that of an activated carbon cartridge, which is used in the hemoperfusion process for paraquat-poisoned humans, and five times higher than that of Fuller's earth, which is used as an adsorbent during the enema. It is also higher than activated bleaching earth which is a new adsorbent of paraquat [33].

Table 6

Comparison of Langmuir and Freundlich adsorption isotherms.

Isotherm	Isotherm equation	<i>r</i>	<i>q<sub>m</sub></i> (mg/g-adsorbent)
Langmuir	$q = 13.98C / (1 + 0.0478C)$	0.9988	292.5
Freundlich	$q = 34.86C^{(1/2.135)}$	0.9792	–

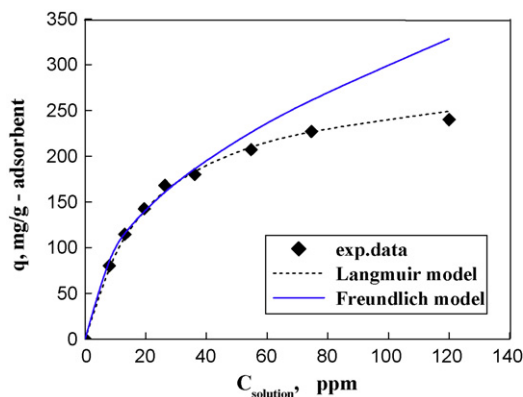
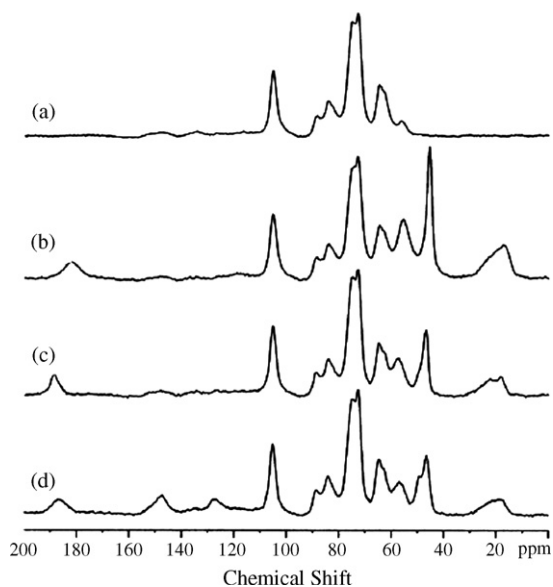


Fig. 2. Langmuir and Freundlich isotherms for paraquat adsorption of hydrolyzed graft copolymer of PMAA and rice husk adsorbent.



**Fig. 3.** Solid-state  $^{13}\text{C}$  NMR spectra of (a) rice husk, (b) graft copolymer of PMAA and rice husk, (c) hydrolyzed copolymer, and (d) hydrolyzed copolymer after adsorption of paraquat.

The results indicate that modifying rice husk by the graft copolymerization of MAA greatly increases the adsorption capacity of paraquat. The PMAA-modified rice husk is a potential future paraquat adsorbent.

Free energy change ( $\Delta G$ ) was evaluated to confirm the adsorption nature. The Langmuir constant  $k$  can be used for calculating the free energy change using the following equation [34]:

$$\Delta G = -RT \ln k$$

where  $R$  is the gas constant,  $T$  is the absolute temperature, and  $k$  is the adsorption constant. The calculated  $\Delta G$  equal to  $-9.983$  kJ/mol, shows that paraquat adsorption is favorable.

#### 3.4. Solid-state $^{13}\text{C}$ NMR characterization

Solid-state  $^{13}\text{C}$  NMR is one of the most convenient techniques for measuring the structures of rice husk and paraquat. Fig. 3 shows the solid-state  $^{13}\text{C}$  NMR spectra. Fig. 3(a) shows the spectrum of pure rice husk. The marked signal at 105 ppm is C-1 of cellulose and the group of weak signals between 115 and 160 ppm reflect the aromatic carbons of lignin [35]. The spectra of PMAA-g-rice husk before and after hydrolysis are shown in Fig. 3(b) and (c), respectively. A broad extra signal at 18 ppm is shown, which is assigned to the methyl carbon of methacrylic acid. Fig. 3(d) shows the spectra after the adsorption of paraquat by the hydrolyzed PMAA-g-rice husk. The signals at 128 and 146 ppm are  $\text{N}^+-\text{CH}=\text{}$  and  $=\text{CH}-$ , respectively, and the shoulder type signal at 48 ppm can be attributed to the  $\text{H}_3\text{C}-\text{N}^+$  of paraquat. The graft of PMAA on rice husk and the adsorption of paraquat are clearly shown.

#### 4. Conclusion

PMAA grafted rice husk can be prepared by grafting copolymerization using Fenton's reagent as the redox initiator. The main factors affecting the grafting percentage and grafting efficiency are the reaction temperature and the concentrations of  $\text{Fe}^{2+}_{(\text{aq})}$  and  $\text{H}_2\text{O}_{2(\text{aq})}$ . The highest grafting percentage of MAA onto rice husk is 44.3% when the conventional copolymerization method is adopted at fixed amounts of MAA monomer and added rice husk. A central composite design, including the three main factors, was used

to improve the grafting behavior. Experimental results for the statistical strategy are consistent with theoretical predictions. The maximum grafting percentage of MAA onto rice husk increased by over 45%, reaching about 65%.

Carboxylic groups grafted to the surface of the rice husk can be hydrolyzed to a salt type with dilute  $\text{NaOH}_{(\text{aq})}$  and readily utilized to adsorb paraquat ions from an aqueous solution. The rapid uptake and high adsorption capacity make the PMAA-modified rice husk a highly promising alternative adsorbent of paraquat. The Langmuir isotherm is more accurate than that of Freundlich. The monolayer adsorption capacity is 292.5 mg/g-adsorbent, which exceeds that of paraquat adsorbents used currently. Therefore, PMAA-modified rice husk is a potential adsorbent in clinical urgent treatment for paraquat-poisoned patients. A series analysis using solid-state  $^{13}\text{C}$  NMR confirms the graft copolymerization and the adsorption of paraquat.

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