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Factorial experimental design for superabsorbent carbonaceous polymer through inverse suspension polymerization method

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Abstract. This paper studies on the effect of synthesis parameters towards the performance of superabsorbent carbonaceous polymer (SPC) via inverse suspension polymerization method. The SPC consists of acrylic acid, acrylamide, and carbon filler. In this work, four independent factors (synthesis parameters) i.e. the content of carbon filler, the content of initiator, the content of crosslinker and reaction temperature that affecting the water absorbency of SPC was investigated. A 2^4 full factorial design was used to investigate the effect of independent factors as well as the interaction factors on the water absorbency of SPC. Apart from reaction temperature, other factors were shown to have the significant effect on the water absorbency of SPC. The results showed the order of significance: initiator's content > crosslinker's content > carbon filler's content > reaction temperature. Meanwhile, interaction factor of carbon filler's and crosslinker's content had the strongest effect on the water absorbency amongst the other interactions. The highest water absorbency of the SPC was achieved at the conditions (filler's content (A): 0.05wt%; initiator's content (B): 0.10wt%; crosslinker's content (C): 0.001wt%, and reaction temperature: 70°C).

1. Introduction

Superabsorbent polymers (SAP) are three-dimensionally cross-linked hydrophilic polymers with the ability to absorb, swell and retain large volumes of water, saline water or aqueous solutions up to hundreds of times their own weight without dissolving [1,2]. High-performance superabsorbent materials conventionally are synthesized from the polymerization process of acrylic esters, polyacrylamide and other unsaturated monomers [3,4]. Inverse suspension polymerization technique is an attractive method to synthesis SAPs in powder or microspheres (beads) form [5].

In this work, SAPs have been incorporated with carbon fiber (filler) due to the value added of the carbon element in soil. The incorporation of these fillers ensures a good balance between high swelling and adequate mechanical properties and even can create new ones (e.g. biocompatibility, biodegradability, antimicrobial, etc.) [6].

Back in the time, one-factor-at-a-time (OFAT) approach is used for running experiments. By using OFAT, the estimation of the factor effects is less precise and interaction between factors cannot be

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estimated because there is no information and this can mislead the optimal conditions of the process. On the other hand, Design of Experiments (DOE) is an alternative answer to the above challenges. DOE is one of the most useful statistical techniques as it offers a number of advantages. It able to cover a wide range of experimental statistics, obtain unambiguous results with a minimum number of experiments and discover the presence of interaction between the factors of the process. When the interaction effect of several factors on the response need to be study, factorial designs are widely applied particularly 2^k factorial design in the beginning stages of experimental work. 2-level factorial designs have been introduced in screening the factors in which to determine the degree of effect from the factors [7,8].

There has not been any literature reported on the application of full factorial design to determine the effects of factors on the water absorbency of superabsorbent carbonaceous fiber polymer (SPC) via inverse suspension polymerization method. In the present study, the SPC will be synthesized by inverse suspension polymerization with acrylic acid (AA), acrylamide (AM) and carbonaceous fiber as raw material. The effects of carbonaceous fiber filler, N,N'-methylenebisacrylamide (NNMBA) crosslinking agent, ammonium persulfate (APS) initiator and reaction temperature on water absorption are explored. This preparation of SPC using inverse suspension polymerization will become the major challenge due to the properties of the materials used and it is still new. Therefore, 2^4 level factorial design was used to design the experiment, generate a model and optimize the process variable. The overall objective is to maximize the water holding capacity as well as improving the properties of SPC.

2. Experimental

2.1. Materials

Chemicals used for synthesizing the SPC were acrylic acid (AA), acrylamide (AM), N,N'-methylenebis(acrylamide) (NNMBA), ammonium persulfate (APS), sodium hydroxide (NaOH), sorbite anhydride monostearic acid ester (Span-80), cyclohexane and methanol supplied by Merck. Carbonaceous fiber (filler) was obtained by processing Kenaf via hydrothermal carbonization process (HTC).

2.2. Methods

2.2.1. Production of superabsorbent carbonaceous fiber polymer (SPC) via inverse suspension polymerization method.

A continuous phase was prepared by mixing cyclohexane and span-80 in a five-neck round bottom flask equipped with a magnetic stirrer, reflux condenser, nitrogen line and immersed in a water bath. Then, the specific amount of carbonaceous fiber (0.01-0.05wt%) and NNMBA (0.001-0.004wt%) were added to the continuous phase. The mixture was then stirred with 300rpm agitation speed until it was well-mixed. Next, a dispersed phase was prepared by adding partially neutralized acrylic acid, sodium hydroxide, acrylamide and the specific amount of APS (0.10-0.25wt%) in a beaker. After that, the dispersed phase was added slowly into the flask that contains the continuous phase and purged with nitrogen gas for 15 minutes. It was then stirred and the reaction was held for 3 hours at the desired temperature (50-70°C). The resulted polymers were then filtered, washed with methanol and dried at 60°C in an oven for 24 hours.

2.2.2. Experimental design.

In the present study, 4 factors e.g. content of filler, initiator, crosslinker, and reaction temperature were taken into account to investigate their effects on the water absorbency of SPC using a 2^4 full factorial design. Table 1 shows the designed factors and levels to be employed for the experiments. A total of 16 experiments runs were conducted. Factor level was coded as -1 (low level) and +1 (high level) where low level indicates the lowest range of the factors and high level indicates the highest range of the factors. The experiments were carried in 3 replicates. The order in which the experiments were run randomized to avoid systematic errors. The outputs of the experimental design were analyzed with Design Expert (DX7) software to evaluate the effects as well as the statistical parameters. The response was analyzed using ANOVA based on the p-value with 95% of confidence level.

Table 1. 2^4 full factorial design matrix and the results.

Standard Order	Run Order	Factor 1 A: Filler wt%	Factor 2 B: Initiator wt%	Factor 3 C: Crosslinker wt%	Factor 4 D: Temperature ^{0}C	Response Water Absorbency g/g	
						Standard Deviation	Average
1	2	0.01 (-1)	0.10 (-1)	0.001 (-1)	50 (-1)	11.218	105.684
2	4	0.05 (+1)	0.10 (-1)	0.001 (-1)	50 (-1)	15.609	160.292
3	5	0.01 (-1)	0.25 (+1)	0.001 (-1)	50 (-1)	16.547	66.311
4	15	0.05 (+1)	0.25 (+1)	0.001 (-1)	50 (-1)	1.591	84.877
5	13	0.01 (-1)	0.10 (-1)	0.004 (+1)	50 (-1)	0.967	105.675
6	1	0.05 (+1)	0.10 (-1)	0.004 (+1)	50 (-1)	2.948	81.873
7	12	0.01 (-1)	0.25 (+1)	0.004 (+1)	50 (-1)	0.613	70.519
8	7	0.05 (+1)	0.25 (+1)	0.004 (+1)	50 (-1)	1.285	64.785
9	11	0.01 (-1)	0.10 (-1)	0.001 (-1)	70 (+1)	14.808	128.644
10	6	0.05 (+1)	0.10 (-1)	0.001 (-1)	70 (+1)	8.130	178.247
11	14	0.01 (-1)	0.25 (+1)	0.001 (-1)	70 (+1)	2.448	64.338
12	3	0.05 (+1)	0.25 (+1)	0.001 (-1)	70 (+1)	8.106	73.260
13	9	0.01 (-1)	0.10 (-1)	0.004 (+1)	70 (+1)	24.271	108.924
14	10	0.05 (+1)	0.10 (-1)	0.004 (+1)	70 (+1)	1.752	101.011
15	16	0.01 (-1)	0.25 (+1)	0.004 (+1)	70 (+1)	3.347	54.644
16	8	0.05 (+1)	0.25 (+1)	0.004 (+1)	70 (+1)	0.853	52.885

Factor	Level		Units	Type
	Low (-1)	High (+1)		
Filler	0.01	0.05	wt%	Numeric
Initiator	0.1	0.25	wt%	Numeric
Crosslinker	0.001	0.004	wt%	Numeric
Temperature	50	70	^{0}C	Numeric

2.2.3. Water absorbency test.
Tea bag method was used to measure the water absorbency of the synthesized SPC. A specific amount of SPC was put into the tea bag and then immersed in a beaker of distilled water. After 24 hours, the tea bag was allowed to drain for 10 minutes to remove the excess water and then been weighed. Water absorbency was calculated using below equation;

$$\boldsymbol{Water\ Absorbency, Q\left(\frac{g(H_2O)}{g\ sample}\right) = \frac{m_2 - m_1}{m_1}} \quad (1)$$

Where m_2 is the weight of tea bag after reach equilibrium and m_1 is the initial weight of tea bag before immersed in distilled water [10].

3. Result and discussion

3.1. Screening of factors affecting the water absorbency of SPC

A total of 16 experimental runs were performed to screen significant process parameters as per 2^4 full factorial design (Table 1). The four parameters were studied simultaneously at a low and high level to determine the degree of the effect of the factors on the response. Independent factor e.g. filler's content (0.01 to 0.05wt %), initiator's content (0.1 to 0.25wt %), crosslinker's content (0.001 to 0.004wt %), and reaction temperature (50 to 70°C) have been taken into account to investigate their effect on the water absorbency. The water absorbency was ranged from 52.885 g water/g sample to 178.247 g water/g sample. The highest water absorbency of the SPC was achieved at the conditions (filler's content (A): 0.05wt%; initiator's content (B): 0.10wt%; crosslinker's content (C): 0.001wt%, and reaction temperature: 70°C).

3.2. Statistical analysis on water absorbency

The significance of the interaction between the factors on water absorbency was evaluated through an effects list of % contribution more than 1 as shown in Table 2. It is noted that the interaction of B*C had the strongest effect on the water absorbency of SPC. The order of significance of main factors: B > C > A > D.

Table 2. Effects list of standardized effects for water absorbency.

Term	Standardized Effects	Sum of Squares	% Contribution
A-filler	11.56	534.66	2.65
B-Initiator	-54.84	12030.31	59.59
C-Crosslinker	-27.67	3061.88	15.17
D-Temperature	2.74	30.08	0.15
AB	-6.56	172.27	0.85
AC	-21.36	1825.58	9.04
AD	0.65	1.70	8.420E-003
BC	16.18	1047.02	5.19
BD	-13.08	684.70	3.39
CD	-4.09	66.88	0.33
ABC	12.62	636.87	3.15
ABD	-2.07	17.13	0.085
ACD	4.31	74.45	0.37
BCD	0.54	1.18	5.839E-003
ABCD	-0.91	3.31	0.016

The relative importance of main effects and their interactions can be seen by Pareto chart as shown in Figure 1. The bonferroni limit line in the chart indicates the maximum statistically significant effect magnitude meanwhile t-value limit line indicates the minimum statistically significant effect magnitude. Any effect that extends beyond this two lines is potentially important. According to the chart in which the bar lengths are proportional to the absolute value of the estimated effects with 95% confidence level, it was possible to verify that the B demonstrates the most significant effect on the water absorbency. The effect of C on water absorbency was half of the effect of B. Even though, the interaction of A*C was lower in comparison with main effects of B and C, but it was also statistically significant at 95% confidence level. The interaction of A*A was followed by the interaction of B*C. Although the main effect of A, the interaction of A*B*C and the interaction of B*D have significant effects on water absorbency, their levels were only a small amount compared to others. Meanwhile, the linear effect of D had been verified as not statistically significant on the water absorbency.

The blue colour bar shows a negative effect of a given factor. A negative effect of a given factor (i.e., B and C) indicates that the respond (water absorbency of SPC) decreases with the increase in the value of that factor. While the orange colour bar shows a positive effect of a given factor. A positive effect of a given factor (i.e., A) indicates that the response increases with the increase in the value of that factor [9]. This was consistent with the findings of [2] and [4] as the increase of carbon filler will give greater values of water absorbency due to the carbonaceous fiber has cross-linked with the polymer chain.

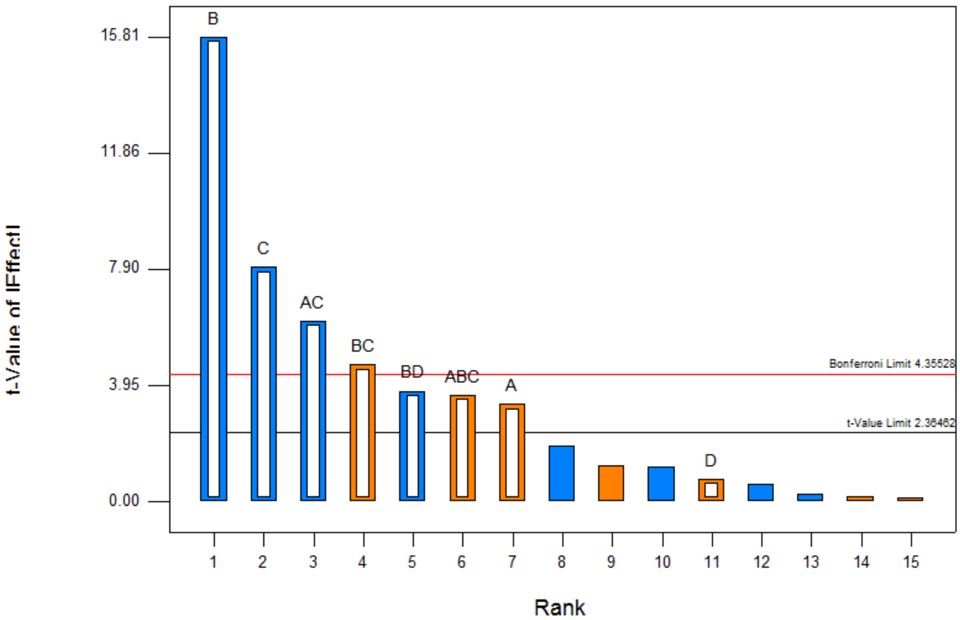

Figure 1. Pareto chart of the standardized effects.

Figure 2 shows the ANOVA analysis for SPC. The p-value of main effects of A, B, and C were less than 0.05 implies the significance of the independent factors. It was necessary to examine any interactions that were important in the experimental design analysis; the interactions of A*C, B*C, B*D, and A*B*C show their significance at p-value smaller than 0.05. The main effects of B and C showed a remarkable model (p<0.0001), thus they were the most statistically significant effects from all.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	19851.09	8	2481.39	51.56	< 0.0001	significant
A-Filler	*534.66*	*1*	*534.66*	*11.11*	*0.0125*	
B-Initiator	*12030.31*	*1*	*12030.31*	*249.95*	*< 0.0001*	
C-Crosslinker	*3061.88*	*1*	*3061.88*	*63.62*	*< 0.0001*	
D-Temperature	*30.08*	*1*	*30.08*	*0.62*	*0.4552*	
AC	*1825.58*	*1*	*1825.58*	*37.93*	*0.0005*	
BC	*1047.02*	*1*	*1047.02*	*21.75*	*0.0023*	
BD	*684.70*	*1*	*684.70*	*14.23*	*0.0070*	
ABC	*636.87*	*1*	*636.87*	*13.23*	*0.0083*	
Residual	336.91	7	48.13			
Cor Total	20188.00	15				

Figure 2. ANOVA analysis.

Two model terms; B and C were selected for model building with values of Prob>F less than 0.0001 which indicate both of the model terms were the most statistically significant. In the valid range from -1 to +1 for the experimental conditions used in this study, the determination coefficient of the proposed mathematical model can explain about 98.33% of the variance (R^2).

4. Conclusion

The effects of four factors e.g. the content of carbon filler (A), the content of initiator (B), the content of crosslinker (C) and reaction temperature (D) on water absorbency of SPC were studied using 2^4 full factorial design. All independent factors except the reaction temperature were found to have a significant effect on the water absorbency. The sequence of the significant main effects with respect to decreasing of effect was found to be: initiator's content > crosslinker's content > carbon filler's content > reaction temperature. Meanwhile, interaction factor of carbon filler's and crosslinker's content had the strongest effect on the water absorbency amongst the other interactions. The highest water absorbency of the SPC was achieved at the conditions (filler's content (A): 0.05wt%; initiator's content (B): 0.10wt%; crosslinker's content (C): 0.001wt%, and reaction temperature: 70°C). The results showed that full factorial design is convenient in investigating the effect of a large number of factors with a minimum number of experiments instead of OFAT.

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