

Oil Palm Ash/ $\text{Ca}(\text{OH})_2/\text{CaSO}_4$ Absorbent for Flue Gas Desulfurization

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The preparation, optimization and activity of active absorbent prepared from oil palm ash for the removal of SO_2 in flue gas from combustion systems were investigated. The absorbent was prepared from oil palm ash, calcium hydroxide and calcium sulfate using a water hydration process. A Central Composite Design (CCD) was used to study the influence of various absorbent preparation variables – hydration period, amount of oil palm ash, and amount of CaSO_4 – on the BET (Brunauer-Emmett-Teller) specific surface area of the resulting absorbent. The surface areas of the absorbents obtained were in the range of 18.7–147.2 m^2/g . It was found that all three absorbent preparation variables studied have a significant positive influence on the BET surface area of the resulting absorbent. An empirical model was then developed to correlate the three absorbent preparation variables to the BET surface area of the resulting absorbent. The model showed significance at a confidence level of 95 % using Analysis of Variance (ANOVA). Based on the empirical model, a maximum specific surface area of 128.6 m^2/g exists within the range of the experimental variables investigated. The hydration conditions that result in the maximum surface area are a hydration period of 10 h, amount of oil palm ash 15.0 g, and amount of CaSO_4 2.7 g. Experimental validations of these predicted optimum hydration conditions gave surface areas in the range of 125.9–129.5 m^2/g . These results are in excellent agreement with the predicted value. In addition, desulfurization activity tests showed that the absorbent derived from oil palm ash/ $\text{Ca}(\text{OH})_2/\text{CaSO}_4$ exhibited a higher desulfurization capacity compared to its starting materials.

1 Introduction

Lately, environmental regulations all over the world are becoming more restrictive concerning the control of atmospheric pollution produced in the flue gas from combustion systems burning liquid and solid fuels such as coal and oil. The control system is mainly focused on sulfur dioxide (SO_2) reduction due to its toxic and acidic characteristics. Apart from being the primary cause of acid rain, which damages buildings, vegetation, and water ground cycles, SO_2 also causes the formation of secondary particles in the atmosphere that impair visibility. Inhalation of SO_2 is also considered to be toxic to humans. Animal tests indicated that SO_2 assists in the carcinogenic activity of other agents [1]. Therefore, there is a need to remove/reduce the SO_2 concentration in the flue gas from combustion systems using appropriate control technology before emitting it to the environment.

Presently, in the practical process SO_2 is removed using various types of flue gas desulfurization (FGD) units. A wet-type FGD unit based on a limestone-gypsum method is most widely used and suitable for large scale boilers such as those installed in coal or oil fired power plants. Although the wet process has a high efficiency in removing SO_2 , it has a lot of disadvantages. The main disadvantages are the large space required for installation, the large volume of water required, and the high capital and operating expenses. On the other hand, dry-type FGDs offer an attractive alternative to the wet-type FGD. Basically, dry-type FGD systems use dry

powdery absorbent to remove SO_2 from the flue gas. Many studies have shown that when siliceous materials such as coal fly ash are mixed with calcium hydroxide ($\text{Ca}(\text{OH})_2$) or calcium oxide (CaO) in a hydration process, absorbents with high SO_2 capture capacities could be attained [2–12]. The absorbents were found to contain complex compounds of Ca, Si, Al, and O ions and hydrated water which has a high surface area [2, 8, 12]. These reactive species are formed from the pozzolanic reaction between silica (SiO_2) and/or alumina (Al_2O_3) eluted from the ash and $\text{Ca}(\text{OH})_2/\text{CaO}$. The structural properties of the absorbent, particularly the specific surface area, are believed to play an important role in SO_2 capture. Some studies have shown that higher desulfurization activity correlates with higher absorbent specific surface area [6, 8].

This study presents the results of using oil palm ash as the source of siliceous material for the synthesis of absorbent for flue gas desulfurization. Oil palm ash is an abundant agricultural solid waste in tropical countries like Malaysia and Thailand. The ash is produced after the burning of oil palm fibers and shells as boiler fuel to produce steam for palm oil mill consumption. It was reported that almost 4 million tons of ash is produced annually in Malaysia. Other than the utilization of oil palm ash as a cement replacement material and as an absorbent for the removal of zinc from aqueous solutions [13], most of the ash is disposed off in landfill that requires a lot of land area. Therefore, utilization of oil palm ash should be further investigated.

In this study, a central composite design (CCD) was conducted to simultaneously study the influence of three absorbent preparation variables (hydration period, amount of oil palm ash, and amount of CaSO_4) on the BET specific surface area of the absorbent. From the results of the CCD, an

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empirical model was then developed to correlate the absorbent surface area to the preparation variables. The empirical model will then be used to optimize the BET surface area of the absorbent. The absorbent will also be tested for its activity in SO₂ absorption.

2 Experimental Section

2.1 Absorbent Preparation

The raw materials used for the absorbent preparation were oil palm ash, calcium hydroxide (Ca(OH)₂) and calcium sulfate (CaSO₄). The oil palm ash was provided by United Oil Palm Mill, Pulau Pinang, Malaysia, while the Ca(OH)₂ and CaSO₄ were obtained from BDH Laboratories, England. The chemical composition of the oil palm ash was determined using a Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer and is shown in Tab. 1. The BET specific surface areas of the raw materials (measured on an Autosorb 1C Quantachrome analyzer) are shown in Tab. 2.

Table 1. Chemical composition of oil palm ash.

Composition	Percentage (%)
SiO ₂	35.6
Al ₂ O ₃	4.8
CaO	12.0
Fe ₂ O ₃	2.0
MgO	7.2
K ₂ O	11.0
P ₂ O ₅	6.8
C	12.0
Others	1.7
Ignition loss	6.9

Table 2. BET specific surface areas of the starting materials.

Starting materials	Specific surface area [m ² /g]
Oil palm ash	8.6
Ca(OH) ₂	6.2
CaSO ₄	4.9

To prepare the absorbent, 5 g of Ca(OH)₂ was added to 100 mL of water at 65 °C. Specific amounts of oil palm ash and CaSO₄ were then added to the slurry simultaneously. The slurry was then heated to 90 °C for a period of time for the hydration process to occur. The resulting slurry was then filtered and dried at 200 °C for 2 h. The prepared powdery absorbent was then palletized, crushed and sieved to produce the required particle size range of 250–300 μm. The hydration period and

amounts of oil palm ash and CaSO₄ were varied in accordance to an experimental design described below. The BET surface areas of the absorbents were analyzed as described above.

2.2 Experimental Design

The experimental design chosen for this study was the Central Composite Design (CCD) that helps in investigating the linear, quadratic and cross-product effects of the three absorbent preparation variables on the specific surface area of the absorbent [14]. The three absorbent preparation variables studied were the hydration period, amount of oil palm ash, and amount of CaSO₄. Tab. 3 lists the range and levels of the three absorbent preparation variables studied. The CCD comprises a two level full factorial design (2³ = 8), six axial or star points and six center points. The value of α for this CCD is fixed at 1.68 [14]. The complete design matrix of the experiments employed and results are given in Tab. 4. All variables at zero level relate to the center points, and the combination of each of the variables at either its lowest level (−1.68) or highest level (+1.68) with the other variables at zero level constitute the axial points. The experimental sequence was randomized in order to minimize the effects of uncontrolled factors.

The responses of the specific surface areas in Tab. 4 were used to develop an empirical model that correlates the specific surface area to the absorbent preparation variables using a second degree polynomial equation, as shown in Eq. (1):

$$Y = b_0 + \sum_{i=1}^3 b_i x_i + \left(\sum_{i=1}^3 b_{ii} x_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (1)$$

where Y is the predicted specific surface area (m²/g), b₀ is the constant coefficient, b_i is the linear coefficient, b_{ij} is the interaction coefficient, b_{ii} is the quadratic coefficient, and x_i, x_j are the coded values of the absorbent preparation variables.

2.3 Model Fitting and Statistical Analysis

Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used for regression analysis of the experimental data to fit the second degree polynomial equation, and also for evaluation of the statistical significance of the empirical model developed. The software was also used to identify the optimum surface area within the range of absorbent preparation variables studied.

2.4 Desulfurization Activity Study

The desulfurization activity of the absorbents was tested using a fixed bed reactor. The reaction zone was contained in a 0.01 m inner diameter stainless steel tube fitted in a furnace for isothermal operation. The absorbent (0.7 g) was packed in the center of the reactor supported by glass wool. A stream of feed gaseous mixture containing 2000 ppm of

Table 3. The absorbent preparation variables chosen for this study.

Variable	Coding	Units	Levels				
			-1.68	-1	0	+1	+1.68
Hydration period	x ₁	h	3.18	10.0	20.0	30.0	36.82
Amount of oil palm ash	x ₂	g	1.6	5.0	10.0	15.0	18.4
Amount of CaSO ₄	x ₃	g	0.32	1.0	2.0	3.0	3.68

Table 4. Experimental design matrix and results.

Solid code	Type	Experimental variables			BET surface area [m ² /g]
		Hydration period, x ₁ [h]	Amount of oil palm ash, x ₂ [g]	Amount of CaSO ₄ , x ₃ [g]	
A1	Center	0	0	0	55.2
A2	Center	0	0	0	54.4
A3	Center	0	0	0	50.3
A4	Center	0	0	0	55.1
A5	Center	0	0	0	56.4
A6	Center	0	0	0	52.7
A7	Axial	0	-1.68	0	26.0
A8	Axial	0	0	-1.68	41.3
A9	Axial	-1.68	0	0	18.7
A10	Axial	1.68	0	0	134.2
A11	Axial	0	1.68	0	105.9
A12	Axial	0	0	1.68	142.4
A13	Factorial	1	-1	1	68.8
A14	Factorial	1	1	-1	126.0
A15	Factorial	-1	1	-1	55.6
A16	Factorial	1	1	1	147.2
A17	Factorial	-1	1	1	128.6
A18	Factorial	-1	-1	1	35.8
A19	Factorial	-1	-1	-1	50.2
A20	Factorial	1	-1	-1	71.7

SO₂, 500 ppm of NO, 12 % of CO₂, 5 % of O₂ and balance nitrogen at a reaction temperature of 100 °C was passed through the absorbent. Prior to that, the N₂ gas stream was humidified using a humidification system which consists of two 250 mL conical flasks immersed in a water bath at constant temperature. The total flow rate of the gas stream was controlled at 150 mL/min using a mass flow controller. The details of the experimental set up are reported elsewhere [15]. The concentration of SO₂ in the flue gas was measured using a Portable Flue Gas Analyzer IMR2800P before and after the absorption process. The concentration of SO₂ was recorded continuously for 60 min. Two or three repeat measurements were made for each activity test. For clarity, only the average is presented in this paper. The activity of the

absorbent was reported in terms of percent SO₂ removal, as shown in Eq. (2):

$$\text{Percent removal of SO}_2 (\%) = \frac{\{[\text{SO}_2]_{\text{inlet}} - [\text{SO}_2]_{\text{outlet}}\}}{[\text{SO}_2]_{\text{inlet}}} \times 100\% \quad (2)$$

3 Results and Discussion

3.1 Development of an Empirical Model

A central composite design (CCD) was used to develop a correlation between the absorbent preparation variables and

the specific surface area of the absorbents. The complete design matrix and surface area responses at various absorbent preparation variables are listed in Tab. 4. The BET surface areas of the absorbents obtained were in the range of 18.7–147.2 m²/g. Runs A1–A6 at the center point of the design were used to determine the experimental error. The results of the surface area of these six runs were found to be quite consistence, indicating that only a single repeat experimental run is essential in this study. The surface area responses obtained in Tab. 4 were correlated with the three absorbent preparation variables studied using the polynomial equation shown in Eq. (1). The coefficients of the full empirical model (polynomial equation) and their statistical significance were determined and evaluated using Design Expert v6.0.6 software. The final model in terms of coded values, after excluding the insignificant terms (identified using Fisher's Test), is as shown in Eq. (3):

$$Y = 54.3 + 24.7x_1 + 26.7x_2 + 18.1x_3 + 9.0x_1^2 + 5.3x_2^2 + 14.5x_3^2 + 14.0x_2x_3 \quad (3)$$

The quality of the model developed was evaluated based on the coefficients of correlation. The value of R² for Eq. (3) was found to be 0.8929. This implied that 89.3 % of the total variation in the surface area responses was attributed to the experimental variables studied.

3.2 Model Adequacy Check

The adequacy of the model was further checked with analysis of variance (ANOVA), as shown in Tab. 5. Based on a 95 % confidence level, the model was found to be significant as the computed F value (14.29) is much higher than the theoretical F_{0.05(7,12)} value (2.91), indicating that the empirical model is reliable in predicting the absorbent surface area. The adequacy of the model was also checked using the normal plot of residues, as shown in Fig. 1. The normal % prob-

ability plot of the studentized residual is an important diagnostic tool to detect systematic departures by assuming that the errors are normally distributed, independent of each other, and that the error variances are homogenous [14]. From Fig. 1, the residuals were found to fall within a straight line, indicating that all the assumptions made in this statistical analysis were correct. From these statistical tests it was found that the empirical model was adequate for predicting the absorbent specific surface area within the range of the absorbent preparation variables studied.

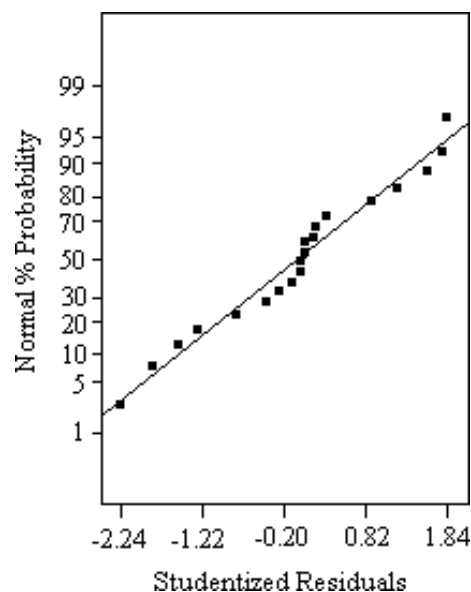


Figure 1. The normal % probability plot of the studentized residuals for the empirical model developed to predict surface area.

3.3 Influences of Absorbent Preparation Variables on Absorbent Surface Area

The results in Tab. 4 show that the absorbent preparation variables have significant influence on the absorbent surface

Table 5. Analysis of Variance (ANOVA) for the regression model equation and coefficients.

Source	Sum of squares	Degrees of freedom	Mean of square	F-test
Model	28131.92	7	4018.85	14.29
x ₁	8348.49	1	8348.49	29.68
x ₂	9765.78	1	9765.78	34.72
x ₃	4463.77	1	4463.77	15.87
x ₁ ²	1172.84	1	1172.84	4.17
x ₂ ²	405.37	1	405.37	1.44
x ₃ ²	3011.35	1	3011.35	10.71
x ₂ x ₃	1556.26	1	1556.26	5.53
Residual	3375.56	12	281.30	–
Total	31507.48	19	–	–

area. It was found that the hydration process improved the surface area of the resulting absorbent as compared to the raw materials. These results also illustrated that there is a possibility of improving the surface area of the absorbent with proper selection of the absorbent preparation variables. As mentioned earlier, higher absorbent surface area may be the key factor to obtaining an absorbent with a higher desulfurization activity.

From the empirical model shown in Eq. (3), it was observed that all the three individual absorbent preparation variables have significant influence on the absorbent surface area. Since the magnitudes of the coefficients of the three individual variables were quite close, it can be concluded that the influences of the three variables on the absorbent surface area were equally important. In addition, the quadratic term of the three absorbent preparation variables also had a significant influence on the absorbent surface area, but less pronounced than the linear term. Also, the influence of the interaction between variables x_2 and x_3 on the absorbent surface area was found to be significant.

Fig. 2 shows the influences of the hydration period and amount of oil palm ash on the absorbent surface area. The amount of CaSO_4 used was held fixed at the zero level (2 g). It was found that higher hydration periods and amounts of oil palm ash resulted in absorbents with higher surface areas. It was reported that for reactions involving siliceous materials such as oil palm ash, pozzolanic reactions typically start with the digestion of vitreous silica and/or alumina by alkaline water, and this process was reported to be very slow [8]. The dissolved silica and/or alumina will then react with $\text{Ca}(\text{OH})_2$ to form the reactive species in the absorbent that absorbs SO_2 . Therefore, it can be concluded that in order to produce absorbent from oil palm ash with a high surface area, sufficient time is required for the hydration process. With a longer hydration period, more silica and/or alumina will dilute out from the oil palm ash to react with $\text{Ca}(\text{OH})_2$ to form the reac-

tive species. On the other hand, the amount of oil palm ash generally determines the amount of silica and alumina available in the preparation mixture for reactions with $\text{Ca}(\text{OH})_2$ to form the reactive species in the absorbent. Thus, with a higher amount of oil palm ash, there will be more silica and alumina available in the preparation mixture to completely react with $\text{Ca}(\text{OH})_2$ to form the reactive species and give a positive influence on the absorbent surface area.

Fig. 3 shows the changes of the absorbent surface area with varying amounts of CaSO_4 and oil palm ash. The hydration period was held fixed at the zero level (20 h). The amount of CaSO_4 used in the preparation mixture was found to give a positive effect on the absorbent surface area. The positive effect of CaSO_4 on the surface area of absorbent prepared from other siliceous material such as coal fly ash has been reported by previous researchers [16]. It was reported that this phenomenon is due to the role played by CaSO_4 where it promotes the reactivity of $\text{Ca}(\text{OH})_2$ towards silica and/or alumina by suppressing crystal growth of $\text{Ca}(\text{OH})_2$.

Based on the results obtained in this study, it could be concluded that CaSO_4 has the same effect on absorbent prepared from oil palm ash as on absorbent prepared from coal fly ash. From the empirical model shown in Eq. (3) it was found that the influence of the interaction between variables x_2 (amount of oil palm ash) and x_3 (amount of CaSO_4) on the absorbent surface area was also significant. The influence of the interaction of these two variables on the absorbent surface area is shown clearly in Fig. 3b). The influence of the amount of oil palm ash on the absorbent surface area was more significant when more CaSO_4 was used in the preparation mixture. The following explanation describes this phenomenon.

When a smaller amount of CaSO_4 is used in the preparation mixture, there is a limited amount of CaSO_4 that could maintain the reactivity of $\text{Ca}(\text{OH})_2$ towards silica and/or alumina. Thus, increasing the amount of oil palm ash in the preparation mixture does not have a significant influence on the absorbent

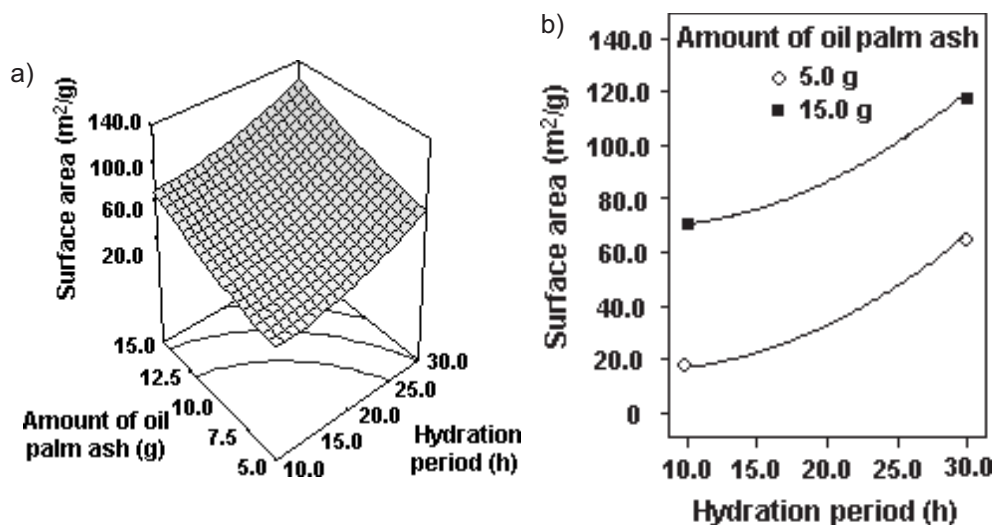


Figure 2. Influence of the amount of oil palm ash and hydration period on the absorbent surface area; (a) Response surface plot and (b) Two dimensional drawing.

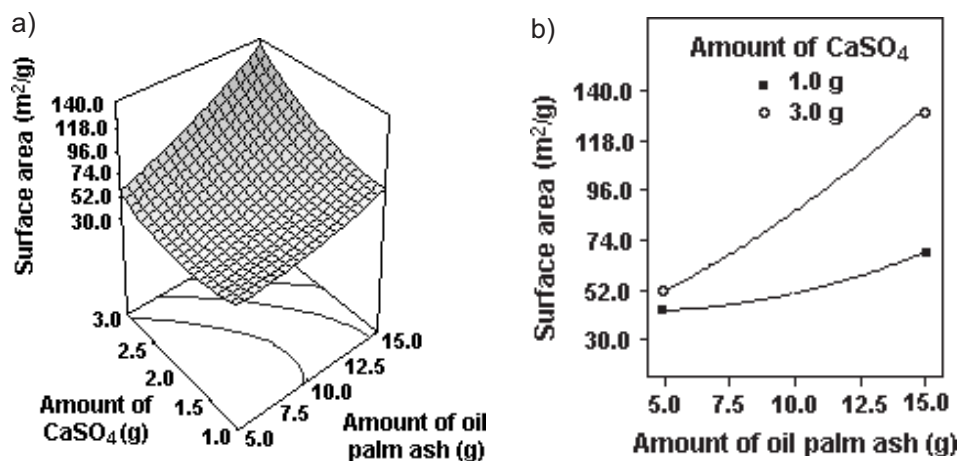


Figure 3. Influence of the amount of CaSO₄ and amount of oil palm ash on the absorbent surface area; (a) Response surface plot and (b) Two dimensional drawing.

surface area as the limited amount of reactive Ca(OH)₂ becomes the limiting factor for the formation of reactive species in the absorbent (the formation of more reactive species will increase the surface area of the absorbent). However, with a higher amount of CaSO₄, the amount of reactive Ca(OH)₂ is no longer the limiting factor for the formation of the reactive species in the absorbent. Thus, increasing the amount of oil palm ash increased the formation of the reactive species (more silica and/or alumina can react with Ca(OH)₂) and thus resulted in a more significant increase in the absorbent surface area.

3.4 Optimization

Based on the data presented in Tab. 4, it was found that a maximum specific surface area of 147.2 m²/g exists within the range of the hydration process variables investigated. The hydration conditions that resulted in the maximum surface area are hydration period (x_1) = 30 h, amount of oil palm ash (x_2) = 15.0 g and amount of CaSO₄ (x_3) = 3.0 g. Although the absorbent with the predicted maximum surface area would be expected to have a very high desulfurization capacity, a major drawback is that a hydration period of 30 h is required. Such a long hydration period is not practical and economical in full scale production of the absorbents. Thus, it was decided to fix the hydration period (x_1) at 10 h and optimize the other two hydration process variables (x_2 and x_3).

Using the point prediction function given in Design Expert v6.0.6 software, it was predicted that a maximum surface area of 128.6 m²/g could be obtained using 15.0 g of oil palm ash and 2.7 g of CaSO₄. To verify the prediction, two experiments were carried out under the conditions predicted and absorbents with surface areas of 125.9 and 129.5 m²/g were obtained. The values obtained were in excellent agreement with the predicted value, and therefore validated the effectiveness of the empirical model in predicting/optimizing the absorbent surface area within the range of variables studied.

3.5 Desulfurization Activity

The extent of SO₂ removal by the absorbent prepared using oil palm ash and the three starting materials is shown in Fig. 4. The absorbent with the optimized surface area was used in the activity test. The fixed bed reactor was subjected to a feed gas consisting of 2000 ppm SO₂, 500 ppm NO, 5 % O₂, 12 % CO₂ and balance N₂ at 100 °C. From Fig. 4 it can be seen that the absorbent prepared from oil palm ash easily outperformed its base components in removing SO₂. The absorbent removed 100 % of the SO₂ in the feed gas during the first 12 min of reaction. The SO₂ started to breakthrough at reaction time > 12 min, resulting in a gradual increase in the outlet concentration of SO₂ from the reactor. In contrast, each of the three starting materials; oil palm ash, Ca(OH)₂, and CaSO₄, did not exhibit any significant desulfurization activity. These results most likely reflect the fact that the specific surface area of the absorbent prepared from oil palm ash (128.6 m²/g) was much larger than those of the starting materials (4.9–10.2 m²/g).

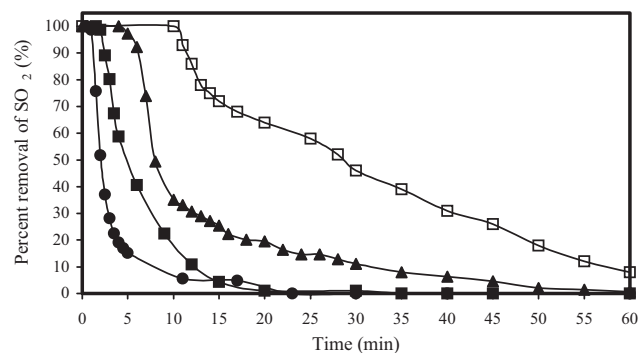


Figure 4. Comparison of the desulfurization activity of the absorbent and its base components. Feed gas composition at 100 °C: 2000 ppm SO₂, 500 ppm NO, 5 % O₂, 12 % CO₂, and the balance N₂; ● Oil palm ash; ▲ Ca(OH)₂; ■ CaSO₄; □ Absorbent.

4 Conclusions

Active absorbents for the removal of SO₂ from flue gas from combustion systems were prepared from oil palm ash, Ca(OH)₂, and CaSO₄ using water hydration. A central composite design (CCD) was used to develop an empirical model that correlates the absorbent surface area with the absorbent preparation variables. Higher hydration periods (x₁), amounts of oil palm ash (x₂) and amounts of CaSO₄ (x₃) used in the preparation mixtures were found to have positive effects on the absorbent surface area. The empirical model was then used to predict the optimum conditions for the preparation of the absorbent with the highest surface area. The predicted values were found to agree very well with the experimental results. The desulfurization activity of the absorbent derived from oil palm ash/Ca(OH)₂/CaSO₄ was found to be significantly higher than that of its starting materials.

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