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# Optimum conditions for preparation of flue gas desulfurization absorbent from rice husk ash

Keat Teong Lee, Atikah Matlina Mohtar, Nor Fatiha Zainudin, Subhash Bhatia, Abdul Rahman Mohamed<sup>\*</sup>

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia

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#### Abstract

Several previous studies have reported the preparation of absorbents from coal fly ash variations as a source of siliceous material for the preparation of absorbents for flue gas desulfurization. On the other hand, this study presents findings from an experimental investigation of the preparation of absorbents from rice husk ash as the source of the siliceous material. The effect of various absorbent preparation variables such as hydration period, amount of rice husk ash, amount of calcium sulfate (CaSO<sub>4</sub>) and hydration temperature on the BET (Brunner–Emmett–Teller) specific surface area of the absorbent were investigated. Based on the Central Composite Design (CCD) of experiments, a third order mathematical model was developed to correlate the absorbent preparation variables to the surface area of the absorbent. The predicted surface area was found to agree satisfactory with the experimental values. The model indicated that lower hydration period and temperature favor the formation of absorbent with higher surface area. Sulfation activity test on the absorbent revealed that the absorbent prepared from rice husk ash does have a high capacity in sulfur dioxide (SO<sub>2</sub>) absorption. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Absorbent; Flue gas desulfurization; Rice husk ash

# 1. Introduction

Demand for energy is expected to increase worldwide over the next 24 years, both in the industrial countries and particularly in the developing countries where rapid economic growth is expected. The total world energy consumption is expected to expand by 58% between 2001 and 2025, from 404 quadrillion kW in 2001 to 640 quadrillion kW in 2025. Coal, being the most abundant energy resource and also the cheapest will have an important role to meet the increasing demand of electricity in the world. For instance, in Malaysia, coal is expected to play a leading role in meeting the increasing demand of energy in the coming years, at least up to the year 2010. This is partly to ensure that Malaysia has a diversified source of fuel for the energy sector. With a balanced energy mix, the economy and particularly the power sector is less vulnerable to shocks in the fuel supply [1].

Although coal has an important role as a source of energy in Malaysia and the world, it faces some challenges. One of the most crucial challenge faced by coal-fired power plants is the emissions of pollutants particularly sulfur dioxide (SO<sub>2</sub>) into the environment. For example, a coal-fired power plant of 600 MW capacity burning coals containing 1.2% sulfur releases 1785 m<sup>3</sup>/h (NTP) of SO<sub>2</sub> with a concentration of 500 ppm. In order to reduce the emission of SO<sub>2</sub> to the environment, appropriate flue gas desulfurization (FGD) technologies must be utilized. Many studies have shown that when coal fly ash is mixed with calcium hydroxide (Ca(OH)<sub>2</sub>) or calcium oxide (CaO) in a hydration process, absorbents with high SO<sub>2</sub> capture capacity could be attained [2–14]. These absorbents with high surface area are products of the pozzolanic reaction between silica eluted

<sup>\*</sup> Corresponding author. Tel.: +60 4 594 1012; fax: +60 4 594 1013. *E-mail address:* chrahman@eng.usm.my (A.R. Mohamed).

from the fly ash and  $Ca(OH)_2$  or CaO to form calcium silicate hydrated compounds. In addition, it has been shown that the addition of  $CaSO_4$  to the preparation mixture has a positive or negative effect on the formation of the hydrated products, depending on the preparation conditions [4,7]. The structural properties of these absorbents, particularly its specific surface area, are believed to play an important role in SO<sub>2</sub> capture. Some studies have shown that higher desulfurization activity correlates with higher specific surface area [9,11]. Apart from that, it was also reported that the content of silica in the siliceous materials used to prepare the absorbent was closely related to the activity of SO<sub>2</sub> absorption [14].

Due to the high content of silica in rice husk ash, there is a possibility to utilize rice husk ash as an alternative source of siliceous material for the synthesis of absorbent for FGD. Rice husk is the natural sheath that forms on paddy grains during their growth. They are removed from the paddy grain during the refining process and are off no commercial value. A huge quantity of rice husks is created worldwide by the rice milling process. It was estimated that 3.6 million tones of rice husk is produced annually in Malaysia. Although rice husk has no commercial value, however, it was reported that if the husks are burned at a controlled low temperature, the ash collected can be ground to produce a pozzolan very similar to (and in some ways superior to) silica fume [15,16]. The white ash obtained from the combustion of rice husk at moderate temperature contains 87-97% silica (SiO<sub>2</sub>) in amorphous form and some amount of metallic impurities [17]. Therefore, the ash produced from burning rice husks can be exploited as a source of silica. The utilization of rice husk ash as a source of silica could help rice millers to meet the increasing cost of rice husk disposal due to increasing restrictions on disposal. Simultaneously, burning of the rice husks could also produce electrical power for mill consumption.

The main aim of this work is to study the feasibility of utilizing rice husk ash as a source of siliceous material for the synthesis of absorbent for dry-type flue gas desulfurization. In this study, a central composite design (CCD) was conducted to study simultaneously the effects of four absorbent preparation variables on the specific surface area of the absorbent. A mathematical model was then developed to correlate the absorbent surface area to the absorbent preparation variables. The absorbent will also be tested for its activity in SO<sub>2</sub> absorption.

### 2. Materials and methods

#### 2.1. Absorbent preparation

The raw materials used to prepare the absorbents were rice husk ash, calcium oxide (CaO) and calcium sulfate dihydrate (CaSO<sub>4</sub>·2H<sub>2</sub>O). The rice husk ash was provided by Padiberas Nasional Berhad (Bernas), Parit Buntar, Perak,

Table 1Chemical composition of rice husk ash

Composition	Percentage (%)		
SiO <sub>2</sub>	88.0		
Al <sub>2</sub> O <sub>3</sub>	0.1		
CaO	0.7		
Fe <sub>2</sub> O <sub>3</sub>	0.1		
MgO	0.9		
K <sub>2</sub> O	0.9		
P <sub>2</sub> O <sub>5</sub>	0.9		
Others	7.2		
Ignition loss	1.2		

Malaysia. The rice husk ash was collected directly after the burning of rice husk without any pre-treatment. The chemical composition of rise husk ash was determined using Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer and is given in Table 1. The CaO and CaSO<sub>4</sub> were obtained from BDH Laboratories, England. The BET specific surface area of these raw materials is given in Table 2.

The procedure used to prepare the absorbents is as follows. A fixed amount of CaO (5 g) was added to 100 ml of water at 65 °C. Upon stirring, the temperature of the slurry increased to about 80 °C. Specific amount of rice husk ash and CaSO<sub>4</sub> were added to the slurry simultaneously. The slurry was then heated to a desirable hydration temperature for a period of time in order for the hydration process to occur. The resulting slurry was filtered and dried at 200 °C for 2 h. The absorbents in powder form were then pelletized, crushed and sieved to produce the required particle size range (250–300  $\mu$ m). The BET surface area of the absorbents were analyzed as described below. The hydration period, amount of rice husk ash, amount of CaSO<sub>4</sub> and hydration temperature were varied according to an experimental design described below.

## 2.2. Designs of experiments

The experimental design chosen for this study was a Central Composite Design (CCD) that helps in investigating linear, quadratic, cubic and cross-product effects of the four absorbent preparation variables on the specific surface area of the absorbent. The four absorbent preparation variables studied are hydration period, amount of rice husk ash, amount of CaSO<sub>4</sub> and hydration temperature. Table 3 list the range and levels of the four independent variables studied. The CCD comprises a two-level full factorial design ( $2^4$ =16), eight axial or

 Table 2

 BET specific surface areas of the starting materials

Starting material	Specific surface area (m <sup>2</sup> /g)
Rice husk ash	3.26
CaO	5.62
CaSO <sub>4</sub>	4.89

Table 3				
Levels of the absorbent preparation	variables	chosen	for this	study

Variable	Coding	Units	Levels				
			-2	-1	0	+1	+2
Hydration period	<i>x</i> <sub>1</sub>	h	2	4	6	8	10
Amount of rice husk ash	<i>x</i> <sub>2</sub>	g	0	5	10	15	20
Amount of CaSO <sub>4</sub>	<i>x</i> <sub>3</sub>	g	0	1	2	3	4
Hydration temperature	<i>x</i> <sub>4</sub>	°C	65	75	85	95	105

star points and six center points. The value of  $\alpha$  for this CCD is fixed at 2 [18]. The complete design matrix of the experiments employed and results are given in Table 4. All variables at zero level constitute to the center points and the combination of each of the variables at either its lowest (-2.0) level or highest (+2.0) level with the other variables at zero level constitute the axial points. The experiment sequence was randomized in order to minimize the effects of the uncontrolled factors.

Each response of the specific surface area was used to develop a mathematical model that correlates the specific surface area to the absorbent preparation variables through first order, second order, third order and interaction terms, according to the following third order polynomial equation

$$Y = b_{o} + \sum_{j=1}^{4} b_{j}x_{j} + \sum_{i,j=1}^{4} b_{ij}x_{i}x_{j} + \sum_{j=1}^{4} b_{jj}x_{j}^{2} + \sum_{k,i,j=1}^{4} b_{kij}x_{k}x_{i}x_{j} + \sum_{j=1}^{4} b_{jjj}x_{j}^{3}$$
(1)

where *Y* is the predicted specific surface area (m<sup>2</sup>/g),  $b_0$  is the offset term,  $b_j$  is the linear effect,  $b_{ij}$  is the first order interaction effect,  $b_{jj}$  is the squared effect,  $b_{kij}$  is the second order interaction effect and  $b_{jjj}$  is the cubic effect.

Table 4 Experimental design matrix and results

Solid code	Experimental variable	Experimental variables					
	Hydration period, $x_1$ (h)	Amount of rice husk ash, $x_2$ (g)	Amount of $CaSO_4$ , $x_3$ (g)	Hydration temperature, $x_4$ (°C)			
E1	4.0	5.0	1.0	75.0	115.9		
E2	8.0	5.0	1.0	75.0	65.4		
E3	4.0	15.0	1.0	75.0	15.4		
E4	8.0	15.0	1.0	75.0	34.6		
E5	4.0	5.0	3.0	75.0	65.7		
E6	8.0	5.0	3.0	75.0	17.6		
E7	4.0	15.0	3.0	75.0	11.8		
E8	8.0	15.0	3.0	75.0	65.3		
E9	4.0	5.0	1.0	95.0	43.5		
E10	8.0	5.0	1.0	95.0	19.2		
E11	4.0	15.0	1.0	95.0	10.3		
E12	8.0	15.0	1.0	95.0	30.4		
E13	4.0	5.0	3.0	95.0	11.9		
E14	8.0	5.0	3.0	95.0	16.7		
E15	4.0	15.0	3.0	95.0	24.6		
E16	8.0	15.0	3.0	95.0	57.6		
E17	2.0	10.0	2.0	85.0	14.6		
E18	10.0	10.0	2.0	85.0	82.8		
E19	6.0	0.0	2.0	85.0	5.4		
E20	6.0	20.0	2.0	85.0	30.2		
E21	6.0	10.0	0.0	85.0	40.1		
E22	6.0	10.0	4.0	85.0	24.1		
E23	6.0	10.0	2.0	65.0	50.5		
E24	6.0	10.0	2.0	105.0	15.5		
E25-I	6.0	10.0	2.0	85.0	30.5		
E25-II	6.0	10.0	2.0	85.0	31.5		
E25-III	6.0	10.0	2.0	85.0	29.2		
E25-IV	6.0	10.0	2.0	85.0	30.5		
E25-V	6.0	10.0	2.0	85.0	31.9		
E25-V1	6.0	10.0	2.0	85.0	32.5		



Fig. 1. Schematic diagram of the experimental set-up for fixed bed desulfurization.

#### 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 third order polynomial equation and also for evaluation of the statistical significance of the equation developed. Additional experiment was carried out to verify the validity of the model equation developed.

# 2.4. Activity study

Desulfurization experiments were performed using a fixed bed test rig, as shown in Fig. 1. 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. The absorbent was then subjected to gas stream consisting of SO<sub>2</sub>, NO, O<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>. Prior to that, the N<sub>2</sub> gas stream was passed through a humidification system consisting of two 250 ml conical flasks immersed in a water bath at constant temperature. The combined feed gas flowed through the reactor at a flow rate of 150 ml/min. The SO<sub>2</sub> concentration of the effluent gas was continuously monitored by an Enerac 2000E flue gas analyzer. The utilization of Ca<sup>2+</sup> ions in the reacted absorbent was determined by taking the ratio of the mole of SO2 absorbed into the absorbent per mole of  $Ca^{2+}$  contained in the absorbent. The mole of SO<sub>2</sub> absorbed into the absorbent was measured by integrating of the difference between the inlet and outlet concentration [14] while the content of  $Ca^{2+}$  in the absorbent was determined using EDTA titration [11].

### 2.5. Physical and chemical analyses

The specific surface area of the absorbents were determined using the BET (Brunner-Emmett-Teller)

methods on an Autosorb 1C Quantachrome analyzer. A Leica Cambridge S360 scanning electron microscope with 15 kV of accelerating voltage was used to examine the absorbent surface morphologies. The chemical composition of rice husk ash was determined using a Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer.

## 3. Results and discussion

## 3.1. Development of regression model equation

A central composite design (CCD) was used to develop a correlation between the absorbent preparation variables to the surface area of the absorbent. The complete design matrix and surface area responses at various absorbent preparation variables are listed in Table 4. As can be seen from Table 4, the surface area obtained range from 5.43 to  $115.9 \text{ m}^2/\text{g}$ . Run E25-I to E25-VI at the center point of the design were used to determine the experimental error. As the result of surface area of these six runs were quite consistence, single replicate experimental run is essential in this study. Apart from that, from the results of these six runs, the experimental error for the surface area of the absorbent could be calculated as 3.1%.

By using multiple regression analysis, the response (surface area) obtained in Table 4 was correlated with the four absorbent preparation variables studied using the polynomial equation as shown in Eq. (1). The coefficients of the full regression model equation and their statistical significance were determined and evaluated using Design-Expert 6.0.6 software. The final model in terms of actual value after excluding the insignificant terms (identified using Fisher's Test) is

$$Y = 859.8 - 31.3x_1 - 53.3x_2 - 85.4x_3 - 8.9x_4$$
  
- 11.1x\_1^2 - 1.1x\_2^2 + 6.8x\_1x\_2 + 2.5x\_1x\_3 + 0.8x\_1x\_4  
+ 2.5x\_2x\_3 + 0.6x\_2x\_4 + 0.5x\_3x\_4 + 0.7x\_1^3 + 0.03x\_2^3  
- 0.06x\_1x\_2x\_4 (2)

Positive sign in front of the terms indicates synergistic effect, while negative sign indicates antagonistic effect. The quality of the model developed could be evaluated from their coefficients of correlation. The value of *R* for Eq. (2) is 0.968. The high value of *R* (very close to 1) shows that there is a very good agreement between the experimental and predicted value from the model. On the other hand, the value of  $R^2$  for Eq. (2) is 0.934. It implies that 93.4% of the total variation in the surface area responses is 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 Table 5.

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	16910.54	15	1127.37	28.37
$x_1$	203.62	1	203.62	5.12
<i>x</i> <sub>2</sub>	950.33	1	950.33	23.92
<i>x</i> <sub>3</sub>	380.81	1	380.81	9.58
$x_4$	2553.58	1	2553.58	64.26
$x_1^2$	697.58	1	697.58	17.56
$x_{2}^{2}$	218.89	1	218.89	5.51
$x_1 x_2$	3719.17	1	3719.17	93.60
$x_1 x_3$	386.52	1	386.52	9.73
$x_1x_4$	221.56	1	221.56	5.58
$x_2 x_3$	2519.04	1	2519.04	63.39
$x_2x_4$	1785.49	1	1785.49	44.93
$x_3x_4$	383.38	1	383.38	9.65
$x_1^3$	1463.24	1	1463.24	36.82
$x_{2}^{3}$	876.38	1	876.38	22.05
$x_1 x_2 x_4$	609.35	1	609.35	15.33
Residual	556.31	14	39.74	-

Based on a 95% confidence level, the model was tested to be significant as the computed *F* value (28.37) is much higher than the theoretical  $F_{0.05(15,14)}$  value (2.46), indicating that the regression model is reliable in predicting the absorbent surface area. Apart from that, each term in the model was also tested to be significant at a 95% confidence level as the computed *F* values for the respective terms are higher than the theoretical  $F_{0.05(1,14)}$  value (4.60). From these statistical tests, it was found that the model is adequate for predicting the absorbent specific surface area within the range of the variables studied.

From Table 5, it was also observed that among the four individual variables studied, hydration temperature  $(x_4)$  has the largest effect on the absorbent surface area (due to the highest *F* value) followed by the amount of rice husk ash  $(x_2)$ . On the other hand, hydration period  $(x_1)$  and amount of CaSO<sub>4</sub>  $(x_3)$  have almost similar effect on the absorbent surface area. The quadratic term of  $x_1$  and  $x_2$  also effect the absorbent surface area significantly, but less pronounced than its cubic term. Besides that, the effect of interaction between variables, particularly between variables  $x_1$  and  $x_2$ , between variables  $x_2$  and  $x_3$  and between variables  $x_2$  and  $x_4$  (due to the relatively very large *F* values), also effect the absorbent surface area significantly.

Fig. 2 shows the experimental values versus predicted values using the model equation developed. A line of unit slope, i.e. the line of perfect fit with points corresponding to zero error between experimental and predicted values is also shown in Fig. 2. This plot therefore visualize the performance of the model in an obvious way. The results in Fig. 2 demonstrated that the regression model equation provided a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the four absorbent preparation variables to the surface area of the absorbent.



Fig. 2. Experimental versus predicted absorbent surface area obtained from the model.

The model was further tested for its validity and adequacy by carrying out 3 additional independent experiments. Table 6 shows the experimental and predicted values using the model developed for the independent experiments. The results demonstrated that the model prediction agrees reasonably very well with the experimental data with the error lower than the experimental error of 3.1%.

### 3.3. Effects of absorbent preparation variables

The results in Table 4 show that the absorbent preparation parameters have great effect on the absorbent surface area. It was found that the hydration process always improve the surface area of the resulting absorbent as compared to the raw materials. These results illustrate that there is a great possibility in improving the surface area of the absorbent with proper selection of absorbent preparation variables. As mentioned earlier, absorbent surface area may be the key factor to obtain absorbent with high desulfurization activity.

Since the model developed in this work was found to have no maximum within the experimental domain examined, therefore the optimum conditions to obtain absorbent with the highest surface area cannot be derived. Thus, the model developed will be utilized to construct three-dimensional response surfaces to facilitate a straightforward examination of the effects of the various absorbent preparation variables on the absorbent surface area.

Fig. 3 shows the response surface of absorbent surface area with varying hydration period  $(x_1)$  and amount of rice husk ash  $(x_2)$ . The other two variables were held fix at zero level. The response surface in Fig. 3 has a saddle behavior or minimax nature. There is a stationary point, which is the point at which the slope of the response surface is zero

Table 6	•
Model	validation

Solid code	Expe	Experimental variables			Surface a	Surface area (m <sup>2</sup> /g)	
	<i>x</i> <sub>1</sub>	<i>x</i> <sub>2</sub>	<i>x</i> <sub>3</sub>	<i>x</i> <sub>4</sub>	Experi- mental	Predicted	(%)
E26	5	7	1.5	80	60.2	61.3	1.9
E27	6	12	2	90	20.0	20.3	1.6
E28	7	9	1.5	80	38.5	37.3	3.1



Fig. 3. Effect of amount of rice husk ash and hydration period on the absorbent surface area; (a) response surface plot and (b) two-dimensional drawing.

when taken from all directions. This indicates that the interaction effect between hydration period and amount of rice husk ash is greatly pronounced, as confirmed by the analysis of variance as shown in Table 5 (the highest F value among all the terms in Eq. (2)). When the amount of rice husk ash was held at 5 g, higher hydration period decreases the surface area of the absorbent, however, when the amount of rice husk ash was held at 15 g, higher hydration period increases the surface area of the absorbent. The following explanation describes this phenomena. When lesser amount of rice husk ash is used (5 g), there is insufficient silica to reacts completely with CaO, producing only limited calcium silicate hydrated compounds. Furthermore, it was reported in the literature that the calcium silicate hydrated compounds form from the pozzolanic reactions could gradually decompose at higher hydration period [13]. Therefore, the limitation of hydrated products formed and the decomposition of the hydrated products caused the surface area of the absorbent to drop at longer hydration period when the amount of rice husk ash was held at 5 g. On the other hand, when the amount of rice husk ash was held at 15 g, there is excess amount of silica present in the preparation mixture for the formation of more calcium silicate hydrated compounds to offset the decomposition of the hydrated compounds formed in the earlier reaction.



Fig. 4. Effect of amount of rice husk ash and hydration temperature on the absorbent surface area; (a) response surface plot and (b) two-dimensional drawing.

Therefore, the surface area of the absorbent increases at longer hydration period.

Fig. 4 shows the changes in absorbent surface area with varying amount of rice husk ash  $(x_2)$  and hydration temperature  $(x_4)$ . The hydration period  $(x_1)$  and amount of  $CaSO_4(x_3)$  were held at 4 h and 1 g, respectively. As seen from Fig. 4, higher hydration temperature decreases the surface area of the absorbent. It was reported that the solubility/dissolution of reactants (siliceous material/ CaO/Ca(OH)<sub>2</sub>) are the major factor affecting the formation of the hydrated products from the pozzolanic reactions [19]. Therefore, the drop in the surface area of the absorbent could be a direct consequences of lower solubility of CaO/  $Ca(OH)_2$  at higher temperature [8,19]. Although, the solubility of SiO<sub>2</sub> from ash was reported to increase with increasing temperature [8], the lower solubility of CaO/ Ca(OH)<sub>2</sub> at higher temperature reduces the amount of hydrated products obtained from the pozzolanic reactions. Apart from that, another possible explanation for the drop in the surface area of the absorbent at higher hydration temperature could be due to the decomposition of the calcium silicate hydrated compounds form from the pozzolanic reactions. Since, it was reported in the literature that the calcium silicate hydrated compounds form from



Fig. 5. Effect of hydration period and amount of  $CaSO_4$  on the absorbent surface area; (a) response surface plot and (b) two-dimensional drawing.

the pozzolanic reactions could gradually decompose at higher hydration period [13], therefore it is also possible to conclude that the calcium silicate hydrated compounds form from the pozzolanic reactions could also gradually decompose at higher hydration temperature.

Fig. 5 shows the changes of absorbent surface area with varying hydration period  $(x_1)$  and amount of CaSO<sub>4</sub>  $(x_3)$ . The amount of rice husk ash  $(x_2)$  and hydration temperature  $(x_4)$ 

were held fixed at 10 g and 75 °C, respectively. The response surface in Fig. 5 shows a minimum ridge in the experimental domain. An increase in the amount of CaSO<sub>4</sub> mixed in the preparation mixture was found to decrease the surface area of the absorbent. The addition of CaSO<sub>4</sub> into the preparation mixture was studied to determine the possibility of recycling the spent absorbent. Furthermore, it was reported that the addition of calcium sulfate (CaSO<sub>4</sub>) to the preparation mixture can further promote the formation of the hydrated products for absorbent prepared from coal fly ash [7]. This phenomena is due to the role played by CaSO<sub>4</sub> where it promotes the formation of hydrated products by suppressing crystal growth of Ca(OH)<sub>2</sub> to keep the reactivity of the Ca(OH)<sub>2</sub> towards silica eluted from coal fly ash. However, this phenomena was found not to be true for absorbent prepared using rice husk ash. The CaSO<sub>4</sub> added to the preparation mixture was found to reduce the reactivity of CaO/Ca(OH)<sub>2</sub> towards silica and thus reduce the formation of the hydrated compounds. This difference could most probably be due to the different content of silica in rice husk ash and coal fly ash. Coal fly ash usually contains about 50% (weight) of silica [4,7]. However, the content of silica in the rice husk ash used in this study is as high as 88% (weight). Due to the high content of silica in rice husk ash, therefore, the reaction between CaO/Ca(OH)2 and the silica eluted from rice husk ash can proceed at a relatively faster rate, as indicated by the formation of an absorbent with a relatively very high surface area even at a short hydration period of 4 h (absorbent E1). Thus, the role of  $CaSO_4$  in keeping the reactivity of the CaO/Ca(OH)2 towards rice husk ash (silica) is no longer necessary. Instead, the presence of CaSO4 covers the surface of CaO/Ca(OH)2 and thus decrease its reactivity towards rice husk ash (silica).

## 3.4. Desulfurization activity

The extents of  $SO_2$  removal by the absorbent prepared using rice husk ash and the three starting materials are



Fig. 6. Comparison of the desulfurization activity of the absorbent prepared from rice husk ash and its base components. Feed gas composition at 150 °C: 2000 ppm SO<sub>2</sub>, 500 ppm NO, 5% O<sub>2</sub>, 12% CO<sub>2</sub>, and balance N<sub>2</sub>.



Fig. 7. SEM micrographs of the absorbent E8 (a) before and (b) after  $SO_2$  capture.

shown in Fig. 6. The absorbent with solid code E1, E8 and E18 were used for this activity study. The fixed bed reactor was subjected to a feed gas consisting of 2000 ppm  $SO_2$ , 500 ppm NO, 5%  $O_2$ , 12%  $CO_2$  and balance  $N_2$  at 150 °C. As can be seen in Fig. 6, all the absorbents (E1, E8 and E18) prepared from rice husk ash easily outperformed its base components in removing SO<sub>2</sub>. Absorbent E8 with a surface area of 65.3  $m^2/g$  removed 100% of the SO<sub>2</sub> in the feed gas during the first 10 min of reaction. On the other hand, absorbent E18 ( $82.8 \text{ m}^2/\text{g}$ ) and absorbent E1  $(115.9 \text{ m}^2/\text{g})$  with a higher surface area exhibited a higher desulfurization activity. The absorbents removed 100% of the  $SO_2$  in the feed gas during the first 16 min (E18) and 28 min (E1), respectively. This result indicated that absorbent surface area is one of the key factors in determining the overall reactivity of the absorbent. After the period of time the absorbents could maintain 100% removal of SO<sub>2</sub>, the outlet concentration of SO<sub>2</sub> gradually increase and eventually reached the same value as the inlet concentration, indicating total deactivation of the absorbents. In contrast, each of the three starting materials; rice husk ash, CaO, and CaSO<sub>4</sub>, did not exhibit any significant desulfurization activity. These results most likely reflect the fact that the specific surface area of the absorbent prepared from rice husk ash (65.3–115.9 m<sup>2</sup>/g) was much larger than those of the starting materials ( $<6.0 \text{ m}^2/\text{g}$ ).

The utilization of  $Ca^{2+}$  ions in the reacted absorbent E1, E8 and E18 was found to be 78.8, 46.7 and 66.3%, respectively. This results showed that the utilization of  $Ca^{2+}$  ions is in accordance with the specific surface area of the absorbent, whereby absorbent with higher surface area resulted in higher utilization of  $Ca^{2+}$  ions. The surface morphology of the absorbent prepared from rice husk ash (E8) before and after SO<sub>2</sub> capture was studied through Scanning Electron Micrograph (SEM). As shown in Fig. 7a, the hydration process produced an absorbent with a needle like appearance. After reacting with SO<sub>2</sub>, Fig. 7b shows that the needle like appearance of the absorbent was no longer discernible. It may be concluded that the surface of the spent absorbent was covered by a layer of the reaction product believed to be  $CaSO_4$ .

## 4. Conclusion

This study has demonstrated the feasibility of using rice husk ash as a source of siliceous material for the preparation of absorbent for flue gas desulfurization. A central composite design was conducted to study simultaneously the effects of hydration period, amount of rice husk ash, amount of CaSO<sub>4</sub> and hydration temperature on the resulting absorbent surface area. A mathematical model was obtained to correlate the various absorbent preparation variables to the surface area using multiple regression analysis. The validity of the model was verified using independent experimental runs and was found to agree very well with experimental data. Analysis of the response surfaces derived from the model developed showed that the absorbent preparation variables have significant effect on the resulting absorbent surface area. The absorbent surface area was found to increase with lower value of all the four absorbent preparation variables studied. The prospect of being able to synthesize absorbent with high surface area at a lower hydration period and temperature could indicate that the preparation of absorbent from rice husk ash might be more economical than the conventional coal fly ash as a source of siliceous material.

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