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Sorption of SO_2 and NO by Modified Palm Shell Activated Carbon: Breakthrough Curve Model

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ABSTRACT

Simultaneous removal of SO_2 and NO from simulated flue gas by cerium oxide supported over palm shell activated carbon (Ce/PSAC) was studied in a fixed bed adsorber. In this study, the adsorption breakthrough of SO_2 and NO on Ce/PSAC at different reaction temperatures was manipulated to test their applicability to a model developed by Yoon and Nelson (1984) for breakthrough curves. Yoon and Nelson (1984) developed a relatively simple model addressing the adsorption and breakthrough of adsorbate vapour with respect to activated charcoal. This model was based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. A regression analysis (least square method) has been used to give the model parameters of k and $t_{1/2}$. The results showed that the agreement between the model and the experimental results is satisfactory. From the observation, it is concluded that the simple two-parameter model of Yoon and Nelson's model can be applied for modelling the breakthrough curves of SO_2 and NO gas adsorption over Ce/PSAC.

Keywords: Palm shell, sulfur doxide (SO_2), nitrogen oxide (NO), breakthrough model

INTRODUCTION

Currently, interests are growing in the use of simultaneous sorption processes to remove pollutant gases such as sulphur dioxide (SO_2) and nitrogen oxide (NO) simultaneous to avoid air pollution and green house effect. One of such process is adsorption. Gas adsorption is a separation process in which adsorbate molecules are adsorbed to the pore surface of solid adsorbents. Activated carbon has been recognized worldwide for its usage as an effective adsorbent for gas phase applications. This is due to its large surface area and pore volume (Barton *et al.*, 1997;

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Bansal *et al*., 1988). Literatures have shown that activated carbon can be used to remove SO_2 and NO (Davini, 2001; Qiang *et al*., 2005; Zhu *et al*., 2005). In previous work, the potential of PSAC (palm shell activated carbon) as a modified (impregnated with cerium oxide) sorbent was tested for its possibility in sorbing both SO_2 and NO gas simultaneously from a simulated flue gas at different temperatures. It was found that the modified PSAC (PSAC-Ce) successfully adsorbed SO_2 and NO simultaneously (Sumathi *et al*., 2010; Sumathi *et al*., 2010) and the adsorption result is presented as breakthrough curves.

Many theoretical or empirical equations have been proposed to model the adsorption breakthrough curves (Wood, 1987; Wood & Moyer, 1989) These equations were theoretically addressed to describe the adsorbate diffusion in the porous adsorbent such as activated carbon. It has been reported that breakthrough times (i.e. the time to reach defined effluent concentrations) and adsorption capacities (amounts held at breakthrough) of adsorbent beds for a given adsorbate gas are functions of the concentration of that gas in air (Yoon & Nelson, 1984). From the perspective of process modelling, the dynamic behaviour of a fixed bed column is described in terms of the effluent concentration–time profile, *i.e.* the breakthrough curve. There are a number of models suggested in the literature, such as Bohart and Adams model, Bed Depth Service Time model (BDST), Yoon and Nelson model, Clark model and Wolborska model (Hamdaoui, 2006). However, one of the most common models used for concentration profile is the Yoon and Nelson model (Yoon & Nelson, 1984).

In this paper, the theoretical breakthrough curves at five different equilibrium temperatures are generated and studied to be compared with the corresponding experimental data using Yoon and Nelson model to give an equation predicting the whole breakthrough curve for sorption of SO_2 and NO on PSAC-Ce.

EXPERIMENTAL

PSAC was impregnated with cerium metal nitrate ($Ce(NO_3)_3{\cdot}6H_2O$) of an appropriate concentration to obtain around 10wt% of metal content per gram of PSAC (10 mL of 10wt % metal solution/gram of PSAC). The preparation method has been reported previously (Sumathi *et al*., 2010). The simultaneous removal activity of the prepared sorbent was carried out in a fixed bed adsorber. The prepared PSAC-Ce sorbent (1.0 g) was placed on borosilicate glass wool (0.05 g) in the centre of the adsorber. A stream of gaseous mixture representing the simulated flue gas, containing SO_2 (2000 ppm) (50%), NO (500 ppm) (11%), oxygen (O_2) (10%), and nitrogen (N_2)(29%) as the balance, was passed through the prepared sorbents. The schematic diagram and parameter control have been reported previously (Sumathi *et al*., 2010). The adsorption temperature was varied from 100ºC to 300ºC. The experimental results have been reported elsewhere (Sumathi *et al*., 2010). This data were used to model the breakthrough curve using Yoon and Nelson Model.

BREAKTHROUGH MODEL

Yoon and Nelson developed a relatively simple model addressing the adsorption and breakthrough of adsorbate vapour with respect to activated charcoal (Yoon & Nelson, 1984). This model was based on the assumption that the rate of decrease in the probability of adsorption

for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. Yoon and Nelson's equation is not only less complicated than other equations, such as the Wheeler equation by Wheeler and Robell in 1963 (Tsai *et al.*, 1999) and Mecklenburg equation by Klotz in 1946 (Tsai *et al.*, 1999), but it also requires no detailed data concerning the characteristics of adsorbate, the type of adsorbent, and the physical properties of adsorption bed.

The Yoon and Nelson's equation (1984) is expressed as:

$$t = t_{1/2} + \frac{1}{K_{YN}} \ln \frac{C_e}{C_o - C_e} \quad (1)$$

$$k = K_{YN} t_{1/2} \quad (2)$$

where K_{YN} is the rate constant (min^{-1}), $t_{1/2}$ the time required for 50% sorbate breakthrough (min), t is the time (min), C_e is the breakthrough concentration of adsorbate in ppm, C_o is the initial inlet concentration of adsorbate in ppm and k is the proportionality constant.

The calculation of the theoretical breakthrough curves for a single-component system requires the determination of the parameters K_{YN} and $t_{1/2}$ for the sorbate of interest. These values may be determined from the available experimental data. The approach involves a plot of $\ln[C_e/(C_o-C_e)]$ versus t, time according to Eq. (1). If the theoretical model accurately characterizes the experimental data, this plot will result in a straight line with slope of K_{YN} and intercept $-t_{1/2}K_{YN}=(-k)$. The proportionality constant, k value can be obtained from Eq. (2).

RESULTS AND DISCUSSION

In this study, the adsorption breakthrough of SO_2 and NO on PSAC-Ce at different reaction temperatures was used as the dataset to analyze the model. The experimental data were obtained from the breakthrough data of different temperature effects on SO_2 and NO sorption which have been reported elsewhere (Sumathi *et al*., 2010). The temperatures were in the range of 100°C to 300°C on each adsorbate respectively. Table 1 shows the saturation time and breakthrough time for SO_2 and NO at different temperatures extracted from the reported data earlier (Sumathi *et al*., 2010). The results show that SO_2 saturates faster than NO. NO takes longer time to achieve breakthrough than SO_2. Using these results, the rate constants were calculated.

In order to find the rate, constant plots of $\ln [C_e/(C_o-C_e)]$ vs. sampling time (t) according to Eq. (1) at various temperatures were done. The plots yield straight lines as expected (Yoon & Nelson, 1984) with the slope of K_{YN} and the intercept of $-k$. The values were used to calculate $t_{1/2}$ and k at each temperature. A regression analysis (least square method) was used to give the model the parameters of k and $t_{1/2}$.

Table 2 shows the tabulated data at each temperature. The model appears to fit the experimental data reasonably well with correlation coefficient factor, (R^2) above 0.95. Both K_{YN} and $t_{1/2}$ are dependent on the adsorbent adsorption capacity. According to Yoon and Nelson, the K_{YN} and parameter values are dependent on the adsorption capacity, whereby the value of

$t_{1/2}$ decreases with decreasing adsorption capacity, while K_{YN} increases (Yoon & Nelson, 1984). This phenomenon was predicted exactly in this case study.

In the case of SO_2, the $t_{1/2}$ values increased from 100°C to 150°C and then decreased from 200°C to 300°C. This is because the adsorption capacity of SO_2 by PSAC-Ce increased when the temperature increased from 100°C to 150°C, whereas when the temperatures were more than 200°C, the adsorption capacity of SO_2 decreased. According to Zhang *et al.,* increment in the operating temperature could enhance the chemical reaction rate and ionic diffusion rate of SO_2 (Zhang *et al*., 2006). Hence in this case at temperature 150°C, SO_2 had a higher ionic diffusion rate into the pores of Ce/PSAC. Furthermore, metal cerium possesses high oxygen mobility at higher temperature, which can easily be oxidized to SO_3 and this scenario indirectly gives a a higher breakthrough time (Trovarelli *et al.*, 1999). However, when the temperature was further increased from 200°C to 300°C, the SO_2 sorption was decreased. This is due to the kinetic energy of SO_2. It is known that at a higher temperature, SO_2 molecules lose their kinetic energies, which make the adsorption an exothermic process (Guo & Lua, 2002). This condition indirectly lessens the amount of SO_2 adsorbed into the pores of Ce/PSAC. The calculated K_{YN} value increased when the temperature was increased from 100°C to 150°C and then decreased accordingly from 200°C to 300°C, as shown in Table 2. These findings indicate that Yoon and Nelson's model fits well with the current SO_2 experimental data vs. different temperature.

As for NO, it was observed that higher temperature (100°C -250°C) increases the adsorption capacity. Higher temperature shows a better removal of NO comparatively because Ce/PSAC is in a more active state to oxidize and reduce NO since cerium oxide has high oxidation activity at high temperature conditions (Waqif *et al*., 1997; Rodas-Grapain *et al*., 2005). Furthermore, at a lower temperature (150°C - 250°C), metal doped carbons showed high catalytic activity due to the disassociation of NO chemisorption, accompanied by N_2O and N_2 evolution and oxygen accumulation on the catalyst surface (Mehandjiev *et al*., 1997). Besides that, when the temperatures were lower (<150°C), the impregnated cerium oxide was most likely in a less active state (whereby lower temperature, the capability of CeO_2 to store and release O_2 via the redox shift between Ce^{4+} and Ce^{3+} under oxidizing and reduction conditions respectively was lesser (Qi & Yang, 2003), thus giving only a moderate removal of NO from the simulated flue gas. Moreover, it was reported that at a higher temperature, AC itself could decompose NO and reduce it to N_2 (Guo *et al*., 2001; Mehandjiev *et al*., 1996).

TABLE 1
Saturation time and breakthrough time for SO_2 and NO at different temperatures (Sumathi *et al*., 2010)

Temp. (°C)	SO_2		NO	
	Breakthrough Time	Saturation Time	Breakthrough Time	Saturation Time
100	180	275	115	265
150	195	285	140	290
200	85	185	170	320
250	45	140	180	335
300	35	120	85	200

TABLE 2
Values of the parameters for SO_2 and NO adsorption at various temperatures

	Temp.	Values of Parameters			R^2	R^2
	(°C)	K_{YN} (min^{-1})	$t_{1/2}$ (min)	k		B/TCurve
SO_2	100	0.0754	228.06	17.20	0.9567	0.9962
	150	0.0714	240.99	17.21	0.9799	0.9978
	200	0.0632	133.81	8.46	0.9644	0.9933
	250	0.0653	90.97	5.94	0.9500	0.9921
	300	0.0832	74.30	6.18	0.9918	0.9987
NO	100	0.0346	195.33	6.76	0.9567	0.9940
	150	0.0324	199.56	6.47	0.9799	0.9937
	200	0.0308	251.95	7.76	0.9529	0.9947
	250	0.0304	260.15	7.91	0.9537	0.9932
	300	0.0443	144.43	6.40	0.9855	0.9964

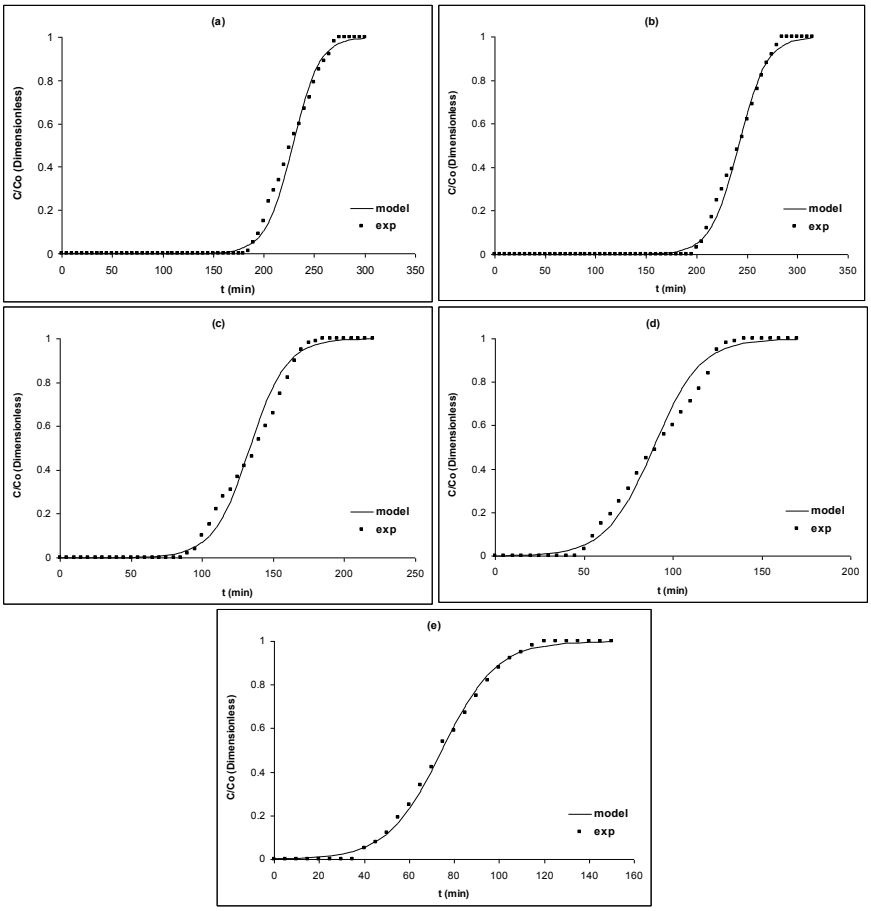

Fig.1: Breakthrough curves for various temperatures of SO_2 adsorption on PSAC-Ce; (a) 100ºC, (b) 150ºC, (c) 200ºC, (d) 250ºC, and (e) 300ºC by Yoon and Nelson's model

In the literature, it is indicated that a catalytic reaction and chemisorption of NO on active centres must occur at a temperature of more than 200°C (Muniz *et al*., 1999). As a result, the value of $t_{1/2}$ increased as the temperature increased. The K_{YN} value decreased consequently. The value of k (proportionality constant), on the other hand, is theoretically independent of the adsorption capacity. This is fairly well-demonstrated by the experimental results in this study. It is noted that different adsorbate gases are characterized by different values of k (Yoon & Nelson, 1984). The k values for NO range from 6.0 to 8.0 at different temperatures. Whereas for SO_2 the first two temperatures were around 17.2 and for the temperatures more than 150°C, it was around 6.0 to 8.5, respectively. The data fit well with the experimental data at different temperatures.

Following the determination of K_{YN} and $t_{1/2}$, one can easily construct the complete breakthrough curves (Fig.1 and Fig.2) for the given set of experimental conditions by applying Eq. 1 and using the determined values in Table 2.

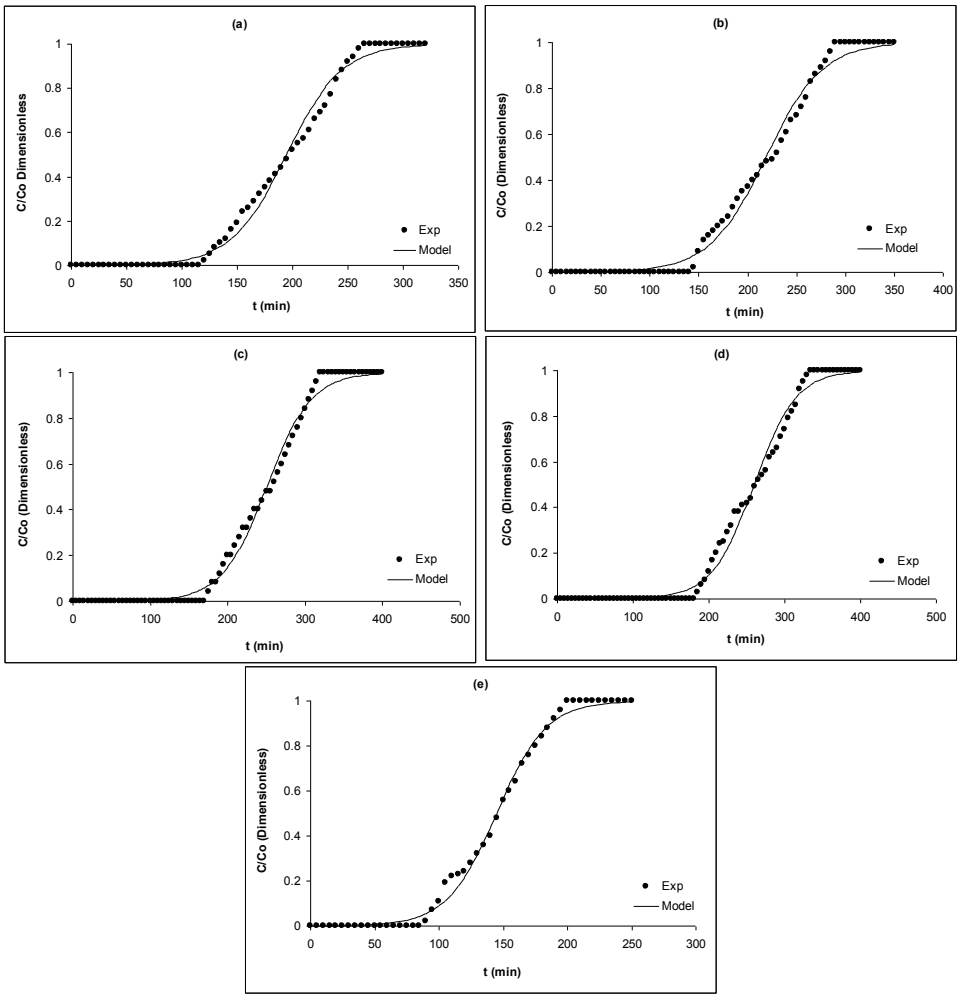

Fig.2: Breakthrough curves for various temperatures of NO adsorption on PSAC-Ce; (a) 100ºC, (b) 150ºC, (c) 200ºC, (d)250ºC, and (e) 300ºC by Yoon and Nelson's model

The calculated breakthrough curves based on Yoon and Nelson's equation were compared with the corresponding experimental data shown in Fig.1 for SO_2 and Fig.2 for NO. It was noted that each solid dot in Fig.1 and Fig.2 represents almost the model data of SO_2 and NO and it fit well with the experimental data at different temperatures. This shows that the agreement between the model and experimental results is very satisfactory. The corresponding coefficient factor was very high (R^2>0.9900) and near 1.0 agreement with the corresponding experimental data at different adsorber temperatures.

This further proves that the calculated theoretical breakthrough curves were in good. Even though the experimental data did show some inconsistent data due to the effects of temperature in this system, the model could still identify the changes and development of the model data accordingly.

CONCLUSION

A simple two-parameter model, *i.e.* rate constant, *k*', and $t_{1/2}$ time required for 50% adsorbate breakthrough, $t_{1/2}$ of Yoon and Nelson's model could be applied for modelling the breakthrough curves of SO_2 and NO gas adsorption through PSAC-Ce. The parameters obtained from the fitting of the experimental data with the model were used to generate the theoretical breakthrough curves. The calculated theoretical breakthrough curves were in good agreement with the corresponding experimental data, whereby the R^2 of the model breakthrough curves was more than 0.9900.

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