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# Characterization of unmodified and chemically modified coal samples by nitrogen adsorption at 77k, and investigation of their interaction with sulphur dioxide, (SO<sub>2</sub>), a known pollutant

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## To cite this article:

Nadiye-Tabbiruka M. S., Unaye Masiya, Salamula, E. J., Obuseng V., Ngila J. C.. Characterization of Unmodified and Chemically Modified Coal Samples by Nitrogen Adsorption at 77k, and Investigation of their Interaction with Sulphur Dioxide, (SO<sub>2</sub>), a Known Pollutant. *Advances in Materials*. Vol. 3, No. 6, 2014, pp. 68-74. doi: 10.11648/j.am.20140306.12

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**Abstract:** Samples of modified and fresh coal from Morupule, in Botswana, were characterized by nitrogen adsorption at 77 K and found to be micro porous materials, with the modified sample having a higher specific surface area ( $S_{\text{BET}} = 282.0 \text{ m}^2/\text{g}$ ) which is 19 times that of the original sample. Modification by activation increased the average pore radius slightly. Interaction of the coals with sulphur dioxide, a known pollutant, was investigated through its adsorption at various temperatures to facilitate the determination of isosteric heats of adsorption. The values obtained indicated physical adsorption of the pollutant indicating the possible reuse over and over again to trap and remove the pollutant in gaseous phase. Results from elemental analyser show that Morupule coal contains  $68.8\% \pm 5.0\%$  carbon.

**Keywords:** Adsorption, Coal, Activated Carbon, Surface Area, Pore Size Distribution

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## 1. Introduction

Air pollution arising from the emission of sulphur dioxide, SO<sub>2</sub>, resulting from combustion in boilers, furnaces in mineral smelters and engines has increasingly been recognized as a problem. SO<sub>2</sub> interacts with gasses such as carbon monoxide, CO, carbon dioxide, CO<sub>2</sub>, and nitrogen oxides, NO<sub>x</sub>, particulate soot and polycyclic aromatic hydrocarbons in the air to form photochemical smog. Dry-regenerative sorption processes based on the chemical reaction of SO<sub>2</sub> with a sorbent or catalyst or adsorptions of SO<sub>2</sub> on solids have attracted increasing attention for SO<sub>2</sub> removal because these methods possess several advantages over conventional wet-scrubbing process [1-3]

Surface area and porosity are important properties in the designing of adsorbents and heterogeneous catalysts since they determine accessibility of active sites which are

important for adsorption and catalytic activity. The distribution of pores of different sizes on a heterogeneous solid controls transport phenomena and influences selectivity in catalyzed reactions. Pore size distribution is therefore an essential parameter especially in shape selective adsorption and catalysis. These important parameters are routinely obtained from gas adsorption among other methods [4]. Generally, specific surface area is determined at the solid/gas interface mainly from N<sub>2</sub> adsorption at 77 K by using the BET method<sup>5</sup>. However, applying the BET surface area to solid/liquid adsorption systems can lead to unrealistic results for surface density of the adsorbate as in the widely known example of the BET surface area of montmorillonite [5, 7, 8, 9].

Micropore size distribution is estimated by using the method of Mikhail R. Sh., Brunauer S., and Bodor E.E., [6] which is based on the plot of mass adsorbed  $X_a$  at a given

relative pressure  $P/P_0$  against the corresponding multilayer thickness,  $t$ , obtained from the appropriate universal “ $t$ ” plot (plot of  $t$  against  $P/P_0$ ). In this method, every change in the gradient of the plot represents a change in the volume  $\Delta V$  filling the micropores of the corresponding change of pore radius  $\Delta r$ . A plot of  $\Delta V/\Delta r$  against  $r$  provides the volume pore-size distribution [10].

Activated carbons are the most widely used adsorbents for removing pollutants from solution [11] and also from gases including air, because of their high surface areas, which are typically in the range 500 – 1400 m<sup>2</sup>/g, mainly in form of large pores (mesopores and macropores of pore radius >10<sup>-1</sup> nm) and micropores (of pore radius in the range 10<sup>-3</sup> – 10<sup>-1</sup> nm) [12, 13]. However these solids do not come cheap, consequently the development of low - cost and readily available materials has gained interest in the field of surface chemistry [11-17]. Activated carbons consist mainly of carbon and are produced from carbonaceous materials such as coal, saw dust, corn cobs and seeds to mention but a few.

The objective of this work is to modify Morupule coal by a chemical activation method. The activated and non-activated samples will then be characterized by gas adsorption and compared paying particular attention to changes in surface area, development of pores and changes in pore size distribution which determine the space available to adsorb pollutants. Heats of adsorption which determine the strength of the adsorption bonds involved are also determined and their changes accompanying activation are monitored. The carbon content of the coal will be investigated.

#### Determination of isosteric heats of adsorption

If we consider adsorption to be similar to liquid to vapour phase change, we can estimate the isosteric heats of adsorption from the Clausius - Clapeyron equation:

$$\frac{dP}{P} = \frac{q_{st}}{RT^2} dT \quad (1)$$

This integrates, for two temperatures  $T_1$  and  $T_2$  and their corresponding relative pressures  $P_1/P_{01}$ , and  $P_2/P_{02}$ , to give

$$\ln \left[ \frac{P_2}{P_{02}} \right]_{T_2, x_2} - \ln \left[ \frac{P_1}{P_{01}} \right]_{T_1, x_1} = \frac{q_{st}}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad (2)$$

$$\text{For } (P_{02})_{T_2} \neq (P_{01})_{T_1}$$

$P_1$  and  $P_2$  are pressures in mm of mercury required to give identical adsorption at temperatures  $T_1$  and  $T_2$ .

$(P_{02})_{T_2}$  is the saturation vapour pressure at temperature  $T_2$  K, and  $(P_{01})_{T_1}$  is the saturation vapour pressure at temperature  $T_1$  K;  $q_{st}$  is the isosteric heat of adsorption, and  $R$  is the universal gas constant.

A plot of  $\ln(P/P_0)$  against  $1/T$  (K) for a given adsorbed mass at the temperatures used yields straight lines (isosters). Isosteric heats of adsorption are obtained from the gradients of the straight line segments for the various coverages.

## 2. Experimental

### 2.1. Materials and Equipment

#### 2.1.1. Nitrogen

The nitrogen gas used was green label of purity 99.999% obtained from Afrox/BOC. It was delivered via liquid nitrogen frozen cold trap containing activated carbon to remove any traces of oxygen. The pure nitrogen was then leaked to the adsorption chamber in small doses.

#### 2.1.2. Sulphur Dioxide

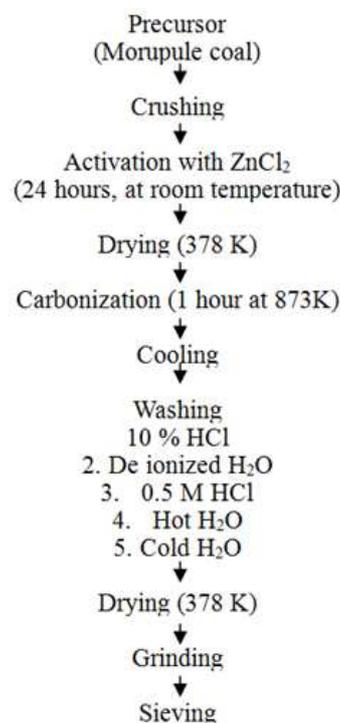
The sulphur dioxide used was of 99.9+% purity obtained from Aldrich. The cylinder was connected to the adsorption apparatus by a Teflon pressure tube. The gas was used without further purification.

#### 2.1.3. Coal

Coal samples obtained from various parts of Morupule coal mine were mixed, and ground to pass through a 0.065 mm sieve. The resulting powder was then heat - treated in an oven for 24 hours at 383.15 K before characterisation using N<sub>2</sub> adsorption. The carbon content was investigated by using an Elemental Analyser.

#### 2.1.4. Activated Coal

A sample of the ground coal was activated by a chemical method using a dehydrating agent. In this study zinc chloride, ZnCl<sub>2</sub>, obtained from Associated Chemical enterprises (96 % purity) was used as the dehydrating agent. The process of activating the coal sample consisted of two consecutive steps: impregnation and carbonization [9].



Flow chart for chemical preparation of activated carbon from Morupule Coal [9]

Impregnation involves mixing of the carbon precursor with the activating agent, ZnCl<sub>2</sub>. The resulting paste was then kept at room temperature for 24 hours before drying and then carbonization. The carbonization process involved heating the precursor (in a ratio of 1:1 by mass of the coal to the drying agent) at 873K under an inert atmosphere of N<sub>2</sub> gas, which was passed through the sample container to minimize the amount of oxygen present during the process. A schematic outline of the procedural steps used in the activation process is given above.

## 2.2. Measurement of Adsorption

### 2.2.1. Adsorption of Nitrogen

Adsorption isotherms of N<sub>2</sub> at 77 K, for the coal samples were obtained gravimetrically by suspending the sample on a calibrated McBain spring balance housed in a glass vacuum apparatus [10]. The balance had been calibrated by loading varying accurately known masses and measuring their corresponding extensions using a cathetometer. The masses were then plotted against the corresponding spring extensions to give an average mass per unit extension from the slope of the resulting straight line.

From the isotherms, the BET specific surface area and pore size distribution were obtained. Pore size distribution was estimated using the micropore method of Mikhail Brunauer and Bodor [7, 8] on the adsorption branch.

### 2.2.2. Adsorption of Sulphur Dioxide

During adsorption of sulphur dioxide, (SO<sub>2</sub>) the adsorbent samples were kept at the required temperature by dipping the adsorption tube containing the suspended coal sample into a Labcon low temperature thermostatic water bath at the required temperature (273 K, 288 K, and 302 K). A thermometer, of accuracy 0.05 K was inserted in the water bath to monitor any temperature changes. Adsorbed weights were obtained from the extensions of the calibrated McBain spring balance.

## 3. Results and Discussions

Elemental Analyser results showed that Morupule coal carbon content is 68.8±5.0%.

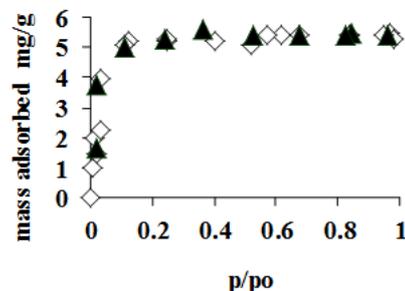
### 3.1. Nitrogen Adsorption

Nitrogen adsorption isotherms on coal are given in figs 1a for unactivated and 1b for activated samples. Fig 2 gives the cross plot of the nitrogen adsorption on unactivated against activated coal samples at the same pressures for comparison. Fig 3 is a plot of the mass of nitrogen adsorbed (X<sub>a</sub>) against film thickness of adsorbed layer, 't' for (a) unactivated and (b) activated Morupule coal. Fig 4 shows the nitrogen pore size distributions of un-activated, (a), and activated, (b), coal samples.

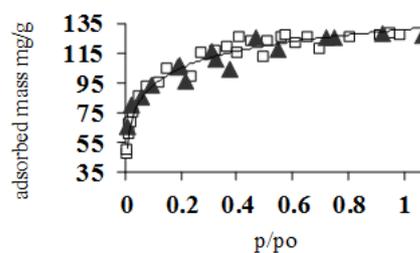
Fig1 shows that the N<sub>2</sub> adsorption isotherms at 77 K on the two coal samples are both type I, with steep rise at low relative pressure (P/P<sub>0</sub>), indicating that both adsorbents are microporous. The BET plots are linear in the range of P/P<sub>0</sub>

between 0.05 and 0.35 giving calculated specific surface areas of 14.7 m<sup>2</sup>/g, for natural coal and 282.0 m<sup>2</sup>/g, for activated coal. The increase in surface area after activation is clearly portrayed in the N<sub>2</sub> adsorption at P/P<sub>0</sub> of 0.2. At this relative pressure activated coal adsorbed more than 100 mg/g of N<sub>2</sub> while natural coal adsorbed barely 6 mg/g of N<sub>2</sub>. The surface area of the activated coal is in good agreement with the surface areas reported for other activated carbons [12]. The increased uptake of adsorbate by adsorbent is clearly shown by the cross-plot given in Fig 2 obtained by plotting the quantity adsorbed by the activated coal at a given pressure against the quantity adsorbed by the natural coal at the same relative pressure. It clearly shows the large change in adsorption that has resulted from modification. A line representing equivalent adsorption is also shown for comparison.

The increase in adsorption per unit pressure for activated coal is much higher for relative pressures lower than 0.2 than for those higher indicating that by this pressure most of the micropores have been filled. The gradual turn of the isotherm also indicates a gradual decrease in adsorption for the activated coal compared to the sudden turn of the isotherm displayed by the unactivated coal. This indicates the presence of larger micropores in the activated stuff. At a relative pressure of 0.3, we are approaching the mesopore region and the natural coal is no longer taking anymore of the adsorbate but the activated coal still adsorbs more indicating that the activated coals pore sizes have been increased and some wider pores were generated during activation.



(a)



(b)

**Fig 1.** Adsorption of nitrogen at 77 K on (a) unactivated coal, ◇ adsorption and ▲ desorption (b) activated coal, □ adsorption and ▲ desorption. The figs show the greatly increased adsorption by the modification

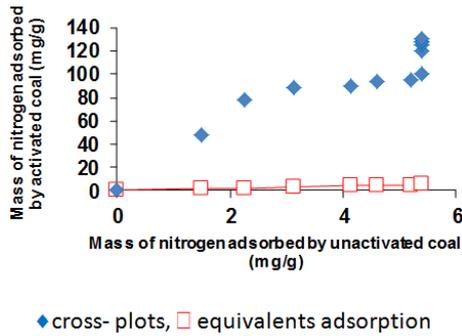


Fig 2. Cross-plots between the adsorption of nitrogen at 77 K on activated and un-activated coal, showing the increased adsorption due to modification by activation.

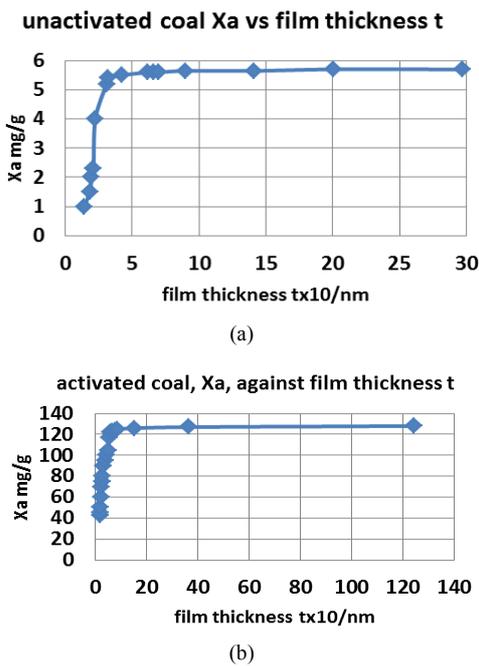


Fig 3. Mass of nitrogen adsorbed ( $X_a$ ) against thickness of adsorbed layer, 't' for (a) unactivated and (b) activated Morupule coal. The figures shows increased adsorption after activation.

Analysis of the  $N_2$  adsorption isotherms as well as the  $X_a$  against  $t$  – plots (Fig 3) shows that the two coal samples are microporous. The entire isotherm is needed or used for calculating the pore size distribution for an adsorbent and from the  $X_a$  against  $t$  - plot, large uptake of nitrogen at low relative pressures indicates filling of micropores ( $r < 2$  nm) in the adsorbent. The concave upward portion of the isotherm represents filling of mesopores (radius,  $r = 2$  nm to 50 nm) and macropores ( $r > 50$  nm) [13-22] and is absent in these samples indicating that there are no mesopores which could falsify the analysis[23]. Pore analysis using Ultra Small Angle Neutron Scattering (USANS) and small angle Neutron scattering (SANS) techniques on a wide range of coal samples from various parts of the globe have yielded higher results for mesopores and macropores than those from adsorption [24-26]. The area and pore size distributions of our coal samples are shown in Fig 4. The peak radius,  $r_{peak}$  for unactivated coal and activated coal were in the ranges 0.2 –

0.3 nm and 0.3 – 0.8 nm respectively confirming that both samples are mostly microporous according to IUPAC classification. Clearly, the activation process created very few new pore types but it did slightly increase the average pore radii over that of the natural coal (see Table 1).

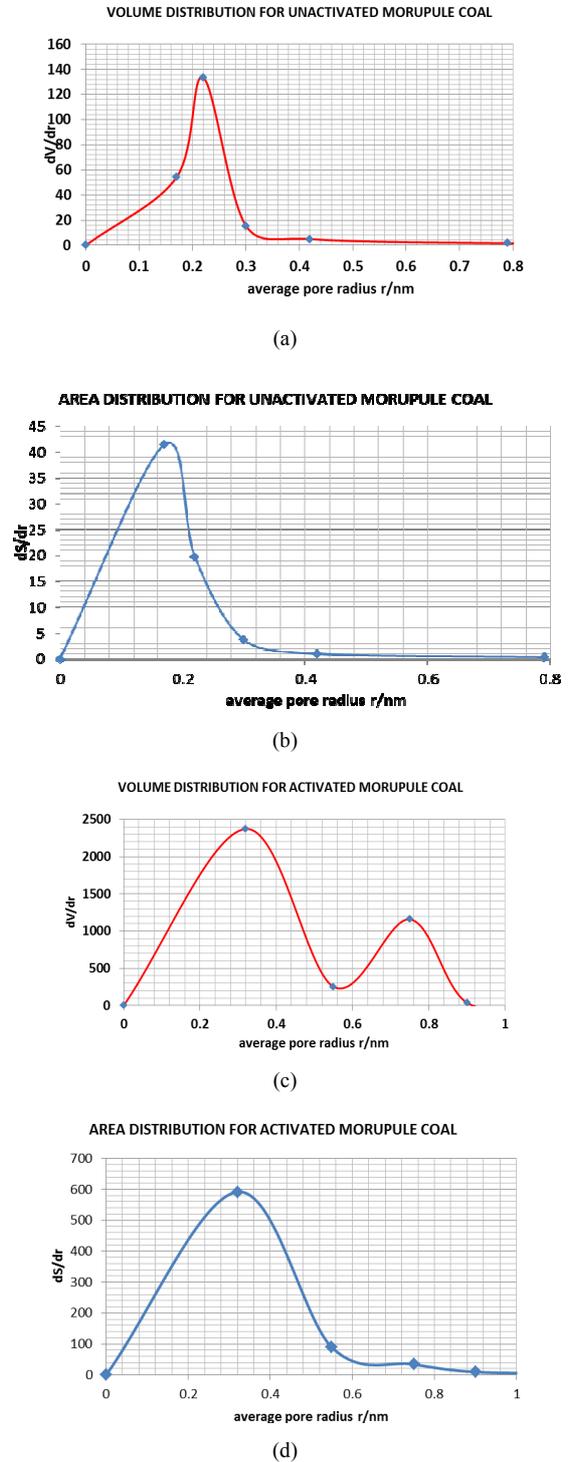


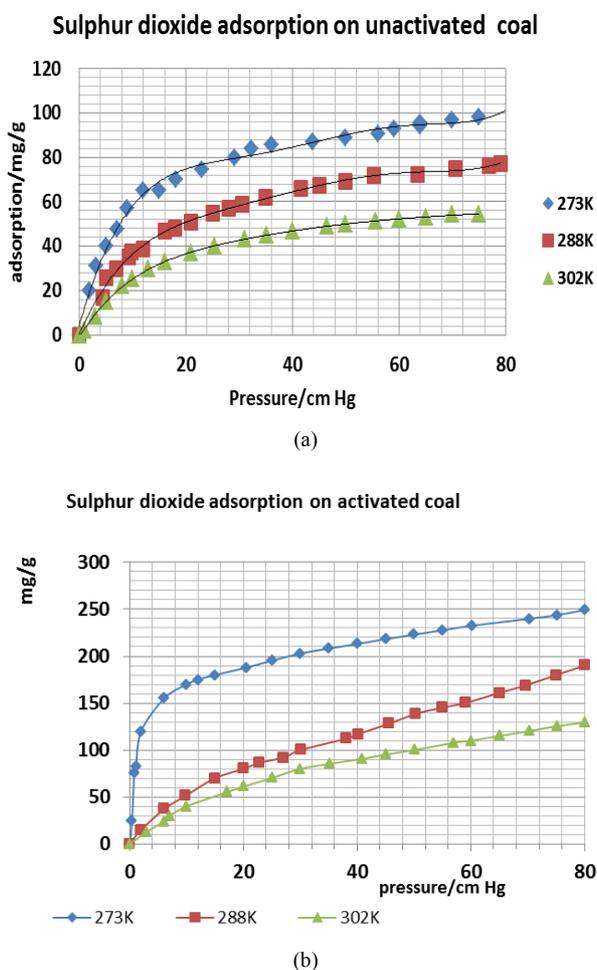
Fig 4. Pore size distributions (a) and area distribution (b) of un-activated coal showing the modal radius at around 0.22 nm for the area and 0.18nm for the area. Pore size distributions (c) and area distribution (d) of activated coal showing the modal radius shift to around 0.3 nm and the creation of new larger pores of average radius 0.74 nm.

**Table 1.** Core properties of the activated and unactivated Morupule coal

Coals	S <sub>BET</sub> / m <sup>2</sup> /g	r <sub>peak</sub> / nm
Fresh (unactivated)	14.7	0.23
Activated	282.0	0.32 and 0.75

### 3.2. Adsorption of Sulphur Dioxide (SO<sub>2</sub>)

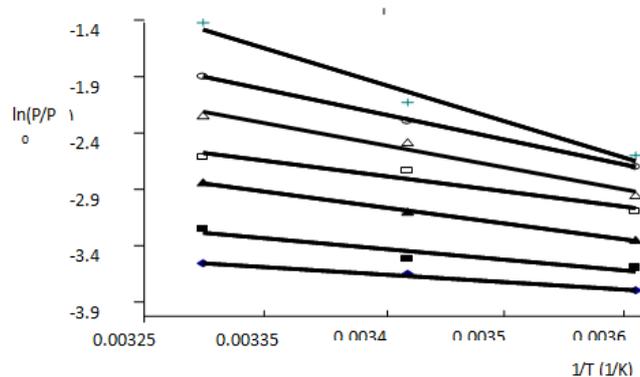
Sulphur dioxide adsorption isotherms are given in Figs 5a for unactivated and 5b for activated coal samples. Fig 6 shows adsorption isosteres for SO<sub>2</sub> on unactivated Morupule coal at various coverages for the studied temperature range. Fig 7 gives the variation of isosteric enthalpy of adsorption of sulphur dioxide with coverage on, (a) unactivated coal and (b) activated coal for the temperature range studied.



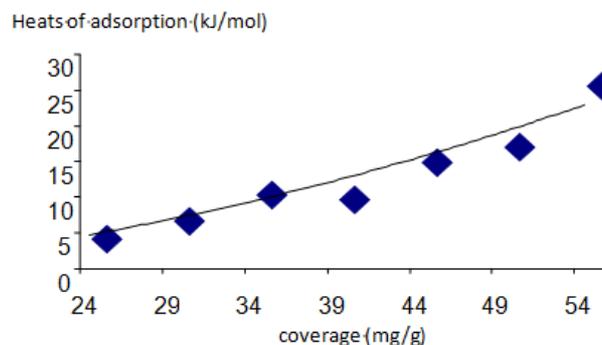
**Fig 5.** Adsorption of SO<sub>2</sub> on (a) unactivated Morupule coal and (b) activated Morupule coal at various temperatures. The increase in monolayer and multilayer adsorption due to activation is shown.

Fig 5 shows that the amounts of SO<sub>2</sub> adsorbed, expressed as mg of SO<sub>2</sub> adsorbed per gram of adsorbent (mg/g) decreases with increasing adsorption temperature indicating that SO<sub>2</sub> adsorption on the studied adsorbents is not activated in the temperature range 273K-302K. High values of adsorption at lower temperatures indicate physical adsorption. These results clearly show that at low temperatures, the activated coal sample adsorbs more of the pollutant than the unactivated sample. Clausius – Clapeyron equation (equation 1) was used

to obtain isosteric heats of adsorption at various coverages  $\theta$  from a plot of  $\ln(P)$  versus  $1/T$  (equation 2). Isosteric heats of adsorption are then obtained from the slopes of the segments of the adsorption isosteres. Fig 6 shows the adsorption isosteres for SO<sub>2</sub> on the unactivated coal sample. The values for activated Morupule coal were obtained in a similar way. Fig 7a shows that the heats of adsorption for SO<sub>2</sub> on unactivated Morupule coal increase with increasing coverage. For a large molecule like sulphur dioxide this trend seems to point to a possibility of surface cooperative effect where the adsorbed molecules stimulate neighbouring empty adsorption sites for further adsorption. It should be borne in mind that coal is very complex and therefore has adsorption sites of different origins and hence different energies. The isosteric heats of adsorption on the unmodified coal ranged from 5.5 kJ/mol at  $\theta = 25$  mg/g to 26.9 kJ/mol at  $\theta = 54$  mg/g, typical of physical adsorption [22]. On the other hand the heats of adsorption on the activated Morupule coal sample decreased with increasing coverage (Fig 7b), ranging from 2 kJ/mol to -12.6 kJ/mol for the temperature range 288 K to 302 K and from 95.5 kJ/mol to 74.7 kJ/mol for the temperature range 273 K to 288 K, for coverage  $\theta = 25$  mg/g to 150 mg/g. The heats of adsorption for SO<sub>2</sub> are higher at lower temperatures and low at high temperatures again indicating physical adsorption. The variations of isosteric heats of adsorption with temperature and with coverage confirm that the two coal samples are heterogeneous.



**Fig 6.** Isosteres for adsorption of SO<sub>2</sub> on unactivated Morupule coal at various coverages: coverage,  $\theta = \blacklozenge$  at 25 mg/g,  $\blacksquare$  at 30 mg/g,  $\blacktriangle$  at 35 mg/g,  $\square$  at 40 mg/g,  $\Delta$  at 45 mg/g,  $\circ$  at 50 mg/g and  $+$  at 60 mg/g.



**Fig 7a.** variation of heats of adsorption of SO<sub>2</sub> on un-activated Morupule coal as a function of coverage.

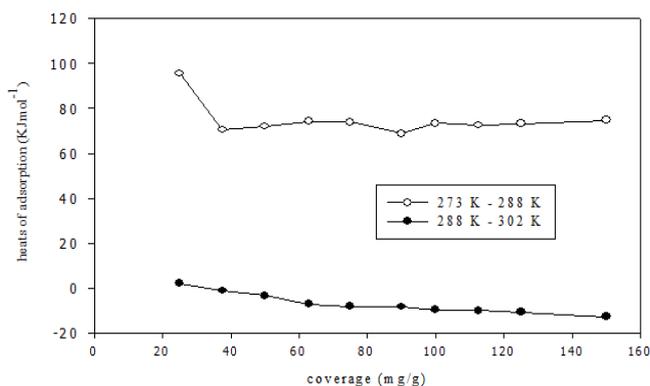


Fig 7b. A comparison of heats of adsorption of  $\text{SO}_2$  at different coverages on activated Morupule coal with different temperature ranges.

## 4. Conclusions

Analysis of Morupule coal using elemental analyser showed that it contains  $68.8\% \pm 5.0\%$  carbon. The coal was successfully modified by dehydrating it using  $\text{ZnCl}_2$  followed by pyrolysis in an inert atmosphere. Characterization of un-modified and activated coal by  $\text{N}_2$  adsorption shows that both samples are microporous with the unmodified coal having a nitrogen specific surface area,  $S_{\text{BET}}$ , of  $14.7 \text{ m}^2/\text{g}$ ; while the activated sample has a higher specific surface area  $S_{\text{BET}}$  of  $282.0 \text{ m}^2/\text{g}$ . Activating Morupule coal increased its specific surface area, slightly increased the average pore radius by creating new wider pores and also altered the trends and magnitudes of  $\text{SO}_2$  heats of adsorption. Adsorption of  $\text{SO}_2$  by the two samples shows that activation immensely increased adsorption capacity of the coal for the pollutant probably because of the increased surface area from the new pores.

Further investigation should focus on other procedures and conditions for activation of the parent coal with the aim of increasing the pore radius that will accommodate larger air pollutant molecules such as the benzenoids. Further work should also include investigating the possible use of the Morupule activated coal to remove other pollutants, from solutions, including heavy metal cations and benzene compounds.

## Acknowledgement

The authors wish to acknowledge financial support provided for this work by the office of research and development of the University of Botswana.

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