Low Cost Microporous Material for Natural Gas Storage: Preparation and Characterization

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Outline

- Introduction
- Problem Statement
- Research Objectives
- Results and Discussion
- Conclusion

Introduction

- Unlocking the energy potential within South Africa's stockpiles of discard coal is a major challenge
- Discard coals are waste material generated from coal beneficiation process
- Stockpiles of discard coals undergo spontaneous combustion thereby polluting the environment with high sulphur content
- There is an accumulated 1.5 billion tons of discard coal stockpiled in South Africa and 60 million tons produced annually

Figure 1: (a) Self-heating of run-of-mine (b) Aerial View of stock pile of coal discard at Mpumalanga Highveld, South Africa (c) Slurry dump, adjacent to a coarse discard coal dump

Critical Need: An urgent need to find beneficial use for the discard coal for the sake of the environment and also for economic benefits.

Product Obtainable: Activated Carbon

Application: Natural Gas Storage

Benefits: low cost adsorbent from waste, drives down the cost of storing natural gas for vehicular and industrial applications

Figure 2: Figure 1: (a) Stock pile of coal discard (b) Activated Carbon (c) Natural Gas Vehicle

Materials

- Run of mine coal (coal delivered to the coal beneficiation plant directly from the mine) and discard coal (waste material from coal beneficiation process) samples were collected from a Mine situated 15 km south-west of Witbank in Mpumalanga, South Africa.
- The samples were ball milled and sieved to particle size 150 – 250 µm
- Potassium hydroxide, KOH (AR Grade) was used as the activation agent.

Table 1: Samples Characterization

Analysis	Run of Mine Coal	Coal Discard
Proximate Analysis (wt.%)		
Moisture Content	1.76	1.37
Volatile Matter	15.08	12.78
Fixed Carbon	37.06	24.65
Ash	46.10	61.20
Ultimate Analysis (wt.%)		
Carbon	56.81	44.07
Hydrogen	3.00	1.44
Nitrogen	1.40	0.64
Oxygen	37.89	41.22
Sulfur	0.89	12.64
Surface Properties		
BET Surface Area (m^2g^{-1})	5.035	3.848
Total Pore Volume (cm^3g^{-1})	0.021	0.014
Pore Size (nm)	17.404	15.111

Preparation of the Activated Carbons

Precursor (ROM & Discard)

Dry, Pulverize & Sieve
150 – 250 µm

Chemical Activation
- KOH
- Ratio: 1:1, 1:2.5, 1:4
- Temp: 400 – 800 °C

Acid Washing & Drying

Activated Carbon

Analysis
BET, SEM, CO_2 and Natural Gas Adsorption Test

Figure 3: Flow Diagram of the Preparation Process

Results and Discussion

Table 2: Surface Characterization Results of Coal Discard Activation Experiment

Sample	Run order	Block	Weight Ratio W	Carbonization Temp. T (°C)	SBET (m^2/g)	Total Pore Volume V (cm^3/g)
AC-1	1	Block 1	2.5	600	471.86	0.655
AC-2	2	Block 1	2.5	800	1374.20	1.037
AC-3	3	Block 1	2.5	600	356.31	0.586
AC-4	4	Block 1	1	600	275.15	0.360
AC-5	5	Block 1	4	800	1766.84	1.016
AC-6	6	Block 1	2.5	400	161.54	0.280
AC-7	7	Block 1	2.5	600	463.67	0.612
AC-8	8	Block 1	1	400	143.84	0.220
AC-9	9	Block 1	1	800	1216.36	0.765
AC-10	10	Block 1	4	600	671.68	0.698
AC-11	11	Block 1	4	400	258.00	0.440
AC-12	12	Block 1	2.5	600	366.54	0.632
AC-13	13	Block 1	2.5	600	453.14	0.568

Results and Discussion

Table 3: Surface Characteristics of Samples and Activated Carbons from Samples

Samples	SBET (m^2/g)	Total Pore Volume VT (cm^3/g)	Micro pore Volume V_{DR} (cm^3/g)	Average Pore Diameter, d (nm)	Meso pore Volume V_{me} ($V-V_{dr}$)	VDR/VT (cm^3/g))
ROM	5.035	0.021	0.0036	17.40	0.0174	0.17
ACR	1827.71	1.046	0.6484	2.92	0.3976	0.62
DS	3.848	0.014	0.0026	15.11	0.0114	0.19
ACD	1766.84	1.016	0.6130	2.77	0.403	0.60

ROM: Run of Mine Coal
ACR: Activated Carbon from Run of Mine Coal
DS: Discard Coal
ACD: Activated Carbon from Discard Coal

Results and Discussion

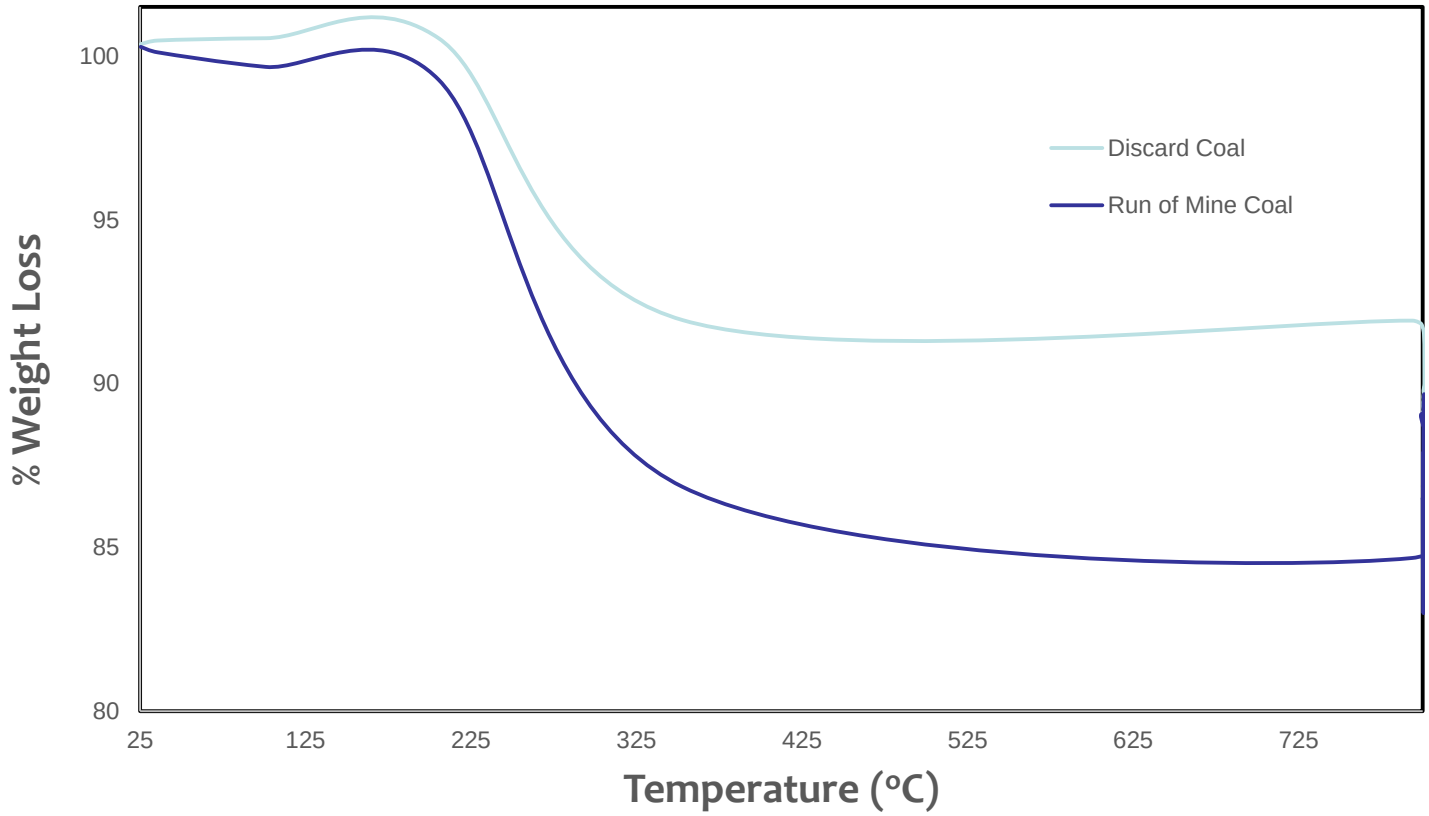


Figure 4: TGA Curves of the Activated Carbon Precursors during Activation Process

Results and Discussion

Table 4: N2 Adsorption Data

ROM

Relative Pressure (P/P₀)	Quantity Adsorbed (cm³/g STP)
0.0517	1.2000
0.1241	1.3688
0.1996	1.4890
0.2746	1.5945
0.3496	1.6884
0.9905	13.5561

ACR

Relative Pressure (P/P₀)	Quantity Adsorbed (cm³/g STP)
0.0522	388.0564
0.1228	452.1542
0.2460	574.3142
0.3160	659.8982
0.4859	734.4788
0.9893	892.2163

DS

Relative Pressure (P/P₀)	Quantity Adsorbed (cm³/g STP)
0.0538	0.9246
0.1243	1.0485
0.1996	1.1340
0.2746	1.2185
0.3494	1.2955
0.9944	9.0168

ACD

Relative Pressure (P/Po)	Quantity Adsorbed (cm³/g STP)
0.0566	392.6872
0.1284	466.6385
0.2393	567.1711
0.3148	592.3061
0.4502	717.0359
0.9873	819.892

Results and Discussion

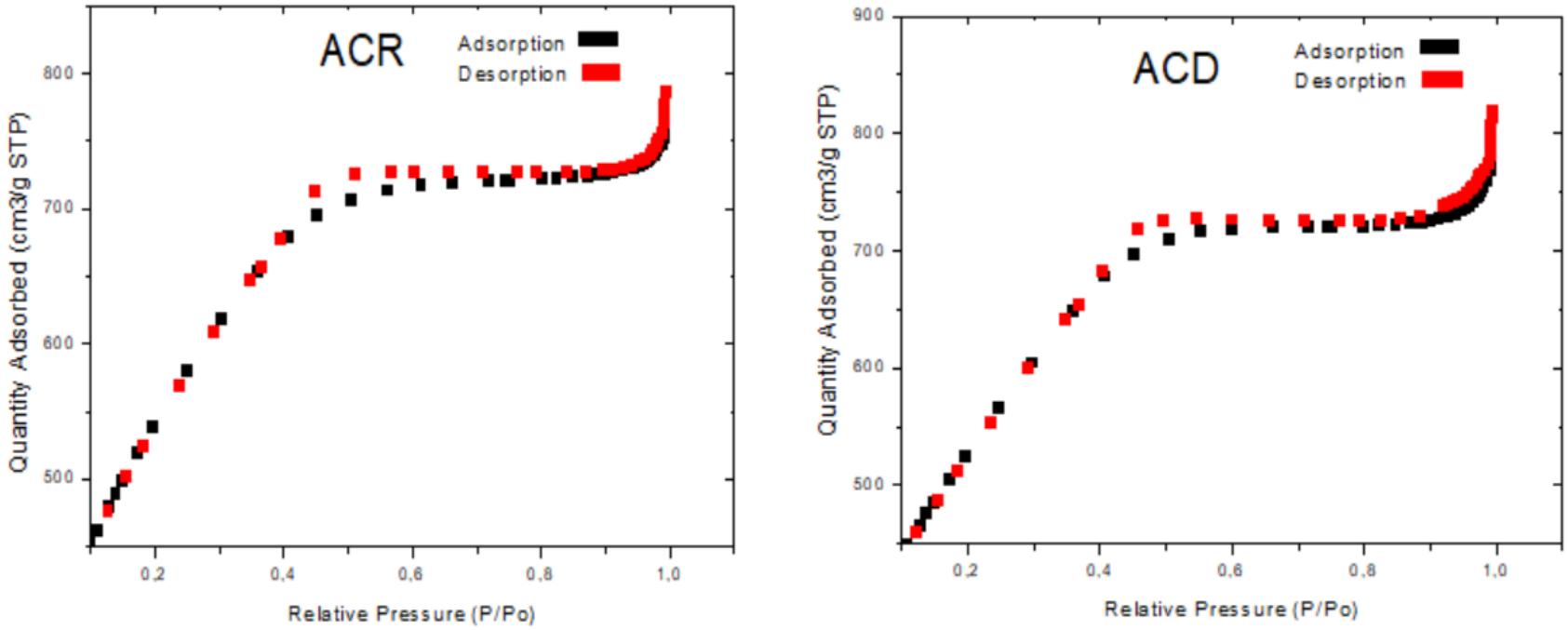


Figure 5: N_2 Adsorption-Desorption Curves of ACR and ACD

Results and Discussion

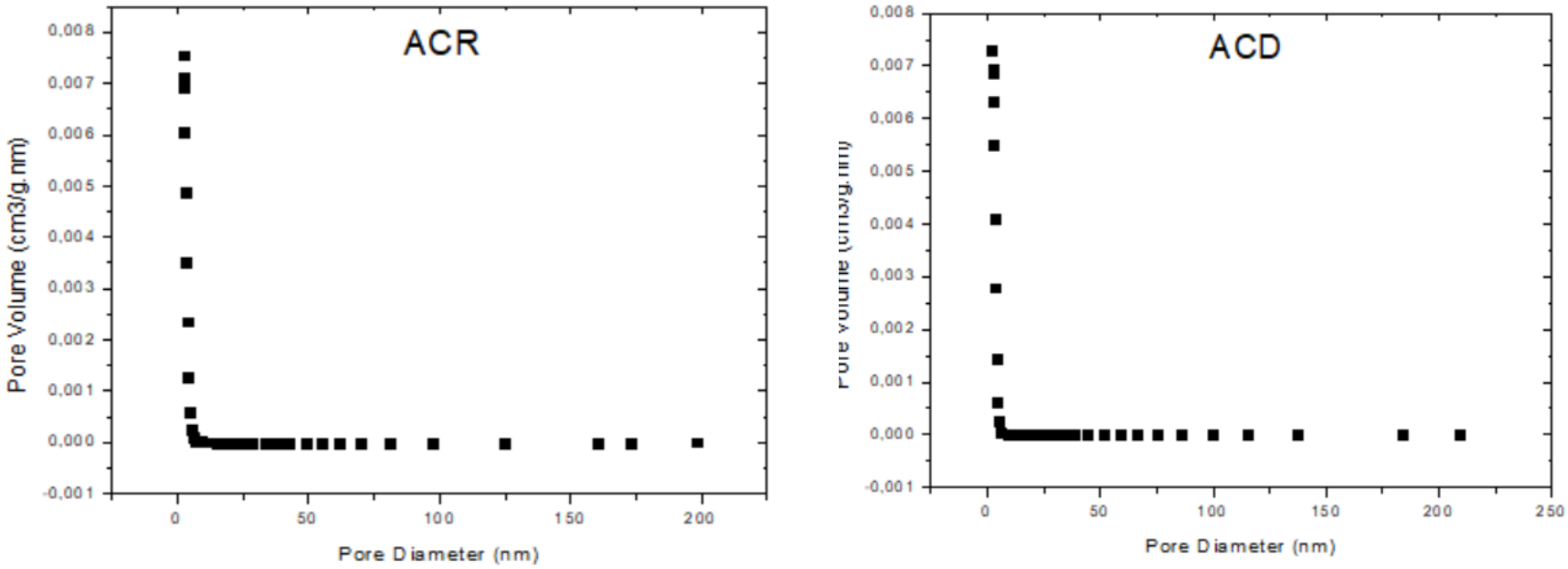


Figure 6: BJH Pore Size Distribution Plot of ACR and ACD

Results and Discussion

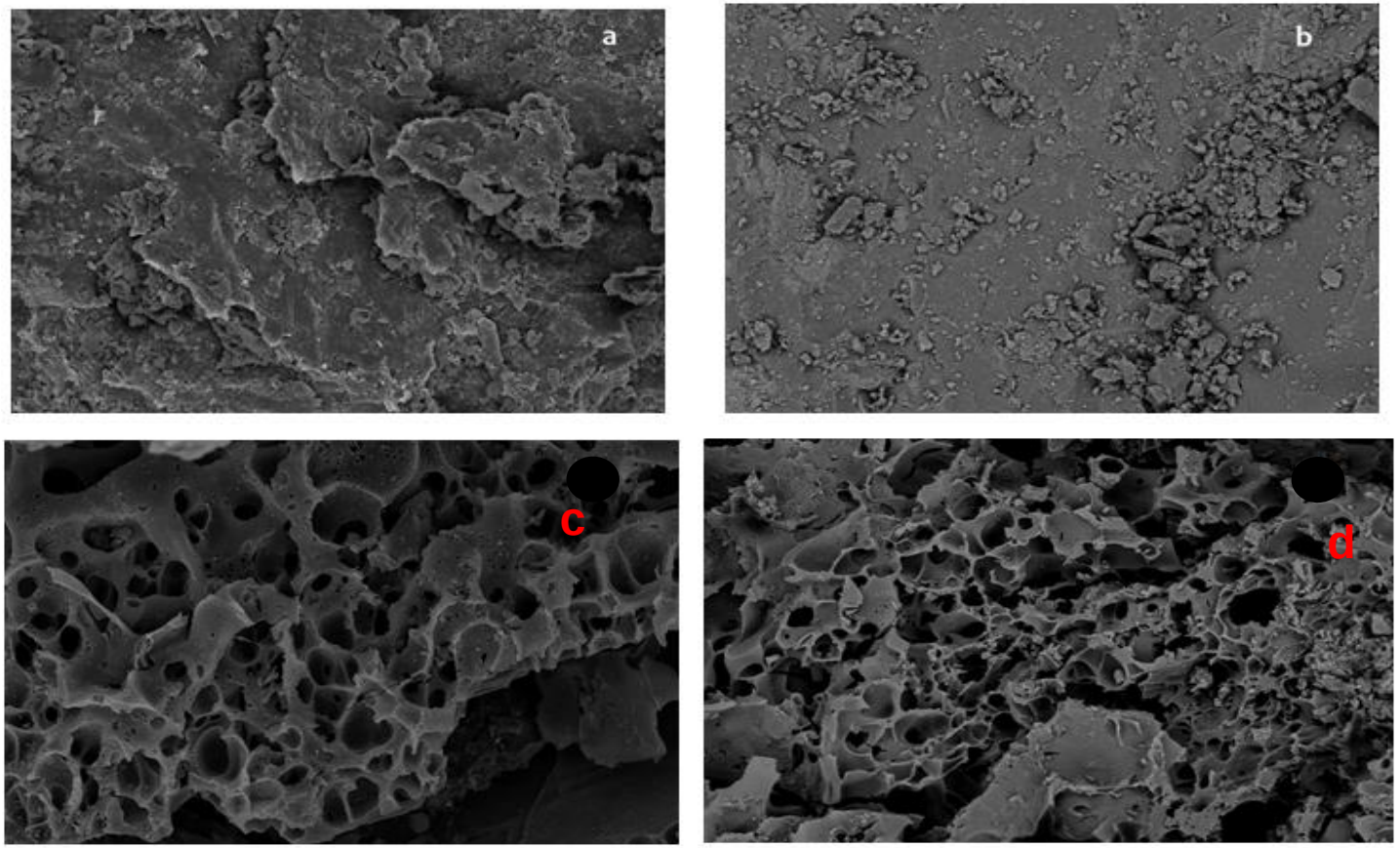


Figure 7: SEM Image of (a) Run of Mine Coal (b) Discard Coal (c) Activated Carbon from Run of Mine Coal (ACR) (d) Activated Carbon from Coal Discard (ACD) at 2000 magnification

Results and Discussion

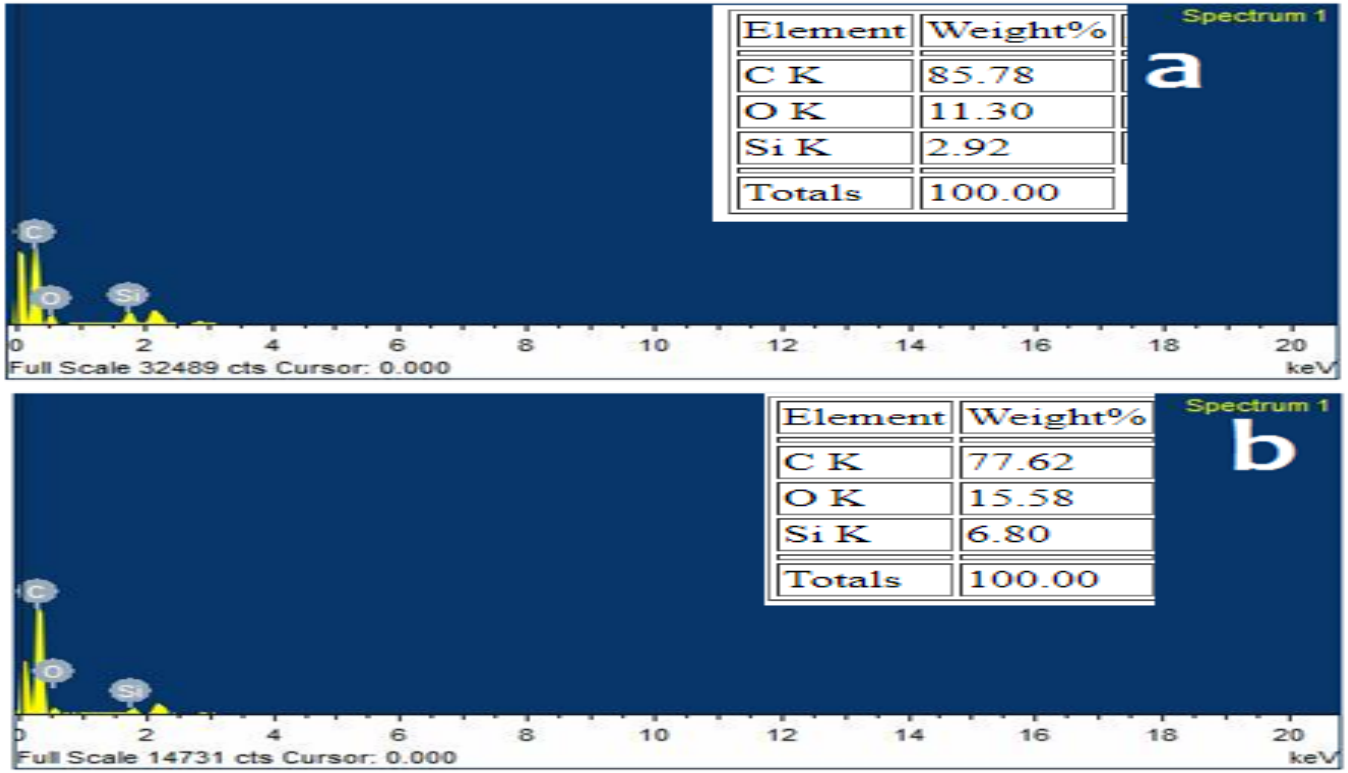


Figure 8: EDS Analysis Spectrum of (a) Activated Carbon from Run of Mine Coal (ACR) and (b) Activated Carbon from Coal Discard (ACD)

Results and Discussion

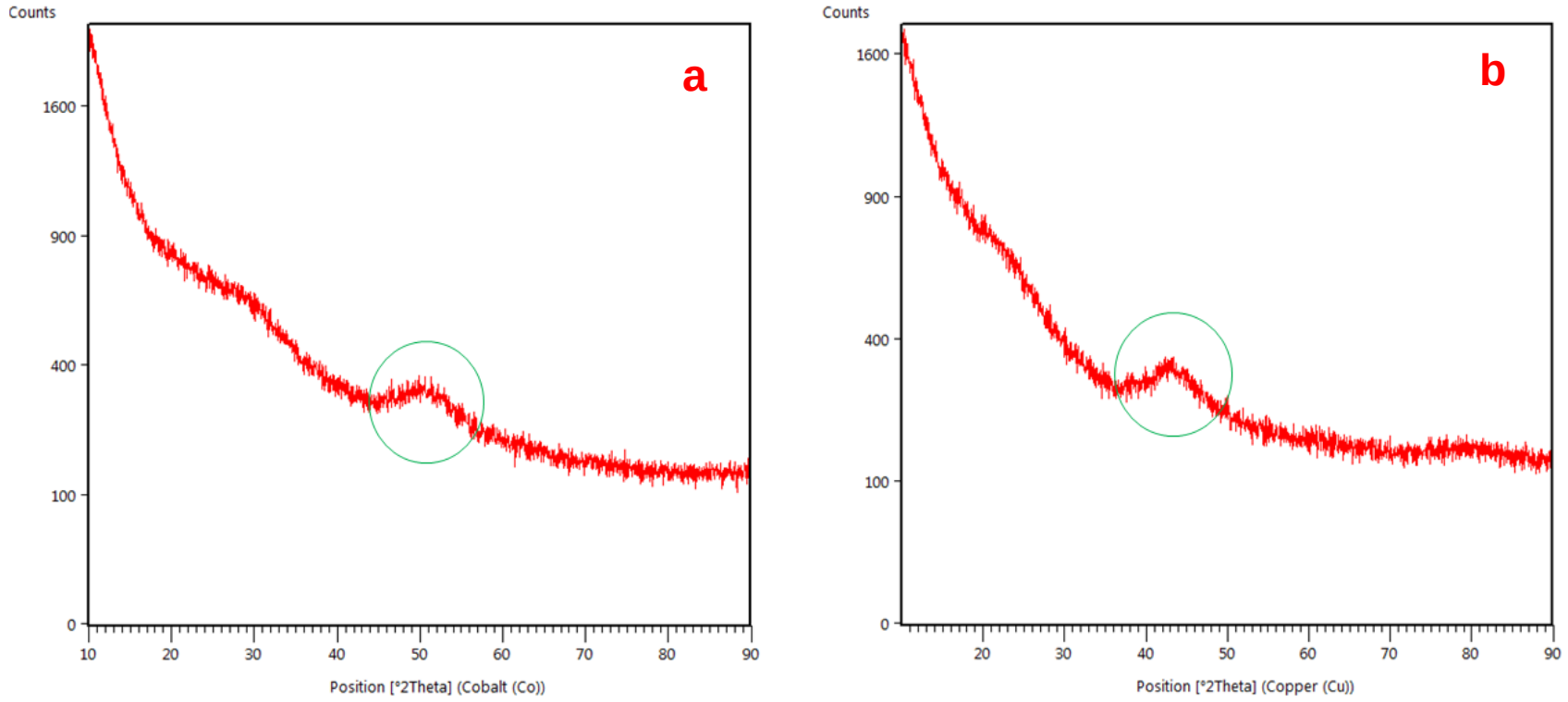
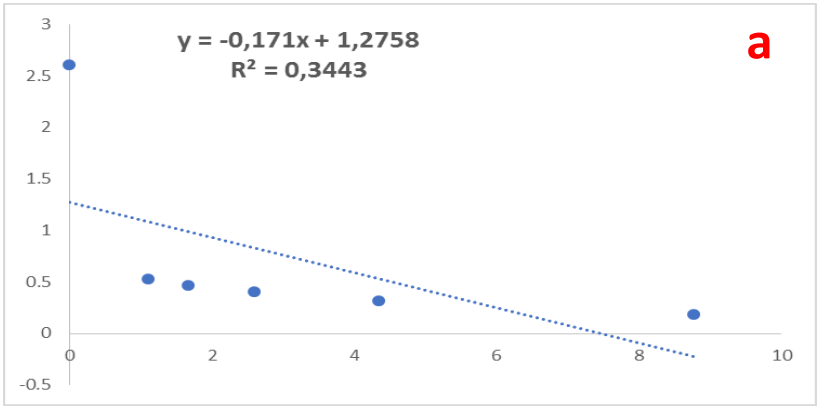
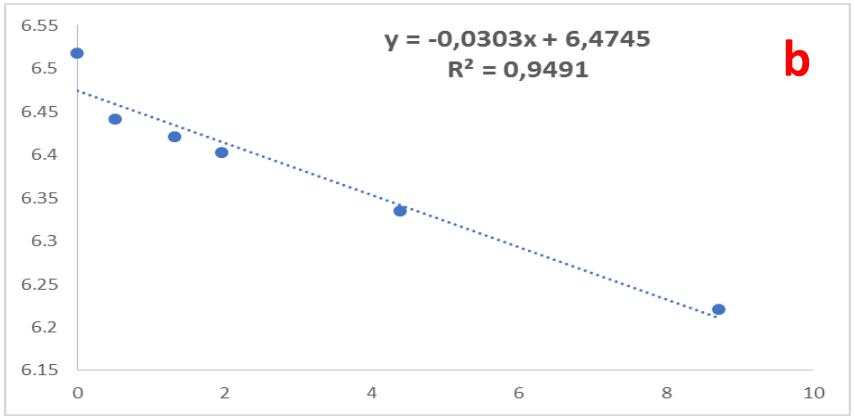
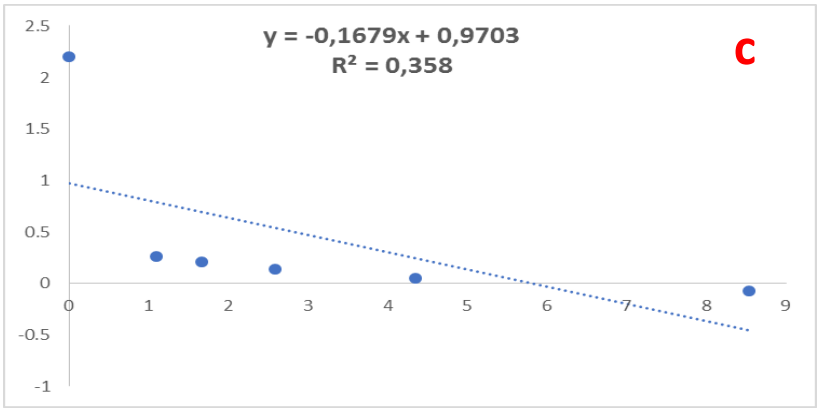


Figure 9: X-Ray Diffraction Profile of (a) Activated Carbon from Coal Discard (ACD) and (b) Activated Carbon from Run of Mine Coal (ACR)

The **Dubinin - Radushkevich (D-R)** model empirically showed the defining characteristic of a microporous material.







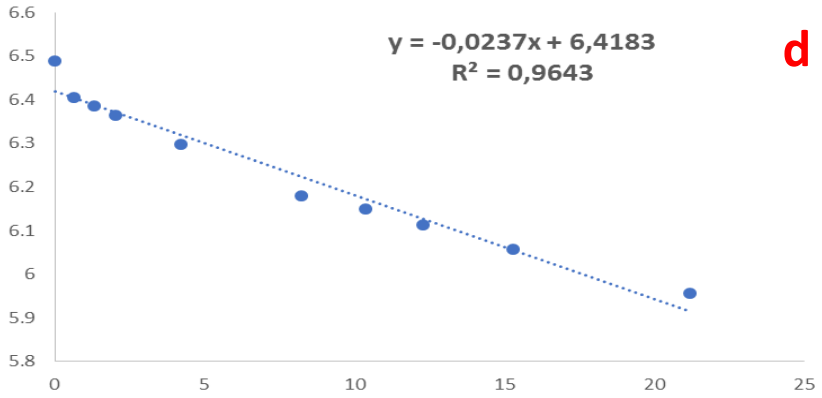


Figure 10: Dubinin-Radushkevich (D-R) plot of CO_2 Adsorption on (a) Run of Mine coal (b) Activated Carbon from Run off Coal (ACR) (c) Discard Coal (d) Activated carbon from Discard coal

Table 5: Surface Area and Application of Activated Carbons Produced from Coal Materials

S/N	Activated Carbon Source	Surface Area (m^2/g)	Application	Reference
1.	Blackwater coal mine in Queensland's Bowen Basin (Australia)	1401	N_2, CO_2 and Methane	(Gao et al., 2017)
2.	Indonesian low grade coal	668	CO_2 and Methane	(Martin et al., 2017)
3.	mineral coal (commercial activated carbon)	900	Removal of organic compounds from gases.	(CarboTech, 2016)
4.	An Illinois Basin coal	1560	N_2	(Sun et al., 1997)
5.	Anthracite coal	2085	Methane	(Lozano-Castello et al., 2002)
6.	Bituminous Coal	1150	Methane	(Himeno et al., 2005)
7.	Ning Xia Anthracite coal, china	2398.1	CO_2 and Methane	(Zou and Han, 2001)
8.	South African bituminous coal	350	Metal extraction	(Campbell et al., 2012)

Conclusions

- Activation carbons were synthesised from discard coal at a temperature of 400 – 800 °C and chemical agent to discard coal ratio of 1:1, 1:2.5 and 1:4 to ascertain the sample with the highest porosity
- The sample run conducted at 800°C and weight ratio 1:4 gave the highest surface area of 1766.8 m^2/g and pore size of 2.77nm.
- Run of mine coal was also activated and used as a reference.
- Activated Carbon obtained from run of mine coal was found to have a surface area of 1827.7 m^2/g and pore size 2.92 nm

Conclusions

- The values obtained meet and exceed the surface area of 1000m^2/g and pore size of 2 nm required for a good carbon adsorbent for gas storage application.
- Discard coal, a waste material from a coal beneficiation process is a good material for producing highly porous activated carbon.
- The textural properties obtained from the characterizations gave an insight into the potential of activated carbons from discard coal in natural gas storage.

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