



OPTIMIZATION OF ACTIVATED CARBON PREPARATION FROM SUGARCANE BAGASSE USING ZINC CHLORIDE AND PHOSPHORIC ACID

WAZIRI JIBRIN., MUSA H. ABDULKADIR,
ABDUL A.

Chemical Engineering Department, Kaduna
Polytechnic, Kaduna Nigeria.

Abstract

Activated carbon preparation from sugarcane bagasse using zinc chloride and phosphoric acid was optimized using one variable at a time (OVAT) method. The sugarcane bagasse in each case was first carbonized at 500 °C at a retention time of 1 h. This was followed by treating the bagasse with 0.5M, 1.0M, 1.5M, 2.0M and 2.5M solutions of zinc chloride and phosphoric acid respectively. The H₃PO₄-AC samples of the aforementioned concentrations were named A1, B1, C1, D1 and E1; while the ZnCl₂AC samples of similar concentrations were named A2, B2, C2, D2 and E2 respectively. The 1.5 M ZnCl₂-AC revealed the highest micropore sized particle of 100 μm and highest surface area of 331.987 m²/g from the Scanning Electron Microscopy (SEM) as well as

Brunauer Emett Teller (BET) surface results respectively among the ZnCl₂-AC. It also gave the most significant drop in absorbance of gum

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Arabic solution, implying a high absorption capacity. On the other hand, the 1.0M H₃PO₄-AC showed the highest micropore sized particle of 50 μm and highest surface area of 301.263 m²/g from the Scanning Electron Microscopy (SEM) and Brunauer Emett Teller (BET) surface results among the H₃PO₄-AC. It further gave the most significant drop in absorbance of the gum Arabic solution,

implying a high absorption capacity. The 1.5 M ZnCl₂-AC had the overall highest pore size as well as BET surface. Both sets of AC were found to best suit Langmuir isotherm indicated by the highest R² values of 0.9941 and 0.9738 respectively. The results of proximate analysis obtained for the entire sets of AC samples conform to ASTM standards.

INTRODUCTION

Activated carbon is a well-known material used in ever increasing numbers of environmental applications, in environment protection, in water and wastewater treatment, in gas filters, etc. Activated carbon can be produced theoretically from any carbonaceous material rich in elemental carbon. In the recent years, there is growing interest in the production of activated carbons from agricultural by products and residual wastes. Agricultural by-products available in large quantities are bagasse- the fibrous by products resulting from the milling of sugarcane- and rice husks. The annual global production of 800 million tonnes of sugarcane results in 240 million tonnes of bagasse while the estimated annual world rice production is about 571million tonnes resulting in approximately 140 million tonnes of rice husk available annually for utilization. Despite the wide consumption of bagasse and rice husks as a fuel for the mill boilers, for electricity and steam generation, animal feed or as a raw material for the manufacture of paper and board, the residues still remain as a surplus which poses a disposal problem for mill owners. The processing and transformation of agricultural residues into activated carbon with good adsorption properties would alleviate problems of disposal and management of these waste byproducts, while providing a high-quality end product for water and wastewater treatment that could potentially expand the carbon market. Production of activated carbon from bagasse and rice husk is achieved through pyrolysis and activation with chemical or physical means. Chemical impregnation with KOH and NaOH of pyrolysed rice husk followed by activation at 650–800°C resulted in activated carbons with extremely high surface areas (1413–3014 m²/g) (Ahmedna *et al.*, 2004; Guo *et al.*, 2003). Pyrolysis of rice husk followed by H₃PO₄ impregnation and activation at high temperatures (700–900°C) produced activated carbon

with a surface area of 450 m²/g (Kennedy et al., 2004). Activated carbon produced by chemical activation with KOH or H₃PO₄ achieved high yield and removal efficiencies comparable to those of commercial products (Lozano-Castello et al., 2002; Nakagawa et al., 2004; Rahman et al., 2005). Other chemical agents studied include ZnCl₂, FeCl₃ · 6H₂O, KCl, CaCl₂ · 7H₂O and FeSO₄ · 7H₂O. Use of these agents and activation at 600°C resulted in activated carbons with surface areas ranging from 168 to 480 m²/g. The optimal chemical mixture was with ZnCl₂ 10% (w/w) (Yalcin and Sevinc, 2000). Physical activation of dry bagasse in a two-stage carbonization/activation process within a temperature range of 750–840 °C produced activated carbon with significant surface areas (404–607 m²/g), the surface area increasing with increasing temperature (Juang et al., 2002). Two-stage steam activation of sugarcane bagasse resulted in activated carbons with 565 m²/g surface area (Ng et al., 2002). Chemical carbonization of bagasse with concentrated sulfuric acid at a 4:3 ratio and subsequent CO₂ activation at 900°C produced activated carbons with very high surface areas (403–1433 m²/g) for long retention times (Valix et al., 2004). Chemical impregnation of bagasse with concentrated sulphuric acid and heating at 150°C for 24 h, produced activated carbons with 312 m²/g surface area, which effectively removed 90% of Pb from samples within 2 h contact time (Ayyappan et al., 2005). Low temperature carbonization of H₂SO₄ impregnated bagasse, followed by subsequent activation with CO₂ at high temperatures (900°C), resulted in activated carbons with surface areas ranging from 403 to 1433 m²/g, the lowest referring to the carbonized only matter (Valix et al., 2004). Zinc chloride up to 1:1 (w/w) was used as the chemical agent for bagasse impregnation in the work of Tsai et al. (2001). The mixture was heated for 0.5 h and the resulting surface areas were up to 790 m²/g for 1:1 (w/w) biomass to chemical ratio.

In all previously cited studies, the produced carbons had significant surface areas and adsorption capabilities, in many cases comparable to the commercially available carbons. However, their production method involved several stages of preparation, long retention times for pyrolysis and activation and often elevated temperatures. This study aimed to

produce activated carbon from **activated** bagasse and rice husk in a single activation process in relatively short retention times. For this purpose, the precursor was impregnated with a chemical agent before being fed to the reactor. Results were compared to those of conventional two-stage physical processes.

Material and Methods

Reagents and Materials used

All reagents/chemicals used in the course of this study were used as purchased. Gum Arabic samples was purchased from Bakindogo market in Kaduna state; the sugarcane bagasse was also collected from the same market. The phosphoric acid, zinc chloride and distilled water were all obtained from chemical engineering laboratory of Kaduna polytechnic, Kaduna.

Preparation of Activated Bagasse

The waste bagasse was first cut into pieces washed thoroughly with tap water and then with distilled water to remove debris and other impurities. It was then dried in an oven at 80°C and then cooled in desiccator. The dried bagasse was further crushed into smaller size of 1mm and charged into a furnace for carbonization at 500°C. The carbonized sample was then chemically activated using phosphoric acid and zinc chloride solutions respectively. In each case, 30 g of the carbonized sample was impregnated in phosphoric acid solutions of 0.5M, 1.0M, 1.5M, 2.0M and 2.5M respectively for a period of 24 h after which the samples were withdrawn, thoroughly washed with distilled water and dried. Fixed beds of the resulting H₃PO₄-AC samples (A1-E1) were prepared in a 18cm by 5 cm plastic cylinder and used individually to decolourize gum Arabic solution. The same chemical activation process was repeated using 0.5M, 1.0M, 1.5M, 2.0M and 2.5M solutions of zinc chloride respectively. A bed of the resulting ZnCl₂- AC samples (A2 to E2) was made and also used individually to decolourize gum Arabic solution.

Decolourization of Gum Arabic Sample

50g of powdered gum Arabic was dissolved in 1000ml of distilled water. 100ml of the solution was carefully measured into 5 different beakers and their initial absorbance recorded. The gum Arabic solution was then introduced into a separating funnel and passed through the AC bed (sample A1) at the rate of 5 m³/s. At the end of the adsorption process, the final absorbance was measured. This procedure was repeated using all other H₃PO₄-AC samples (B1 – E1) as well as the ZnCl₂- AC samples (A2 to E2).

RESULTS AND DISCUSSION

Results

Table 1: Proximate Analysis of the Various Samples of H₃PO₄-AC

<i>Samples</i>	<i>Moisture Content (%)</i>	<i>Content (%)</i>	<i>Volatile (%)</i>	<i>Matter (%)</i>	<i>Ash</i>	<i>Fixed Carbon (%)</i>
<i>A1</i>	14.040	67.380	5.706			15.446
<i>B1</i>	10.320	68.517	5.526			25.763
<i>C1</i>	10.920	68.388	5.682			22.010
<i>D1</i>	10.860	68.533	5.681			22.082
<i>E1</i>	10.460	68.684	5.679			18.935

Table 2: Proximate Analysis of the Various Samples of ZnCl₂- AC

<i>Samples</i>	<i>Moisture (%)</i>	<i>Content (%)</i>	<i>Volatile (%)</i>	<i>Matter</i>	<i>Ash Content (%)</i>	<i>Fixed Carbon (%)</i>
<i>A2</i>	14.580		67.160		4.749	13.511
<i>B2</i>	14.418		67.194		4.901	13.487
<i>C2</i>	14.020		67.330		4.735	13.924
<i>D2</i>	14.100		67.367		4.609	13.916
<i>E2</i>	14.248		67.236		4.826	13.690

Table 3: Physical Properties and Yield of H₃PO₄-AC

<i>Samples</i>	<i>Density (g/cm³)</i>	<i>pH</i>	<i>Yield (%)</i>
A1	0.28	6.60	21.007

B1	0.28	6.67	21.020	
C1	0.27	6.43	20.737	
D1	0.30	7.10	20.847	
E1	0.29	7.15	21.007	

Table 4: Physical Properties and Yield of ZnCl₂ – AC

Samples	Density (g/cm ³)	pH	Yield (%)
A2	0.27	6.90	22.202
B2	0.29	7.43	24.312
C2	0.28	7.30	22.067
D2	0.28	7.50	22.210
E2	0.27	7.50	22.207

Table 5: Concentration of Gum Arabic solution before and after Adsorption using H₃PO₄ -AC

AC Samples	Sample A2	Sample B2	Sample C2	Sample D2	Sample E2
Initial Absorbance	0.487	0.487	0.487	0.487	0.487
Final Absorbance	0.400	0.298	0.107	0.104	0.103

Table 6: Concentration of Gum Arabic solution before and after Adsorption using ZnCl₂ – AC

AC Samples	Sample A1	Sample B1	Sample C1	Sample D1	Sample E1
Initial Absorbance	0.487	0.487	0.487	0.487	0.487
Final Absorbance	0.204	0.103	0.107	0.104	0.103

Table 7: Freundlich isotherm parameters for gum Arabic decolorization

Parameter	H ₃ PO ₄ – AC	ZnCl ₂ - AC
Intercept	3.443	3.329
Kf	31.274	27.919

1/n	-0.547	-0.437
N	-1.827	-2.291
R ²	0.929	0.9574

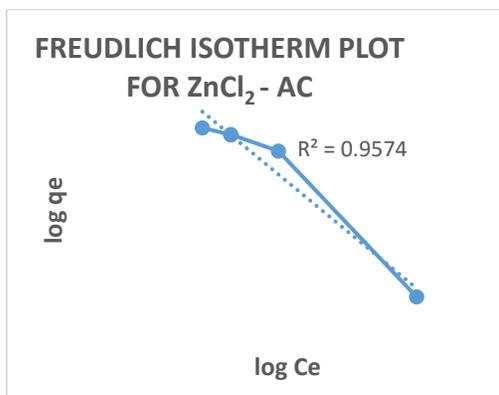


Fig 1: Freudlinch isotherm plot for ZnCl₂- AC

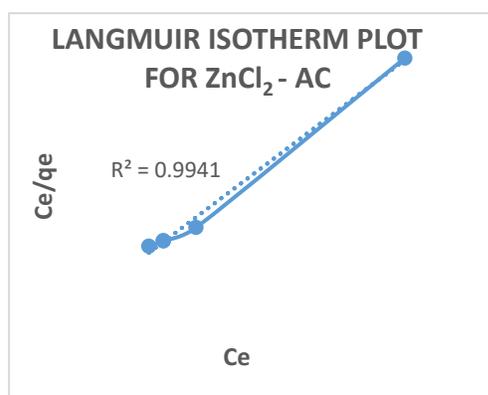
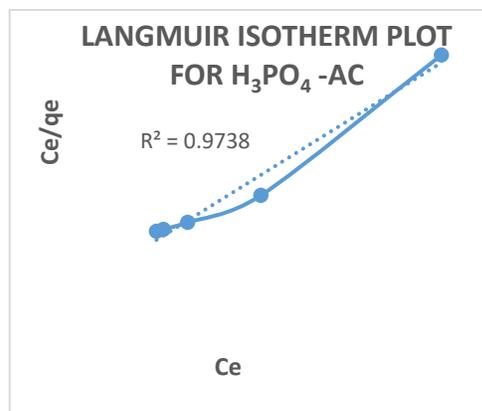
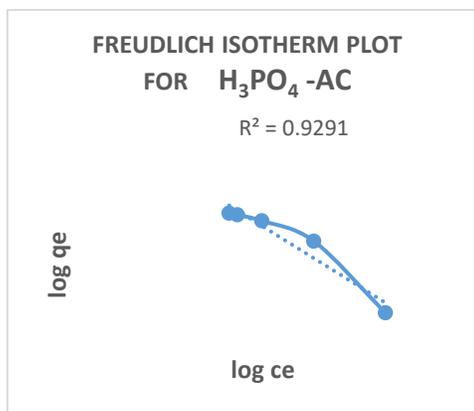


Fig.2: Langmuir Isotherm Plot for H₃PO₄ - AC

Table 8: Langmuir isotherm parameters for gum Arabic decolourization

Parameter	H ₃ PO ₄ - AC	ZnCl ₂ - AC
Intercept	0.007	0.004
Slope	0.002	0.002
q _{max} (mg/g)	454.545	555.556
K _L (L/mg)	0.310	0.474
R _L	0.129	0.081
R ²	0.9738	0.9942



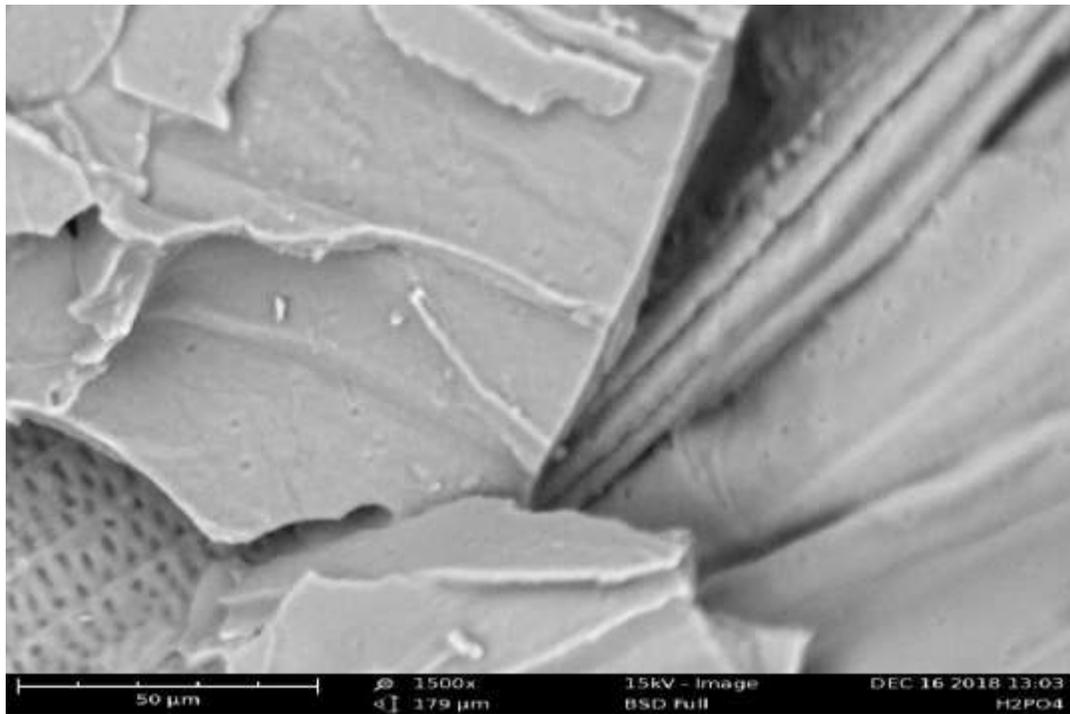


Fig5: SEM image for H₃PO₄ – AC activated using 1.0 M solution of phosphoric acid

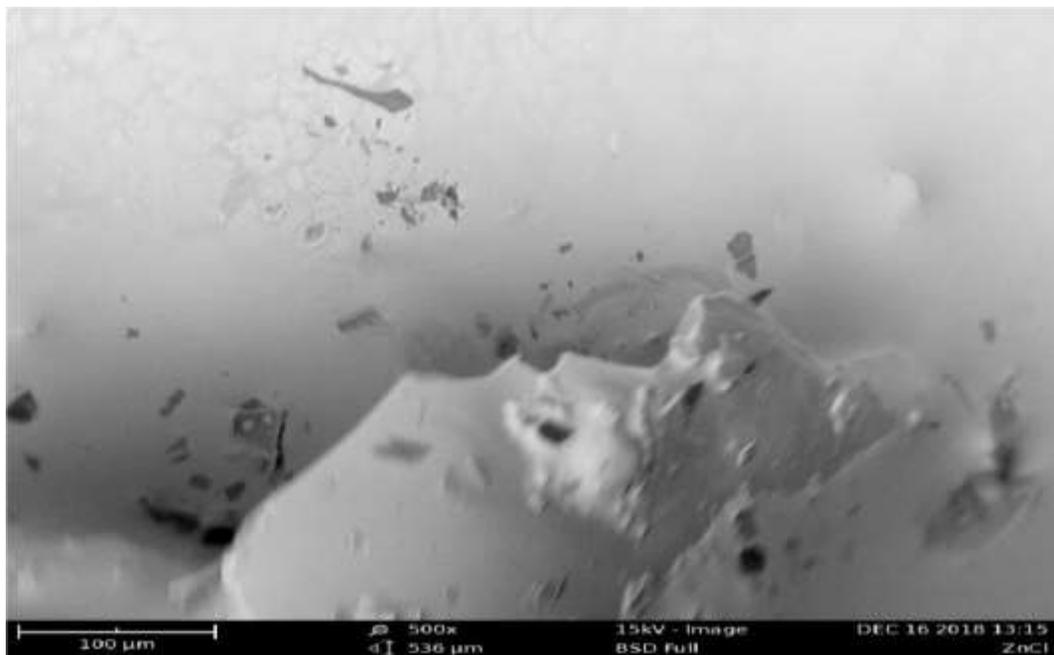


Fig 6: SEM image for ZnCl₂- AC activated using 1.5 M solution of zinc chloride

In this study, five different samples of H_3PO_4 – AC and $ZnCl_2$ -AC were separately prepared using 0.5M, 1.0M, 1.5M, 2.0M and 2.5M concentrations of phosphoric acid and zinc chloride respectively.

Proximate Analyses

Proximate analyses of the various AC samples prepared are as presented in Tables 1 and 2 respectively. In both cases, the moisture content falls within the ASTM standard. The moisture content of the $ZnCl_2$ -AC is within the range of 14.040% - 10.460%, while those of H_3PO_4 – AC falls within 14.580% - 14.248%. It can be observed that the $ZnCl_2$ -AC shows less moisture content compared to H_3PO_4 – AC. This implies that the $ZnCl_2$ -AC will show better adsorption properties than the H_3PO_4 -AC samples.

It can be observed from the two tables that the ash contents of the AC samples all fall within the ASTM standard limit of <8%. The H_3PO_4 – AC is within the range of 5.706% - 5.679% while the $ZnCl_2$ -AC falls within the range of 4.749% - 4.826%. This implies that the major part of the combustible matter in the activated carbon have been burnt off. However, the ash content of the $ZnCl_2$ -AC is lower than that of the H_3PO_4 -AC at equivalent activation conditions.

The volatile matter of the H_3PO_4 – AC falls within the range of 67.380 - 68.684 while that of the $ZnCl_2$ -AC is within the range of 67.160- 67.236. These range of values falls within the ASTM standard of 56.81 to 74.86% as obtained by Lee and Ao, (2005). The $ZnCl_2$ -AC revealed a lower volatile matter which makes it a better adsorbent than the H_3PO_4 -AC and connotes higher pore volume (Rashidi *et al.*, 2014). In general, low amount of moisture, ash and volatile matter indicates that the particle density is relatively small and the bagasse should be an excellent material for adsorbents to be used in columns and fixed bed reactors. The fixed carbon content of the activated carbon was within the range of 15.446 to 25.763% which is in line with values obtained by (Võ-Ngọc *et al*, 2016)

Physical Properties

The bulk density was estimated on dry basis. It is an indication of the floatability property of the adsorbent. It was observed to fall within the range of 0.27 – 0.30 g/cm³ for H₃PO₄-AC and within 0.27 – 0.29 for ZnCl₂-AC. The values obtained for all samples show good floatability of the ACs shows compared favorably with values of 0.25 – 0.28 g/cm³ reported by Qureshi *et al.*, (2008).

The pH values of the H₃PO₄-AC set of samples is within the range of 6.60 - 7.15 and those of ZnCl₂-AC range between 6.90 – 7.5. This is in line with the ASTM standard range of 6-8 corresponding to results obtained by Williams *et al.*, (2004).

The percentage yield of the H₃PO₄-AC was obtained within the range of 22.067 to 24.312%. The highest percentage yield of 24.312 was obtained with the sample prepared using phosphoric acid of 1.0 M solution. Similarly, percentage yield of the ZnCl₂-AC is within 20.737% - 21.020%. The highest percentage yield was obtained at with sample activated with 1.0M ZnCl₂. This value is in agreement with that obtained by Qureshi *et al.*, (2008) and Patil and Kulkarni, (2012) connoting the fact that the difference between the mass of the carbon sample before and after activation at this chemical concentration is significant.

The absorbance of the gum Arabic solution by the two sets of AC samples was measured using the COLE- UV-7120 spectrophotometer at a wavelength of 581 nm. The initial absorbance of the gum Arabic stock solution was 0.487. This concentration was reduced to 0.103 after treating it with ZnCl₂-AC. A significant drop in the value of the absorbance was observed with bagasse activated using 1.5 M solution of ZnCl₂. This implies that the colour was absorbed most with the AC sample activated with 1.5M solution of ZnCl₂. Thereafter the colour absorption was found to be infinitesimal using AC prepared with ZnCl₂ solution of 2.0 M and 2.5 M respectively. Similarly, the colour absorption of gum Arabic decreased to the range 0.103 when treated with the H₃PO₄AC. A significant drop in the value of the absorbance was observed using bagasse activated using 1.0 M solution of H₃PO₄. This implies that the colour was absorbed most with the AC sample activated

with 1.0 M solution of H_3PO_4 . Thereafter the colour absorption was found to be infinitesimal using AC prepared with H_3PO_4 solution of 1.5 M, 2.0 M and 2.5 M respectively. These range of values conform to those reported by Qureshi *et al*, (2008) and Rodriquz *et al.*, (2014).

Adsorption Isotherms

Table 7 shows the slope $1/n$ for Langmuir isotherm parameters for H_3PO_4 -AC and $ZnCl_2$ -AC. The slope of the $ZnCl_2$ -AC was obtained as 0.437 which is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Okoli, 2014). The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which describes the type of isotherm. A value of $R_L > 1$ implies Langmuir isotherm unfavorable, $R_L = 1$ implies Langmuir isotherm linear, $0 < R_L < 1$ implies Langmuir isotherm favorable and $R_L = 0$ implies is Langmuir isotherm irreversible (Võ-Ngọc, 2016). The R_L value for AC is 0.081 which indicates that it favours ($0 < R_L < 1$) Langmuir isotherm for gum Arabic decolourization. From the Freundlich and Langmuir isotherm plots for $ZnCl_2$ -AC as shown in Figures 1 and 2, the R^2 values was obtained as 0.9574 and 0.9941 respectively. This shows that the regression value with respect to Langmuir is higher than that obtained with respect to Freundlich isotherm thus indicating that the AC best suit the Langmuir isotherm.

Tables 8 shows the Freundlich isotherm parameters for both the $ZnCl_2$ -AC and H_3PO_4 -AC respectively. The slope $1/n$ for the H_3PO_4 – AC range between 0.547 which is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Okoli, 2014). A value for $1/n$ below one indicates a normal Langmiur isotherm while $1/n$ above one is indicative of cooperative adsorption (Okoli, 2014). Regression values of 0.9291 and 0.9738 are obtained for Freudlinch and Langmuir plots for H_3PO_4 – AC as shown in Figures 3 and 4 respectively. In general, it is revealed that both the Freundlich and Langmuir isotherm values for the $ZnCl_2$ -AC are greater than those of H_3PO_4 -AC

Figure 2 shows the SEM analysis carried out using a resolution of 1500X and 15kV for the H_3PO_4 -AC sample. A micropore size of 50 μ m was obtained with rough agglomerates. This conforms to results obtained by Rodriguez *et al*, (2014), Lozano *et al*, (2002) and Rahman *et al.*, (2005). Figure 3 shows the SEM analysis carried out using a resolution of 500X and 15kV of the sample. A micropore size of 100 μ m was obtained with smooth agglomerates. This conforms to results obtained by (Odebunmi & Okeola, 2001) and (Devnarain *et al*, 2002). The result obtained for the $ZnCl_2$ -AC sample using 1.5 M gave the best SEM result.

The Brunauer Emmett Teller (BET) surface area was obtained as 331.987 m²/g for the $ZnCl_2$ -AC while that of H_3PO_4 – AC was obtained as 301.263 m²/g. The duo implies a surface area significant enough for effective adsorption of the gum Arabic solution. This is complemented with the increased pore volume as indicated by the volatile matter. This is in line with results obtained by Encinar *et al.*, (1998), Guo *et al.*, (2008) and Kennedy *et al.*, (2004).

Conclusion and Recommendation

Conclusion

From the results obtained, it can be concluded that the 1.5 M $ZnCl_2$ -AC gave the highest pore size as well as surface area from the SEM and BET results respectively. It also showed a high colour absorption of the gum Arabic solution compared to other activated carbon samples thereby revealing the highest absorption capacity. The proximate analysis of all the activated carbon samples prepared all conform to ASTM standard; and its isotherm best suits Langmuir model.

Recommendation

Studies on the efficacy of activated carbon preparation should be carried out using various agricultural wastes in order to promote local content and to enhance solid waste management and control.

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