

SORPTION AND CHARACTERIZATION STUDIES OF ACTIVATED CARBON PREPARED FROM POLYETHYLENE TEREPHTHALATE (PET)

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ABSTRACT. *A series of activated carbons (ACs) were prepared from cut pieces of polyethylene terephthalate (PET) via semi-carbonization followed by physical activation using a two-stage self-generated atmosphere method. The best AC was obtained by using a temperature of 700°C and 5 hours of carbonization period. The percentage yield decreased with increasing activation temperature, whereas the activation time did not have a significant effect on the yield. With a moisture content and ash content of less than 10% and 1% respectively, this material was suitable for AC production. The BET surface area was measured at 515.41 m²/g, with a Type I isotherm and an H4-type adsorption hysteresis loop concurring that the AC was a microporous solid with chemisorption properties.*

KEYWORDS. Activated carbon (AC), 2,5-dichlorophenol (2,5- DCP), polyethylene terephthalate (PET), physical activation

INTRODUCTION

Anthropogenic activities, particularly agricultural, domestic, industrial, recreational and environmental activities, have greatly contributed to water pollution. Water consumption is increasing at a rapid rate as the global population continues to increase at a remarkable rate, which implies that our utilizable water resources are decreasing over time. Drinking water that has been contaminated by chemicals and minerals, such as pesticides and arsenic, can have chronic effects on human health (Tatiya, 2010). Therefore, water pollution has become an increasingly critical issue and is a major concern to our research group.

Considerable effort has currently been focused on finding a more effective solution for treating polluted water, and one method for treating wastewater is the use of carbon adsorbents. The reason for the use of adsorbents is because adsorption has become a well-established technique for removing pollutants, and activated carbon (AC) has been found to possess suitable characteristics as an adsorbent for the purification of water with a low pollutant concentration (Mestre *et al.*, 2009). AC primarily consists of an amorphous solid that has an extraordinarily large internal surface area and pore volume (Tsai *et al.*, 2001). The adsorptive property of AC is mainly due to the porosity of the AC and, to a smaller extent, the surface oxygen sites on the AC's active sites.

AC can be produced from any material that is rich in carbon, and one example of such a material is polyethylene terephthalate (PET). PET is a thermoplastic polyester resin that contains alternating ethylene and terephthalate groups (Beswick & Dunn 2002; Joseph *et al.*, 2011; Nakagawa *et al.*, 2003).

PET is also known as the number one plastic because it has high clarity, high strength, toughness and it is non-permeable to gases and moisture. Presently, this material is widely used as a packaging material for soft drink bottles, dressing bottles and peanut butter jars. It has been reported that PET consumption currently has the fastest growth rate in the global plastic market due to ongoing expansion of the PET bottle market (Mestre *et al.*, 2009). Consequently, there is an issue related to the recycling and disposal of PET due to its low bio- and photo-degradability. The choice of PET as the raw material in this study is due to its widespread commercial use for replacing glass in soft drink bottles and containers and because it has produced considerable amounts of solid waste. This study proposes to utilize PET waste as a precursor for high-value carbon adsorbents that can serve as a solution to the problem of recycling and disposing of PET wastes and at the same time generate a waste-to-wealth opportunity. The AC was prepared using the physical activation method, and the preparation temperature and time were optimized and evaluated. The physical activation method was selected to limit the use of chemicals, which is in line with our continuous efforts to promote the green chemistry concept.

EXPERIMENTAL

Sample preparation and activation

The PET was cut into small pieces, approximately 1 cm². Twelve samples (labeled AC-A to AC-L), 20 g each, were placed in a stainless steel petri dish. The samples were semi-carbonized at 200°C in a muffle furnace for 15 minutes and were then carbonized using various activation times and temperatures in the same muffle furnace. The activation time, activation temperature and the label for each of the ACs represented in Table 1. The prepared samples were washed with 0.1M nitric acid to remove any heavy metals that were present, followed by washing with distilled water to ensure the complete removal of unwanted substances in the samples.

Determination of percentage yield

The percentage yield was calculated using Eqn. 1. This analysis was performed to estimate the economics of scale for this process.

$$\% \text{ of yield} = \frac{W_f}{W_i} \times 100 \quad (1)$$

where, W_f = final mass of sample at the end of activation process and W_i = initial mass of the dry sample .

Determination of moisture content

Approximately 1.0 g of the AC was weighed and dried at 120°C in an oven for two hours. The sample was cooled in a desiccator (SIRIM, 1984) and the final weight was recorded. Eqn. 2 was used to calculate the moisture content in the prepared carbon.

$$\% \text{ of moisture content} = \frac{\text{Loss of weight}}{\text{Weight of sample after drying}} \times 100 \quad (2)$$

Determination of ash content

Approximately 1.0 g of the AC was weighed (dry weight) and transferred into a stainless steel petri dish. The carbon was then pyrolyzed at 500°C in a muffle furnace for 4 hours (SIRIM, 1984). The sample was then cooled in a desiccator and weighed. The ash content was estimated using Eqn. 3.

$$\% \text{ of ash content} = \frac{\text{Weight of sample after ash process}}{\text{Weight of sample before ash process}} \times 100 \quad (3)$$

Determination of pH

Approximately 0.1 g of the AC (dry weight) was weighed and added to a beaker with 20 mL of distilled water. This beaker was then heated for 5 minutes under gentle boiling. The contents were allowed to cool to room temperature, and with continuous stirring, the solution pH was measured with a pH meter (SIRIM, 1984).

Scanning electron microscopy (SEM)

The morphology of the sample was determined using SEM (JOEL JSM-5610LV). The granular form of the carbon was placed in a 100 mm tub and coated with gold for conductivity purposes. The micrographs were recorded under various angles and magnifications to evaluate the surface morphological structures that influence the adsorption process.

Fourier transform-infrared spectrometry (FTIR)

Surface oxygen sites are greatly influenced by the functional groups present on the carbon surface. Therefore, the types of functional groups present on the surface of the AC were determined using a Fourier transform-infrared spectrometer (Perkin Elmer Spectrum 100). The recorded spectrum was then evaluated to obtain an understanding of the prepared carbon material.

N₂ adsorption isotherm analysis

The specific surface area and the pore-size distribution were determined using the Brunauer, Emmet and Teller (BET) and Barret, Joyner and Halenda (BJH) methods, respectively. The BET surface area and pore size distribution were determined from nitrogen isotherm at 77.3K using Quanta chrome autosorb automated gas sorption instrument. Prior to analysis, the adsorbents are out gassed for 12 h under vacuum at 110°C. The specific surface area was determined according to the BET method at the relative pressure range of 0.05-0.30.

RESULTS AND DISCUSSION

Physical characteristics of AC

Physically, the produced ACs were black, porous and brittle solids. According to Husseien *et al.*, 2007, pyrolysis of the raw material at a temperature of 300°C or greater yielded a black carbonaceous material, which is known as carbon. In addition, the produced ACs were very lightweight. In this study, the pyrolysis of the raw material was conducted at temperatures of 400°C and greater. The yield, burn-off and a few other tests, such as the determination of pH, moisture and ash contents based on the SIRIM method, were performed on the pyrolyzed samples. The results of these tests are presented in Table 1. The yield percentages were analyzed based on the activation times and temperatures. As shown in Table 1, the yields of the produced ACs ranged from 12.65 to 24.47%. Sample AC-B exhibited the highest yield of 24.47%, whereas sample AC-L exhibited the lowest yield of 12.65%. The activation temperature was found to have a greater effect on the yield than the activation time. As shown in Table 1, the yield of the produced AC decreased with increasing activation temperature. The yield of the AC produced at 400°C ranged from 22.40 to 24.47%, which decreased to approximately 12.65 to 13.33% at 700°C. This decrease in yield was due to the removal of volatile components through enhanced dehydration and elimination reactions (Lua & Yang, 2004; Cao *et al.*, 2006). Moreover, the PET was partially decomposed into liquid and gaseous products during the process. At temperatures above 600°C, the yield became almost constant because all major components of PET were completely decomposed (Bouchelta *et al.*, 2008).

The results presented in Table 1 also indicate that the overall yield decreased with increasing activation time. The AC produced with 2 hours of pyrolysis had a yield of 13.13 – 23.73 %, which decreased to 12.65 – 22.40 % with 5 hours of pyrolysis. The slight decrease of approximately 2% suggested that the activation time had a less significant effect on the yield than did the activation temperature. This result was further supported by the study conducted by Sudaryanto *et al.*, 2006, in which the activation time did not have a considerable effect on the AC yield. In most cases, however, as the activation time increases, the extractives and high-molecular-weight hydrocarbons undergo devolatilization and thermal degradation, thereby decreasing the yield. Furthermore, the volatile components in the carbon decrease while the fixed carbon increases ^[13]. Therefore, it can be concluded that the most

suitable activation temperature and time for the preparation of activated carbon are 700°C and 5 hours. The moisture contents were analyzed based on the activation times and temperatures. As shown in Table 1, AC-H possessed the lowest moisture content of 4.6%, whereas AC-C had the highest moisture content of 9%. In general, all of the ACs had moisture contents of less than 10%. Based on Table 1, the moisture content generally decreased as the activation temperature increased from 400 to 700°C. The moisture content at the activation temperature of 400°C was approximately 6.8 to 9.0% which decreased to approximately 6.0 to 7.2% at the activation temperature of 700°C. No apparent trend was observed for the moisture content of these carbons as the activation temperature increased. This result was explained by Ahmad *et al.*, 2007, in which they were able to absorb moisture from the surrounding atmosphere due to the hygroscopic nature of AC.

Table 1 show that the overall moisture content increased as the activation time increased from 2 hours to 5 hours. The moisture content in the AC with 2 hours of pyrolysis ranged from 6.2 to 7.2 %, which increased to 5.2 to 9 % for AC with 5 hours of pyrolysis. The result also showed no significant trend for the moisture content as the activation time increased. According to Abiko *et al.*, 2010, a water adsorption of 30% or higher for the AC would result in a sharp reduction in the adsorption capacity of the AC for organic pollutants. Because the moisture contents of all the PET-based ACs were generally less than 10%, they are suitable for use in the removal of organic pollutants from aqueous solutions.

Ash content

The ash contents were analyzed based on the activation times and temperatures. As shown in Table 1, AC-I had the lowest ash content of 0.4 %, whereas AC-B had the highest ash content of 0.98%. High ash contents would cause the AC to be inefficient because high ash content could decrease the adsorption capacity and mechanical strength of the AC. Therefore, the ash content in AC should be as low as possible. As shown in Table1, the overall ash content decreased as the activation temperature increased from 400 to 700°C. The ash content decreased from a range of 0.8-0.98% to a range of 0.42-0.7%. This decrease could be due to the degradation of material into volatile products at higher activation temperatures (Jagtoyen *et al.*, 1992).

Table 1 also shows that the overall ash content decreased as the activation time increased from 2 to 5 hours. The ash content decreased to a range of 0.38 – 0.8% from a range of 0.52-0.92%. However, the reduction was not apparent because the ash was not completely destroyed during pyrolysis (Raveendran *et al.*, 1995). The ash contents in all of the PET-based ACs decreased with increasing activation time and temperature. Moreover, all of the ash contents were generally less than 1%, and this could be an advantage for AC production. According to Karthikeyan *et al.*, 2008, the low ash content value may be attributed to the high amount of elemental carbon in the starting material. Yang & Lua, 2003 reported that ACs with ash contents greater than 10% are considered as non-ideal. Because the PET-based AC had an ash content of less than 1%, which is ideal, PET is a suitable precursor for the preparation of AC.

pH

Overall, all of the prepared ACs had pH values in the range of 5 to 6, as shown in Table 1. The pH values for the samples do not show any significant pattern. The solution pH will affect the adsorption capacity of the AC, and therefore, it needs to be considered during the determination of the adsorption capacity of the AC (Abuzaid & Nakhla, 1996. According to Weber, 1972, acidic conditions favor adsorption; therefore, a decrease in pH will increase the AC adsorption capacity toward common organic pollutants from water. Thus, it can be concluded that the PET-based ACs are suitable for removing 2,5-DCP from water.

Functional groups of AC

Figure 1 presents the FTIR spectra of the PET ACs from A to L, which were prepared using different times and temperatures. In general, all of the spectra exhibit similar patterns. The FTIR spectrum of the PET-based AC was observed to have absorbance peaks at 3700, 1733, 1500, 1300, 1050, 890 and 750 cm^{-1} . The band at approximately 3700 cm^{-1} can be assigned to OH stretching, which might have contributions from hydroxyl functional groups or adsorbed moisture. The peak at 1500 cm^{-1} corresponds to C=C stretching vibrations. The peak at approximately 1300 cm^{-1} corresponds to vibrations of the C-O bond. The peak at 1733 cm^{-1} is characteristic of C=O stretching, where as the peak at approximately 1050 cm^{-1} corresponds to C-H stretching. Finally, the peaks at approximately 890 cm^{-1} and 750 cm^{-1} are indicative of an aromatic ring, which means that aromatic groups are present. According to Esfandiari et al., 2012, the PET-based AC has a few principal groups, namely the O-H stretching vibration, graphitic carbon near 1600 cm^{-1} , and C=C stretching vibrations.

Morphological characteristics of AC

Scanning electron microscopy (SEM) was used to study the morphological structure of the prepared ACs. Figure 2 presents the morphological characteristics of all the ACs prepared using different temperatures at same activation time (2 hours) in comparison with the unprocessed PET (Figure 2 (e)). As shown in these figures, the surface of the PET precursor (Figure 2 (e)) is very smooth and non-porous (even at 1000x magnification), which is different from the morphological structure of the prepared ACs, which showed a surface that was full of pores because at elevated temperatures, holes were blown into the molten originally cut PET polymers by gases that evolved during activation while the previously smooth surface of the PET polymer was strongly eroded by the heat treatment and activation (László *et al.*, 1999).

Most of the ACs have regularly arranged pores, and most have pores on the inner walls of the larger pores. A significant but ordered increasing trend was observed in the surface area and both pore volumes as the activation temperature increased. By comparing Figure 2 (c) and (d), the temperature used to prepare AC-J was 700°C, which was 100°C higher than the temperature used to prepare AC-G. This difference in temperature resulted in a considerably larger surface area of the AC, which indicates that the influence of temperature on the preparation of AC is geometrically related. These results suggest that

the activation temperature played an important role in the morphological characteristics of the ACs. However, the activation time does not appear to have any significant effect on the morphological structure of the AC.

As shown in Figure 2(d), the surface of the AC possesses circular pores that are highly regular. It can also be observed that AC-J contains a large amount of pores on its surface. Sample AC-A is observed to have the least-developed pore structure among all the ACs. As shown in Figure 2, the surface of the AC possesses highly irregular circular pores. In addition, it was observed that most of the pores on the surface of AC-A have a large diameter by comparison. This is due to its short activation time of 2 hours, which gave limited enhancement to the formation of porosity (Cao *et al.*, 2006). From the SEM micrographs, some white fine particles observed on the surface of the AC are ash, which has the ability to fill or block some portion of the micropores (Sun & Jian, 2010). The SEM micrographs showed that the majority of the pores on the surface of the prepared AC are generally macropores. However, it was observed that the PET-based AC was primarily microporous with some mesoporosity (László *et al.*, 1999; Sun & Jian, 2010; László & Szűcs, 2001).

N₂ adsorption isotherm

The surface area and pore volume obtained for the AC-L from the Langmuir equation was 738.61 m²/g, the BET surface area was determined to be 515.41 m²/g. The BET isotherm, shown in Figure 3, exhibited a Type I isotherm with an H4 adsorption hysteresis loop. This is typical of a microporous solid with chemisorption properties, which is corroborated by the compliance to the pseudo-second-order model. As shown in Figure 3, during the initial stage, the adsorbed volume significantly increased in the low relative pressure region ($P/P_0 < 0.1$). This result provides a strong indication that the prepared carbon is primarily microporous in nature. The pore volume, which was measured to be 0.5436 cm³/g, also supported the microporous nature of the prepared carbon.

CONCLUSION

The results of this work demonstrate that PET is a promising precursor source for preparing high-quality AC. The results revealed that PET-based AC has low moisture and ash contents, which resulted in the production of high-efficiency ACs. The SEM analysis demonstrated that AC-L had well-developed pores in comparison to the other samples. Under the investigated experimental conditions, the optimum values of the parameters for the production of AC from PET via physical activation are as follows: an activation temperature of 700°C and an activation time of 5 hours. The use of PET waste as a precursor for high-value carbon adsorbents, can serve as a solution to the problem of recycling and disposing of PET wastes while simultaneously generating a waste-to-wealth opportunity. Spent adsorbents can be turned into biomass, effectively eliminating the adsorbents and the pollutant molecules, simultaneously.

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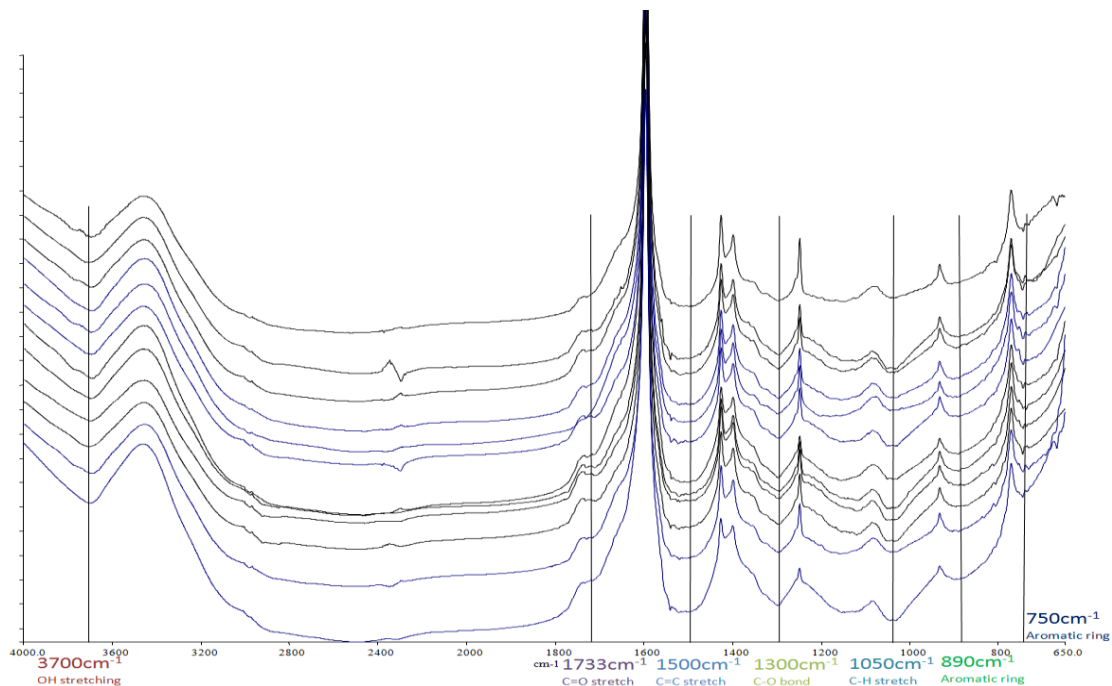
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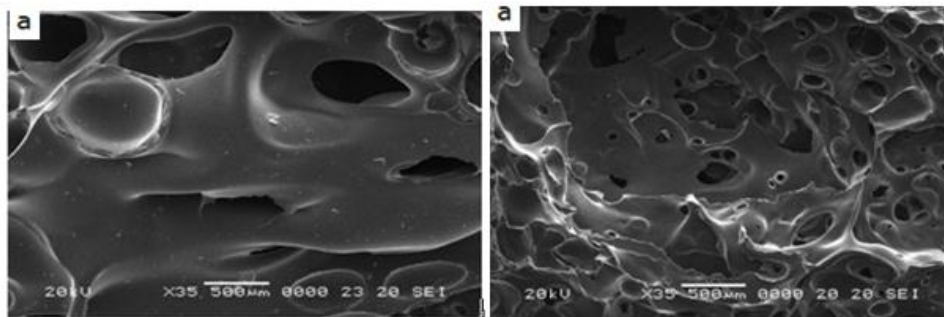
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Table 1: Preparation parameters and physical characterizations for prepared ACs.

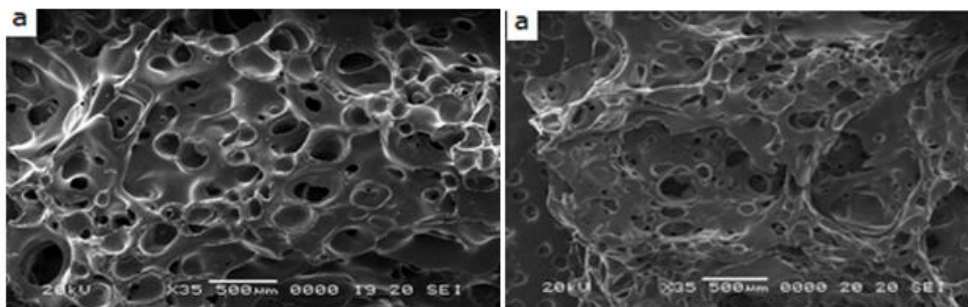
Sample	Activation temperature (°C)	Activation time (hr)	Yield (%)	pH	Moisture (%)	Ash (%)
AC-A	400	2	23.73	5.53	7.2	0.92
AC-B	400	3	24.47	5.27	6.8	0.98
AC-C	400	5	22.40	5.28	9.0	0.80
AC-D	500	2	19.17	5.07	6.8	0.52
AC-E	500	3	19.95	5.48	6.6	0.54
AC-F	500	5	15.47	5.23	8.0	0.38
AC-G	600	2	13.90	5.27	6.2	0.62
AC-H	600	3	15.45	5.10	4.6	0.64
AC-I	600	5	13.43	5.32	5.2	0.40
AC-J	700	2	13.13	5.09	7.2	0.68
AC-K	700	3	13.33	5.15	6.0	0.70
AC-L	700	5	12.65	5.40	6.4	0.42

**Figure 1:** FTIR spectra of AC-A to AC-L



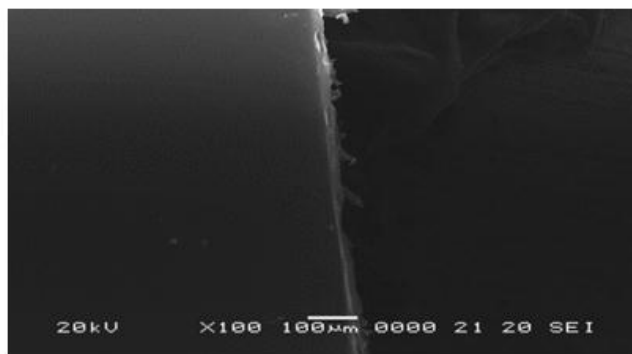
(a)

(b)



(c)

(d)



(e)

Figure 2: SEM of the PET-based AC: (a) AC-A (b) AC-D (c) AC-G (d) AC-J in comparison with (e) unprocessed PET waste.

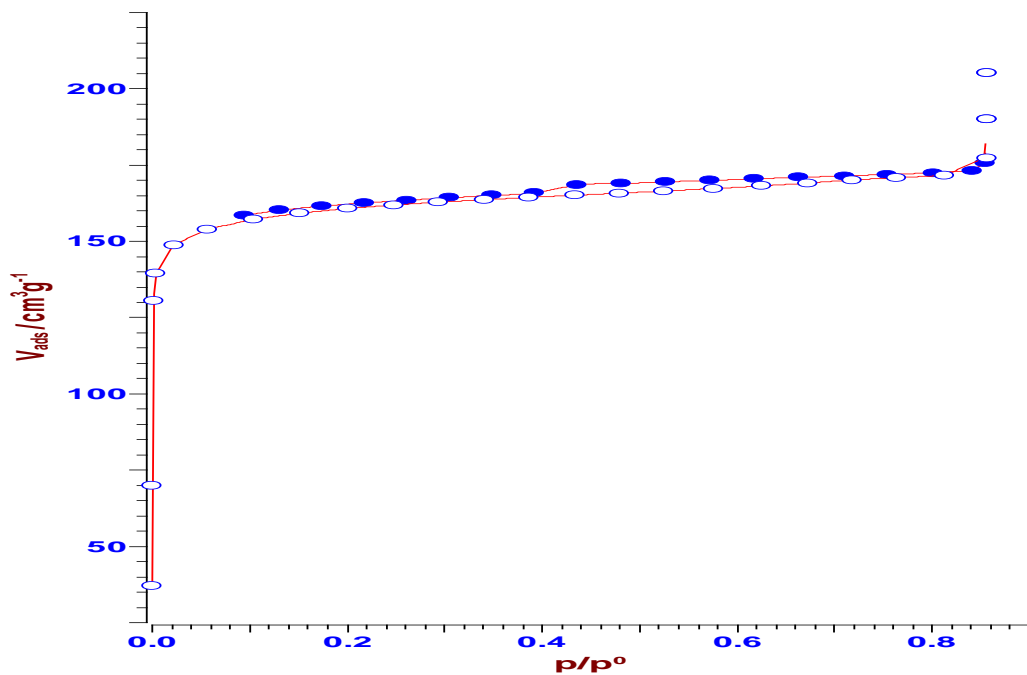


Figure 3: The N₂ adsorption-desorption isotherms of the activated carbon (AC-L).