

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED
SCIENCES

PREPARATION AND CHARACTERIZATION
OF ACTIVATED CARBON FROM *POSIDONIA*
***OCEANICA* (L.) DEAD LEAVES**

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August, 2010
İZMİR

**PREPARATION AND CHARACTERIZATION
OF ACTIVATED CARBON FROM *POSIDONIA
OCEANICA* (L.) DEAD LEAVES**

**A Thesis Submitted to the
Graduate School of Natural and Applied Sciences of Dokuz Eylül University
In Partial Fulfillment of the Requirements for the Degree of Master of
Science in
Chemistry Department**

**by
Mehmet Ulaş DURAL**

**August, 2010
İZMİR**

M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM *POSIDONIA OCEANICA* (L.) DEAD LEAVES**” completed by **MEHMET ULAŞ DURAL** under supervision of **ASSOCIATED PROFESSOR LEVENT ÇAVAŞ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Mehmet Ulaş DURAL

PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON FROM *POSIDONIA OCEANICA* (L.) DEAD LEAVES

ABSTRACT

Posidonia oceanica (L.) is an endemic species in the Mediterranean Sea. As other terrestrial plants, *Posidonia oceanica* (L.) patches off seasonally and these dead leaves of *Posidonia oceanica* (L.) accumulate on the beaches. However, tonnes of this dead leaves on the beaches are considered as the waste material in Turkey. These wastes can be used as raw materials for the production of activated carbons. In this study activated carbons were prepared by chemical activation from *Posidonia oceanica* (L.) dead leaves. The preparation process consisted of zinc chloride impregnation followed by carbonization in nitrogen atmosphere. The carbonization temperature was raised to 600 centigrade degree from room temperature. Prepared activated carbons were characterized by SEM, FT-IR, SBET and pore structural parameters. The adsorption capacities of *Posidonia oceanica* (L.) dead leaves based chemically activated carbons to remove methylene blue (MB) from aqueous solution under varying conditions of initial concentration, carbon dosage, pH, temperature were investigated. The results showed that the increased ZnCl₂ concentration (0 percentage to 45 percentage), increased BET surface area, micro and mezo pore volume and the adsorption capacity on MB as well. In conclusion, dead leaves of *Posidonia oceanica* (L.) can be used as a raw material for preparation of activated carbon.

Keywords: Activated carbon, adsorption, chemical activation, *Posidonia oceanica* (L.), zinc chloride.

POSIDONIA OCEANICA (L.) ÖLÜ YAPRAKLARINDAN AKTİF KARBON ELDESİ ve KARAKTERİZASYONU

ÖZ

Posidonia oceanica (L.) Akdeniz’de yaşayan endemik bir türdür. *Posidonia oceanica* (L.) diğer kara bitkileri gibi sezonal olarak yapraklarını dökmekte ve dökülen bu yapraklar kıyılarda birikim yapmaktadır. Ancak, kıyılarda birikim yapan bu ölü yapraklar Türkiye’de çöp olarak nitelendirilmektedir. Bu atık maddeler aktif karbon üretiminde öncü madde olarak kullanılabilir. Bu çalışmada *Posidonia oceanica* (L.) ölü yapraklarından kimyasal aktivasyon ile aktif karbon üretimi yapılmıştır. Üretimde ilk önce çinko klorür ile doyurulma yapılmış, daha sonra azot atmosferinde karbonizasyon işlemi yapılmıştır. Karbonizasyon sıcaklığı oda sıcaklığından 600 santigrat derece’ye kadar çıkarılmıştır. Üretilen aktif karbonların SEM, FT-IR, SBET ve por yapısı parametreleri ile karakterizasyonu yapılmıştır. Üretilen *Posidonia oceanica* (L.) ölü yaprakları tabanlı kimyasal aktivasyonu yapılmış aktif karbonların, farklı başlangıç konsantrasyonlarında, farklı karbon miktarlarında, farklı pH’larda, farklı sıcaklıklarda sulu çözeltilerden metilen mavisini uzaklaştırmadaki adsorpsiyon potansiyeli bulunmuştur. Sonuçlar artan $ZnCl_2$ konsantrasyonunun (yüzde 0’dan yüzde 45’e) BET yüzey alanını, mikro ve mezo por hacmini ve metilen mavisi adsorpsiyon kapasitesini arttırdığı gözlenmiştir. Sonuç olarak *Posidonia oceanica* (L.) ölü yaprakları aktif karbon üretiminde öncü madde olarak kullanılabilir.

Anahtar kelimeler: Aktif karbon, adsorpsiyon, çinko klorür, kimyasal aktivasyon, *Posidonia oceanica* (L.).

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CHAPTER ONE

INTRODUCTION

1.1 Activated Carbon

Activated carbon is a member of a family of carbons ranging from carbon blacks to nuclear graphites and many more. All carbonaceous material can be used as an activated carbon with some processes. Mechanisms of carbonizations are different, so creations of activated carbons are important from selecting of raw material to product. Activated carbons are prepared from via carbonizations of parent organic materials. Activated carbons are widely used for adsorption studies because of their porous structure and large surface area. Woods, coconut shell, coal, lignite, peat, etc. are usually chosen as raw materials for preparation of activated carbons. Various carbons differing in porous properties can be obtained by changing the precursor and the preparation conditions such as carbonization temperature and/or time and activation conditions. Activated carbons can be prepared with 2 main methods. They are physical and chemical activations (Demirbas, 2009; Marsh & Rodríguez-Reinoso, 2006)

Physical activation: The physically activated carbons are developed by using of gases. After carbonization of precursor (600 – 1000 °C) in inert atmosphere (argon, nitrogen), steam, O₂, CO₂ is used for doing activation of carbons.

Chemical activation : The chemically activated carbons are developed with reaction of precursor before carbonization process by using of some salts and acids such as, K₂CO₃, H₂SO₄, H₃PO₄, ZnCl₂, FeCl₃ etc.. Then, the raw material is carbonized at lower temperatures (450–900 °C) at inert atmosphere. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material.

Many investigations have been performed to explore novel raw materials (such as waste materials) and to optimize the preparation conditions to obtain activated carbons with the desired porous and large surface areas properties. The using of

activated carbon in purification process provides the cheap, easy and fast applications. Thus recent times activated carbons are used in so many different areas. Some activated carbons can have about 1000 m² surface area just in its 1 gram. There are several types of activated carbon. Powdered activated carbons and granular activated carbons are widely used activated carbons in the adsorption studies (Ahmad & Hameed, 2010; Yorgun et al., 2009)

Powdered Activated Carbons : The size of powdered activated carbons (PAC) particles are between 0.15-0.25 mm. Because of their small particles they have large surface area. They usually used in gas adsorption studies.

Granular Activated Carbons : The size of granular activated carbons (GAC) particles are between 0.30-0.50 mm. Granulated carbons are used for water treatment, deodourisation and separation of components of flow system.

1.2 Activated Carbon Applications

After the adsorptive capabilities of activated carbons were discovered, the charcoals have been used for adsorption of colour and odours. In 19th century powdered activated carbons used in industry usually in sugar refining (Bansal et al., 1988). Then activated carbons were used for removal of dyes or other toxic substances from waste water especially in textile industry (Bergna et al., 1999; Robinson et al., 2001) The physically activated carbon production with steam and CO₂ was first done and patented by Ostrejko in 1901. After 1918 activated carbons were used in the adsorption of the hazardous gases and different raw materials have been tried for production of activated carbons. Researchers enable to producing several activated carbons derived from different raw materials such as bituminous coal and coconut shell. Produced activated carbons from different material have different properties, such as different surface area, pore size distribution, size and shape. Nowadays activated carbons are applied purification of gases and liquids because of their high surface area and big adsorption capacity (Derbyshire et al., 1995). Mainly three types of activated carbons are produced by companies. They are named as granular, powder and extruded (pellet) activated carbons. All types of

activated carbons have different using area with their suitable applications. Last decades activated carbon is used as the best adsorbent for industrial air purification, water treatment, and solvent recovery (Radovic & Sudhakar, 1997). Conventionally, the applications of the activated carbon can be broadly divided into two categories:

- Adsorption of gases and vapors,
- Purification of liquids.

The summary of industrial and municipal applications of activated carbon is presented in Table 1.1 (Prezepiórski, 2006).

Table 1.1 Industrial applications of activated carbons as filtering material

Industrial applications of activated carbons as filtering material	
<i>Application field</i>	Adsorption from liquid phase
Potable water treatment	Removal of dissolved organics, control of taste and odor, lead, chlorine, colour
Food industry	Decolourization of liquid sugars (glucose, maltose)
Soft drinks and brewing	Removal of chlorine and dissolved organic contaminants from potable water, after disinfection with chlorine
Pharmaceutical	Purification and separation of antibiotics, vitamins, hormones, etc.
Semi-conductors	Production of ultra high purity water
Petrochemical	Removal of oil and hydrocarbon contaminations from recycled steam condensate for boiler feed water
Groundwater	Reduction of total organic halogens and adsorbable organic halogens in industrial reserves of contaminated groundwater
Industrial waste water	Process effluent treatment to meet the environmental legislation
Swimming pools	Removal of residual ozone and control of chloramine levels
Adsorption from gas phase	
Solvent recovery	Control of vapour emissions and recovery of organic solvents
Carbon dioxide	Purification of carbon dioxide from fermentation processes
Industrial respirators	Adsorption of organic vapours and inorganic gases
Waste disposal	Removal of heavy metals and dioxins from flue gas formed during incineration of various wastes
Cigarettes	Removal of some harmful substances (nicotine and tar)
Air conditioning	Removal of contaminants from air subjected to heating, ventilation, and air conditioning in airports, offices, hospitals
Semi-conductors	Production of ultra high purity air
Toxic gas removal	Purification of industrial off-gases
Fridge deodorizers	Removal of general food odours

1.2.1 Air Treatment

Activated carbon is a good adsorbent for removal of organic compounds from gas phase. With air treatment, control of potentially harmful or environmentally damaging substances to the atmosphere is provided. Some of environmental problems such as some gases or vapours can damage human body. Some of them are eye irritation, toxic or carcinogenic problems. For these reasons carbon filtration units get more importance (Mills, 1995). Activated carbon is the leading technology for the removal of Volatile Organic Compounds (VOCs) with its highly porous structure and large surface area. High adsorption capacities of activated carbons makes this material the most appropriate material used for the removal of VOCs from air and other gases (Kim et al., 1997; Mohr, 1997; Nevers, 1995; Noll et al., 1992; Pamele & Kovalcson, 1998). Prevention of odour from sewage is an important application for the prevention of environment. Consequently, with the decomposition of some compounds are the biggest reason of an unpleasant odour. The odor source is VOCs. This may cause of the some symptoms for the building occupants (Anonymous, 2002). With the activated carbons some dangerous can be adsorbed by carbon. The adsorption capacities of activated carbon are lower for SO₂ and NO_x compared with VOCs. There are many processes for applied the industrial fumes from SO₂ and NO_x compounds. Usually activated cokes which produced from hard coals has low surface area (~ 400 m²g⁻¹) and pore volume (~0.25 cm³g⁻¹). Depending on the material origin and the manufacturing process, either adsorptive or catalytic characteristics may play a dominant role in the removal of contaminants on this adsorbent. The big amount of activated cokes are widely used for the adsorption of SO₂ and dioxins from waste and flue gases (Ashford, 1994; Derbyshire et al., 2001; Jungten & Kuhl 1989).

1.2.2 Water Treatment

Activated carbons are used for the treatment of the municipal, industrial or ground water treatments. Because of their structure the carbon adsorbents efficiently adsorb pollutants and contaminants from water. The treatment can be done with granular activated carbon (GAC) or powdered activated carbon (PAC). The treatment of water

with GAC has some advantages than the treatment with powdered activated carbon. The biggest advantage is the low cost treatment and the other advantage is the large amounts of carbon can be employed in the filtering system series units. Today, granular activated carbon is widely used in the clarification of surface sourced drinking water and contaminated ground water. With this application the quality of drinking waters are improved. Other applications for waters are the removal of substance from industrial and municipal waste waters by using activated carbons. Treatment of waste water is an environmental application for the world. With this application the toxic, colours, organics, pesticides etc. molecules which are dangerous and harmful for both animals, plants and humans are removed from the wastes (Culp & Culp, 1974; Matson & Mark; 1971; Ruthven, 1984).

1.2.3 Application in Food Industry

Activated carbons have a wide range of application for the treatments of foods, beverages and cooking oil production for the increase the quality of product. Big amount of activated carbons are used for the removal of color. Significant amounts of activated carbons are used for the decolorization of sucrose sugar. For the removal of caffeine from tea or coffee the activated carbons are used. Activated carbons are important adsorbents for the production of caffeine-free coffee. For the production of alcoholic beverages activated carbons are used for the removal of fusel oil (Achaerandio et al., 2002; Bernardo et al., 1997).

1.2.4 Application in Pharmaceutical and Chemical Industries.

Activated carbons are consumed in the industrial applications for purification of the products of pharmaceutical. The main application of activated carbon is purify the antibiotics, vitamins, steroids. Purification is an important parameter for the pharmaceutical industry from the beginning process of production until the product with the removal of color, protein, organic compounds, contaminants etc. (Elga, 1997)

In chemical industry activated carbons is again used for the purification of product or by products. Activated carbons are used for the decolorisation and removal of contaminants from organic acids, amines, hydrocarbons etc.

1.2.5 Liquid Phase Applications

Some activated carbons are can be used for the purification of tap water in the filters. It is a kind of water treatment for the removal of the contaminants. With this application it can gained ultrapure water for some suitable areas. In the small water filters activated carbons also can remove some contaminants which come from aquatic environment such as, agricultural ingredients, some metals, hydrocarbons, some toxins from patients. The other effect of activated carbon is removal of chlorination residues of the water. This residues can be found in the municipal drinking water and have to removed before drinking (Abbasi & Streat, 1994; Edris et al., 2003; Song et al., 1997)

1.2.6 Medical Applications

Activated Carbon has been used after the adsorption capacity of this porous material discovered. Egyptians started to use its use in medicinal treatment for food poisoning and after 18th Century this material have been started to use in various medical applications (Cheremisinoff & Morresi, 1980). There are so many examples about activated carbons application on medical. After some suicide actions with lethal dose of some toxic compounds or drugs, activated carbons are used to clear the body from those toxic chemicals. It is showed that the power of activated carbon on adsorption. Activated charcoal is considered to be the most effective single agent available. It is used after a person swallows or absorbs almost any toxic drug or chemical.

1.2.7 Personal and Collective Protection

Among activated carbons applications protection from toxic gases is one of the oldest applications. During World War I for the protection from toxic gases to soldier, masks were containing the activated carbon. Today also the activated carbons are used in mask and also in the clothes for the protection from not only possible gases effect but also viruses and bacterias (Prezepiórski, 2006).

1.3 Activated Carbon Productions and Applications in Adsorption Studies

It is common knowledge that industrial wastewaters are discharged into the aquatic environments - in many cases without any treatment – causing severe environmental pollution. Industrial wastewaters may include toxic substances such as heavy metals, dyes, organic compounds etc. These toxic pollutants are harmful for living organisms (Anliker, 1979). Dural et al. (2007) have reported that due to the accumulation of pollutants in the aquatic environment toxic substances can be found in fish tissues which are consumed by humans. The propagation of pollutants into the marine food chain, their bioaccumulation and biomagnification as well as their detrimental effects after human consumption have made wastewater treatment imperative for the sustainability of the ecosystems. Various water treatment methods based on filtration, oxidation, ultrafiltration, ozonation, precipitation, sedimentation, adsorption etc. have been applied for the removal of pollutants from wastewaters. (Tan et al., 2008). In the last few decades, adsorption has been proved to be a well established and cheap pollutant removal process among other purification techniques. Activated carbons (AC) are porous carbon based materials with high adsorption capacity and have developed into the prevailing adsorbent for both liquids and gases purification (Lin & Juang, 2009). The adsorption capacity of AC is strongly dependent on its surface area, pore structure and existing surface functional groups with the latter determining its behaviour during interaction with polar, non-polar, anionic and cationic adsorbates (Wibowo et al., 2007). AC has a very complicated structure, with different pore sizes and a variety of surface groups with

its textural and surface properties being related to the precursor and the method used for its preparation (Ismadji et al., 2005; Spahis et al., 2008).

Because of its availability, coal is the most commonly used precursor for activated carbon production. Nowadays, several studies have been focused on low cost, renewable alternative materials for the production of rich carbon content and low inorganic content AC (Demirbas, 2009). A variety of starting materials have been already used for the preparation of AC such as coconut shells, wood char, lignin, petroleum coke, bone char, peat, sawdust, carbon black, rice hulls, sugar, peach pits, fish, fertilizer waste, waste rubber tire, etc. These precursors are being used in large quantities: some examples include wood (130,000 tonnes/year), coal (100,000 tonnes/year), lignite (50,000 tonnes/year), coconut shell (35,000 tonnes/year), and peat (35,000 tonnes/year) (Mohan & Pittman, 2006).

Turkey has 8333 km coastline on the Mediterranean Sea, the Black Sea and the Aegean Sea. This coastline provides various sea plants, seaweed and animals. *Posidonia oceanica* (L.) is an indicator plant and endemic species in the Mediterranean Sea. Especially in autumn *Posidonia oceanica* (L.) leaves fall off and accumulate on the beaches as biomass waste. Unfortunately this abundant biomass material has not yet been utilized economically in Turkey. Recently, various activated carbons derived from waste materials have been investigated for dye removal from contaminated wastewaters. In this context, *Posidonia oceanica* (L.) dead leaves, a renewable, highly available, and low cost biomass resource was used in this study as raw material for the production of activated carbon.

Activation of the precursor can be carried out by two different methods, physical (or thermal) and chemical activation (Ichcho et al., 2005). The physical preparation process consists of the pyrolysis of the precursor material, at temperatures usually between 600-800 °C, in an inert atmosphere, followed by the gasification of the resulting char under an oxidizing agent (Carbon dioxide, air, water) at about 800-900 °C (Katsaros et al. 2006; Yorgun et al., 2009).

The chemical route involves the impregnation of the precursor by a chemical agent (H_2SO_4 , H_3PO_4 , ZnCl_2 , alkali metal hydroxides) and then the heat-treatment at moderate temperatures (400–600°C) in a one-step process (Ahmad & Hameed, 2010).

Chemical reagents may cause the formation of cross-links and volume contraction (Illán-Gómez et al., 1996). Among the chemically activation agents, zinc chloride is the widely used chemical agent in the preparation of chemically activated carbon (Teng & Yeh, 1998). The advantages of chemical activation are taken place at a lower temperature, low energy cost and shorter time than those used in physical activation (Lozano-Castello et al 2001). The carbon yield in chemical activation is usually higher than in physical activation, since the chemical agents are substances that inhibit the formation of tar and reduce the production of other volatile substances (Sudaryanto et al., 2006). Furthermore chemical activation leads to the development of improved pore structure with tunable characteristics (Ahmadpour & Do, 1996). Zinc chloride is generally used for the activation of lignocellulosic materials before a carbonization process (Prahas et al., 2008). Chemical activation of raw material with ZnCl_2 causes the decomposition of the cellulosic structure of the material. In conclusion after activation with some agents, materials are pyrolysing for creates aromatisation of the carbon skeleton and creation of the pore structure (Olivares-Marín et al., 2006).

In the present study, *Posidonia oceanica* (L.) dead leaves have been chosen as the precursor for the preparation of activated carbon by chemical activation with zinc chloride, and the influence of ZnCl_2 impregnation ratio on its structure (characterised using BET, SEM and FT-IR) and methylene blue adsorption properties were investigated.

Methylene blue is accepted as a model dye for adsorption studies (Caparkaya & Cavas, 2008; Cengiz & Cavas, 2007). Although there have been many reports in the literature on the preparation and characterization of activated carbon from waste

biomass this is the first attempt to prepare activated carbon from *Posidonia oceanica* (L.) dead leaves.

CHAPTER TWO

MATERIALS AND METHODS

2.1 Preparation of Activated Carbons

Posidonia oceanica (L.) dead leaves were collected from the coast of Urla/IZMIR in February 2010. The collected biomass was put into plastic bags and immediately transported to the laboratory. The dead leaves were washed with tap water to remove salt, impurities and epiphytes, subsequently was washed with distilled water, dried at 70 ± 2 °C for 16 hours and ground by means of a crusher machine. The resulting ground *Posidonia oceanica* (L.) dead leaves (GPO) having a mean particle size of 500 μm were activated with different concentration of ZnCl_2 .

20g of GPO was added into 200 mL of ZnCl_2 solution of desired concentration (0, 15, 30, 45%, w/v) and stirred for 2 hours. The excess of ZnCl_2 solution was then decanted and the zinc treated GPO (ZTGPO) was subsequently dried in a stove for 24 h at 70 ± 2 °C. ZTGPO was then placed in porcelain capsule and kept in a muffle furnace. The temperature was raised by 10°C/min from room temperature to 600 °C where it was kept for 2 h. The experiments were carried out under nitrogen atmosphere at a flow rate of 10 ml/min. After pyrolysis the resultant material was *Posidonia oceanica* (L.) dead leaves derived activated carbons (POAC). The resultant chemically activated carbons which reacted with %15 concentration of ZnCl_2 (15%-AC), %30 concentration of ZnCl_2 (30%-AC) and %45 concentration of ZnCl_2 (45%-AC), was washed with hot 0.5N HCl solution for 30 min to remove excess ZnCl_2 and subsequently washed 3 times with warm water until a zinc ion free effluent. After pyrolysis untreated activated carbon (0%-AC) was not washed. The resulting material was dried in an air oven at 70 °C for 16 h.

2.2 Preparation of Methylene Blue Solution

The methylene blue (MB) ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, MW 319.87 g/mol) was supplied by Fluka MB adsorption is a well known technique for the determination of the pore

volume of activated carbons (Pelekani & Snoeyink, 2000). Double distilled water was used for the preparation of all the solutions and reagents (pH: 6.5). A 1000 mg/L stock solution was prepared and 250 mg/L, 500 mg/L, 750 mg/L solutions were prepared with the necessary dilution from stock solution. The concentrations of the MB solutions were obtained from standard calibration curve.

2. 3 Characterization of Activated Carbon

The surface physical characteristics of POAC were analyzed by scanning electron microscopy (SEM). A Jeol JSM 7401F Field Emission Scanning Electron Microscope equipped with Gentle Beam mode was used to characterize the morphology of the activated carbon. The specific surface area and pore structure parameters of POAC were determined from the adsorption–desorption isotherm of nitrogen at $-196\text{ }^{\circ}\text{C}$ using an automated volumetric system (AUTOSORB-1 -Krypton version - Quantachrome Instruments). Prior to their measurement, the samples were outgassed at 200°C for 48h. The functional carbon–oxygen groups on the surface of active carbon were identified by means of a Thermo Scientific Nicolet 6700 FTIR with N_2 purging system. The instrument was also equipped with a LN_2 cooled wide range Mercuric Cadmium Telluride detector (MCT-B), which exhibits 4–10 times higher sensitivity and better linearity than classic DTGS detectors. Spectra were acquired using a single reflection ATR (Attenuated Total Reflection) SmartOrbit accessory equipped with a single-bounce diamond crystal (Spectral range: $10,000\text{--}55\text{ cm}^{-1}$, Angle of incidence: 45°).

2. 4 Adsorption Experiments

Sorption kinetics experiments were carried out at 25°C using 8 different initial Methylene Blue concentrations, namely 25, 50, 75, 100, 250, 500, 750 and 1000 mg/L. All the kinetics measurements were performed at pH 6.5, with a maximum contact time of 360 min (for 15%-AC 480 min). The samples were taken out at preset time intervals and centrifuged at 5000 rpm for 4 min. Dye concentrations in the

supernatant solutions were determined by means of a Shimadzu UV-VIS 1601 spectrophotometer at 665 nm.

The amount of dye adsorbed onto POAC at equilibrium was calculated by using the equation as shown below:

$$q = \frac{C_0 - C_e}{M} V \quad (1)$$

Where;

q: adsorbed dye amount (mg/g)

C₀: initial dye concentration (mg/L)

C_e: dye concentration at equilibrium (mg/L)

V: volume of dye solution (L)

M: amount of adsorbent (g)

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Characterization of Activated Carbons

For the characterization of prepared activated carbons SEM, FT-IR, SBET and pore structural parameters techniques were used. The adsorption capacities of *Posidonia oceanica* (L.) dead leaves based activated carbons were investigated with methylene blue adsorption.

3.1.1 SEM Analysis of the Activated Carbons

Scanning electron microscopy (SEM) was used in order to obtain information about the surface morphology of the POAC. Figure 3.1-3.4 show the SEM photographs of the POAC with different impregnation ratios. The untreated sample (0%-AC) has a relatively smooth surface without large defects. On the other hand the chemically activated carbons (15%-AC, 30%-AC, 45%-AC) exhibit larger cavities and rougher surfaces compared to the initial sample. These surface characteristics are more pronounced as the impregnation ratio increases. Thus, while the 15% sample has some large cavities in the range of 10-20nm, the 45% sample shows additional small pores and extremely rough surface. The large pores which were created by the chemical treatment, promote effectively the activation in the internal surface of the carbon particles. Therefore, the $ZnCl_2$ is an effective activating agent for the production of high-surface area activated carbon.

White spots observed in the samples, may be due to the presence of salt residues at 0%-AC. 0%-AC was not treated with $ZnCl_2$ it can be concluded that traces of salts are still present in the precursor indicating that after collection of *Posidonia oceanica* (L.) dead leaves, materials should be washed more thoroughly.

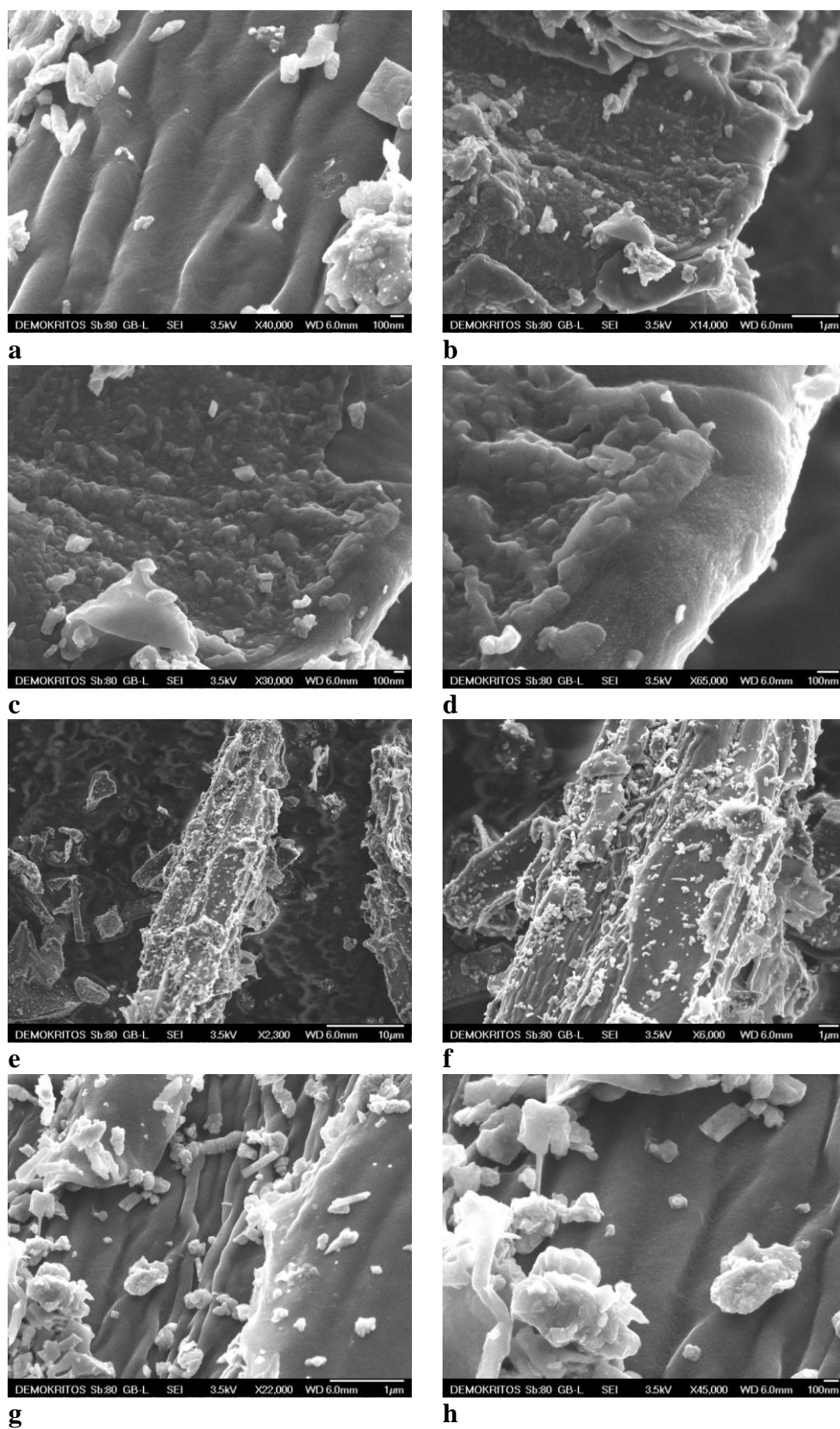


Figure 3.1 (a-h) Scanning electron micrographs of the 0%-AC

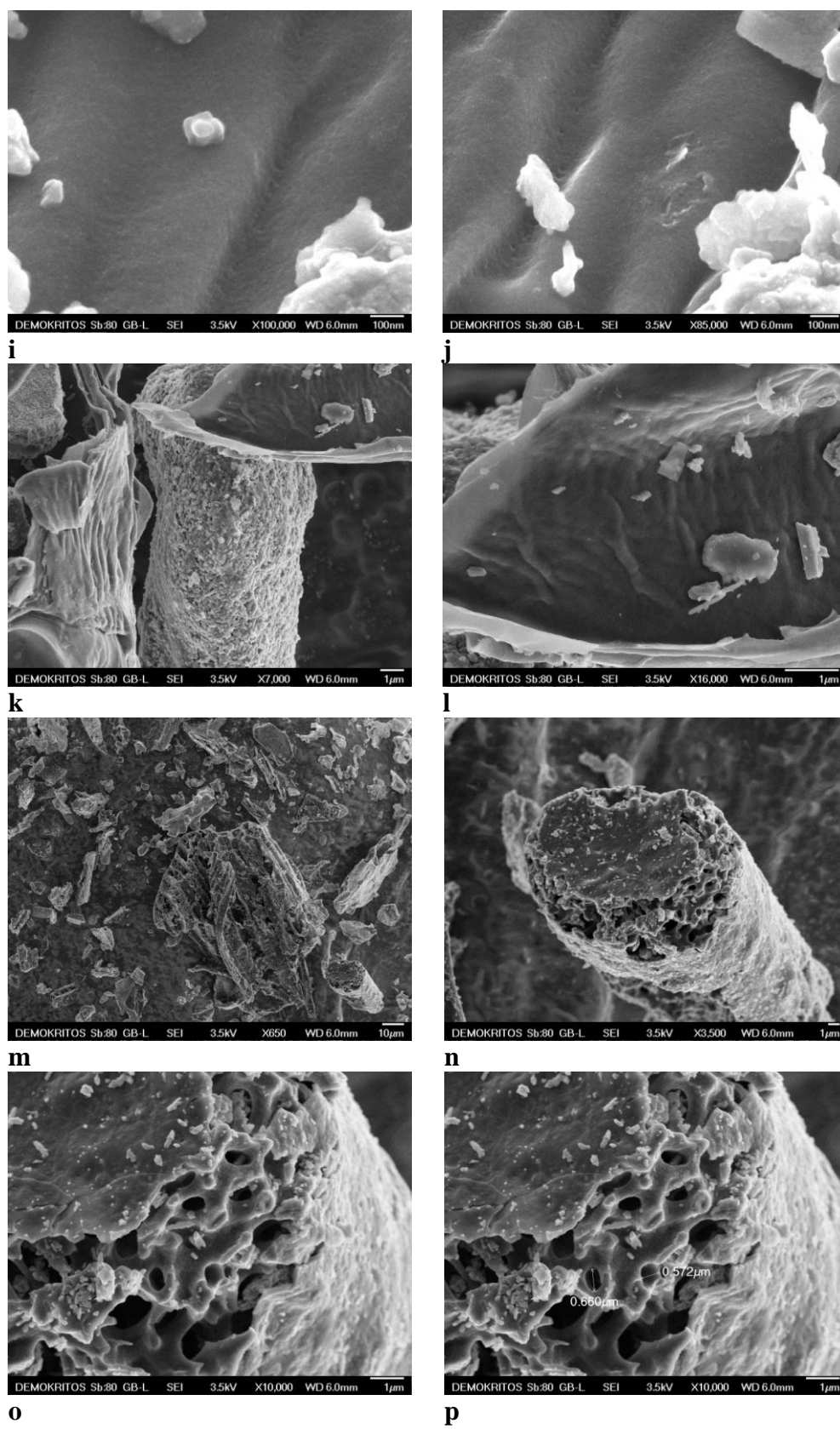


Figure 3.1 (i-p) Scanning electron micrographs of the 0%-AC

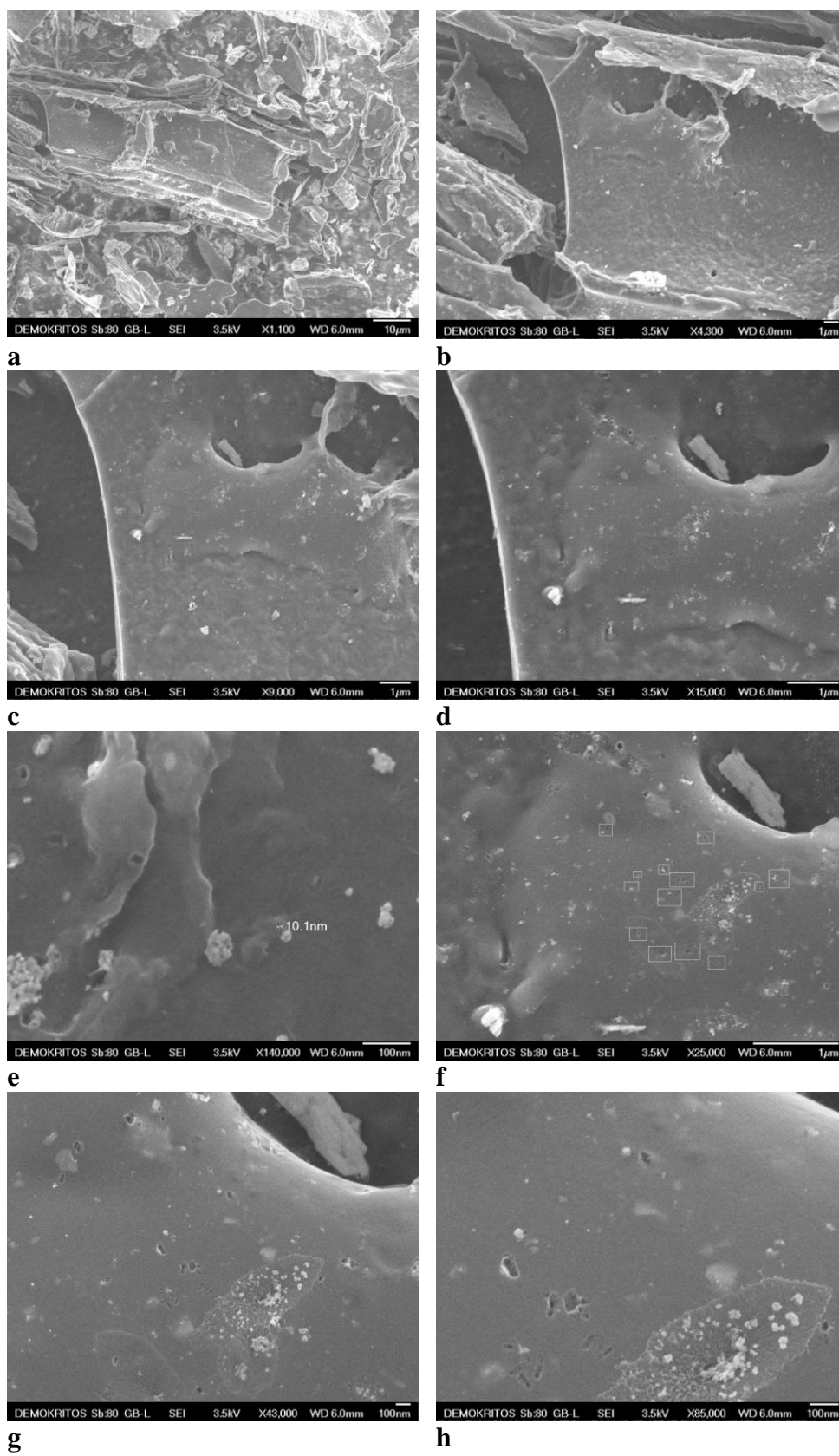


Figure 3.2 (a-h) Scanning electron micrographs of the 15%-AC

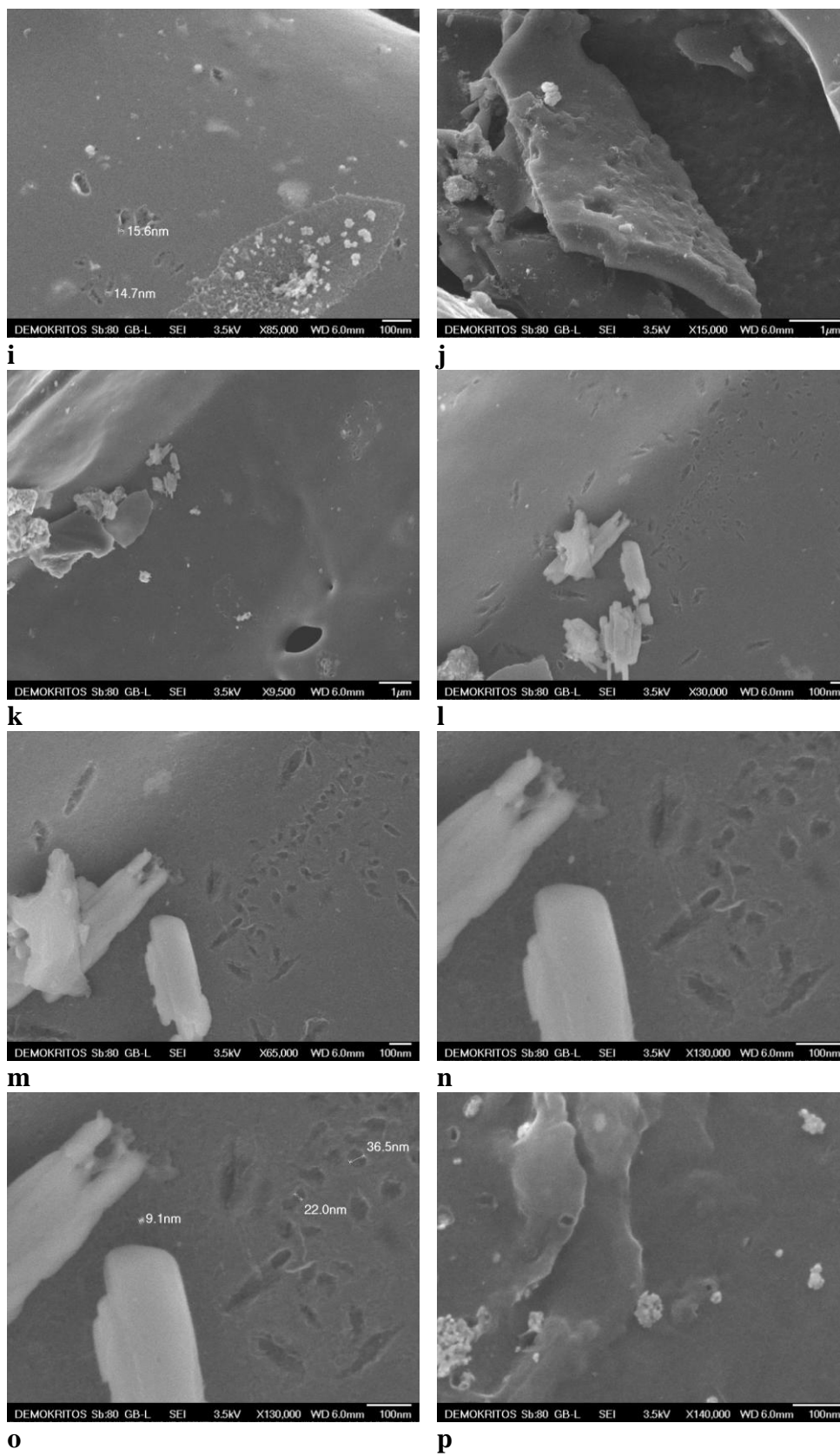


Figure 3.2 (i-p) Scanning electron micrographs of the 15%-AC

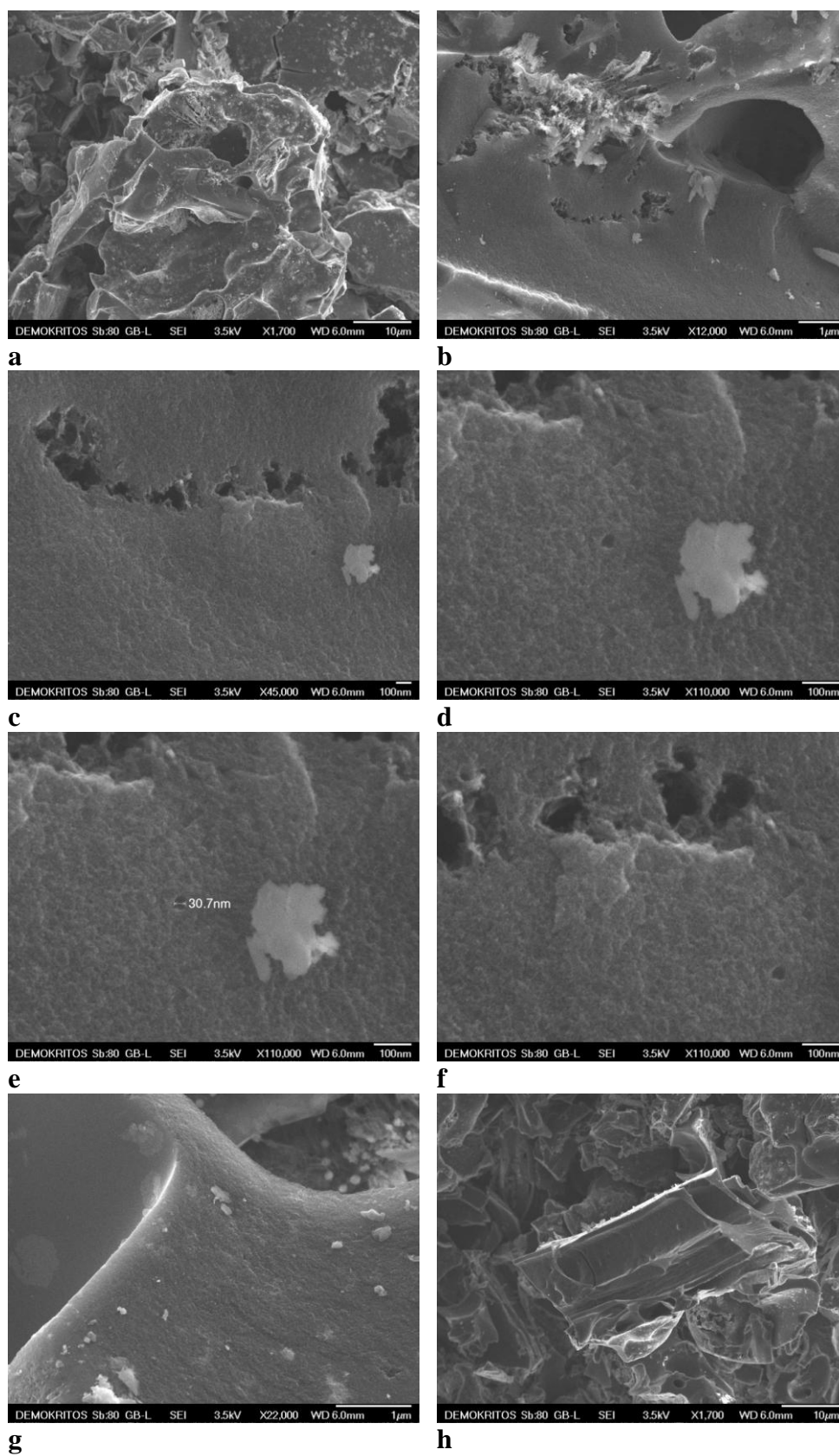


Figure 3.3 (a-h) Scanning electron micrographs of the 30%-AC

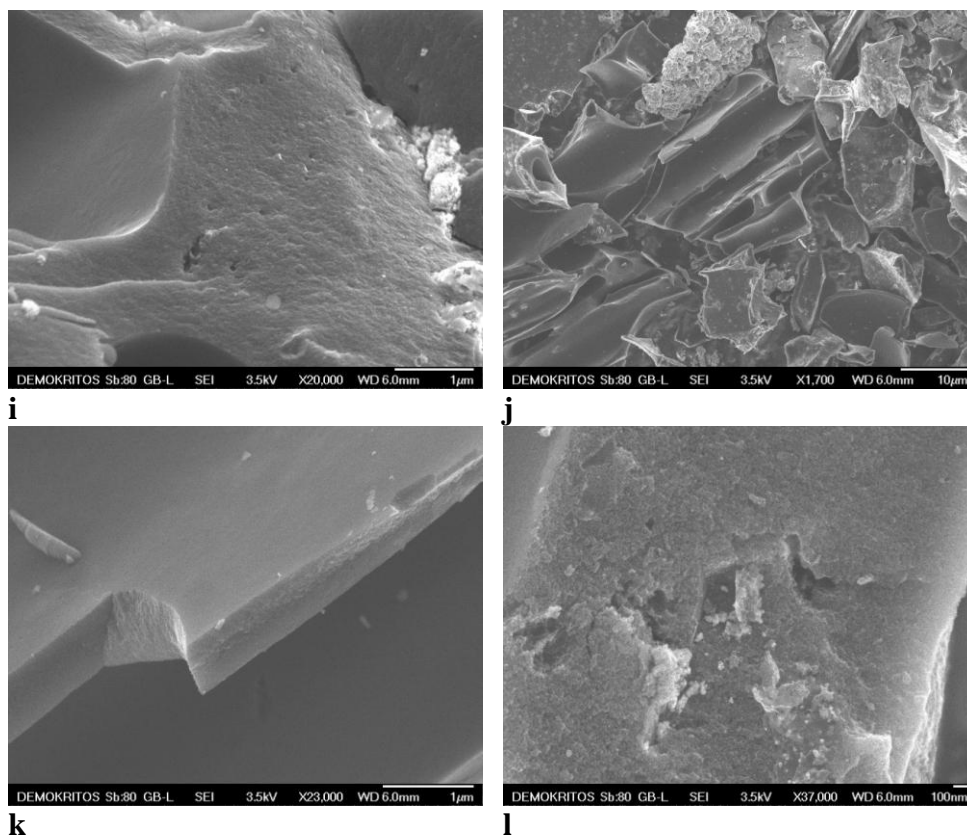


Figure 3.3 (i-l) Scanning electron micrographs of the 30%-AC

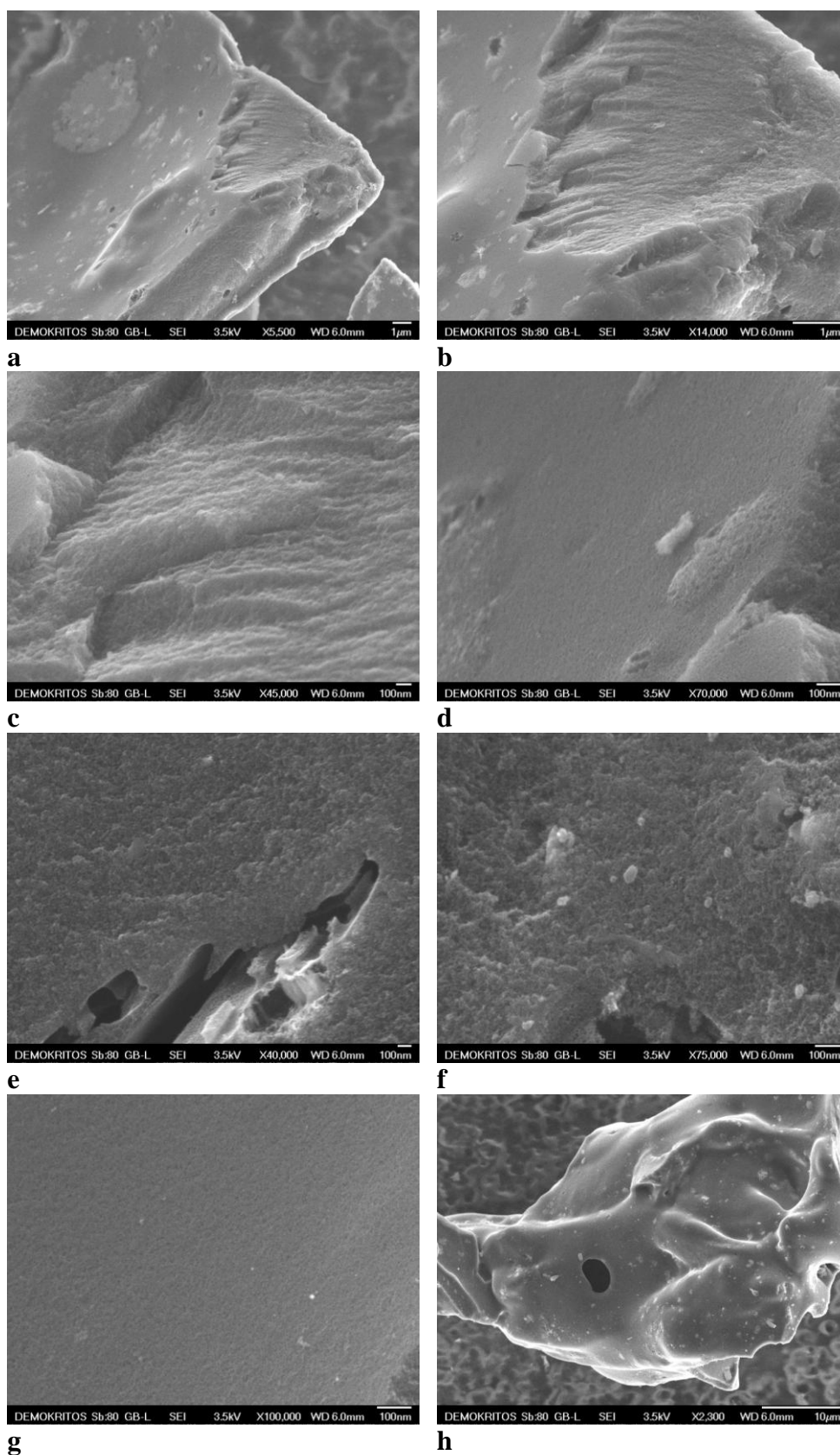


Figure 3.4 (a-h) Scanning electron micrographs of the 45%-AC

3.1.2 Specific Surface Area and Pore Structural Characterization Analysis of the Activated Carbon

The N₂ adsorption isotherms at 77 K of both untreated sample and chemically activated carbons are shown in Figure 3.5. The adsorption isotherms of the activated carbons are type I isotherms, indicating the presence of large fractions of micropores and in some cases mesopores, while the isotherm of untreated sample can be considered as non-porous. According to the International Union of Pure and Applied Chemistry (IUPAC), adsorption pores can be classified into three groups: micropore (diameter <2 nm), mesopore (2 nm < diameter <50 nm), and macropore (diameter >50 nm).

Isotherm data were analyzed for BET area, total pore volume, micropore volume and average pore width. Specific surface areas were calculated according to the BET method. Total pore volumes were directly derived from the adsorbed quantity at high relative pressures ($p/p_0 \sim 0.95$). Adsorption data were analyzed by NLDFT equilibrium model for slit pores and the pore size distributions (PSD) were calculated (Figure 3.6) (Roussel et al. 2006). The results obtained from nitrogen isotherms are presented in Table 1.

The activation of *Posidonia oceanica* (L.) dead leaves without ZnCl₂ impregnation resulted in a non-porous sample with relatively low carbon yield. The carbon produced from the untreated sample has very low surface area and pore volume: 33.4 m²/g and 0.041 cc/g respectively. On the contrary, the impregnation process leads to samples with increased surface area from 839.9 m²/g (15%) and 1063.4 m²/g (30%) up to 1230 m²/g for the sample with impregnation ratio 45%.

In all samples there is no evidence of ultra micropores, the average micropore size was in the range of 7-15 nm. Concerning the pore volume of the carbons samples, activation up to 15% leads mainly to the formation of micropores (increase from 0.001 to 0.322 cc/g) while the mesoporosity remains unaffected. This implies that the treatment initially creates new rather than increasing the size of the already existing

ones. This may be attributed to the removal of amorphous material which increases the micropore volume, without significant alteration of the pore sizes.

Higher degree of activation (up to 30%) increases both the micropore and the mesopore volume. This implies that the treatment beyond the development of new micropores, affects also the pre-existing porosity by increasing its pore size. Thus, there is a shift in PSD of the sample 30% to higher micropore sizes (the average is increased from 0.75 nm to 1. nm). In addition the PSD is broader and a shoulder appears at about 15nm. Finally treatment up to 45% leads only to the formation of mesopores. In this case, the PSD shows a significant increase in mesopore volume, while the microporosity region remains almost the same. These results are very interesting as one can tune the pore size of the AC (micropores and mesopores) by using different impregnation ratios.

Concerning the mechanism of the preparation process, the initial step involves the mixing and the chemical attack of the biomass by the activating agent. During the subsequent step of thermal treatment, dehydration and cross-linking reactions are taking place leading to the formation of aromatic rings in the char product. The volatile organic material is also removed in this step (Rodríguez-Reinoso & Molina-Sabio, 1992). The heating rate, the residence time and the final temperature are the crucial parameters that determine the structural properties of the carbon. Furthermore the final washing process (with hot acid water and water) has a great influence on the final porous structure of the carbon (Williams & Reed, 2006).

In general *Posidonia oceanica* (L.) dead leaves can effectively be used as precursor for the preparation of high quality carbon. In addition, it is very interesting that by applying different impregnation ratios, one can tune the pore size of the final carbon product (micropores and mesopores). Furthermore the carbons produced in this study have superior characteristics compared to the properties of activated carbons derived by other low cost materials. Table 2 summarises the structural properties of the carbon produced by *Posidonia oceanica* (L.) dead leaves in regard to the corresponding properties of other carbons from the literature.

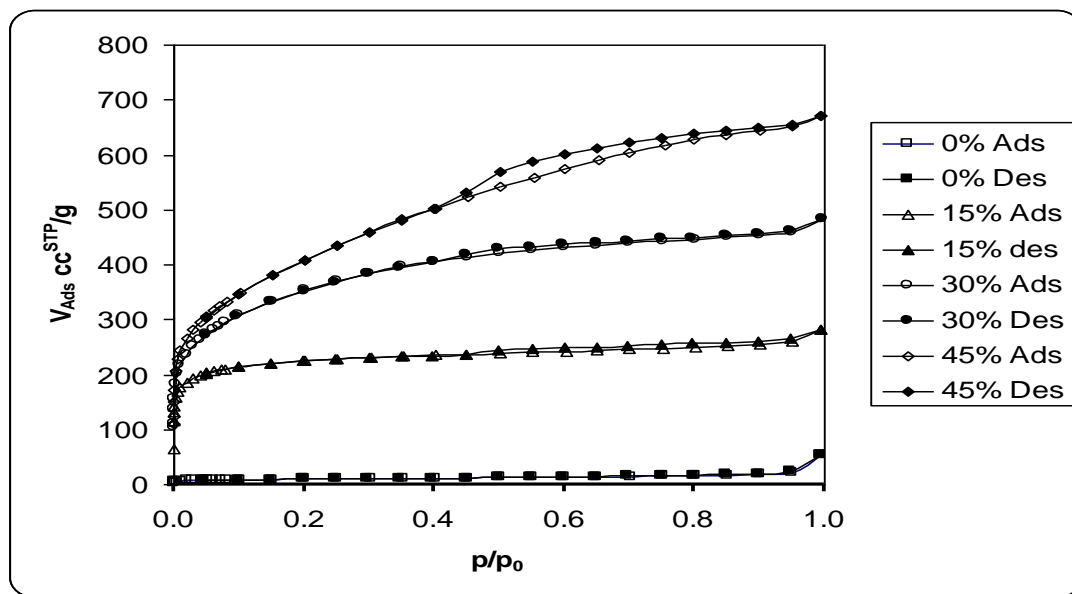


Figure 3.5 N₂ Adsorption Isotherms at 77K on POAC

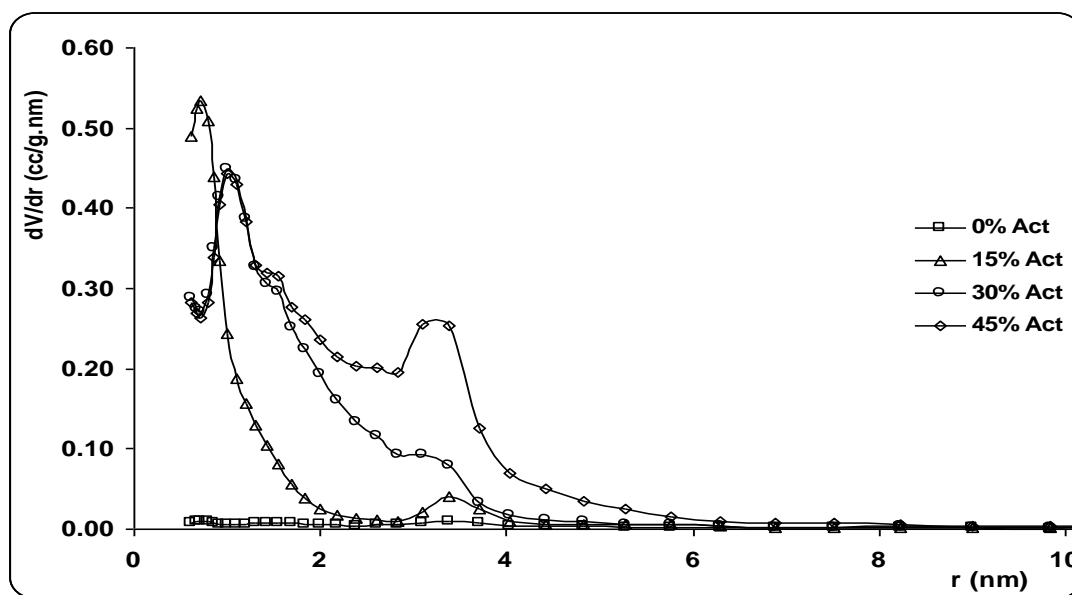


Figure 3.6 Pore size distribution of activated carbons derived by *Posidonia oceanica* (L.) dead zleaves

Table 3.1 Textural characteristics of the produced activated carbons derived by *Posidonia oceanica* (L.) dead leaves.

Sample	Surface area (m ² /g)	Pore Volume (cm ³ /g)		
		V _{micro}	V _{meso}	V _{total}
0%	33.4	0.011	0.025	0.041
15%	839.9	0.322	0.063	0.415
30%	1063.4	0.479	0.197	0.723
45%	1230.4	0.494	0.456	1.022

Table 3.2 Comparison of textural characteristics of some activated carbons.

Activated carbon type	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	Referance
Sunflower oil cake	240	0.111	0.005	0.116	Karagöz et al., 2008
Bean pods	258	0.080	0.013	0.206	Budinova et al., 2009
Cotton stalk	594	0.280	0.030	0.381	Girgis et al., 2009
Cotton stalk	794	0.083	not available	0.630	Deng et al., 2009
Macadamia nut-shell	844	0.391	0.094	0.485	Aworn et al., 2008
Bituminous coal	857	0.390	not available	0.450	El Qada et al. 2006
Commercial AC	924	0.426	0.041	0.466	Aworn et al., 2008
Coffee ground	925	0.046	0.666	0.718	Reffas et al., 2010
Coal	970	0.481	0.180	not available	Gong et al., 2009
Coffee ground	1021	0.350	0.950	1.300	Rufford et al., 2009
Chinese firsawdust	1079	0.502	0.050	0.558	Juan and Ke-Qiang, 2009
Commercial AC	1118	0.415	0.203	0.618	Wang et al., 2005
<i>Posidonia oceanica</i> (L.) dead leaves	1230	0.494	0.456	1.022	This study

3.1.3 FT-IR analysis of the activated carbon

The FTIR spectra of the raw *Posidonia oceanica* (L.) dead leaves and the carbon samples produced are shown in Figure 3.7. The raw biomass spectrum is very complex comprising of bands assigned to the main components from *Posidonia*: cellulose, hemicellulose and lignin. The wide band around $3450\text{--}3200\text{cm}^{-1}$ (maximum absorption being at 3320cm^{-1}) is indicative of the existence of hydroxyl groups and amines. The spectrum also displays an absorption peak at 2919 and 2851cm^{-1} , corresponding to the $-\text{CH}_2$ group (asymmetric and symmetric stretching vibrations respectively). In addition the peaks at 1261cm^{-1} (rocking) and 1150cm^{-1} (wagging) are related to the presence of methylene groups. The peak in 1603cm^{-1} is attributed to the C=O stretching, while the small shoulder at 1727cm^{-1} can be related with the presence of carboxylic acids. The peak at around 1020cm^{-1} is mainly due to the C-O stretching vibrations. Finally the peaks at 1417, 875 and 713cm^{-1} can be assigned to the inorganic carbonates and mainly to calcite (CaCO_3).

The FTIR spectrum of carbon produced without impregnation clearly shows that most of the functional groups, present in the precursor, were removed by the heating treatment. Only a small shoulder at 1603cm^{-1} demonstrates the presence of some

C=O groups on the carbon surface, while the peaks that correspond to calcium carbonate are quite obvious. On the other hand, the spectra of the activated samples are typical for activated carbon, revealing the almost complete absence of functional groups. Some small shoulders, in the range 1200-1000 cm^{-1} , can be attributed to C=C and to aromatic groups.

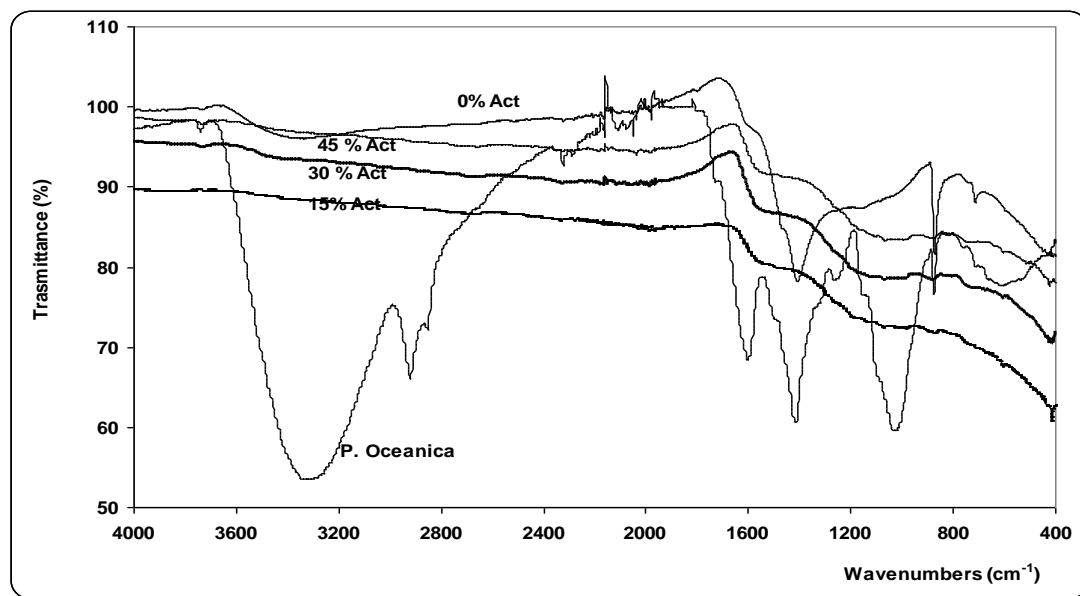


Figure 3.7 Fourier transform infrared spectra of activated carbons.

3. 2 Effect of pH

Initial pH of the methylene blue solutions were varied in range of 3.0-11.0. For adjusting pH either 0.1 N NaOH or 0.1 N HCl solutions were added to assess the effect of pH on the dye adsorption onto the POAC. The experiments were also performed at 50 mg/L for untreated activated carbon (%0) and 500 mg/L initial dye concentration for chemically activated carbons (%15, %30, %45) with 5 g/L adsorbent dose for a 60-min equilibrium time at 25 °C.

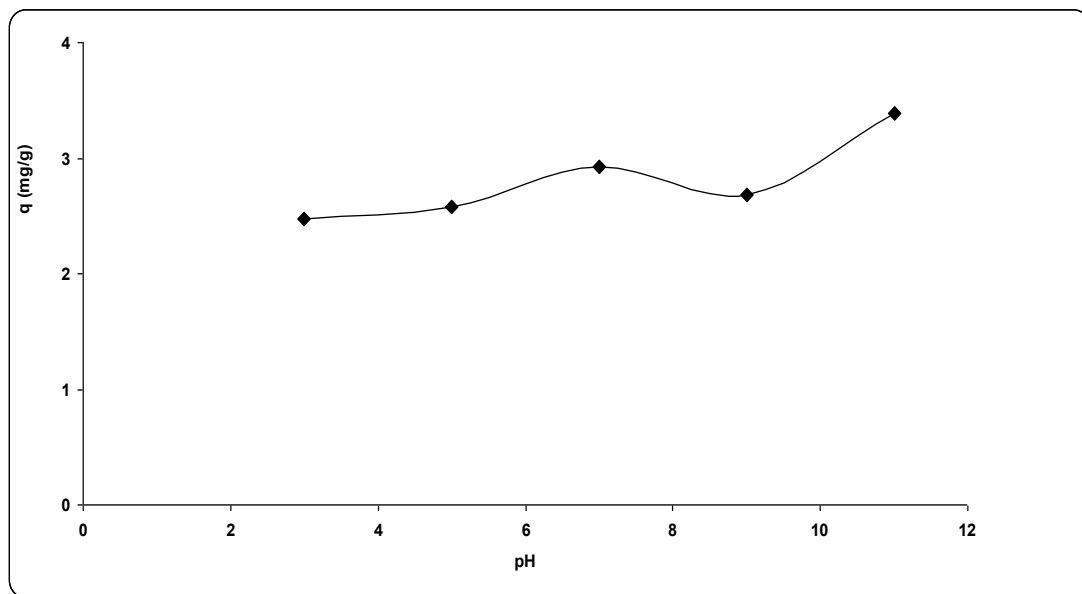


Figure 3.8 Effect of pH on MB adsorption onto 0%-AC (initial dye concentration = 500 mg/L, temperature = 298 K, adsorbent dosage = 5 g/L, agitation rate= 130 rpm).

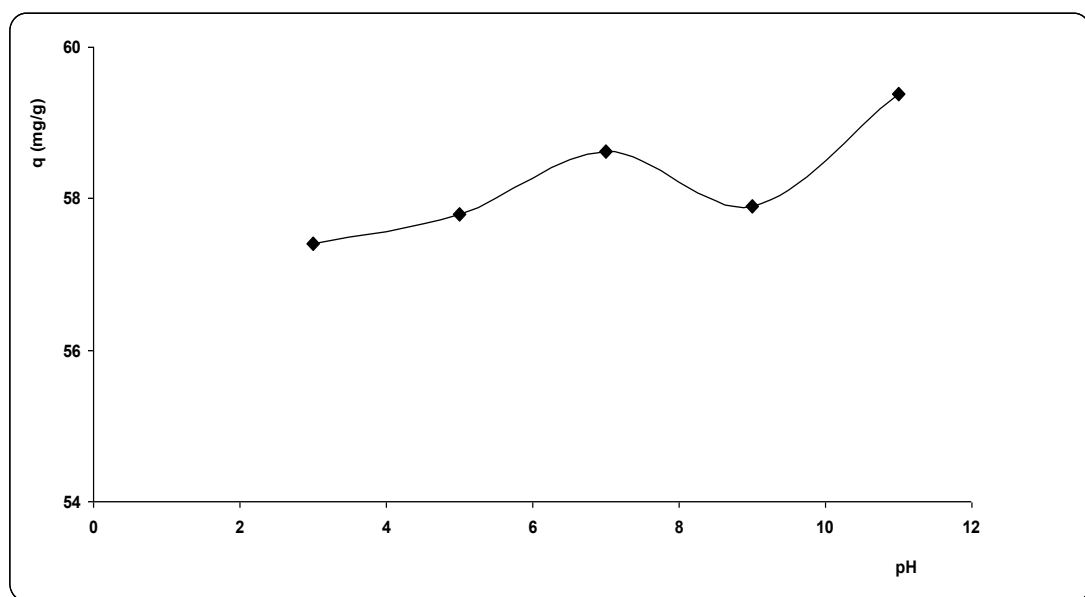


Figure 3.9 Effect of pH on MB adsorption onto 15%-AC (initial dye concentration = 500 mg/L, temperature = 298 K, adsorbent dosage = 5 g/L, agitation rate= 130 rpm)

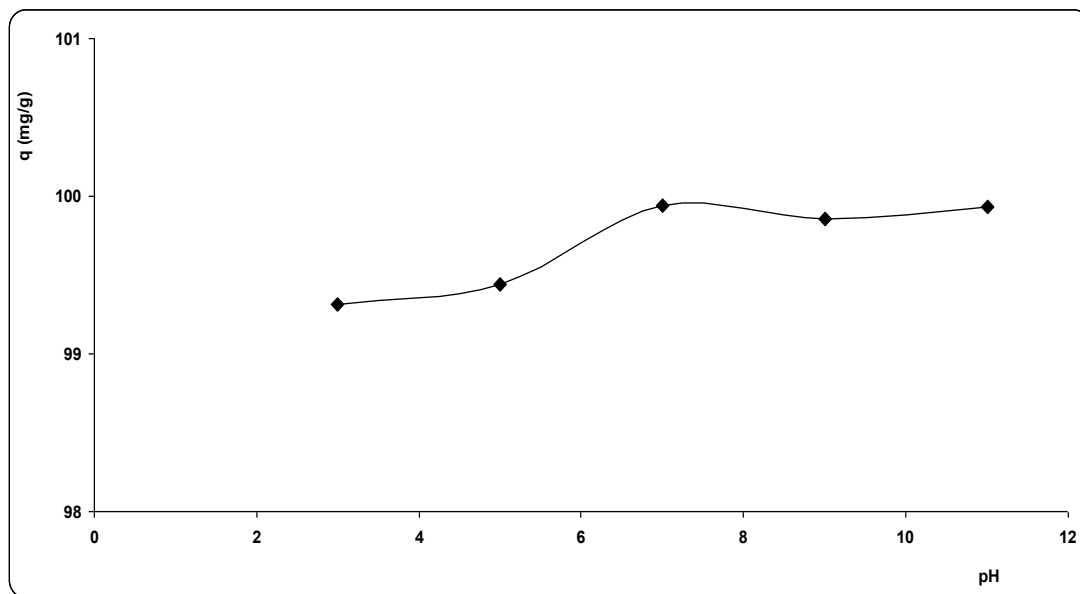


Figure 3.10 Effect of pH on MB adsorption onto 30%-AC (initial dye concentration = 500 mg/L, temperature = 298 K, adsorbent dosage = 5 g/L, agitation rate= 130 rpm).

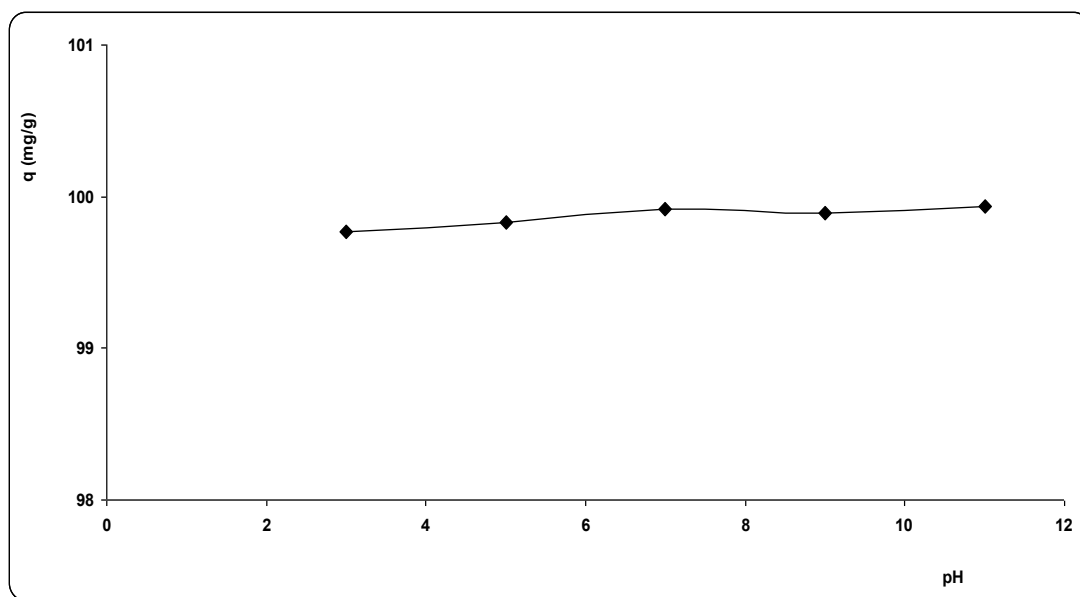


Figure 3.11 Effect of pH on MB adsorption onto 45%-AC (initial dye concentration = 500 mg/L, temperature = 298 K, adsorbent dosage = 5 g/L, agitation rate= 130 rpm).

As can be seen in Figure 3.8-3.11 MB adsorption capacity of POAC is not significantly affected by pH variation. This fact may indicate that the adsorption process mainly consists of physical adsorption in the pores of the material rather than

chemical adsorption on surface reactive sites. Thus all the methylene blue adsorption experiments were carried out at the double distilled water pH (6.5 ± 0.2).

3. 2 Effect of Adsorbent Dosage

The influence of adsorbent dosage on the efficiency of MB removal is shown in Figure 3.12-3.15

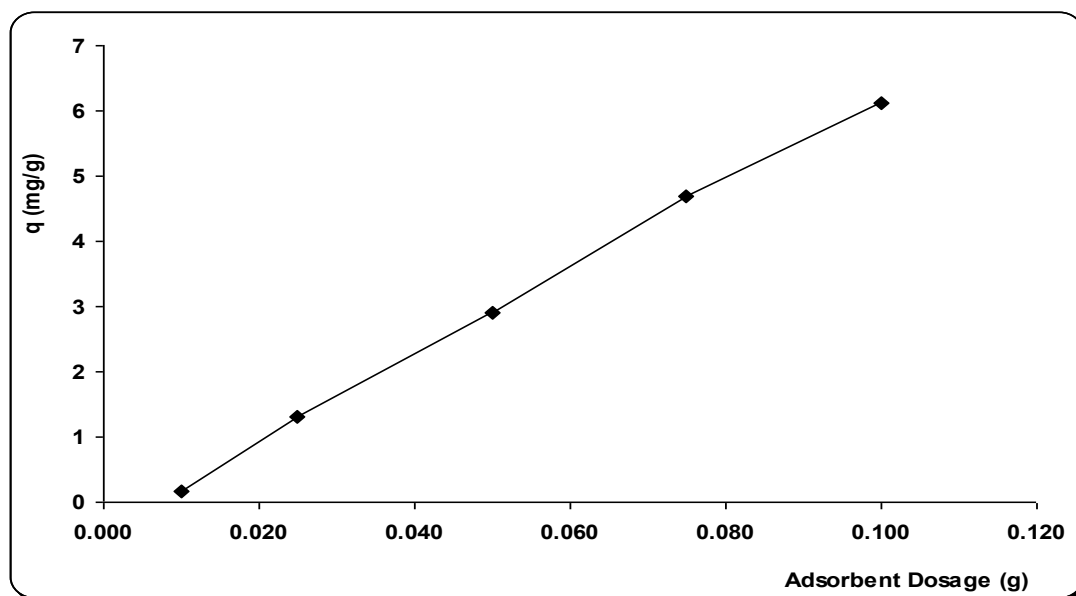


Figure 3.12 Effect of adsorbent dosage on MB adsorption onto 0%-AC (pH =6.5, initial dye concentration = 50 mg/L, temperature = 298 K, agitation rate= 130 rpm).

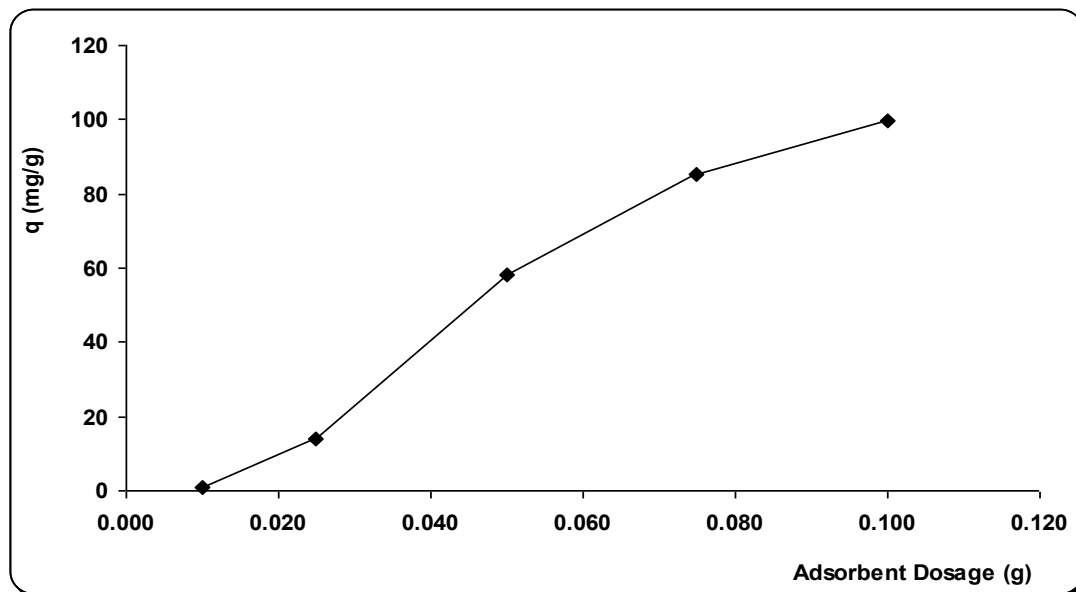


Figure 3.13 Effect of adsorbent dosage on MB adsorption onto 15%-AC (pH =6.5, initial dye concentration = 50 mg/L, temperature = 298 K, agitation rate= 130 rpm).

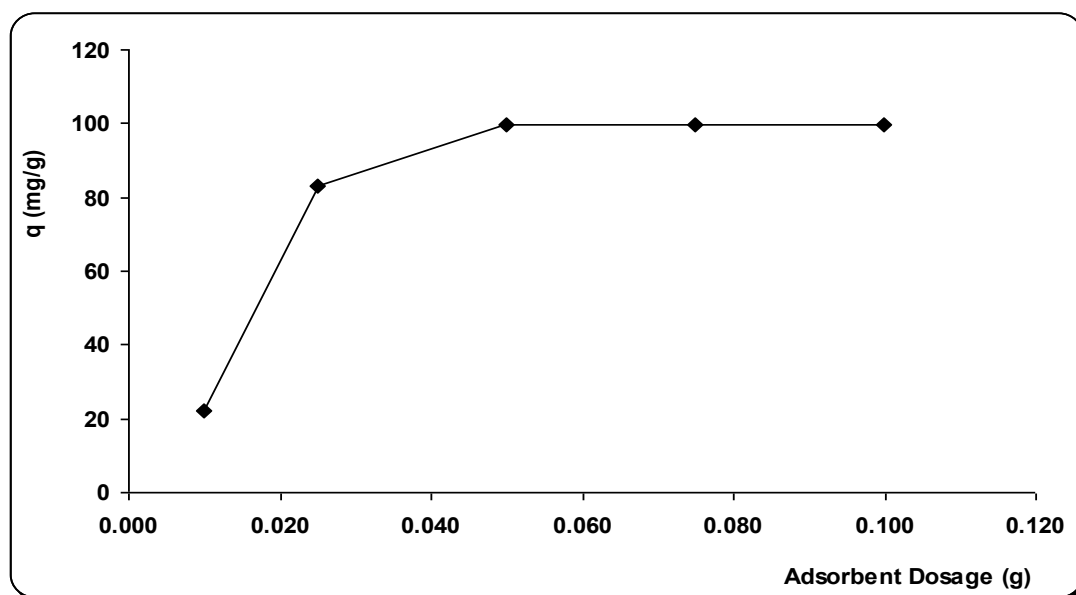


Figure 3.14 Effect of adsorbent dosage on MB adsorption onto 30%-AC (pH =6.5, initial dye concentration = 50 mg/L, temperature = 298 K, agitation rate= 130 rpm).

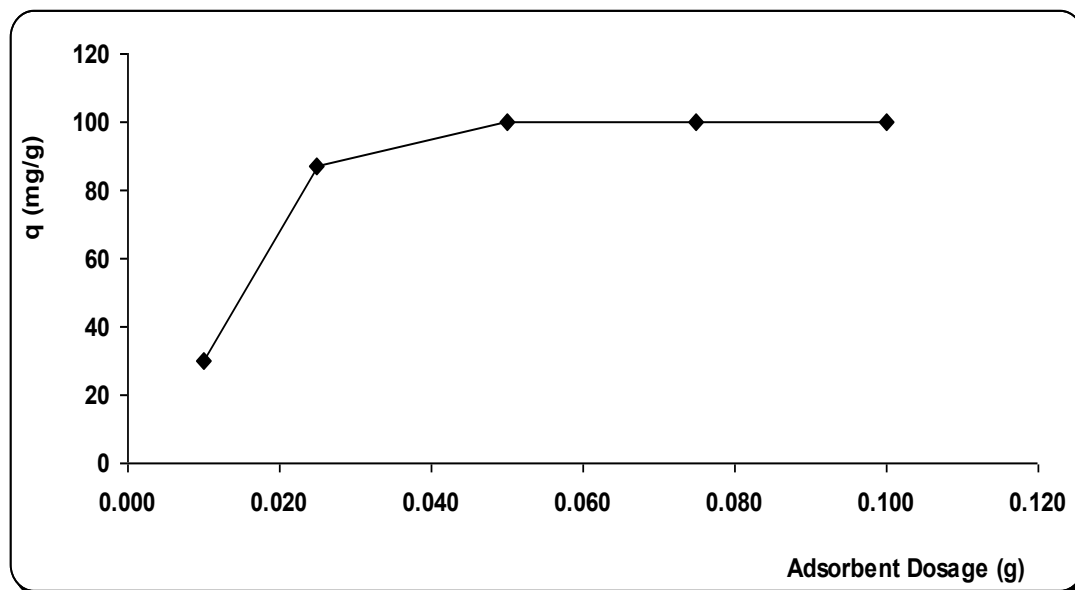


Figure 3.15 Effect of adsorbent dosage on MB adsorption onto 45%-AC (pH =6.5, initial dye concentration = 50 mg/L, temperature = 298 K, agitation rate= 130 rpm).

An adsorbent concentration range of 1–10 g/L was studied at initial dye concentration of 500 mg/L (50 mg/mL for %0-AC) at 10ml volume. Significant increases of MB adsorption on the POAC were noted with increasing adsorbent dosage. After 1 h, adsorption of MB increased from 0.16 to 6.11 mg/g for %0-AC, 0.93 to 99.50 mg/g for %15-AC, 22.11 to 99.83 mg/g for %30-AC, 29.80 to 99.84 mg/g for %45-AC. When adsorbent dosage was increased from 0.010 to 0.100 g, maximum adsorption capacities of activated carbons were also increased.

3. 3 Effect of Contact Time

The amount of adsorbed MB onto the activated carbon was evaluated at time periods ranging from 5 min to 6 h (for 15%-AC 5 min to 8h) and initial dye concentrations ranging from 250 to 1000 mg/L for chemically activated carbon and 25 to 100 mg/L for %0-AC. The adsorption reached equilibrium after 240 minutes for 0%-AC (Figure 3.16), 360 minutes for 15%-AC (Figure 3.17) and 60 minutes for 30%-AC and 45%AC (Figure 3.18-3.19). It can be said that there is almost no significant increase in MB adsorption after the equilibrium contact time.

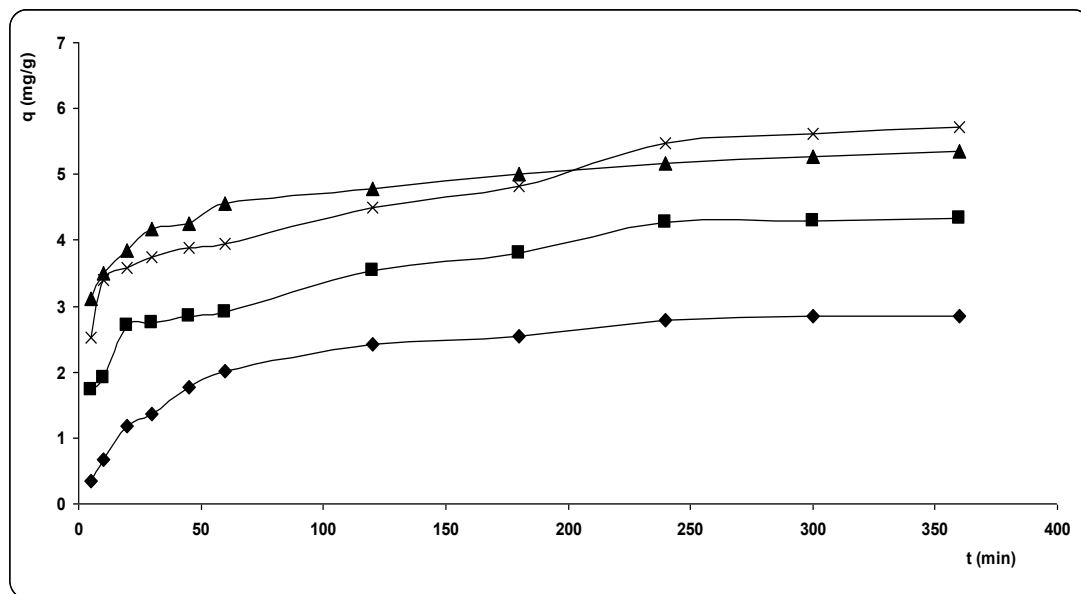


Figure 3.16 The adsorption of MB onto 0%-AC (temperature = 298 K, pH = 6.5, adsorbent dosage = 10 g/L) (-◆- 250 mg/L; -■- 500 mg/L; -▲- 750 mg/L; -×- 1000 mg/L).

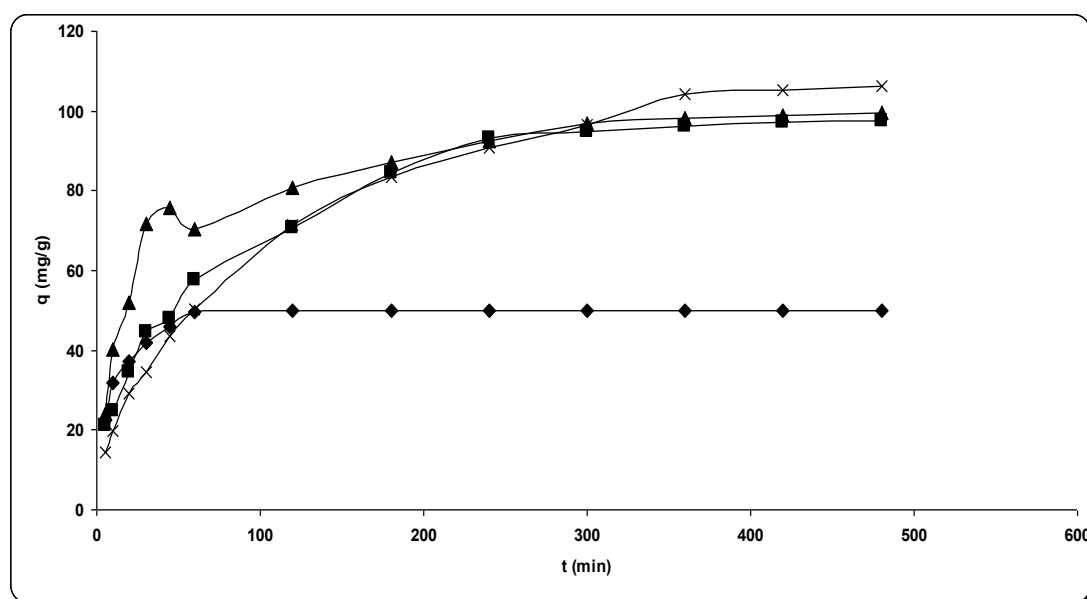


Figure 3.17 The adsorption of MB onto 15%-AC (temperature = 298 K, pH = 6.5, adsorbent dosage = 10 g/L) (-◆- 250 mg/L; -■- 500 mg/L; -▲- 750 mg/L; -×- 1000 mg/L).

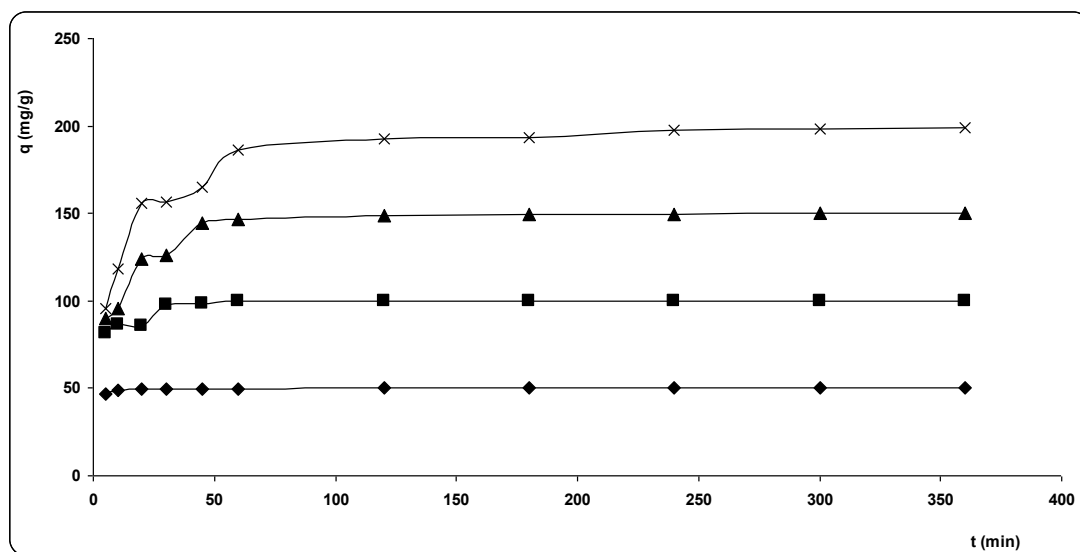


Figure 3.18 The adsorption of MB onto 30%-AC (temperature = 298 K, pH = 6.5, adsorbent dosage = 10 g/L) (-♦- 250 mg/L; -■- 500 mg/L; -▲- 750 mg/L; -×- 1000 mg/L).

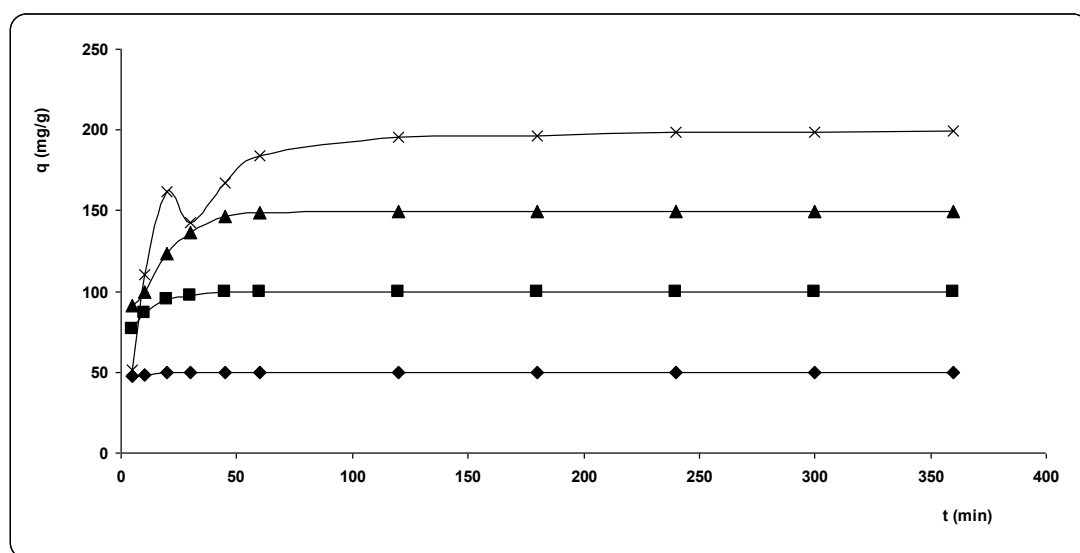


Figure 3.19 The adsorption of MB onto 45%-AC (temperature = 298 K, pH = 6.5, adsorbent dosage = 10 g/L) (-♦- 250 mg/L; -■- 500 mg/L; -▲- 750 mg/L; -×- 1000 mg/L).

3.4 Adsorption Kinetics

Adsorption kinetics is one of the most important parameters for the evaluation of adsorption efficiency. Two main kinetic models namely the pseudo-first order (Lagergren, 1898) and pseudo-second order (Ho, 2004) were used in this study to characterize adsorption kinetics.

The linearised form of the Pseudo first-order kinetic model is given by the equation:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

q_e : The amount of dye adsorbed at equilibrium (mg/g)

q : The amount of dye adsorbed (mg/g)

t : time (min)

k_1 : The pseudo first order rate constant (1/min).

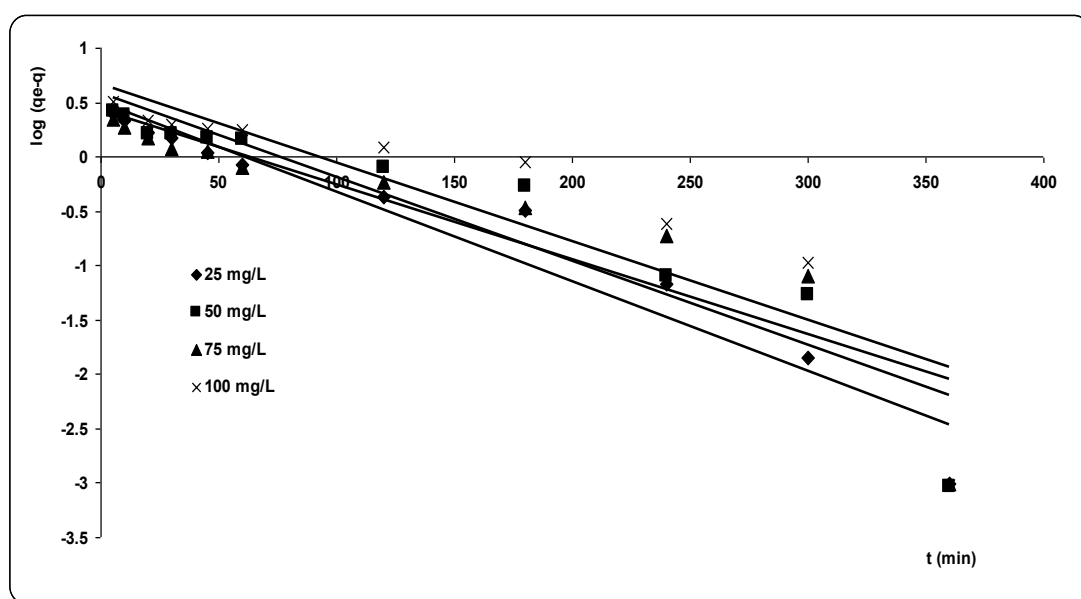


Figure 3.20 First-order sorption kinetics of methylene blue by 0%-AC at different dye concentrations (temperature = 298 K, solution pH = 6.5, adsorbent dosage = 5 g/L)

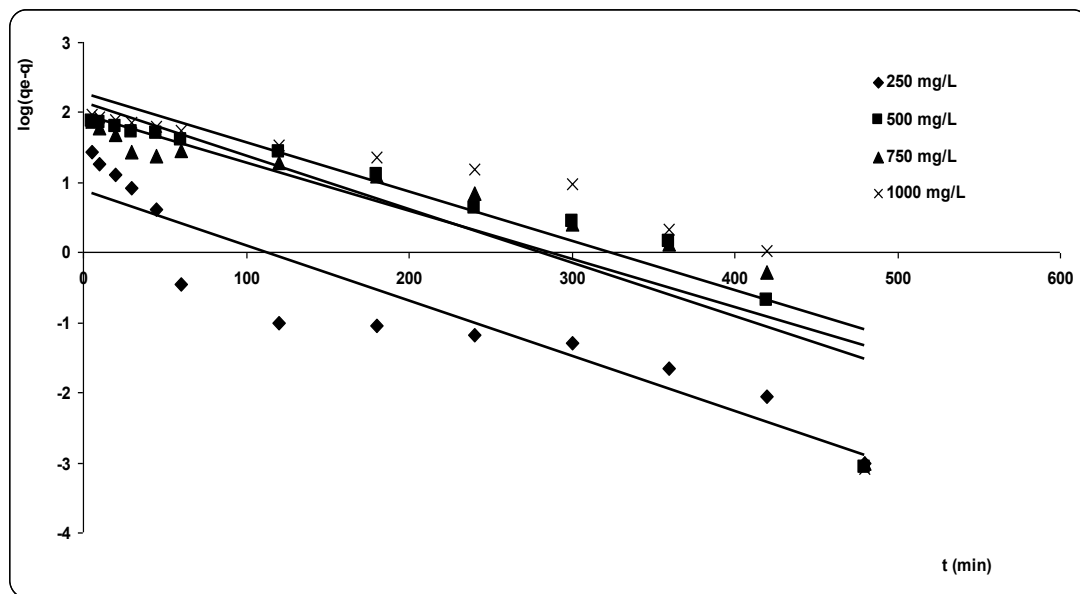


Figure 3.21 First-order sorption kinetics of methylene blue by 15%-AC at different dye concentrations (temperature = 298 K, solution pH = 6.5, adsorbent dosage = 5 g/L).

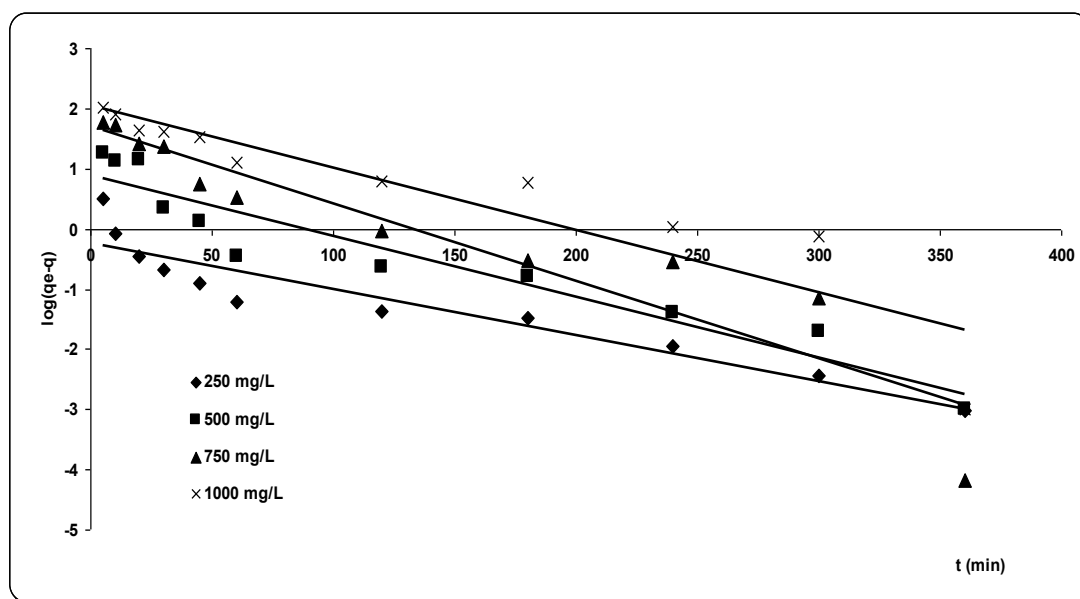


Figure 3.22 First-order sorption kinetics of methylene blue by 30%-AC at different dye concentrations (temperature = 298 K, solution pH = 6.5, adsorbent dosage = 5 g/L).

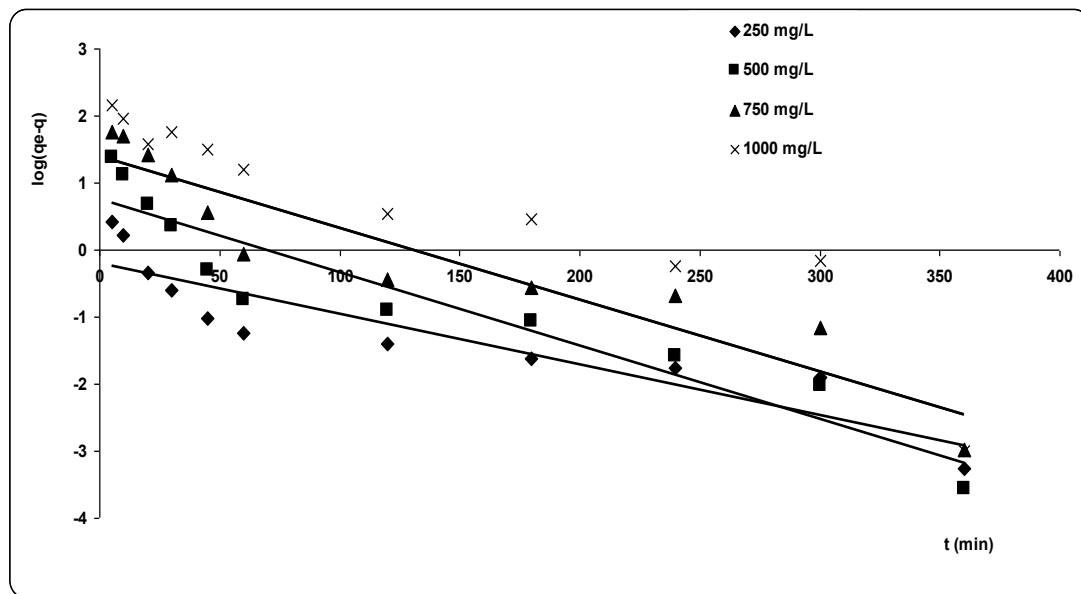


Figure 3.23 First-order sorption kinetics of methylene blue by 45%-AC at different dye concentrations (temperature = 298 K, solution pH = 6.5, adsorbent dosage = 5 g/L).

The Pseudo second-order kinetic model can be expressed by the following equation (in the linear form):

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

q_e : The amount of dye adsorbed at equilibrium (mg/g),

q : The amount of dye adsorbed (mg/g)

t : Time (min)

k_2 : The pseudo second order rate constant (g/mg min)

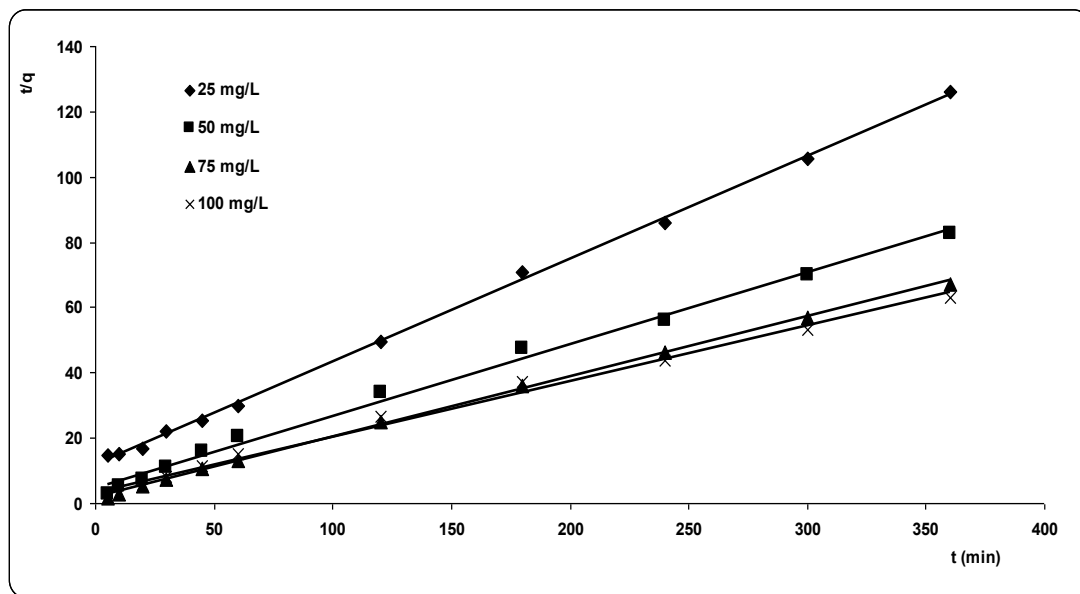


Figure 3.24 Pseudo-second order sorption kinetics of methylene blue by 0%-AC at different dye concentrations (temperature = 298 K, solution pH = 6.5, adsorbent dosage = 5 g/L)

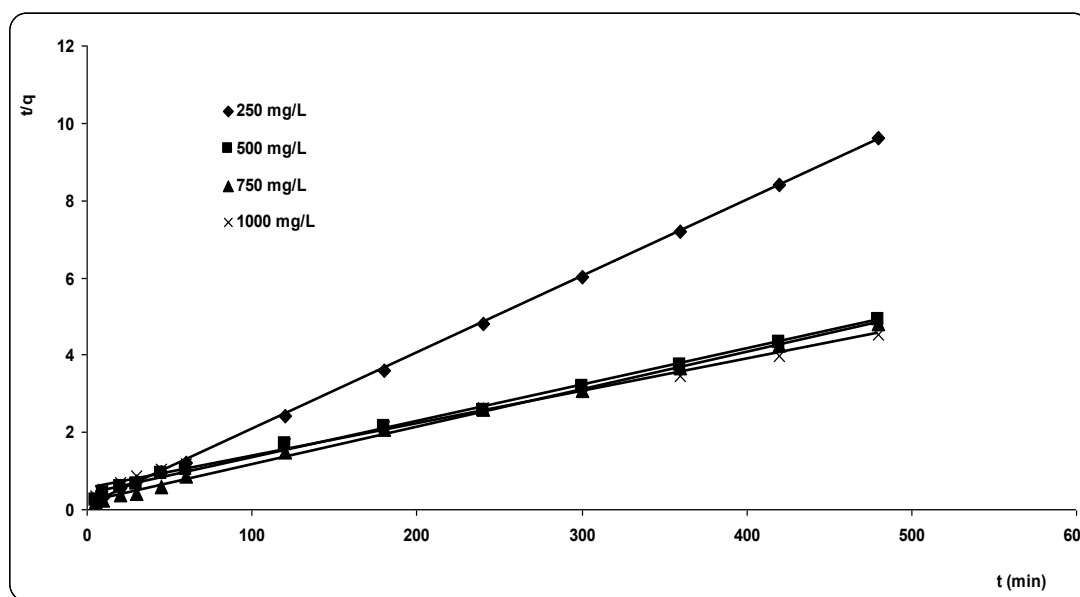


Figure 3.25 Pseudo-second order sorption kinetics of methylene blue by 15%-AC at different dye concentrations (temperature = 298 K, solution pH = 6.5, adsorbent dosage = 5 g/L)

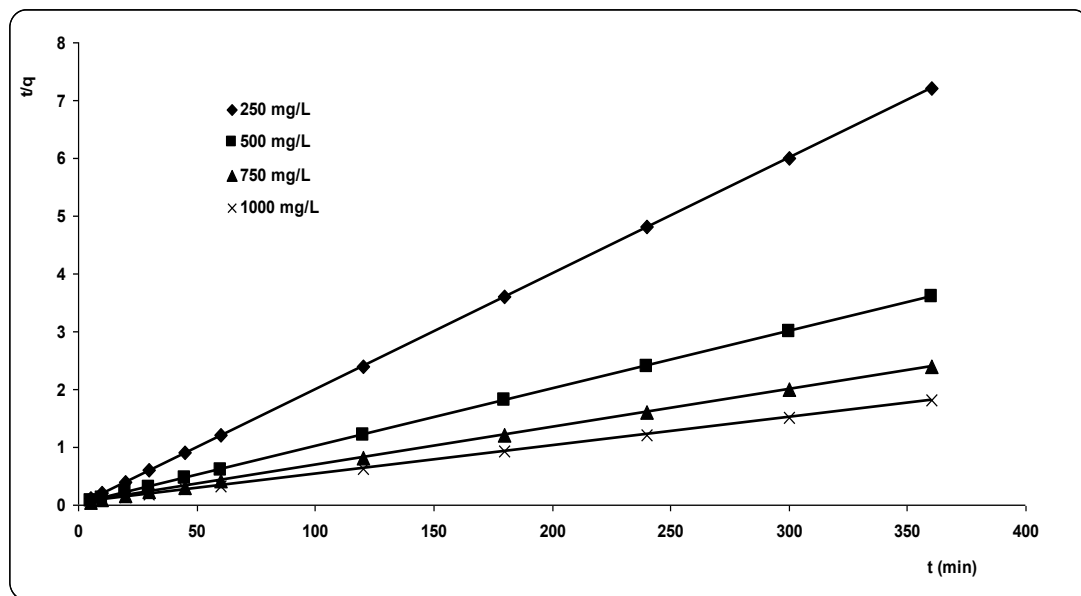


Figure 3.26 Pseudo-second order sorption kinetics of methylene blue by 30%-AC at different dye concentrations (temperature = 298 K, solution pH = 6.5, adsorbent dosage = 5 g/L)

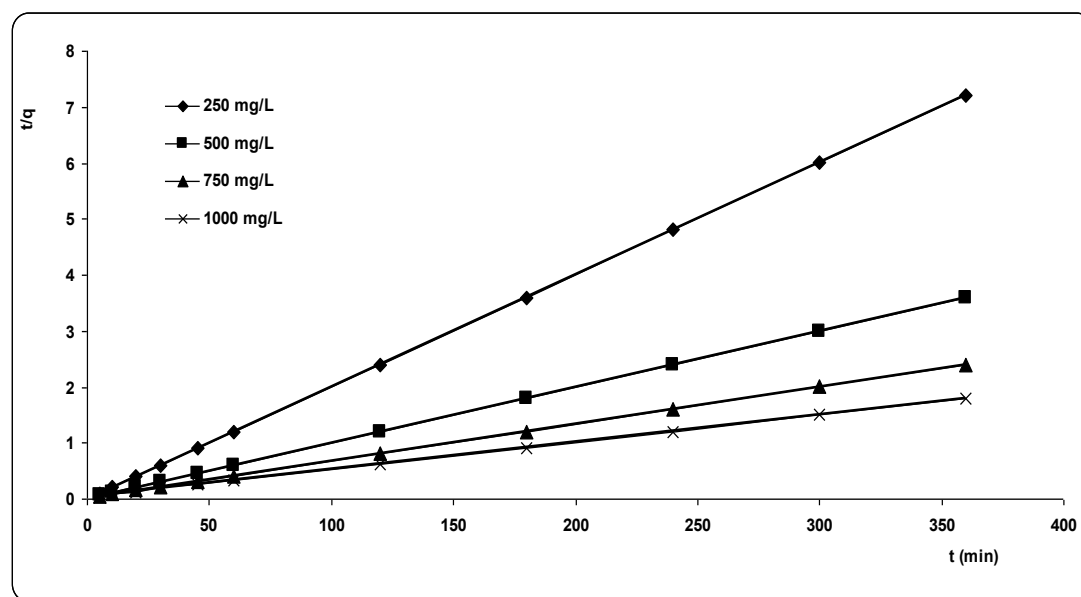


Figure 3.27 Pseudo-second order sorption kinetics of methylene blue by 45%-AC at different dye concentrations (temperature = 298 K, solution pH = 6.5, adsorbent dosage = 5 g/L)

The fit of the kinetic models to the experimental results for MB adsorption onto the POAC is shown in Figure 3.20-3.27 and derived kinetic parameters are shown in Table 3.3. As can be seen by the values for R^2 the pseudo-second-order kinetic model fits the experimental results more accurately than the pseudo-first-order

kinetic model for all produced activated carbons (Table 3.3). Thus, it can be concluded that MB adsorption on POAC follows the second order rate equation.

Table 3.3 Pseudo first and second order adsorption kinetics at different initial dye concentrations for the adsorption of MB onto POAC at 298 K.

Act Perc.	Dye Conc. (mg/mL)	Temp. (K)	q_{exp} (mg/g)	Pseudo First Order-Kinetics			Pseudo Second Order Kinetics		
				q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2
0%	25	298	2.86	3.13	0.019	0.940	3.17	0.84×10^{-3}	0.999
	50	298	4.35	3.79	0.018	0.872	4.53	11×10^{-3}	0.995
	75	298	5.36	2.69	0.016	0.821	5.42	19×10^{-3}	0.999
	100	298	5.72	4.65	0.017	0.790	5.86	8.96×10^{-3}	0.992
15%	250	298	49.97	7.82	0.018	0.878	50.5	4.27×10^{-3}	1.000
	500	298	97.48	140.31	0.017	0.836	106.38	0.23×10^{-3}	0.996
	750	298	99.54	94.08	0.016	0.781	103.09	0.46×10^{-3}	0.998
	1000	298	106.23	183.95	0.016	0.730	120.48	0.12×10^{-3}	0.993
30%	250	298	49.98	0.58	0.018	0.890	50	11×10^{-3}	1.000
	500	298	99.83	8.02	0.027	0.928	100	7.58×10^{-3}	1.000
	750	298	149.91	50.48	0.029	0.877	151.51	1.72×10^{-3}	1.000
	1000	298	199.01	100.79	0.023	0.838	204.08	0.67×10^{-3}	1.000
45%	250	298	49.98	0.064	0.017	0.828	50	98×10^{-3}	1.000
	500	298	99.94	5.75	0.025	0.891	100	10×10^{-3}	1.000
	750	298	149.85	24.83	0.025	0.883	151.51	2.21×10^{-3}	1.000
	1000	298	199.33	115.32	0.025	0.883	204.08	0.52×10^{-3}	1.000

3.5 Adsorption Isotherms

The experimental results of MB adsorption on POAC were represented by adsorption isotherms and fitted with three model equations in order to obtain information about the properties and mechanism of the sorption process. Langmuir, Freundlich and Dubinin-Raduschkevich model equations were used in this study.

3.5.1 Langmuir Isotherm Model

The Langmuir isotherm model (Langmuir, 1916) is based on the assumption that the adsorption process takes place on a homogeneous surface, assuming mono-layer adsorption onto a surface with a finite number of identical sites, so a monolayer of adsorbate is formed at saturation on the adsorbent surface.

The linear expression of the Langmuir Isotherm model is represented by the equation:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{bq_m} \frac{1}{C_e} \quad (4)$$

q_m : maximum adsorption capacity (mg/g)

C_e : equilibrium concentration of dye at the equilibrium time (mg/L)

b : Langmuir constant (L/mg).

The plot of specific adsorption ($1/q_e$) against the equilibrium concentration ($1/C_e$) (Figure 9) shows that MB adsorption follows the Langmuir model. The Langmuir constants q_m and b were determined from the slope and intercept of the plot. The Langmuir constant q_m is related to the adsorption capacity (amount of adsorbate adsorbed per unit mass of the adsorbent to complete monolayer coverage). The calculated Langmuir isotherm parameters were given in Table 3.4. Maximum adsorption capacity of POAC were found 285.7 mg/g at 45 °C for 45%-AC.

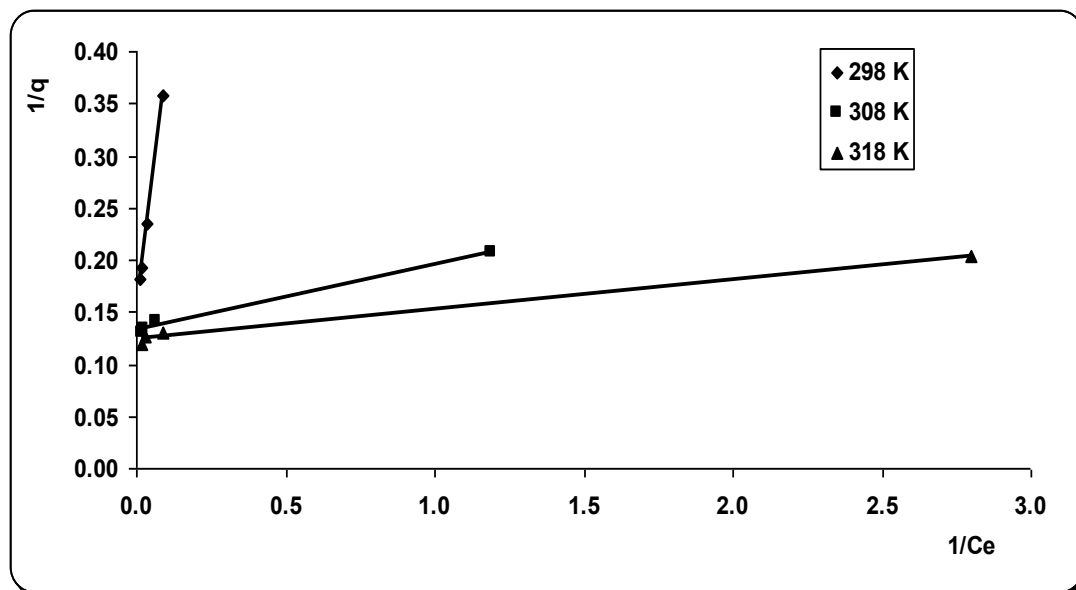


Figure 3.28 Langmuir isotherm plots for the adsorption of methylene blue, by 0%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

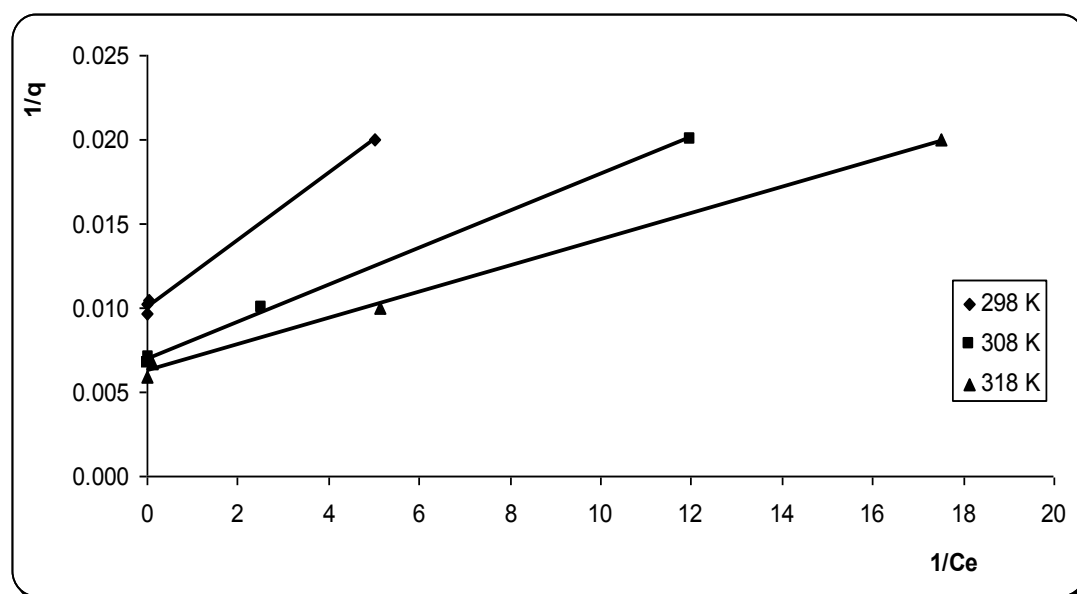


Figure 3.29 Langmuir isotherm plots for the adsorption of methylene blue, by 15%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

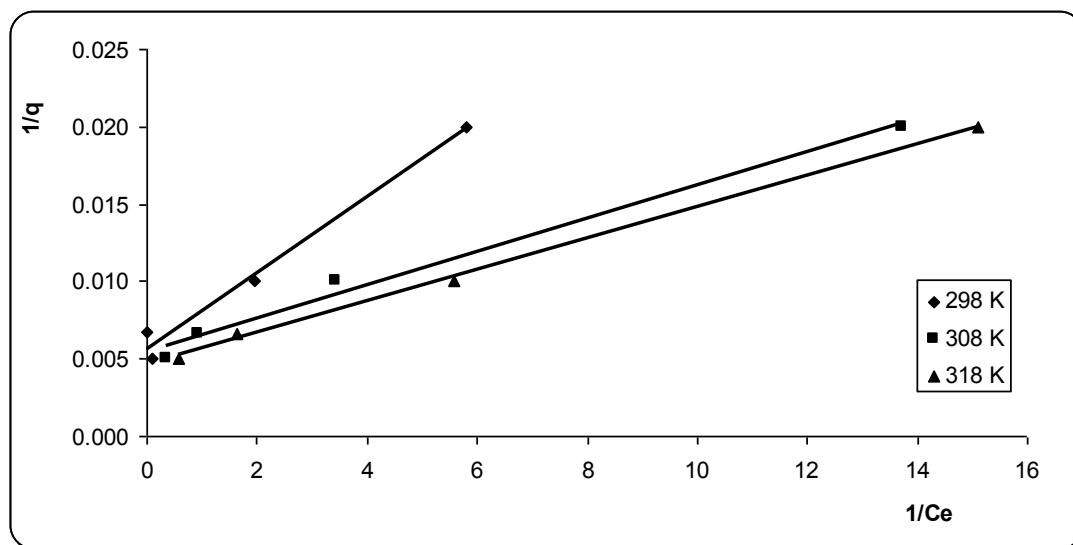


Figure 3.30 Langmuir isotherm plots for the adsorption of methylene blue, by 30%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

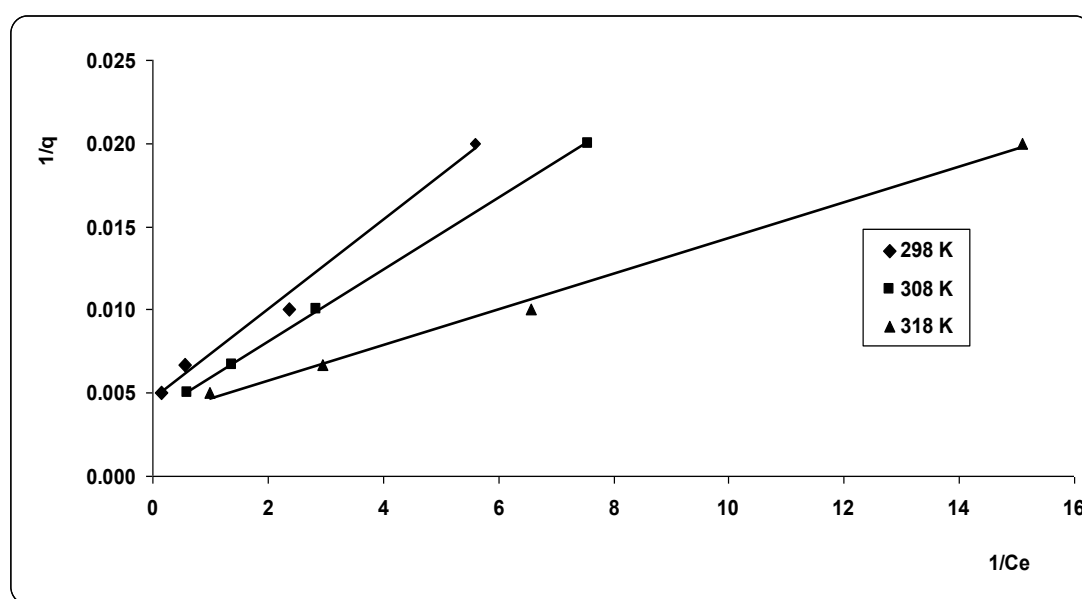


Figure 3.31 Langmuir isotherm plots for the adsorption of methylene blue, by 45%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

3.5.2 Freundlich Isotherm Model

Freundlich 1906 presented a fairly satisfactory empirical model to describe non-ideal adsorption on heterogeneous surfaces as well as multiplayer adsorption expressed by the equation:

$$\log q = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

C_e : equilibrium concentration of dye at the equilibrium time (mg/L),

n : Freundlich constant related to adsorption intensity (dimensionless),

K_f : Freundlich constant represents the relative adsorption capacity (mg/g).

Freundlich isotherm constant, n_f , indicating the surface heterogeneity factor.

The equation was given as:

$$n_f = \frac{1}{n} \quad (7)$$

The Freundlich heterogeneity parameter (n_f) provides a convenient measure of equilibrium nonlinearity, with n_f equal to 1 implying a linear equilibrium relationship. On the contrary n_f values close to 0 can be related to an adsorption process on a highly heterogeneous surface. In Figure 3.32-3.35 the Freundlich plots can be seen while constants K_f and n were calculated from equation 6, and n_f was calculated from equation 7 and tabulated in Table 3.4. The obtained all n_f values for 30%-AC and 45%-AC was 0.32, 0.37, 0.41 and 0.37, 0.55, 0.50 at 25, 35, 45 °C respectively. This values indicate that the dye is favourably adsorbed ($0.2 < n_f < 0.8$) by the activated carbon (Ho & McKay, 1998), while the surface of the POAC is heterogeneous.

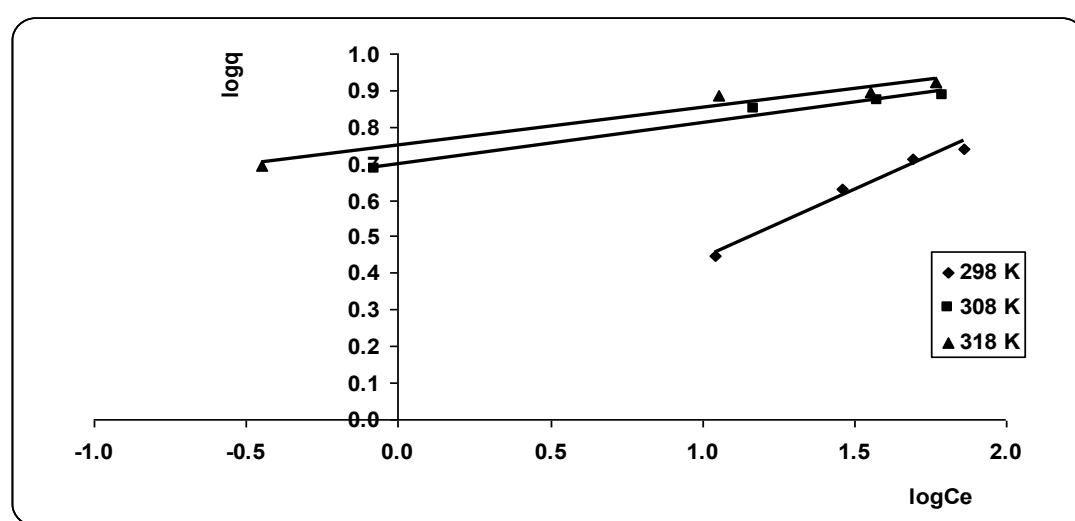


Figure 3.32 Freundlich isotherm plots for the adsorption of methylene blue by 0%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

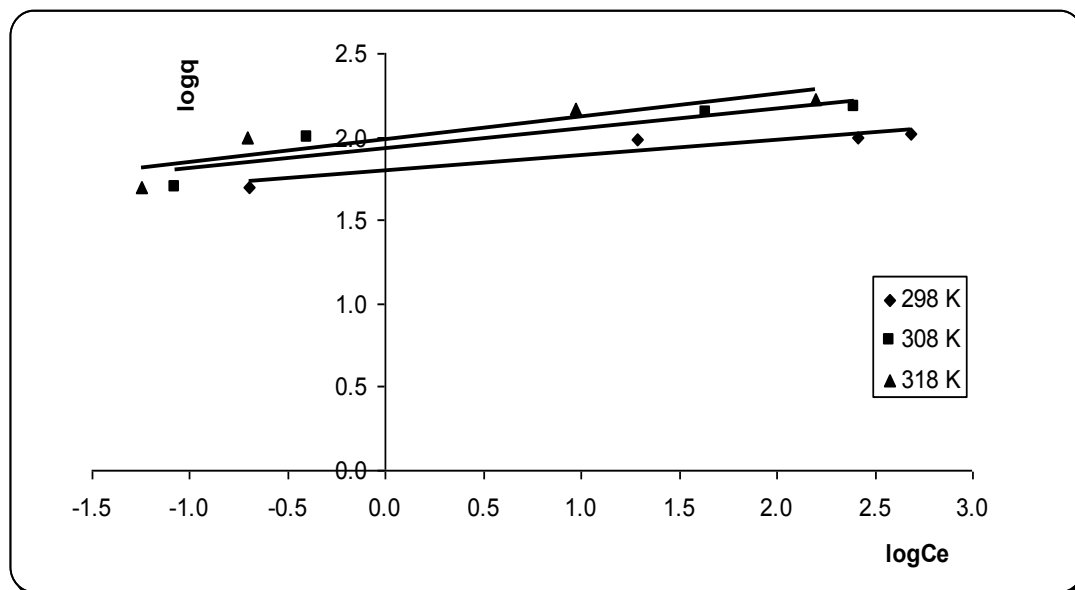


Figure 3.33 Freundlich isotherm plots for the adsorption of methylene blue by 15%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L)

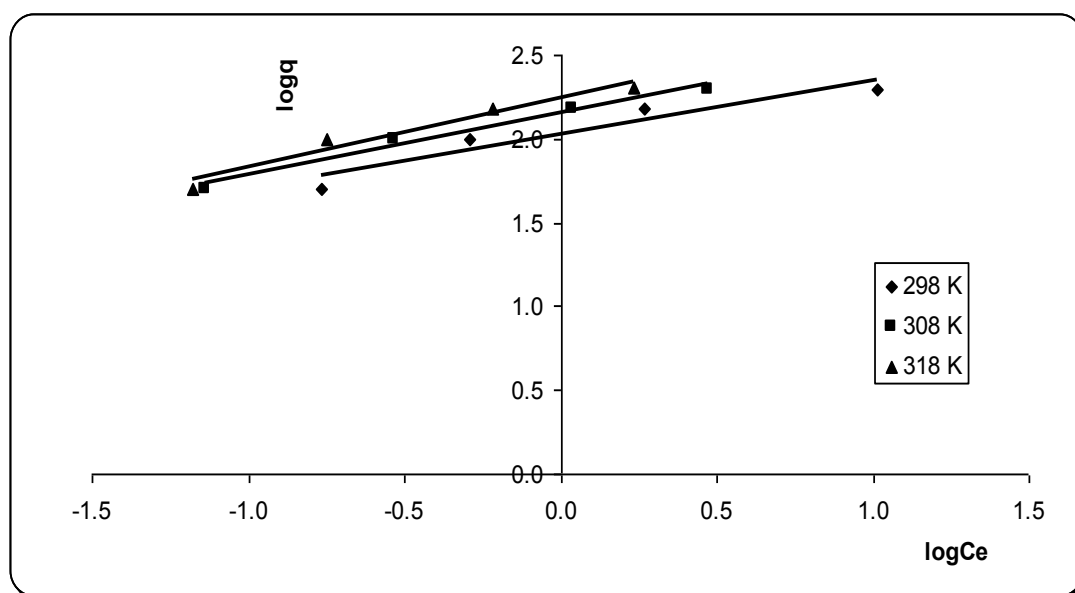


Figure 3.34 Freundlich isotherm plots for the adsorption of methylene blue by 30%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

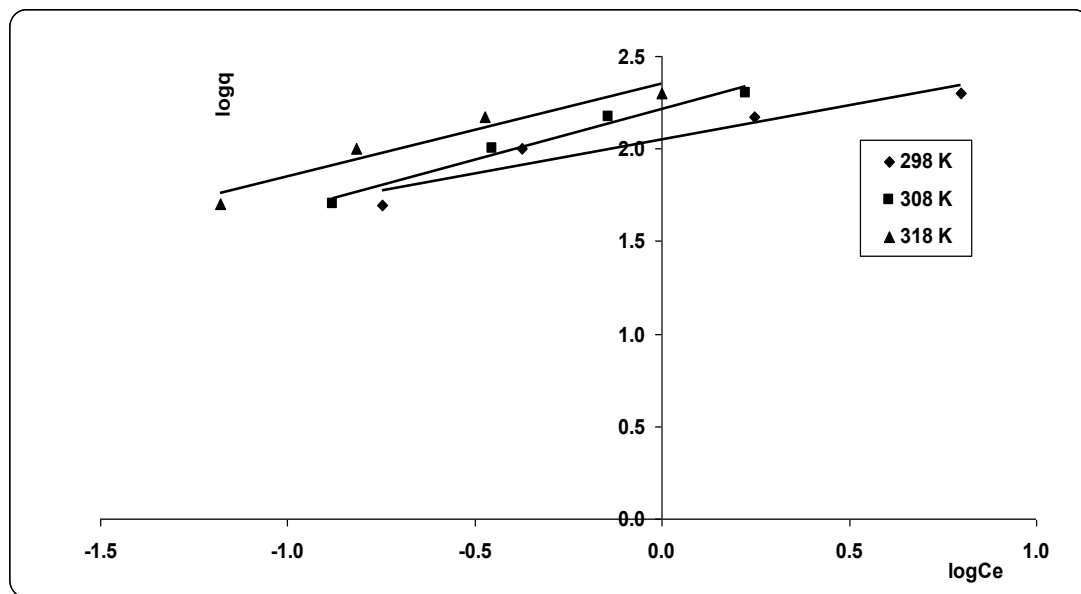


Figure 3.35 Freundlich isotherm plots for the adsorption of methylene blue by 45%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L)

3.5.3 Dubinin-Raduchkevich Isotherm Model

The Dubinin-Radushkevich equation (Dubinin & Radushkevich, 1947; Fu et al., 2008) was used in order to determine whether MB adsorption on the activated carbon is physical, chemical or ion-exchange.

Dubinin-Raduchkevich Isotherm is expressed by the equation;

$$\ln q_e = \ln q_m - B\varepsilon^2 \quad (8)$$

q_m : amount of the max ions sorbed onto POAC (mg/g)

B : a constant related to the sorption energy (mol^2/J^2)

C_e : equilibrium concentration of dye (mg/L),

R : ideal gas constant (8.314 J/mol.K)

T : temperature (Kelvin)

ε is Polanyi potential is shown as follows:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (9)$$

$\ln q_e$ versus ε^2 was plotted as shown in Figure 3.36-3.39 to obtain the q_m and B values from the slopes and intercepts. Results are shown in Table 3.4. Energy related to adsorption can be found from the equation below (Hobson, 1969):

$$E = \frac{B^{-1/2}}{\sqrt{2}} \quad (10)$$

Energy values for MB adsorption onto POAC were found to be 4.08, 5.00 and 5.00 kJ/mol for 15%-AC, 2.89, 4.08 and 4.08 kJ/mol for 30%AC, 2.89, 3.16 and 4.08 kJ/mol for 45%-AC at 298, 308, and 318 K, respectively. Energy values which in the range of between 2–20 kJ/mol, represent the physical interactions between adsorbent and adsorbate (Smith, 1981; Apiraticul & Pavasant, 2008). Energy values of adsorption between MB and 45%-AC were within this range, thus indicating physical adsorption.

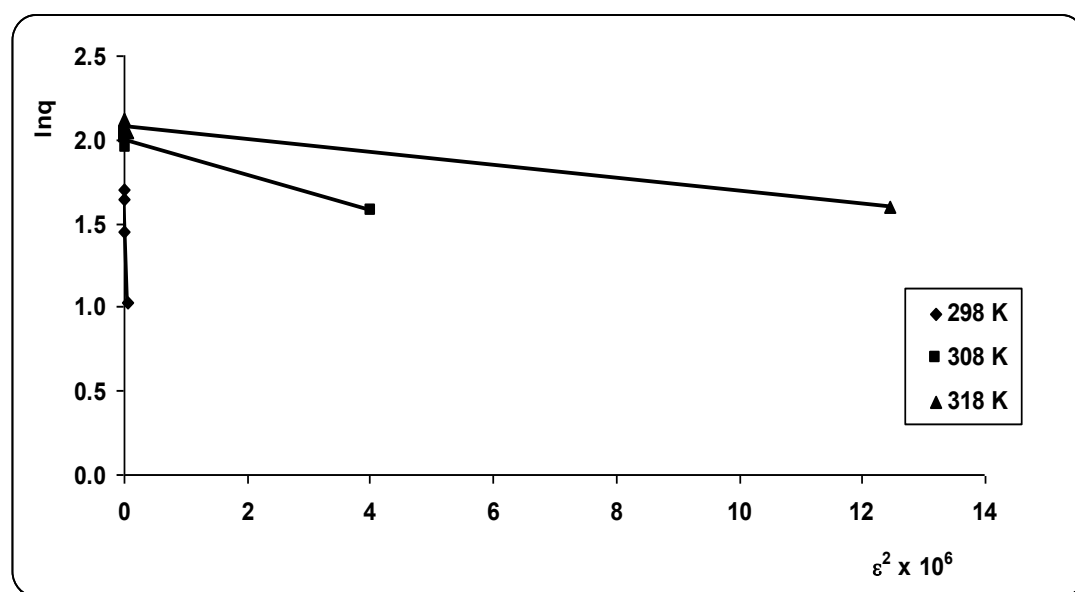


Figure 3.36 Dubinin-Radushkevich isotherm plots for the adsorption of methylene blue by 0%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

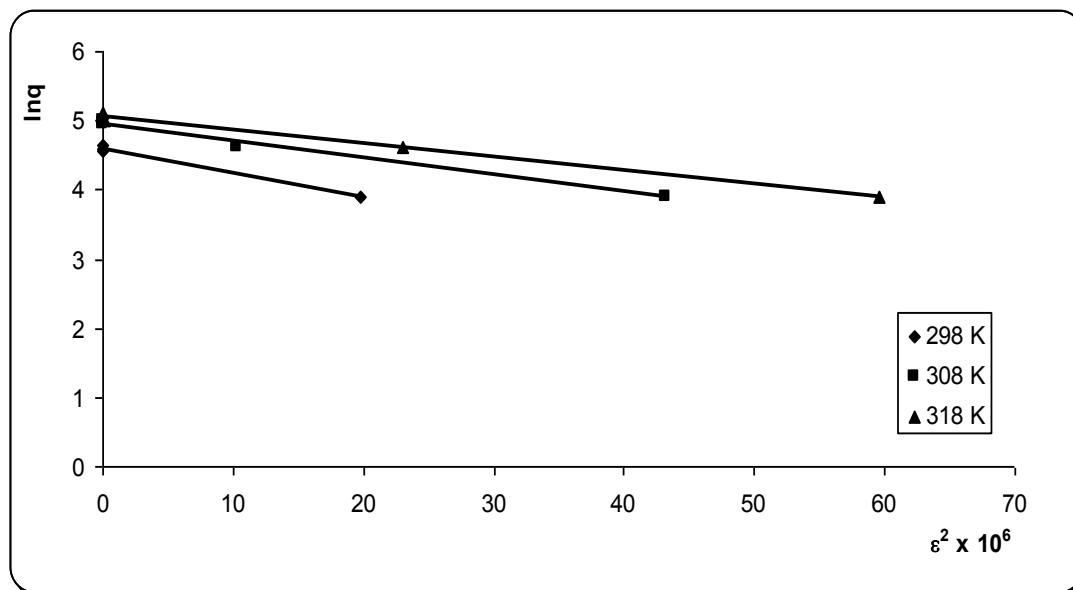


Figure 3.37 Dubinin-Radushkevich isotherm plots for the adsorption of methylene blue by 15%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L)

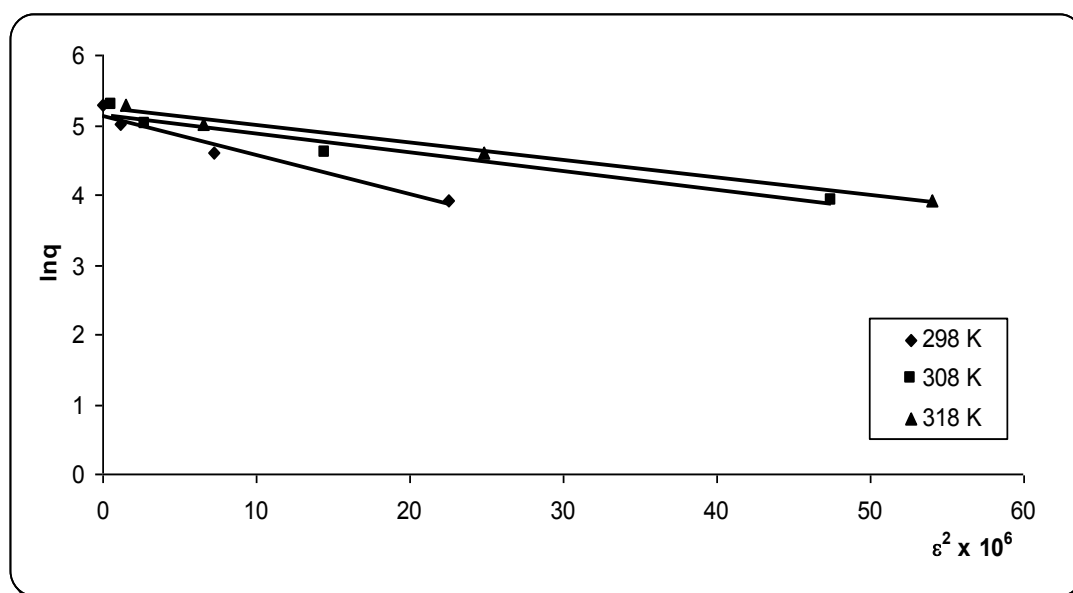


Figure 3.38 Dubinin-Radushkevich isotherm plots for the adsorption of methylene blue by 30%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

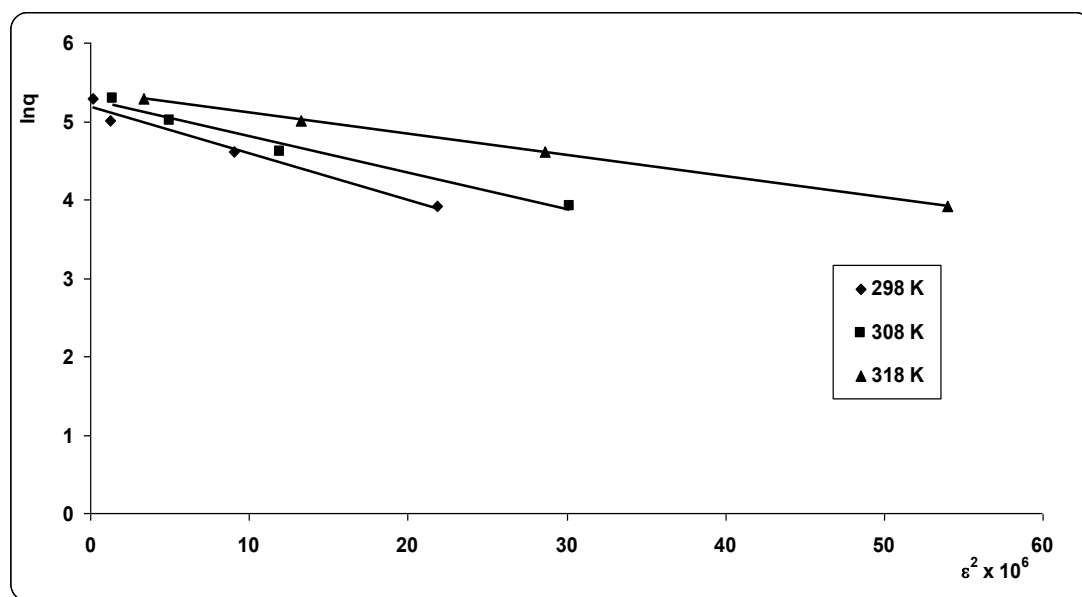


Figure 3.39 Dubinin-Radushkevich isotherm plots for the adsorption of methylene blue by 45%-AC at different temperatures. (solution pH = 6.5, adsorbent dosage = 5 g/L).

Table 3.4 Langmuir, Freundlich and Dubinin-Radushkevich isotherm constants for the adsorption of methylene blue by POAC (solution pH = 6.5, adsorbent dosage = 10 g/L).

Act Perc.	Temp. (K)	Langmuir Constants			Freundlich Constants				Dubinin-Radushkevich Constants			
		q_m (mg/g)	b (L/mg)	R^2	K_f (mg/g)	N	nf	R^2	q_m (mg/g)	B (mol^2/kJ^2)	E (kJ/mol)	R^2
0%	298	6.68	0.07	0.999	1.17	2.7	0.37	0.977	5.22	1000×10^{-8}	0.22	0.945
	308	7.53	2.13	0.990	5.00	8.94	0.11	0.981	7.71	10×10^{-8}	2.24	0.972
	318	8.05	4.42	0.992	5.59	9.66	0.10	0.961	7.97	4×10^{-8}	3.54	0.982
15%	298	100	5.00	0.996	61.84	10.81	0.09	0.898	99.41	3×10^{-8}	4.08	0.991
	308	142.5	6.36	0.998	84.94	8.33	0.12	0.816	140.64	2×10^{-8}	5.00	0.984
	318	161.3	7.75	0.997	96.18	7.37	0.14	0.810	157.67	2×10^{-8}	5.00	0.991
30%	298	178.6	2.24	0.972	105.75	3.13	0.32	0.909	170.70	6×10^{-8}	2.89	0.957
	308	181.8	5.00	0.989	141.68	2.71	0.37	0.981	171.86	3×10^{-8}	4.08	0.949
	318	217.4	4.60	0.998	173.86	2.42	0.41	0.945	190.99	3×10^{-8}	4.08	0.988
45%	298	217.4	1.70	0.990	112.12	2.74	0.37	0.918	177.76	6×10^{-8}	2.89	0.975
	308	270.3	1.68	1.000	164.21	1.82	0.55	0.974	193.97	5×10^{-8}	3.16	0.978
	318	285.7	3.18	0.996	225.63	1.99	0.50	0.934	217.39	3×10^{-8}	4.08	1.000

Table 3.5 lists a comparison of maximum monolayer MB adsorption capacity on activated carbons between some low cost materials, commercial activated carbon and 45%-AC. The MB adsorption capacity of the 45%-AC was higher compared to other adsorbents studied and reported in the literature. This shows that *Posidonia oceanica* (L.) dead leaves can be used for the preparation of activated carbon and especially

via chemical activation with %45 impregnation ratio it can produce a material with very high MB adsorption efficiency.

Table 3.5 Monolayer adsorption capacities of various activated carbon against methylene blue.

Activated carbon type	q_m (mg/g)	References
Hazelnut shell-based	8.82	Aygun et al., 2003
Oil palm wood-based	90.90	Ahmad et al., 2007
Bamboo dust-based	143.20	Kannan & Sundaram, 2001
Ground shell-based	164.90	Kannan & Sundaram, 2001
Cotton Stalk-based	180.00	Girgis et al., 2009
Jute fiber-based	225.64	Senthilkumaar et al., 2005
Oil Palm Fiber-based	227.78	Tan et al., 2007
Coal-based	234.00	Gong et al., 2009
Oil Palm Shell-based	243.90	Tan et al., 2008
FiltrisorbF300	240.00	Stavropoulos & Zabaniotou, 2005
<i>Posidonia oceanica</i> (L.) dead leaves-derived	285.70	Present study

3.6 Thermodynamic Parameters

In order to determine the thermodynamic parameters of the MB-POAC adsorption system Gibbs free energy was used since Entropy, S , and free energy, G cannot be measured directly. The values of Gibbs free energy and entropy were used to predict the nature of the adsorption phenomenon.

Thermodynamic parameters (ΔG , ΔH and ΔS) were calculated from the equations below:

$$\ln K_d = \frac{-\Delta H}{R} \frac{1}{T} + \frac{\Delta S}{R} \quad (\text{van't Hoff Equation}) \quad (11)$$

$$K_d = \frac{q}{C_e} \quad (12)$$

$$\Delta G = \Delta H - T\Delta S \quad (13)$$

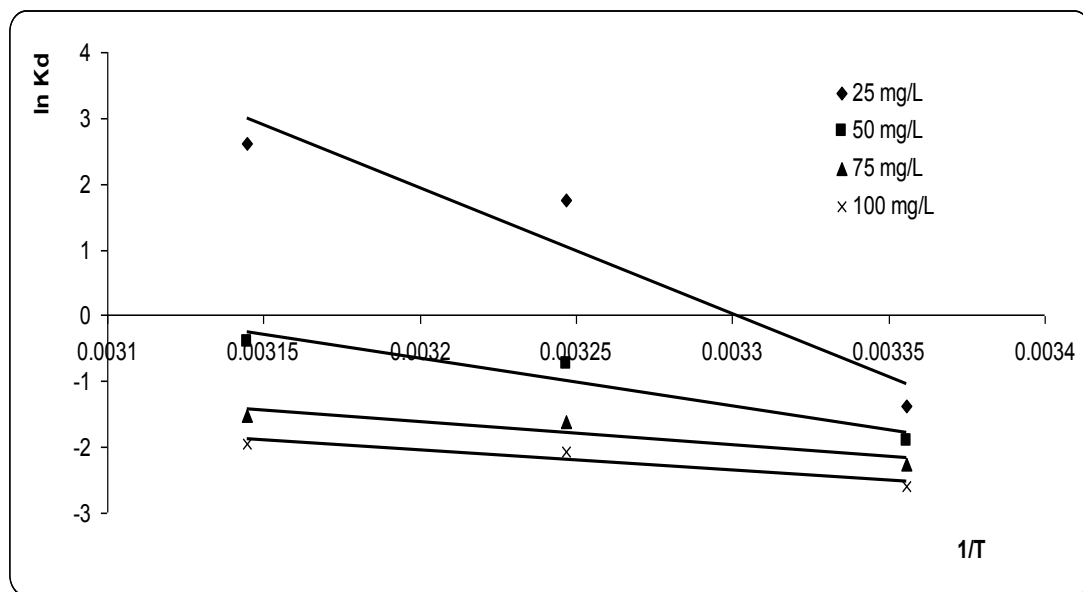


Figure 3.40 Plots of $\ln K_d$ versus $1/T$ for the adsorption of methylene blue by 0%-AC at different dye concentrations. (solution pH = 6.5, adsorbent dosage = 5 g/L).

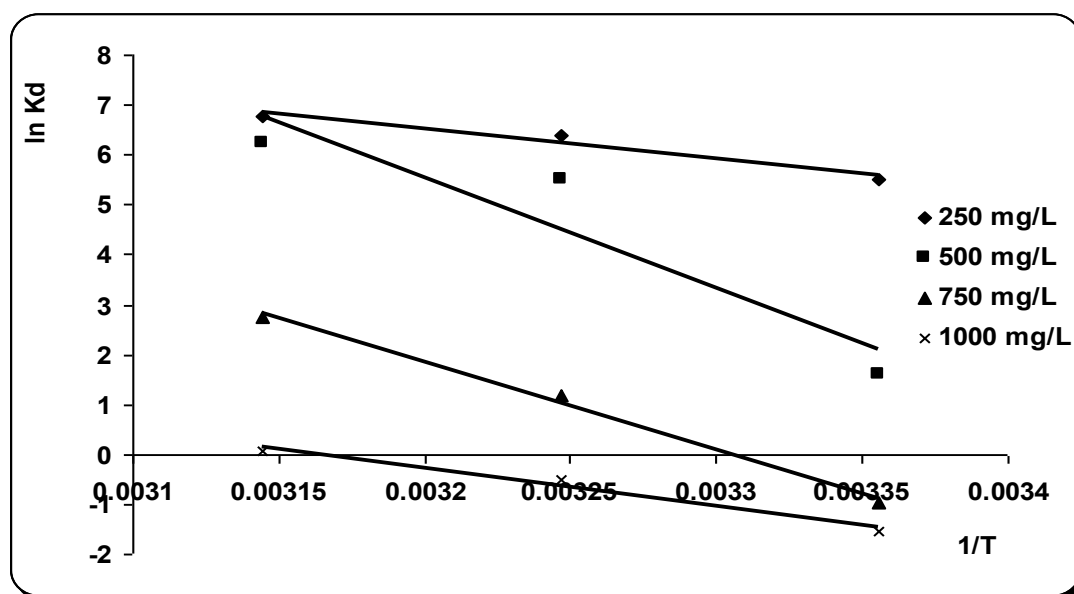


Figure 3.41 Plots of $\ln K_d$ versus $1/T$ for the adsorption of methylene blue by 15%-AC at different dye concentrations. (solution pH = 6.5, adsorbent dosage = 5 g/L).

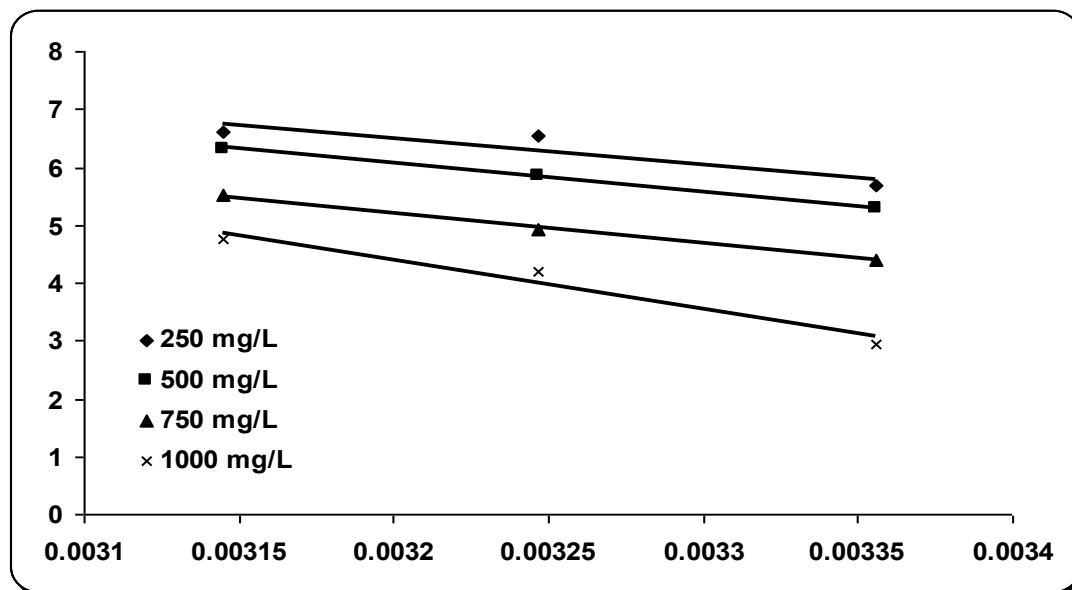


Figure 3.42 Plots of $\ln K_d$ versus $1/T$ for the adsorption of methylene blue by 30%-AC at different dye concentrations. (solution pH = 6.5, adsorbent dosage = 5 g/L).

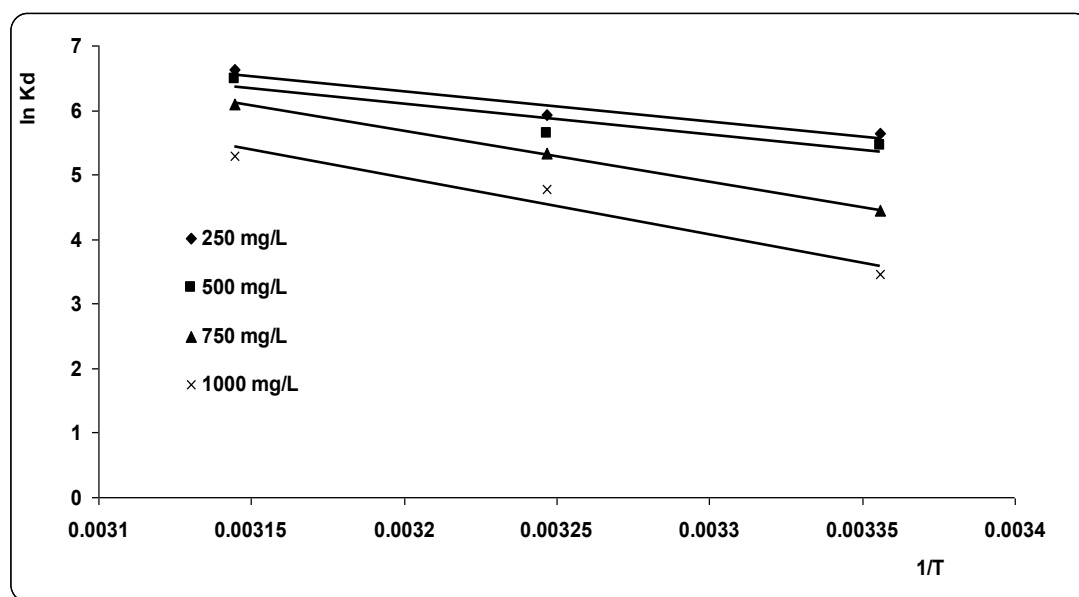


Figure 3.43 Plots of $\ln K_d$ versus $1/T$ for the adsorption of methylene blue by 45%-AC at different dye concentrations. (solution pH = 6.5, adsorbent dosage = 5 g/L).

As seen in Table 3.6, all ΔH values were found positive at all dye concentrations studied. This indicates that the interactions between MB and POAC were endothermic. Moreover ΔG values values of 30%-AC and 45%-AC were negative at all temperatures indicating that the adsorption of MB on 30%-AC and 45%AC are spontaneous at all dye concentration and at all temperature.

Table 3.6 Thermodynamic parameters of MB adsorption onto POAC (T = 298, 308, 318 K).

Activation Percentage	Dye concentration (mg/L)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)		
				298 K	308 K	318 K
0%	25	158.53	0.52	3.57	-1.63	-6.83
	50	60.19	0.19	3.57	1.67	-0.23
	75	29.16	0.08	5.32	4.52	3.72
	100	25.33	0.06	7.45	6.85	6.25
15%	250	49.35	0.21	-13.23	-15.33	-17.43
	500	184.25	0.64	-6.47	-12.87	-19.27
	750	147.42	0.49	1.40	-3.50	-8.40
	1000	63.24	0.20	3.64	1.64	-0.36
30%	250	37.97	0.17	-12.69	-14.39	-16.09
	500	41.32	0.18	-12.32	-14.12	-15.92
	750	43.73	0.18	-9.91	-11.71	-13.51
	1000	71.20	0.26	-6.28	-8.88	-11.48
45%	250	38.96	0.18	-14.68	-16.48	-18.28
	500	40.04	0.18	-13.60	-15.40	-17.20
	750	65.32	0.26	-12.16	-14.76	-17.36
	1000	72.98	0.27	-7.48	-10.18	-12.88

CHAPTER FOUR

CONCLUSION

In this study, *Posidonia oceanica* (L.) dead leaves were used as the precursor for the preparation of activated carbon by chemical activation with zinc chloride. The influence of ZnCl₂ impregnation ratio on the yield of activated carbon as well as its structure was investigated and the material was evaluated as to its methylene blue adsorption properties.

The yields of produced activated carbons were 36%, 48%, 44% and 40% for 0%, 15%, 30% and 45% activation percentage respectively. The best yield of produced activated carbon was observed in 15% activated carbon; however activation with %45 ZnCl₂ showed better results on methylene blue adsorption at 45 °C. An impregnation ratio of 45% ZnCl₂ was found to be the optimum treatment for the preparation of activated carbons from *Posidonia oceanica* (L.) dead leaves. Both microporosity and mesoporosity depending on the activation conditions were reported from the analysis of the textural properties of the POAC samples. SEM images showed that the surface roughness depended on the impregnation ratio . The highest specific surface area (SBET) of POAC was obtained with 45%-AC reaching a value of 1230.4 m²/g combining both microporous and mesoporous structure.

Methylene blue adsorption isotherm experiments validated the superiority of the activated carbon prepared via 45% ZnCl₂ activation. Specifically its adsorption capacity reached 285,7 mg/gr higher than other low cost adsorbents and commercial activated carbons.

The analysis of adsorption data by different models revealed strong interactions between sorbent and adsorbate and energetically heterogeneous surface for the POAC samples. In addition, the adsorption energy, calculated by the Dubinin-Raduchkevich equation, reaches a value of 4.08 kJ/mol, implying that the adsorption is dominated by the physical interactions between MB and POAC.

Several parameters affecting the MB sorption quantity such as temperature, initial dye concentration, contact time, sorbent dosage and pH were investigated, and the optimum adsorption conditions were found. As expected for physical adsorption, pH does not affect significantly the adsorption of MB on 45%-AC while the adsorption increased with increasing temperature.

Kinetic experiments have shown that MB adsorption onto 45%-AC reaches equilibrium after a little over 60 mins and follows second order kinetics

Overall *Posidonia oceanica* (L.) dead leaves can be effectively used as a precursor for the preparation of high sorption efficiency activated carbon by chemical activation with zinc chloride.

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