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Présentée par : **FRIKECHE Fatima**

**Thème**

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**Influence d'un traitement chimique de la houille actifs sur  
l'élimination de composés organiques**

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Soutenu le, 19/06/2022

**Devant le Jury :**

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Faculty of Science and Technology

Department of Material Science

Final dissertation for the graduation of Academic Master in

Faculty: **Chemistry**

Specialty: **Molecular Chemistry**

Presented by: **FRIKECHE Fatima**

**Theme**

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**Influence of chemical treatment of active coal on the  
elimination of organic compounds**

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Supported on, 19/06/2022

**Before the Jury:**

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## **Abstract:**

This research is focused on recycling polluted water and rehabilitating it to make it portable by removing organic matter that contaminates the water's purity.

This study is based on the expertise of adsorption of activated carbon to methylene blue, which plays the function of these pollutants, and knowledge of the regular circumstances to achieve optimum performance for this study, as well as the ability of coal from the Bechar City mine to purify wastewater.

Carbon activation experiments have been conducted with two chemicals, one of which is known to be powerful in terms of activation and the other weak. The study's goal is to demonstrate the effectiveness of these two substances in chemical activation, as well as the essential settings, such as the amount of coal, methylene blue concentration, heat of activation, and time.

The collected results were used to identify the grade of the coal in Bechar City, as well as the kind of adsorption, by comparing the data to the Langmuir and Freundlich models.

**Keywords:** Coal, carbon, water, purification, adsorption, activation.

## **ملخص:**

تم تخصيص هذه الدراسة من اجل اعادة رسكلة المياه الملوثة و تأهيلها لتصبح قابلة للشرب ، و ذلك بأزالة المواد العضوية التي تعكر نقاوة هذه المياه .

تقوم هذه الدراسة على تجربة ادمصاص الفحم المنشط لازرق الميثيلين الذي يلعب دور هذه المواد الملوثة ، و معرفة الشروط النظامية للحصول على أفضل نتائج لهذه الدراسة و قدرة الفحم الحجري من منجم مدينة بشار بحد ذاته على تنقية المياه العكرة .

تمت تجربة تنشيط الفحم بمادتين احدهما يعرف انها قوية من ناحية التنشيط اما الاخرى ضعيفة ، هدف الدراسة هو اثبات فعالية المادتين في التنشيط الكيميائي و كذا الشروط اللازمة لذلك من كمية فحم، تركيز ازرق الميثيلين، حرارة التنشيط و المدة الزمنية .

ثم بعد ذلك اختبار النتائج المتحصل عليها لمعرفة جودة فحم مدينة بشار ، و نوع الادمصاص الذي تم من خلال مقارنة تطابق البيانات مع نموذج لونجمير و فريندليتش.

**الكلمات المفتاحية:** فحم، كربون، ماء، تنقية، امتزاز، تنشيط

## **Résumé:**

Cette étude est consacrée à recycler l'eau polluée et à la réhabiliter pour la rendre potable, en éliminant la matière organique qui perturbe la pureté de cette eau.

Cette étude est basée sur l'expérience de l'adsorption du charbon actif au bleu de méthylène, qui joue le rôle de ces polluants, et la connaissance des conditions régulières pour obtenir les meilleurs résultats pour cette étude, et la capacité du charbon de la mine de bechar ville lui-même pour purifier les eaux usées.

L'activation du carbone a été expérimentée avec deux substances, dont l'une est connue pour être forte en termes d'activation, tandis que l'autre est faible. Le but de l'étude est de prouver l'efficacité des deux substances dans l'activation chimique, ainsi que les conditions nécessaires pour cela, telles que la quantité de charbon, la concentration de bleu de méthylène, la chaleur d'activation et la durée.

Ensuite, les résultats obtenus ont été testés pour déterminer la qualité du charbon de la ville de Béchar, et le type d'adsorption, ce qui a été fait en comparant les données avec le modèle de Langmuir et Freundlich.

**Mots-clés** : Charbon, carbone, eau, purification, adsorption, activation.

## **Acknowledgment**

For my mom, my family that we share the same house same goal, and the same feeling of getting graduating.

For all my teachers.

For my friends who gave me their support.

For my hard work, patience, and belief in how far I could go if I just kept looking forward.

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**Abbreviation list:**

AC	Activated carbon
MB	Methylene blue
PAC	Powder activated carbon
GAC	Granular activated carbon
TEC	Trichloroethylene
PCE	Perchloroethylene
HS	Bisulfide (inorganic anion)
MIB	2-Methylisoborneol

# **General Introduction**

## **General Introduction:**

The expansion of civilization is accompanied by an increase in consumer demand. The generation of solid waste and wastewater is a byproduct of the manufacturing and usage of these commodities. Municipal and industrial wastewater are the main sources of these compounds' pollution of the aquatic environment and typically comprise substantial amounts of different organic compounds. Therefore, finding efficient ways to manage wastewater and other contaminated water is a crucial part of protecting the environment.

As an efficient way, we made up our research on the adsorption of this organic material with bechar coal as an effective adsorbent, In addition, we chose methylene blue as a pollutant.

Coal with a complex porous medium and abundant oxygen function can be used as an adsorbent to adsorb organic compounds. Molecular dynamics and adsorption experiments were performed to study the activity of methylene blue (MB) on the Wiser bituminous coal surface. The effect of adsorption through factors such as powdered carbon dosage, adsorption reaction time, initial concentration, and influence of temperature was investigated. MB removal efficiency reached 98.5% under optimal reaction conditions. The adsorption equilibrium was adjusted by an adsorption equation of Langmuir or Freundlich isotherms. The adsorption of BM on carbon is a spontaneous process because the free energy of the adsorption is negative. It is consistent with the conclusion about negative interaction energies between bituminous coal and MB obtained by molecular dynamics simulation. Furthermore, the density distribution along the z-axis of each constitutive molecule shows that the MB molecules are adsorbed on the carbon surface due to polar interactions between the MB methyl groups and the hydrophilic sites on the surface. coal face. Furthermore, the degree of diffusion of the water molecule in the liquid phase suggests that when the MB molecule forms hydrogen bonds with the water molecule, the water molecule's activity is restricted.

In order to clarify all the above, we divide this work into four chapters. The first one will set out some definitions of coal and its activation, The second one delineates the phenomena of adsorption, its types, isotherms, and kinetics. The last chapter is the experiment of what we had in the two previous chapters and the results we got.

# **Chapter 1: Activated carbon and water treatment**



## **Chapter 1: Activated carbon and water treatment**

### **Part A - Coal:**

#### **1- History:**

Coal production began around 300 million years ago, during the Carboniferous period. At that time, the earth was covered in wide, shallow seas and dense forests. The seas flooded the forested areas on occasion, trapping plants and algae at the bottom of a swampy wetland. [0]

Coal is the most abundant fossil fuel and the world's largest source of energy for generating electricity. [0]

Although coal as a source of energy (fuel) may continue to be necessary, "nonfuel" coal use is an important part of coal utilization. [1]

The use of activated coal in its current form has only a short history. On the other hand, according to records, the use of carbon itself dates back to ancient times. [2]

Activated coal has been used for medicinal purposes since (1500 B.C.). Then Scheele discovered activated carbon adsorption in 1773. [3]

Scheele et al [1773] recognized the adsorptive power of charcoal by the use of adsorption of gases on the coal surface. [3]

After this discovery, many scientists started their work to expand the uses of activated carbon as an adsorbent in diverse fields, In [1862], Lipscombe prepared carbon for potable water purification.

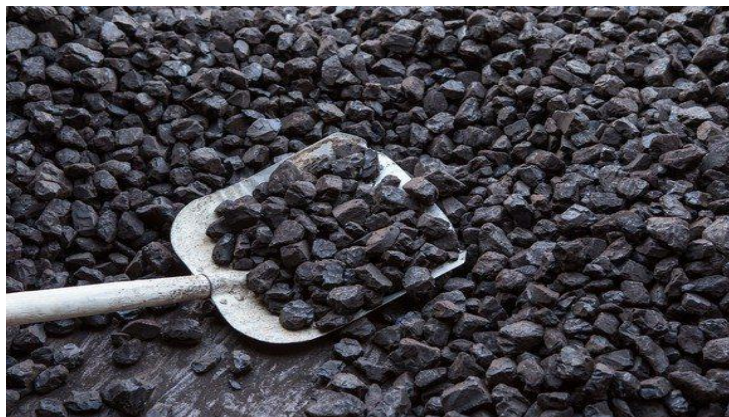


Fig 1. New coal mine starts operations in Hwange - tradelink Publications.

## **2- Definition:**

Coal is a typical conventional solid fuel that used as a source of energy by humans for thousands of years. It accounts for approximately 75% of total global fossil fuel resources. Coal has more known international reserves than any other fossil fuel. [1]

Coal is primarily composed of carbon, hydrogen, and oxygen, with trace amounts of sulfur and nitrogen. Coal is made of a diverse range of ash-forming compounds that are distributed throughout the coal. It is found in deposits known as seams that formed from the accumulation of vegetation that has undergone physical and chemical changes. [4]

Coal is a porous material and, thus, the porosity and surface area of coal has a large influence on coal behavior during mining, preparation, and utilization. As previously stated, coal porosity declines with carbon content, with a minimum of around 89 % carbon followed by a significant increase in porosity. [5]

About Coal density, it is often lower than that of conventional reservoirs and varies by coal rank and purity from seam to seam. [6]

## **3- Formation:**

Coal is formed from plant remains through a process known as coalification. The entire process begins with the remains of dead plants, which must be buried in an oxygen-deficient or oxygen-free environment to prevent complete decomposition. Typically, these are swampy environments. The coalification process takes millions of years. [4]

Biochemical degradation, which involves the chemical disintegration of plant material with the help of microorganisms, is the first stage of coalification. The amount of coal heating and the pressure circumstances during the coal's history induce physicochemical coalification, which occurs after biochemical degradation. [8]

## **4- The molecule structure of coal:**

Coal structure is intrinsically complicated and changes greatly depending on the origin, history, age, and rank of the coal under consideration. Nonetheless, due to the association between coal structure and reactivity in combustion, pyrolysis, and liquefaction processes, much research

has been conducted to describe its molecular (chemical) and conformational (physical) structure and characteristics. Initially, scientists thought coal had the same structure as graphite and/or black carbon. Fuchs and Sandhoff (1942) suggested one model of coal structure based on this assumption, as shown in Fig. The main constituent of coal in this model is an enormous aromatic condensed ring, and naphthene ring, alkyl side chain, endocyclic carbon combination, carbonyl substituents, etc. surround the circumference of the ring, which is estimated by the elemental analysis value and product properties in pyrolysis. [7]

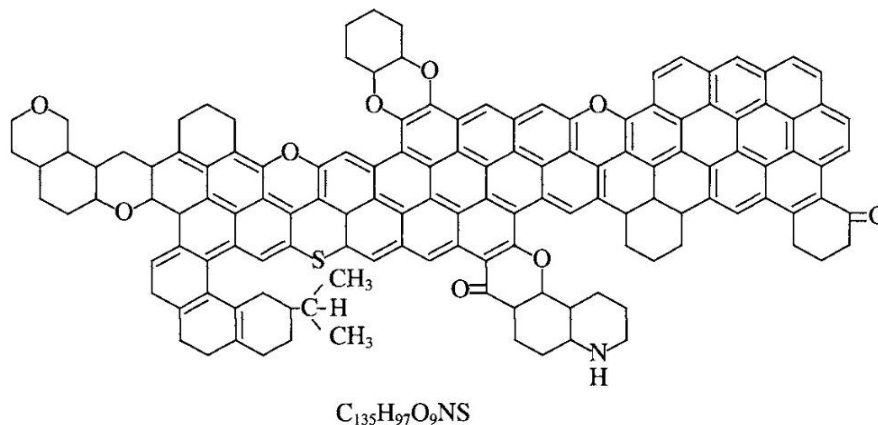


Fig 2. Structure model of coal (by Fuchs, W. and Sandhoff).

## **5- Coal rank:**

Coal ranking is a measure of the degree of organic metamorphosis (coalification) of coal, ranging from low-grade peat to high-grade anthracite. [8]

In order to define rank, we can use a multitude of chemical and physical parameters. [8]

The types and amounts of carbon in the coal, as well as the quantity of heat energy it can provide determine the ranking of coal. The amount of pressure and heat that operated on the plants throughout time determines the rank of a coal deposit as well. [9]

**Anthracite:** contains between 86% and 97% carbon and has the highest heating value of all coal grades. [9]

**Bituminous:** composed of 45% – 86% carbon, it is an important fuel employed to generate electricity and raw ingredient in the production of iron and steel. [9]

**Subbituminous:** has a lower heating value than bituminous coal and typically includes 35%–45% of carbon. [9]

**Lignite:** has the lowest energy content of all coal grades and contains 25–35 percent carbon. Lignite coal resources are typically fresh and have not been subjected to intense heat or pressure. In addition, it is flaky and contains a lot of moisture, which adds to its low heating value. [9]

## **6- Algeria Coal:**

Algeria had 65 million tons of confirmed coal reserves in 2016, ranking 63rd in the world and accounting for around 0% of total global coal reserves of 1,139,471 million tons. It has proven to be a reserve of 2,380.4 times yearly usage. This means it has around 2,380 years of coal remaining (at current consumption and excluding unproven reserves).

Bechar is a town in Algeria's western region. It is a major administrative center in the mining (coal, copper, magnesium, iron) and industrial sector, located in the northern regions of the Sahara. Bechar is also an important coal shipping point. [10]



Fig 3. Abandoned mine of Kenadsa Bechar, Algeria, by Tamale Mohammed.

## **7- Water:**

### **7.1- Portable water:**

Water is a chemical molecule that contains two hydrogen atoms and one oxygen atom. The term water often refers to the compound's liquid state. Ice refers to the solid phase, while steam refers to the gas phase. Water can also be a supercritical fluid under specific conditions. [11]

### **7.2- Wastewater:**

Water that has already been used is referred to as wastewater. Therefore, it is a mixture of wastewater from homes, offices, and industrial effluents in metropolitan areas. Suspended solids, ammonia, nitrate, and phosphate concentration are all relevant properties, which include a wide range of pathogens.

Water is contaminated by a variety of sources, we can classify it as organic pollutants, inorganic fertilizers, metals, and radioactive isotopes which results in wastewater. [12]

## **8- Coal and Carbon:**

Coal is an extremely complex mixture of carbon molecules and this number cannot be precisely determined. [13]

Carbon is by far the most important component of coal. [13]

The carbon content of coal (dry basis) typically ranges from more than 60% for lignite to more than 80% for anthracite. [13]

## **Part B - Activated carbon:**

### **1- Definition of Activated coal:**

In general, activated carbon can be regarded as a solid foam. It has a massive interior surface area along the sidewalls of an intricate network of internal pores (holes). The ideal activated carbon would have the internal surface area and enough volume in the pores to hold the most weight of adsorbed material. Because of its high porosity, activated carbon is one of the few materials that can deliver a very high surface area and pore volume per unit weight or volume at a reasonable cost. [14]

### **2- Proprieties:**

Activated carbon has low selectivity (ability to separate two chemicals) as compared to other adsorbents because of its large pore size distribution. However, this wide distribution makes it possible to absorb a wide variety of chemicals, especially volatile organic compounds. [15]

Activated carbons have pore volumes of 0.7 to 1.8 mug and a total surface area of 450 to 1800 m<sup>2</sup>/g. Only the fraction of that area and pore volume that is in pores of the appropriate size is available for adsorption. As a result, total surface area and pore volume statistics should not be utilized to estimate activated carbon's likely effectiveness. Although activated carbon with a large surface area may adsorb quickly, its adsorptive capacity may be limited due to a lack of pore volume to store the adsorbed material. Gas-adsorbing carbons, for example, have a large total surface area (> 1000 m<sup>2</sup>/g) but a small pore volume (0.6 mUg), making them poor at removing most pollutants from wastewater. [16]

### **3- Characteristics of Activated Carbon:**

A typical activated carbon elemental composition is 88% C, 0.5% H, 0.5% N, 1.0% S, and 6% to 7% O, with the remainder comprising inorganic ash components. However, the oxygen concentration of activated carbon might vary depending on the type of raw material used and the parameters of the activation process. [17]

Activated carbon also contains some ash produced from the raw material, with the amount ranging from 1% to 12%. The ash contains primarily silica, alumina, iron oxides, and

alkaline and alkaline earth metals. The ash in activated carbon makes it more hydrophilic. When powder-activated carbon is used for water treatment, it does not stick on the reactor walls if the ash content is high. [18]

#### **4- Classification:**

Activated carbons are complex products that are difficult to classify based on their behavior, surface characteristics, and preparation methods. However, for general purposes, this classification is based on physical characteristics. [19]

#### **4.1- Powdered Activated Carbon (PAC):**

Active carbons are traditionally manufactured as powders or fine granules less than 1.0 mm in size with an average diameter of 0.15 to 0.25 mm. As a result, they have a high surface-to-volume ratio and a short diffusion distance. [19]



Fig 4. Powder Activated Coal by Suto Norbert.

## **4.2- Granular Activated Carbon (GAC):**

Granular activated carbon has a bigger particle size than powdered activated carbon, which means it has a lesser exterior surface area. As a result, these carbons are preferable for all gas and vapor adsorption because their diffusion rates are faster. [19]

GAC filters are frequently employed as an advanced treatment stage in purification processes for drinking water, groundwater, and wastewater, particularly for the elimination of harmful organic compounds. A microbial layer can form on the particles in some GAC uses in drinking water and wastewater treatment. As a result, biological pollution removal is integrated with GAC adsorption. [19]



Fig 5. Activated granular coal by Winai Tepsuttinun.

## **5- The activation of carbon:**

The initial step in providing activated carbon is carbonization. This technique removes all moisture and volatile chemicals before proceeding to physical or chemical activation. Physical activation uses activating agents at temperatures ranging from 800 to 1250 K, while chemical activation uses basics and acids. [21]



## **6- Carbonization:**

It is a complicated method for concentrating and purifying carbon by denaturing organic substances with heat in the absence of oxygen. In the case of coal, carbonization is made up of a few processes that are partially complementary and partly antagonistic. The mobile and readily moving volatile and semi-volatile hydrocarbons are first vaporized by heat distillation. Second, excess heat pyrolysis hydrocarbon vapors, causing some to all carbon-carbon bonds to break or "crack," resulting in lighter and smaller hydrocarbon gases. The presence of metallic surfaces frequently catalyzes this process. [20]

During the carbonization process, the pyrolytic decomposition of the starting material eliminates the majority of noncarbonated components such as oxygen, hydrogen, and nitrogen as volatile gaseous species. The remaining carbon atoms form stacks of flat, aromatic sheets that are randomly cross-linked. Because the aromatic sheets are positioned randomly, there are gaps between them. Activated carbons are effective adsorbents because of these interstices, which result in pores. These pores are filled with tarry matter or decomposition products during carbonization or are partially blocked by disordered carbon. This pore structure in carbonized char is further developed and enhanced during the activation process, which converts the carbonized raw material into a form with the greatest possible number of randomly distributed pores of various sizes and shapes, resulting in a product with an extended and extremely high surface area. [17]

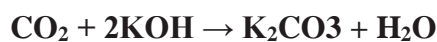
## **7- Chemical activation:**

Chemical activation combines carbonization and activation in a single phase in which the raw material, impregnated with particular chemical agents, is thermally decomposed. In industrial, the most widely utilized reagents are zinc chloride, phosphoric acid, and sulfuric acid. These function both as dehydrating agents and as oxidants, resulting in simultaneous carbonization and activation. The chemical activator dehydrates the raw material at this stage, resulting in the charring and aromatization of the carbon skeleton and the formation of a porous structure. The product is subsequently cooled and cleaned to remove the activating agent, which is then recycled. [22]

### **7.1- Chemical activation by KOH:**

In the manufacture of activated carbon, potassium hydroxide is extensively utilized as an activating agent. Although it is obvious that KOH activation creates activated carbon with a higher specific surface area and good pore formation, the resulting yield is often poor (between 10% and 40%) when compared to other activators such as ZnCl<sub>2</sub> and H<sub>3</sub>PO<sub>4</sub>. This is most likely related to the formation of pores, which increases carbon loss as a result of metallic potassium ion intercalation into the carbon network. KOH functions as a dehydrating agent during carbonization to eliminate the presence of water in the precursor, which would otherwise promote the production of tar, which might clog the pores. [23]

During the activation process, the reaction would be:



### **7.2- Chemical activation by Nitric Acid:**

HNO<sub>3</sub> treatment increases the quantity of acidic surface functional groups, resulting in the formation of various surface oxygen groups and structures containing N-O linkages (nitro groups and nitrate complexes). The effect of nitrate acid treatment on carbon surface area is inconclusive. [24]

The equation of the reaction of Carbon nitric acid



## **8- Principal Applications:**

When activated carbon was first employed in water treatment in the early 1960s in granular or powdered form, the primary goal was to remove flavor and odor. [23]

The presence of chlorophenols generated in water because of phenol chlorination at the disinfection stage was primarily responsible for the disagreeable taste and odor in drinking water. [25]

Activated carbon is now widely utilized to remove organic and inorganic pollutants from surface water, groundwater, and wastewater.

Therefore, its applications are as follows:

- Removal of volatile organic compounds such as benzene, TCE, and PCE.
- Removal of Hydrogen Sulfide (HS) and Exhaust Gas.
- Impregnated activated carbon is used as a bacteriostatic agent in drinking water filters.
- Removes taste and odor compounds such as MIB.
- Gold recovery in the mining process.
- Dechlorination and chloramine. [26]

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## **References:**

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- [0] National Geographic Society. (2012, December 18). Coal. National Geographic Society. Retrieved May 24, 2022, from <https://www.nationalgeographic.org/encyclopedia/coal/>
- [1] Toshiaki Kabe, Atsushi Ishihara, Eika Weihua Qian, I. Putu Sutrisna, Yaeko Kabe. (2004). Coal and Coal-Related Compounds: Structures, Reactivity and Catalytic Reactions (p. 127). Elsevier.
- [2] Çeçen, F., & Aktaş, Ö. (Eds.). (2012). Activated carbon for water and wastewater treatment: Integration of adsorption and biological treatment (p. 1). Wiley-VCH-Verl.
- [3] Sadashiv Bubanale, M Shivashankar, & SIDDAGANGA INSTITUTE OF TECHNOLOGY. (2017). History, Method of Production, Structure, and Applications of Activated Carbon. International Journal of Engineering Research and, V6 (06), IJERTV6IS060277.
- [4] Voncken, J. H. L. (2020). The Origin and Classification of Coal. In J. H. L. Voncken, Geology of Coal Deposits of South Limburg, the Netherlands (pp. 25–40). Springer International Publishing.
- [5] James G. Speight PhD, DSC, Ph.D. (2020). Chapter 5—Hydrocarbons from coal. In Handbook of Industrial Hydrocarbon Processes (Second, pp. 193–242). CD & W Inc. Laramie, WY, United States.
- [6] Alireza K, Hamed A, Masoumeh Z. (2018). Enhanced Gas Recovery Techniques From Coalbed Methane Reservoirs (pp. 233–268). In Fundamentals of Enhanced Oil and Gas Recovery from Conventional and Unconventional Reservoirs.
- [7] Toshiaki Kabe, Atsushi Ishihara, Eika Weihua Qian, I. Putu Sutrisna, Yaeko Kabe. (2004). Coal and Coal-Related Compounds: Structures, Reactivity and Catalytic Reactions (p. 85). Elsevier.
- [8] Mastalerz, M., Drobnik, A., Hower, J. C., & O’Keefe, J. M. K. (2011). Spontaneous Combustion and Coal Petrology. In Coal and Peat Fires: A Global Perspective (pp. 47–62). Elsevier.

- [9] U.S. Energy Information Administration - EIA - independent statistics and analysis. Coal explained - U.S. Energy Information Administration (EIA). (n.d.). Retrieved May 20, 2022, from <https://www.eia.gov/energyexplained/coal/>
- [10] Columbia Encyclopedia 6th edition. (2001). Reference Reviews, 15(7), 6–6.
- [11] Anne Marie Helmenstine, P. D. (2020, February 6). What is water, according to Chemistry's definition? ThoughtCo. Retrieved May 20, 2022, from <https://www.thoughtco.com/definition-of-water-in-chemistry-605946>
- [12] one. Smith, P. G., & Scott, J. S. (2005). Dictionary of water and waste management. IWA Publishing.
- [13] B.D. Hong and E. R. Slatick. (1994). Carbon Dioxide Emission Factors for Coal. Energy Information Administration, Quarterly Coal Report 1-8.
- [14] Perich, Jerry. R. (2017). Activated Carbon Adsorption For Wastewater Treatment (p. 35).
- [15] Khelaifia Lemya, Mazouz Manel. (2017). In Dr : Mecheri Ghania (Ed.), EVALUATION DU POUVOIR D'ADSORPTION D'UN CHARBON ACTIF COMMERCIAL (p. 18).
- [16] Perich, Jerry. R. (2017). Activated Carbon Adsorption For Wastewater Treatment (p. 36).
- [17] Bansal, R. C., & Goyal, M. (2005). Activated carbon adsorption. Taylor & Francis. (p. 1)
- [18] Çeçen, F., & Aktaş, Ö. (Eds.). (2012). Activated carbon for water and wastewater treatment: Integration of adsorption and biological treatment (p. 14). Wiley-VCH-Verl.
- [19] Kwiatkowski, J. F. (Ed.). (2012). Activated carbon: classifications, properties, and applications (p. 251). Nova Science Publishers.
- [20] Stracher, G. B., Prakash, A., & Sokol, E. V. (Eds.). (2011). Coal and peat fires: A global perspective (1st Ed) (pp. 173-208). Elsevier.
- [21] Núñez-Delgado, A. (Ed.). (2021). Sorbents materials for controlling environmental pollution: Current state and trends (pp. 575-594). Elsevier.
- [22] Dąbrowski, A. (Ed.). (1999). Adsorption and its applications in industry and environmental protection (pp. 69-94). Elsevier
- [23] Tang Shu Hui1, M. A. A. Z. (2015). Potassium hydroxide activation of activated carbon: A commentary. Carbon Letters, Vol.16.

[24] J. Paul Chen, S. W. (2004). Acid/Base-Treated Activated Carbons: Characterization of Functional Groups and Metal Adsorptive Properties. *Langmuir : The ACS Journal of Surfaces and Colloids*.

[25] Çeçen, F., & Aktaş, Ö. (Eds.). (2012). *Activated carbon for water and wastewater treatment: Integration of adsorption and biological treatment* (p. 4). Wiley-VCH-Verl.

[26] Carbons. Centralstatescarbon. (n.d.). Retrieved May 27, 2022, from <https://www.centralstatescarbonllc.com/carbon-types>

**Chapter 2: The phenomenon of  
adsorption: Its isotherms, kinetics,  
and thermodynamics**

## **Chapter 2: The phenomenon of adsorption: Its isotherms, kinetics, and thermodynamics**

### **1- History:**

On the suggestion of physiologist Du Bois-Reymond, Kayser create the phrase adsorption at the outer and inner surface, as opposed to absorption in the mass. [0]

Adsorption technology has been largely employed for water treatment for about 100 years, and it has not lost importance throughout this time. On the contrary, new application fields, in addition to the traditional application in drinking water treatment, have been added in recent decades, such as groundwater remediation or enhanced wastewater treatment. [1]

Adsorption history is divided into three periods: the Pioneering Age, the Middle Age, and the Modern Age. The Pioneering Age is defined by the experimental or theoretical discovery of new adsorption isotherms; this time is denoted by equations. The Middle Age is distinguished by attempts to explain the most often seen experimental isotherms in terms of surface attributes such as the adsorption-energy distribution; this period is distinguished by the methodologies. The Modern Age is defined by attempts to explain specific behaviors of complex adsorbents; it is distinguished by the absence of generic approaches or equations and by the extensive use of big computational methods. [2]

### **2- Introduction:**

Some solids have been known for almost a century for their ability to remove the color from dye-containing solutions. Similarly, air tainted with disagreeable odors could be turned odorless by passing it through a tank containing coal. Although such processes were not fully understood before the early twentieth century, they constitute the beginning of adsorption technology, which has lasted to the present day as a method of purifying and separating both gases and liquids. Indeed, the subject is constantly evolving as new and improved applications compete with other well-established process technologies such as distillation and absorption. [3]



### **3- Definition:**

Adsorption is thought to be a significant phenomenon in most natural physical, biological, and chemical processes, and activated carbon is the most commonly employed adsorbent material in water and wastewater treatment. [4]

Adsorption is an interfacial process in which molecules from a gaseous or liquid phase bind to the surface of a solid. Different forces create the attraction between the molecules (adsorbate) and the solid (adsorbent).

The van der Waals and Columbia forces, polar interactions, and specific bond formation are the key attraction forces in the adsorption process. [5]

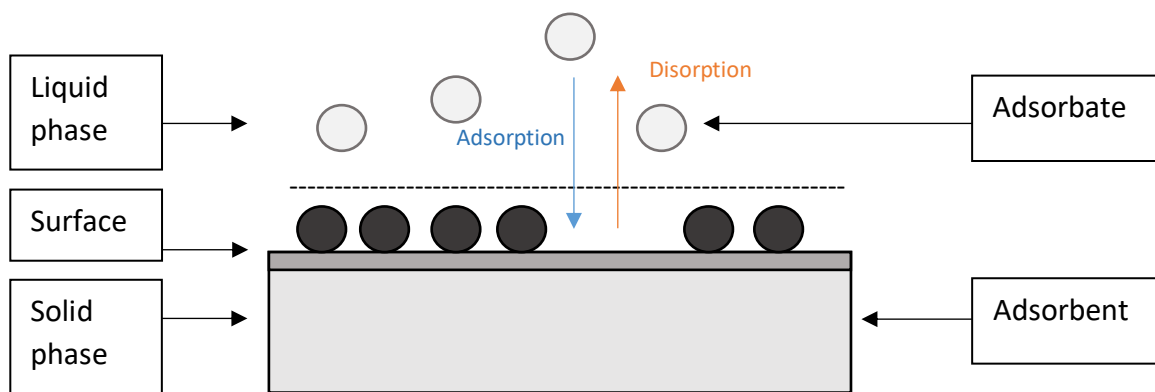


Fig 1. Basic terms of adsorption.

### **4- Difference between Adsorption and absorption:**

The absorption and adsorption procedures are essentially separation methods that work on the same principle. [6]

Adsorption is the enrichment of adsorbates on the surface of an adsorbent. In contrast, absorption is defined as the transfer of material from one bulk phase to another. The material is enriched within the receiving phase rather than only on its surface in this case. Absorption is most commonly seen in the dissolving of gases in liquids. [7]

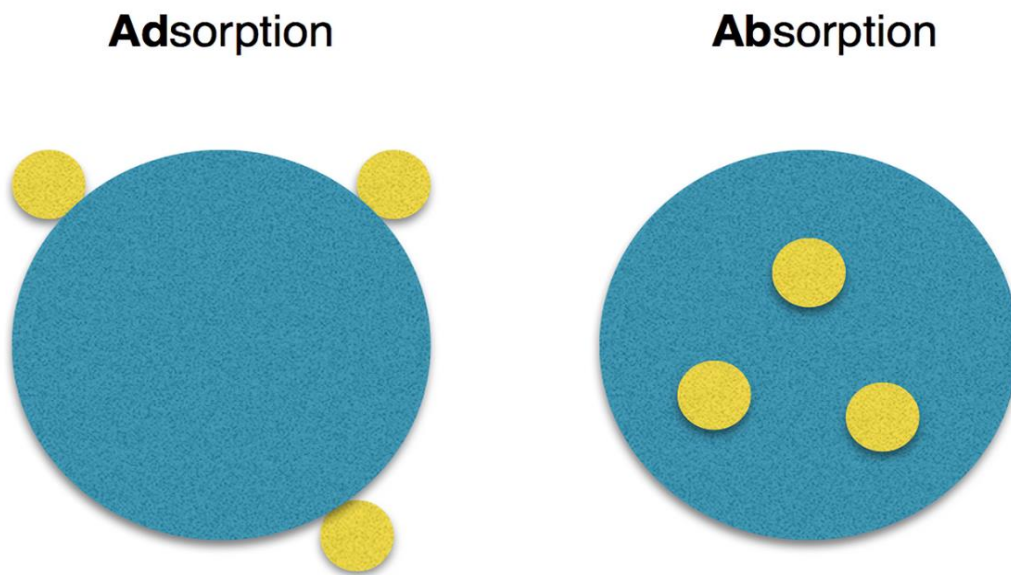


Fig 2. Difference between absorption and adsorption, The daily garden

### **5- Types of adsorption:**

There are two types of adsorption, depending on the nature of the forces involved:

#### **5.1- Physical adsorption:**

Physical adsorption is a simple process distinguished by weak forces such as hydrogen bonding, van der Waals forces, electrostatic forces, and hydrophobic interactions. [8]

Physical adsorption is caused by interactions between fluid species and practically any solid surface. [9]

Adsorbed solutes (surfactants, hydrophilic polymers, etc.) form multilayers on the membrane surface because of physical adsorption. [10]

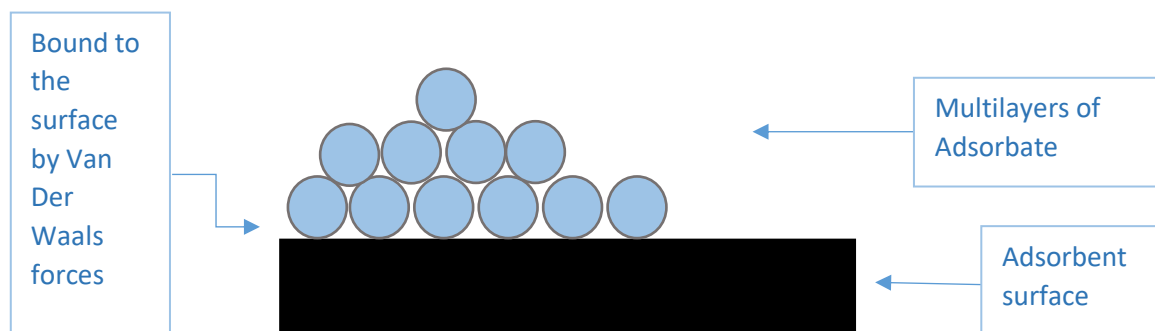


Fig 3. Physical adsorption.

## **5.2- Chemical adsorption:**

Chemisorption, on the other hand, is an adsorption process that involves a chemical reaction and the formation of a covalent connection between the molecule and one or more atoms on the surface. [11]

Chemical adsorption on solid materials is accomplished through significant electron sharing between the surfaces of adsorbent and adsorbate to form a covalent or ionic connection. As a result, chemical adsorption may not be reversible and may necessitate a large amount of energy for regeneration. [12]

Chemical adsorption is distinguished by a strong chemical connection between the adsorbant and the adsorbent. As a result, it is more difficult to reverse and hence requires more energy to remove the bound molecules than physical adsorption does. [13]

The quantitative treatment of chemisorption is based on Langmuir's original model proposed in 1916, and the type isotherm obtained, known as the Langmuir isotherm, is the most widely used functional form for characterizing monolayer gas adsorption on solid surfaces. [14]

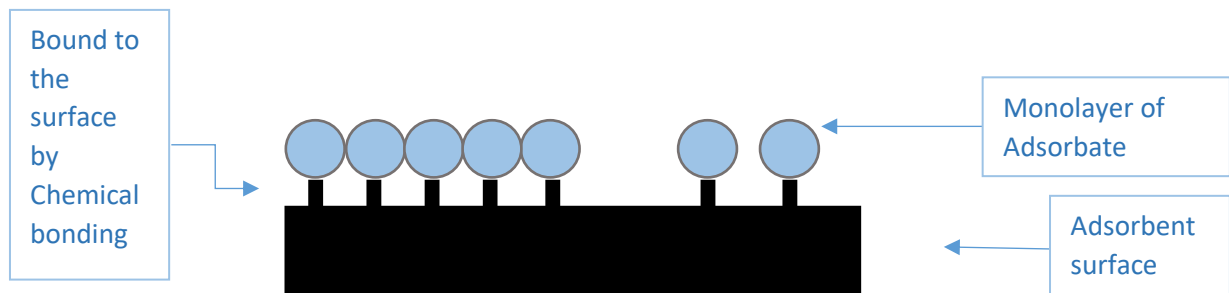


Fig 4. Chemical adsorption.

## **6- Adsorption Characteristics:**

### **6.1- Characteristics of physical adsorption:**

- Physical forces are responsible for this form of adsorption.
- Physical adsorption is a weak phenomenon.
- This adsorption is a multilayer process.
- Physical adsorption is nonspecific and takes place throughout the entire adsorbent.

- The physical adsorption process is influenced by the surface, temperature, pressure, and type of the adsorbent.
- Low activation energy (20 - 40 kJ/mol). [30]

### **6.2- Characteristics of chemical adsorption:**

- Chemical forces cause this type of adsorption.
- Chemical adsorption is a strong phenomenon.
- This type of adsorption is almost a monolayer phenomenon.
- Chemisorption is affected by the surface, temperature, and type of the adsorbent as well.
- High activation energy 40 - 400 kJ/mol. [30]

### **7- Adsorption equilibrium:**

If the adsorbent and adsorbate are in contact for a long enough time, an equilibrium will be created between the amount of adsorbate adsorbed and the amount of adsorbate in the solution. Adsorption isotherms are utilized to describe the equilibrium relationship. [15]

The relevant adsorption equilibria are required for the analysis and design of adsorption separation processes, which is the most important piece of information in understanding an adsorption process. [16]

An adsorption isotherm, which can take several forms, can be applied to determine the adsorption capacity of activated carbon. Lab tests are used to discover isotherms. [17]

### **8- Adsorption isotherms:**

An adsorption isotherm is defined by certain constant values that describe the surface characteristics and affinity of the adsorbent and may be utilized to compare the adsorbent's adsorptive capabilities for different contaminants. Equilibrium data can be evaluated using well-known adsorption systems. Several mathematical models can be used to describe experimental data of adsorption isotherms. The Freundlich and Langmuir equations are used to calculate the amount of adsorption that occurred in the experiment. [18]

The analysis of isotherm data is critical for determining the adsorbent's strength. Adsorption isotherms can describe the relationship between an adsorbate (heavy metal ion) and an

adsorbent (activated carbon), which aids in optimizing the use of the adsorbent. It is common practice to use several isotherm models to connect the amount of heavy metal ions absorbed by an adsorbent and their concentration in a solution. [19]

The adsorption isotherm is defined as the quantity  $q$  of a gas, vapor, or liquid that is absorbed by a porous solid at constant temperature and the steady-state equilibrium partial pressure is  $p$  (or concentration  $c$ ). [20]

### **8.1- Langmuir isotherm:**

The Langmuir adsorption isotherm model was designed to simulate the adsorption of a gas on a solid adsorbent. The isotherm model assumes monolayer surface coverage, similar and equivalent surface sites with the equal sorption activation energy of each molecule resulting in inhomogeneous adsorption, and no transmigration or interaction between the adsorbed species in the plane of the surface. [21]

The mathematical expression of the Langmuir isotherm is as follows: [21]

$$Q_e = \frac{Q_{\max} B C_e}{1 + B C_e}$$

Where  $Q_e$  is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mol/g) and  $C_e$  is the solute concentration at equilibrium (mol/L). The Langmuir constants are represented by the parameters  $q_{\max}$  and  $b$ .  $Q_{\max}$  is the maximal monolayer adsorption capacity, while  $b$  is the adsorption system's binding energy or affinity parameter. For the adsorption of a solute from an aqueous solution on a solid substrate,  $C_e$  is commonly expressed in mg/L and  $Q_e$  in mg/g. As a result, the units for  $q_{\max}$  and  $b$  are mg/g and L/mg, respectively. [21]

### **8.2- Freundlich isotherm:**

Freundlich developed an empirical equation to depict a heterogeneous system of non-identical adsorption sites in 1906. Each adsorbate molecule could only be adsorbed on one adsorption site, according to the model. [19]

The Freundlich equation, also known as the Freundlich adsorption isotherm, is a curve that connects the concentration of a solute on an adsorbent's surface to the concentration of the solute in the liquid with which it comes into contact. [18]

The equation is:

$$q_e = k_f C_e^{1/n}$$

$q_e$  is the amount of adsorbing material on the adsorbent surface,  $C_e^{1/n}$  &  $k_f$  are adsorbate concentrations into the solution at the balance moment, from Freundlich constants respectively. [18]

## **9- Adsorption Kinetics:**

Adsorption kinetics is the measurement of adsorption uptake over time at constant pressure or concentration, and it is used to determine Adsorbate diffusion in pores. Adsorption kinetics, or the fluctuation of water intake over time, is affected by the material's structural properties. [22]

### **9.1- Pseudo-first-order model:**

Lagergren (1898) proposed a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto the coal, which is believed to be the first model based on adsorption capacity. [23]

The equation is:

$$\text{Log}(q_e - q_t) = \log q_e - kt$$

where  $q_t$  is the amount of lead ions removed at time  $t$  (mg/g),  $q_e$  is the adsorption capacity at equilibrium (mg/g),  $K_i$  is the pseudo-first-order rate constant (1/min), and  $t$  is the contact time (min). [24]

### **9.2- Pseudo-second-order:**

The pseudo-second-order kinetic equation has been widely utilized in the study of adsorption kinetics to characterize the time development of adsorption under non-equilibrium conditions. Its equation is:

$$\frac{dqt}{dt} = k (qe - qt)^2$$

In which  $Q_t$  is the amount of adsorbate adsorbed at time  $t$ ,  $Q_e$  is its value at equilibrium, and  $k$  is constant. [25]

### **10- Thermodynamics of Adsorption:**

Thermodynamics has a unique capacity to connect properties that appear to be unrelated. The heat of immersion of the solid adsorbent in the liquid or gas, for example, is directly proportional to the temperature coefficient of adsorption. The computation of phase equilibrium between a mixture and a solid adsorbent is the most important use of thermodynamics in adsorption. [26]

The adsorption isotherm, which gives the quantity of adsorbed in nanopores as a function of external pressure, is the basis for thermodynamic calculations. Thermodynamics only applies to equilibrium adsorption isotherms. [26]

### **11- Adsorption ability of activated carbon:**

Activated carbons can adsorb a wide range of organic compounds primarily through weak intermolecular interactions (van der Waals forces), particularly dispersion forces. In the case of aromatic adsorbates,  $\pi$ -interactions can be superimposed, whereas electrostatic interactions between surface oxide groups and ionic adsorbates can be overlaid. Activated carbons are the preferred adsorbents in all water treatment processes that need the removal of organic pollutants due to their high adsorption capabilities. Activated carbon may effectively remove not just trace pollutants (micropollutants), but also natural organic matter (NOM).

Some general trends in activated carbon adsorption are listed below. [27]

- The adsorption increases with increasing internal surface (increasing micropore volume) of the adsorbent.
- Adsorption increases with the increasing molecular size of the adsorbates.
- The adsorbability of organic substances onto activated carbon increases with decreasing polarity (solubility, hydrophilicity) of the adsorbate.
- Aromatic compounds are better adsorbed than aliphatic compounds of comparable size.

- In multicomponent systems, competitive adsorption takes place, resulting in decreased adsorption of a considered compound in comparison with its single solute adsorption.
- Inorganic ions (e.g. metal ions) can be adsorbed by interactions with the functional groups of the adsorbent surface but much lower extent than organic substances, which are adsorbed by dispersion forces and hydrophobic interactions. [27]

## **12- Methylene blue:**

MB is an aromatic heterocyclic basic dye with a molecular weight of 319.85 g/mol. MB is a well-known cationic and primary thiazine dye with the chemical formula  $C_{16}H_{18}N_3Cl$  and a maximum wavelength of 663 nm. It is extremely water-soluble and so forms a stable solution with water at room temperature. MB is a positively charged polymethine dye with an amino autochrome unit. Its chemical name is [3,7-bis (dimethylamine) phenothiazine chloride tetra methylthionine chloride].

P.S (Dyes are colored aromatic organic compounds that absorb light and lend color to the visible region.) [28]

Methylene blue (MB) is utilized by several companies, resulting in contaminated industrial wastewaters that must be cleaned before being discharged into the environment. The adsorption method can remove MB, and readily available materials should be used as adsorbents. [29]



Fig 5. Methylene Blue - Existing research and clinical potential - mitolab.



### **13- Spectrophotometry:**

Spectrophotometry is a science based on the idea that every chemical molecule absorbs, reflects, or transmits light throughout a certain wavelength spectrum. It is widely used in chemistry, physics, biochemistry, biology, and clinical investigations, and allows for qualitative and quantitative examination. [31]

### **14- Spectrophotometer:**

In today's laboratories, the spectrophotometer is a common sight. Most laboratories concerned with the identification and quantification of organic and inorganic substances across a wide variety of goods and processes have turned to ultraviolet (UV) and visible (VIS) spectrophotometry as the method of choice. [32]

Spectrophotometers today are fast, precise, and dependable. They put less strain on the operator's time and abilities. [32]

To put it another way, it's employed to measure the quantity of light that goes through a sample material and, by comparing that to the original intensity of light reaching the sample, indirectly estimate the amount of light absorbed by that sample. [33]

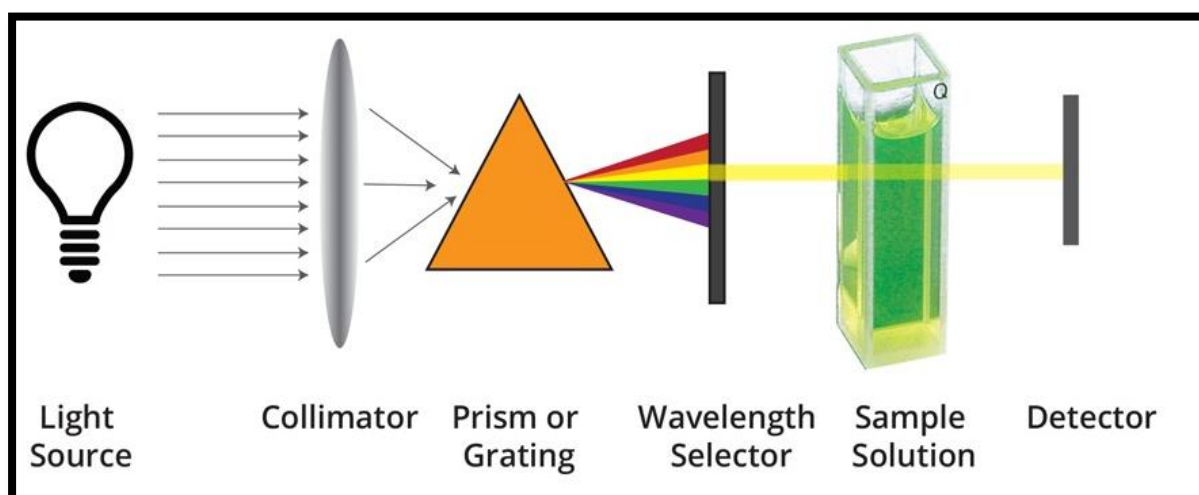


Fig 6. Molecular analysis UV/Visible spectra - eurekalect.

## **References:**

- [0] E. Robens. (1994). Some intriguing items in the history of adsorption. In *Studies in Surface Science and Catalysis* (Vol. 87, pp. 109–118).
- [1] Worch, E. (2012). *Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling* (p. Preface). DE GRUYTER.
- [2] Rudziński, W., Steele, W. A., & Zgrablich, G. (1997). *Equilibria and dynamics of gas adsorption on heterogeneous solid surfaces* (p. history page). Elsevier.
- [3] Thomas, W. J., & Crittenden, B. D. (1998). *Adsorption technology and design* (p. 1). Butterworth-Heinemann.
- [4] Çeçen, F., & Aktaş, Ö. (Eds.). (2012). *Activated carbon for water and wastewater treatment: Integration of adsorption and biological treatment* (p. 16). Wiley-VCH-Verl.
- [5] Inamuddin, Mohd Imran Ahamed, & Eric Lichtfouse. (2021). In *Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water* (p. 66).
- [6] Rudziński, W., Steele, W. A., & Zgrablich, G. (Eds.). (1997). In *Equilibria and dynamics of gas adsorption on heterogeneous solid surfaces* (p. 46). Elsevier.
- [7] Thomas, W. J., & Crittenden, B. D. (1998). *Adsorption technology and design* (p. 3). Butterworth-Heinemann.
- [8] Peng Zhang, You PengChen, & Jin-SongGuob. (2021). Chapter Five—SPR for water pollutant detection and water process analysis. In *Comprehensive Analytical Chemistry* (Vol. 95, p. 148).
- [9] Karl D. Hammond. (2013). Chapter One—Analysis of Catalyst Surface Structure by Physical Sorption. In *Advances in Catalysis* (Vol. 56, p. 2).
- [10] Lichao Xia, Bhuvan Vemuri, Sambhu Saptoka, Namita Shrestha, Govinda Chilkoor, James Kilduff, & Venkataramana Gadhamshetty. (n.d.). Chapter 1.8—Antifouling Membranes for Bioelectrochemistry Applications. In *Microbial Electrochemical Technology* (2019th ed., pp. 195–224).
- [11] Bârsan, N. (Ed.). (2019). In *Gas sensors based on conducting metal oxides: Basic understanding, technology, and applications* (pp. 61–165). Elsevier.

- [12] Soonchul Kwon & Maohong Fan. (2011). Chapter 10—CO<sub>2</sub> Sorption. In *Coal Gasification and Its Applications* (pp. 293–339).
- [13] Ioan Sarbu & Calin Sebarchievici. (n.d.). In *Solar Heating and Cooling Systems, Fundamentals, Experiments, and Applications* (2017th ed., pp. 241–313).
- [14] Ahmet K.Avci & Z . IlsenÖnsan. (2018). In *Comprehensive Energy Systems* (Vol. 2, pp. 475–523).
- [15] Lecture 4. Adsorption - Islamic University of Gaza. (n.d.). Retrieved May 20, 2022.
- [16] Thio Christine Chandra, M.M. Mirna, Y. Sudaryanto, & S. Ismadji. (2006). Adsorption of basic dye onto activated carbon prepared from durian shell: Studies of adsorption equilibrium and kinetics. *Chemical Engineering Journal*.
- [17] Adsorption Equilibria - mimoza.marmara.edu.tr. (n.d.). Retrieved May 20, 2022, from <https://mimoza.marmara.edu.tr/~zehra.can/ENVE401/3.%20Adsorption%20Equilibria.pdf>
- [18] Mehdi Vadi, M. R. (2014). Langmuir, Freundlich and Temkin Adsorption Isotherms of Propranolol on Multi-Wall Carbon Nanotube. *JOURNAL OF MODERN DRUG DISCOVERY AND DRUG DELIVERY RESEARCH*.
- [19] Inamuddin, Ahamed, M. I., Lichtfouse, E., & Asiri, A. M. (2021). Green adsorbents remove metals, dyes, and boron from polluted water (p. 19).
- [20] Thomas, W. J., & Crittenden, B. D. (1998). *Adsorption technology and design* (p. 38). Butterworth-Heinemann.
- [21] Partha S.Ghosal & Ashok K.Gupta. (2017). Determination of thermodynamic parameters from Langmuir isotherm constant-revisited. In *Journal of Molecular Liquids* (Vol. 225, pp. 137–146).
- [22] D.Saha, H. A. G. (2017). *Activated Carbon Fiber and Textiles* (pp. 143–165). Woodhead Publishing Series in Textiles.
- [23] Bing-cai PAN Hui QIU. (2009). Critical review in adsorption kinetic models. *Journal of Zhejiang University SCIENCE A*.
- [24] Dariush Robati. (2013). Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube. *Journal of Nanostructure in Chemistry*.

- [25] YuLiu. (2008). New insights into pseud the o-second-order kinetic equation for adsorption. In *Colloids and Surfaces A: Physicochemical and Engineering Aspects* (Vol. 320, pp. 275–278).
- [26] Trevor Letche, A. L. M. (2004). *Thermodynamics of Adsorption*. In *Chemical Thermodynamics for Industry* (p. 243). Royal Society of Chemistry.
- [27] Worch, E. (2012). In *Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling* (p. 15). DE GRUYTER.
- [28] Tariq Shah, Baoliang Zhang, & Idrees Khan. (2022). Review on Methylene Blue: Its Properties, Uses, Toxicity, and Photodegradation. *Water*.
- [29] Capela, M. N., Cesconeto, F. R., Pinto, P. C., Tarelho, L. A. C., Seabra, M. P., & Labrincha, J. A. (2022, May 19). Biomass fly ash self-hardened adsorbent monoliths for methylene blue removal from aqueous solutions. MDPI. Retrieved May 20, 2022.
- [30] Admin. (2022, April 26). Adsorption - definition, applications, types of adsorption, isotherm. BYJUS. Retrieved May 20, 2022, from <https://byjus.com/jee/adsorption/>
- [31] Ken PhillipsMr. Philips has spent the last 30 years in product development and management. (2022, March 30). Spectrophotometry vs. spectroscopy. HunterLab Horizons Blog. Retrieved May 21, 2022, from <https://blog.hunterlab.com/blog/color-measurement/spectrophotometry-vs-spectroscopy/>
- [32] A brief background to spectrophotometry - biochrom home. (n.d). Retrieved May 21, 2022, from [https://biochromspectros.com/media/wysiwyg/support\\_page/UV-Visible\\_Spectrophotometry.pdf](https://biochromspectros.com/media/wysiwyg/support_page/UV-Visible_Spectrophotometry.pdf)
- [33] Spectrophotometry page 1 10 lab #4 spectrophotometry. (n.d). Retrieved May 21, 2022, from [http://gervind.faculty.mjc.edu/biology\\_101/101\\_lab/spectrophotometry/4%20Spectrophotometer%20Fa17.pdf](http://gervind.faculty.mjc.edu/biology_101/101_lab/spectrophotometry/4%20Spectrophotometer%20Fa17.pdf)

# **Experiment Part**

## **Experiment Part**

### **1- Introduction:**

In this chapter, we will use chemical products to increase carbon's adsorption capability; otherwise, we will come to know about the types of adsorption that can be produced as a result of this chemical activation, as well as the factors that influence this process.

### **2- Products and equipment used:**

I utilized in this scientific research some products and equipment that made this experiment doable and practical, as well as to grant us a good result.

#### **So as products I utilized:**

- Raw coal ( powder )
- Distilled water
- Nitric acid
- Potassium hydroxide
- Methylene blue

#### **As equipment, I utilized:**

- Spatula
- Beaker
- Graduated cylinder
- Test tube
- Filter paper and funnel
- Vacuum pump
- Dropper
- Erlenmeyer flask
- Round bottom flasks
- Watch glass
- Electronic analytical balance
- Wash bottle
- Volumetric flask
- Parafilm
- Benchtop PH/MV meter

- Magnetic stirrer
- Magnetic stir bar
- Pipet volumetric
- Air drying oven
- Jaw crusher
- Soxhlet extraction
- Orbital shaker

### **3- Preparation of activated carbon:**

#### **3.1- Purification:**

The raw coal we used came straightly from the mine of bechar, therefore containing associations with impurities that have to be removed to get pure coal ready for laboratory modifications.

I followed some steps, which are:

##### **3.1.1 - Sieving:**

This raw coal was mixed with dirt and sand so I had to separate them through a sieve

##### **3.1.2 - Washing:**

In this step, I used only distiller water. To give more details I took a beaker, fill it with raw granular coal, add water, a magnetic stir bar, and then put it on a magnetic stirrer for 10 min (without turning on the heat ) to make those impurities unstuck from the coal.



Fig 1. Raw granular coal after washing.

### **3.1.3 - Drying:**

Put it in an air drying oven for 24 hours at 100° temperature.

### **3.1.4 - Crushing:**

I used the Jaw machine in this process.



Fig 2 and 3. Raw coal before and after crashing on Jaw crusher.

- ✓ After this last step of purification got powder coal of diameters 1 mm and 250 $\mu$ m.

### **3.2- Activation:**

For the activation of carbon, I used two chemical products one of them acidotic and the basic, those products are **Nitric acid** (HNO<sub>3</sub>) and **Potassium hydroxide** (KOH).



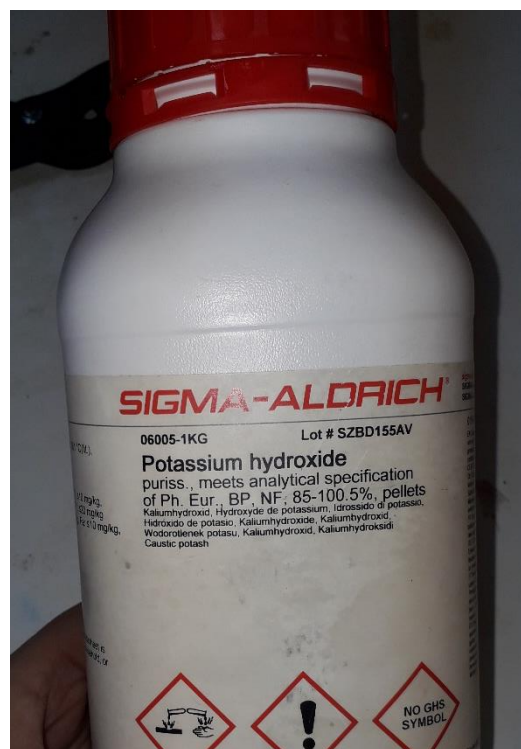
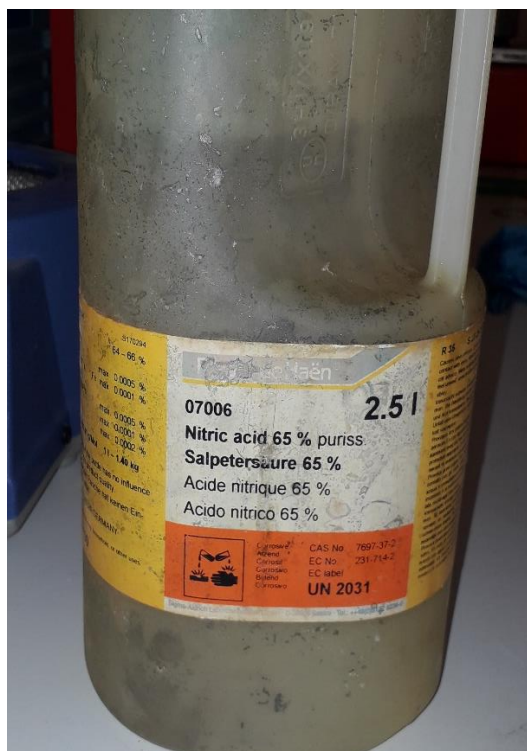


Fig 4 and 5. Chemical products (KOH, HNO<sub>3</sub>).

As an equipment, I employed soxhlet extraction

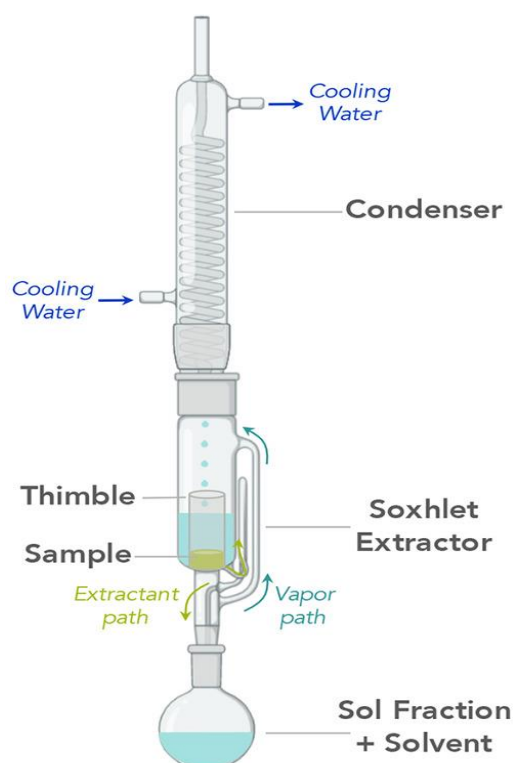


Fig 6. Schematic of a Soxhlet extraction by Shu Wang.

### **3.2.1- Activation of carbon by KOH:**

First, the KOH solution with 100 ml of distilled water and 16.88 g of the agent ( the concentration of the solution was 3M), and 20 g of coal were put in a filter, both placed on a Soxhlet extraction assembly indicated below at a temperature of 80° C for 2 hours.

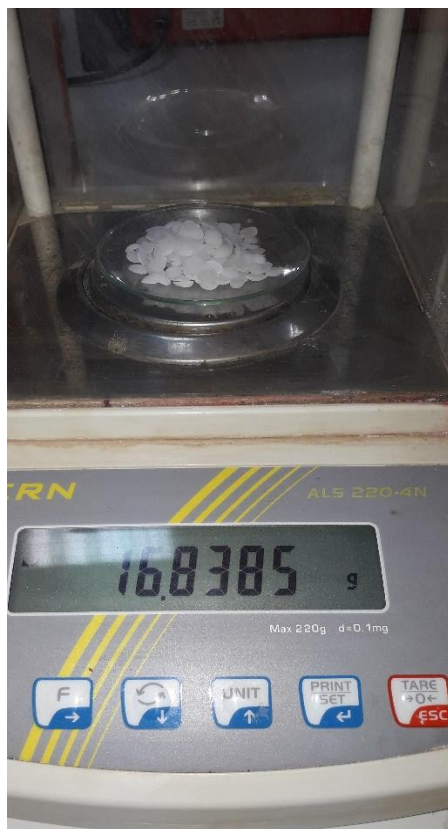


Fig 7 and 8. Activation process by KOH (measure of the agent and assembly used).

### **3.2.2- Activation of carbon by HNO<sub>3</sub>:**

The HNO<sub>3</sub> solution of 28,28 ml of the agent that got completed with distilled water till it reaches 100 ml, put on a round bottom flasks (Its concentration was 4 M), with 20 g of carbon inside a filter, all placed on the Soxhlet extraction assembly at a temperature of 80° C for 2 hours.



Fig 9. Montage employed for the coal activation process.

### **3.2.3- Washing and drying:**

I washed the carbon multiple times until its PH reaches 7, filtrate it every time washed using filter paper and vacuum pump, Put on the air oven to dry for 24 h at 100 temperature.



Fig 10 and 11. Filtration of carbon by the Vacuum pump and filter paper.

✓ The samples of activated carbon are ready for the test.

#### **4- Preparation of dye (MB):**

##### **4.1- Method:**

Preparation of the mother solution using 1 L of distilled water and 1 g of methylene blue, then diluting to six degrees to make a calibration curve by adding 1 ml of mother solution to a volumetric flask, then filling it with distilled water until it reaches 50 ml for the first diluent sample.

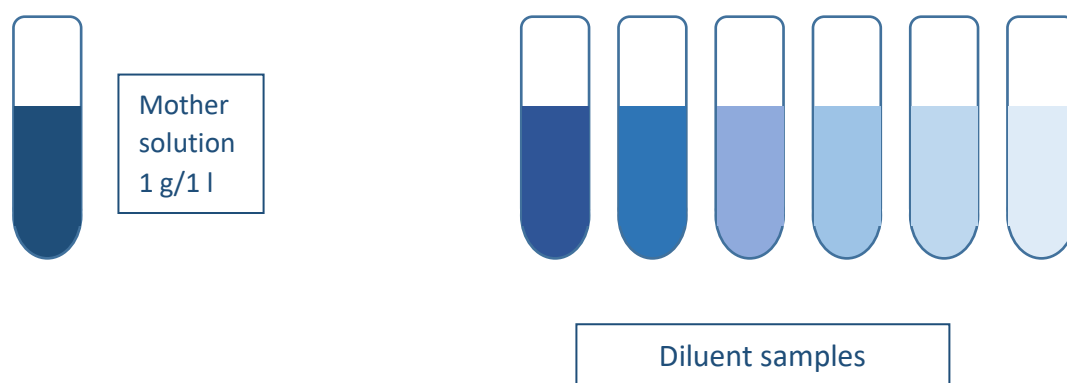


Fig 12. Test tubes of mother solution and diluent samples.

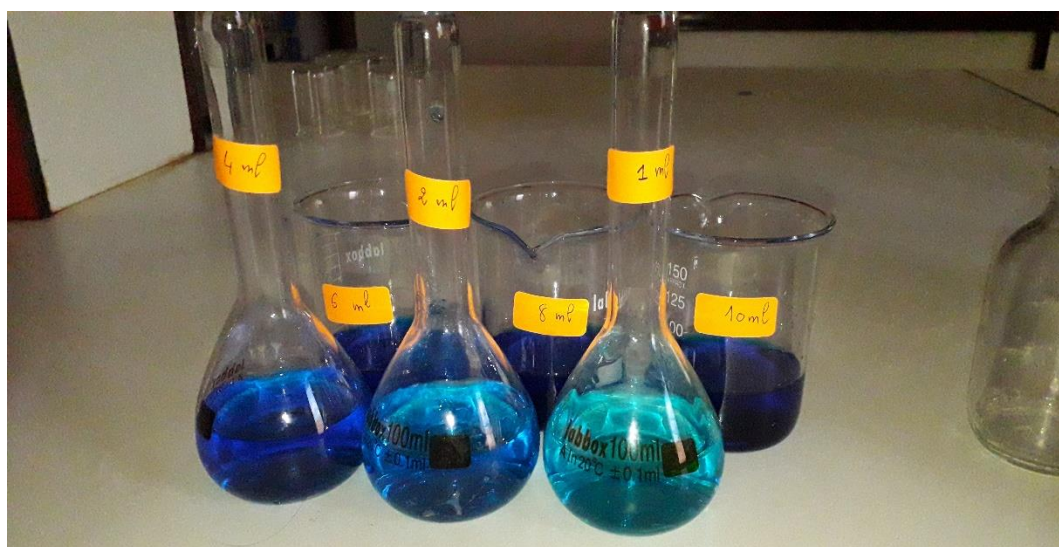


Fig 13. Methylene blue diluent samples.

The preparation of the other samples are indicated in the table below:

Mother solution Methylene blue 1 g/L	Concentration $C_0$ (mg/L) for volume of 50 ml
Volume (ml)	ml
1	20
2	40
3	60
4	80
6	120
8	160

Table 1. Preparation of mother solution and diluted samples.

#### **4.2- Calibration curve:**

To draw a calibration curve line, I made a quick test of those six different concentrations of methylene blue on a spectrophotometer to know the adsorption degree on each one of them, and I got the results below.

c	1	2	3	4	6	8
Abs	0,510	1,027	1,512	2,031	3000	3000

The linear fit of the calibration curve:

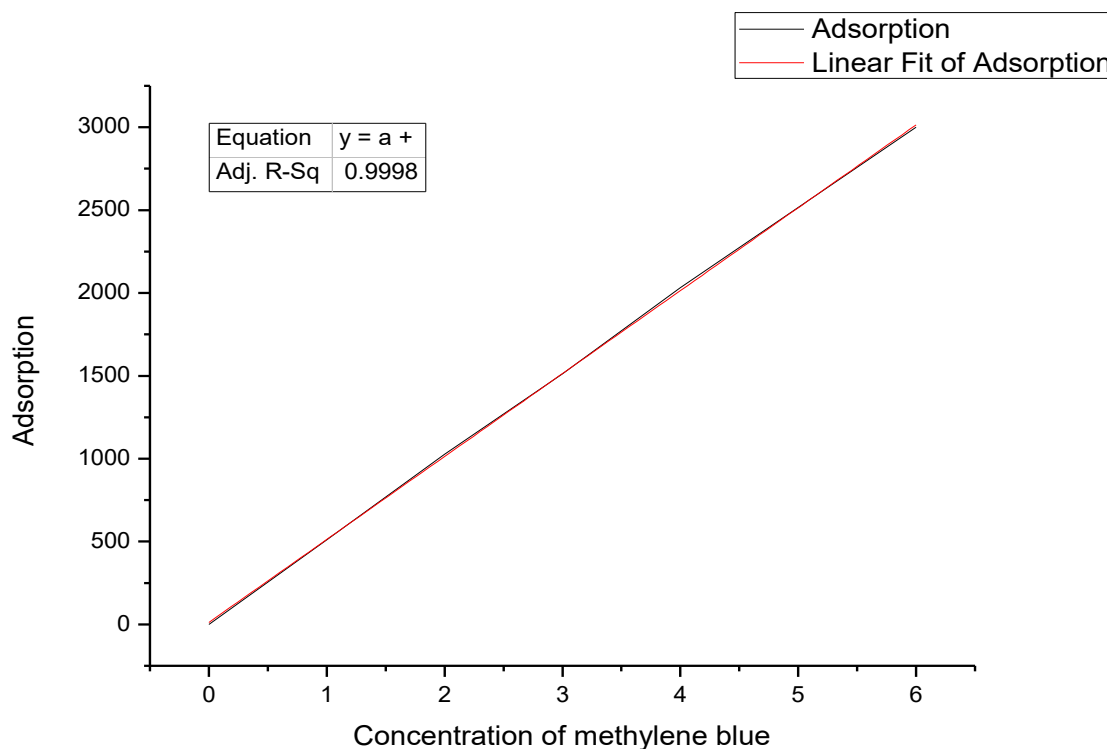


Fig 14. Calibration curve of methylene blue.

## **5- Studies of the ideal condition of this process:**

In this part of my experiment, I tried to fix the ideal quantity of coal that can absorb the maximum of MB meanwhile the examination of the perfect concentration of that last (MB),

Besides another assay to fix the perfect temperature of the activation of the adsorbent, all results are included below.

Regarding equipment, I utilized beakers, parafilm, and Orbital shaker to agitate the mixture.

### **5.1- Study of ideal weight of coal:**

With a fixed C of MB (80 mg/L), I prepared 6 samples with different “w” of coal starting from 0.1 g till 2 g on 10 ml of MB solution, I got the results shown in table 2.

	Q(g)	0,1	0,3	0,5	1	1,5	2
Adsorption	Raw coal	0,678	1,382				
	AC with KOH	0,257	0,179	0,389			
	AC with HNO <sub>3</sub>	0,515	0,185	0,007	0,166		

Table 2. Study of the ideal weight of coal.

These values that I got after the spectrophotometer test, the ideal “w” of raw coal was 0.1 g, about both of the activated coal either with KOH or HNO<sub>3</sub> the ideal “w” was more than 0,1 g, So the mutual “w” between all of them is 0,1 g.

The gray color means that I could not obtain any results because I failed to separate the coal from the solution to make the test, using available equipment, as it shown in fig 14 and 15.



Fig 15 and 16. Coal and MB solution that I could not separate.

## **5.2- Study of the temperature of coal activation:**

The aim of this experiment is to determine the optimal temperature for activating carbon. I followed the same steps as described above for the activation part (3.2), with the exception that the temperature on the Soxhlet extraction assembly was changed to 80 mg/L and the weight of coal was 0.1 g in 10 ml of the solution, with the following results.

### **5.2.1 Activated carbon with KOH:**

T°	20	40	60	80	100	120
Ads	1,030	0,675	0,421	0,276	0,243	0,201
C <sub>e</sub>	5,576	3,581	2,153	1,338	1,152	0,916
C Ads	74,424	76,419	77,847	78,662	78,848	79,084
X	0,744	0,764	0,778	0,786	0,788	0,790
Q ads	7,442	7,641	7,784	7,866	7,884	7,908
Ads %	93,03	95,52	97,30	98,32	98,56	98,85

Table 3. Study of the ideal activation temperature for AC with KOH.

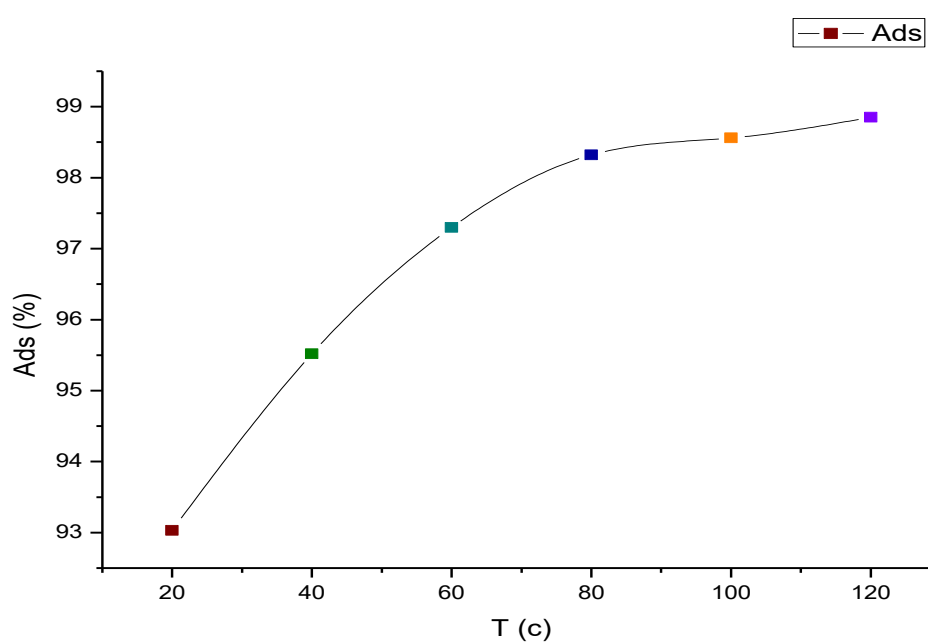


Fig 17. Graph of the percentage of adsorption of activated carbon in different temperatures.



### 5.2.2 Activated carbon with HNO<sub>3</sub>:

T°	20	40	60	80	100	120
Ads	1,798	1,390	0,898	0,561	0,539	0,514
C <sub>e</sub>	9,983	7,600	4,834	2,940	2,816	2,676
C Ads	70,017	72,400	75,166	77,06	77,184	77,324
X	0,700	0,724	0,751	0,770	0,771	0,773
Q ads	7,001	7,240	7,516	7,706	7,718	7,732
Ads %	87,52	90,50	93,95	96,32	96,48	96,65

Table 4. Study of the ideal activation temperature for AC with HNO<sub>3</sub>.

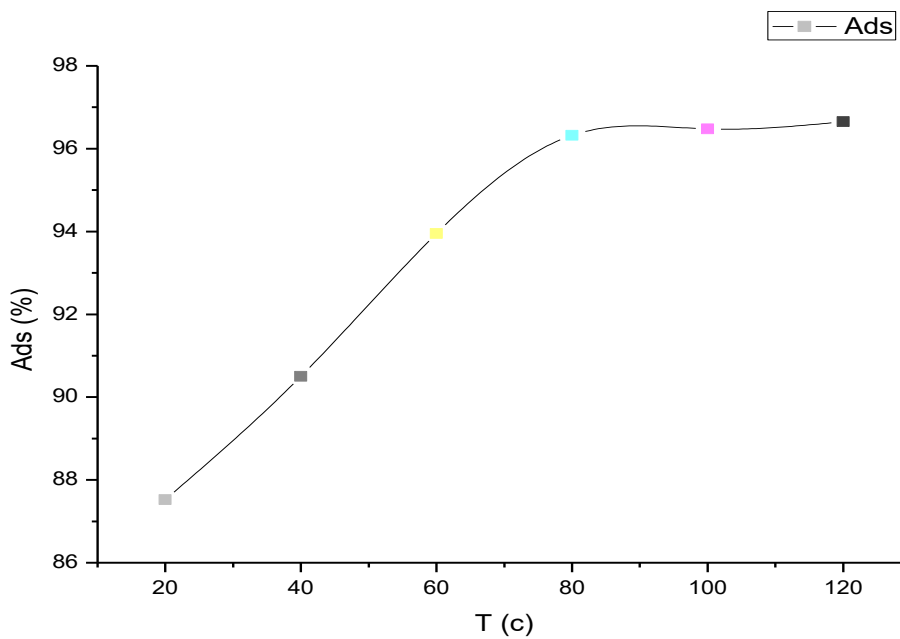


Fig 18. Graph of the percentage of adsorption of activated carbon in different temperatures.

- ✓ Based on these results, the lower temperature that provided the best adsorption rate it 80° C, therefore I employed it in all other experiments.

### **5.3- Study of the ideal concentration of methylene blue:**

After fixing the weight of coal, I prepared 6 samples each one of them has 0.1 g, in 10 ml of MB solution with different concentrations starting from  $C_i=20$  till  $C_i =160$ .

I got the results below:

#### **5.3.1- Raw coal:**

C	1	2	3	4	6	8
Ads	0,193	0,451	0,545	0,639	1,173	1,897
$C_e$	0,873	2,237	2,856	3,386	6,394	10,47
C Ads	19,127	37,763	57,114	76,614	113,606	149,53
X	0,191	0,377	0,571	0,766	1,136	1,495
Q ads	1,912	3,776	5,711	7,661	11,360	14,953
Ads%	95,63	94,40	95,19	95,76	94,67	93,45

Table 5. Study of the ideal concentration of MB for raw coal.

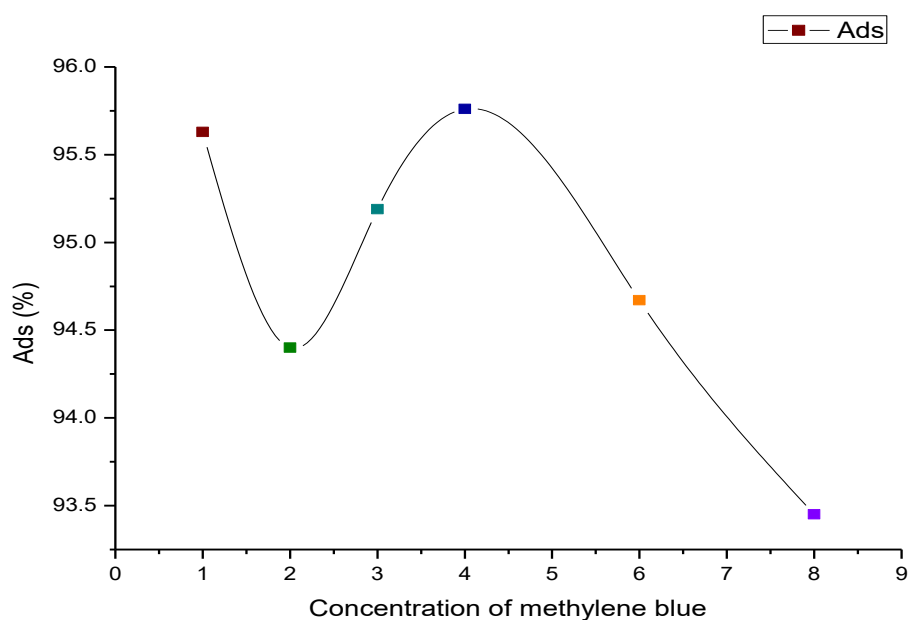


Fig 19. Graph of the percentage of adsorption of raw coal in different concentrations.

### 5.3.2- Activated carbon with KOH:

C	1	2	3	4	6	8
Ads	0,003	0,059	0,115	0,260	1,050	1,973
$C_e$		0,118	0,434	1,259	5,723	10,937
C ads		19,882	59,566	78,75	114,277	149,063
X		0,198	0,595	0,787	1,142	1,490
Q ads		1,988	5,956	7,875	11,427	14,906
Ads %		99,41	99,27	98,43	95,23	93,16

Table 6. Study of the ideal concentration of MB for AC with KOH.

### Langmuir isotherm of activated carbon with KOH:

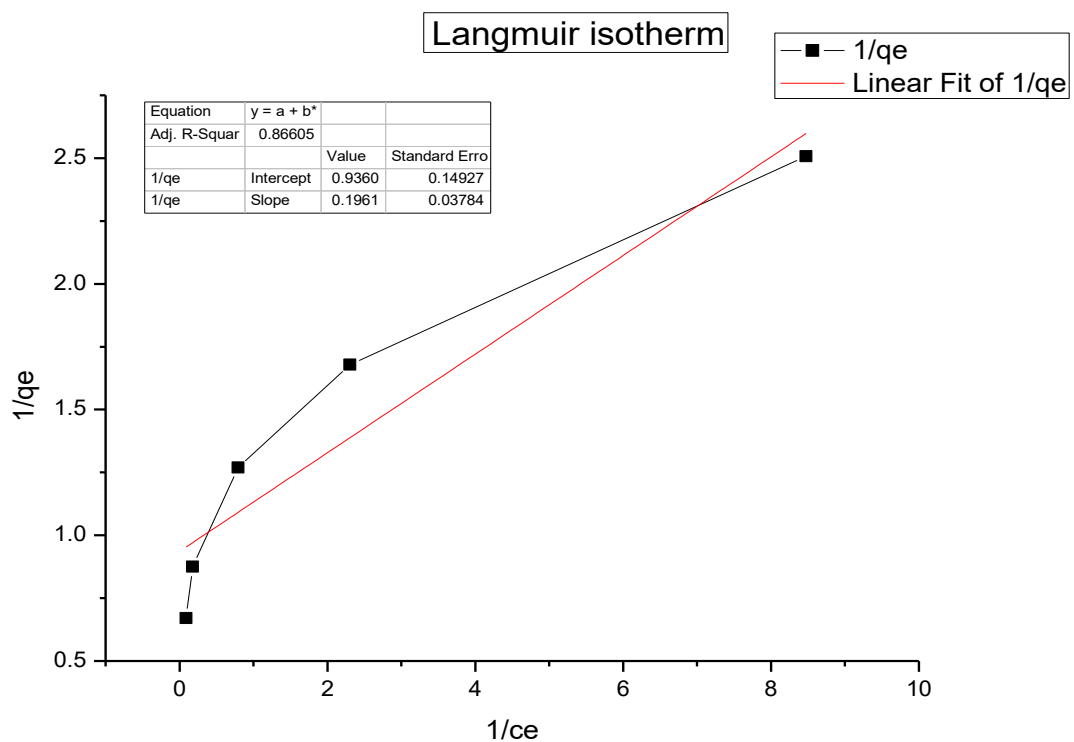


Fig 20. Langmuir isotherm of activated carbon with KOH.

### Freundlich isotherm for activated carbon with KOH:

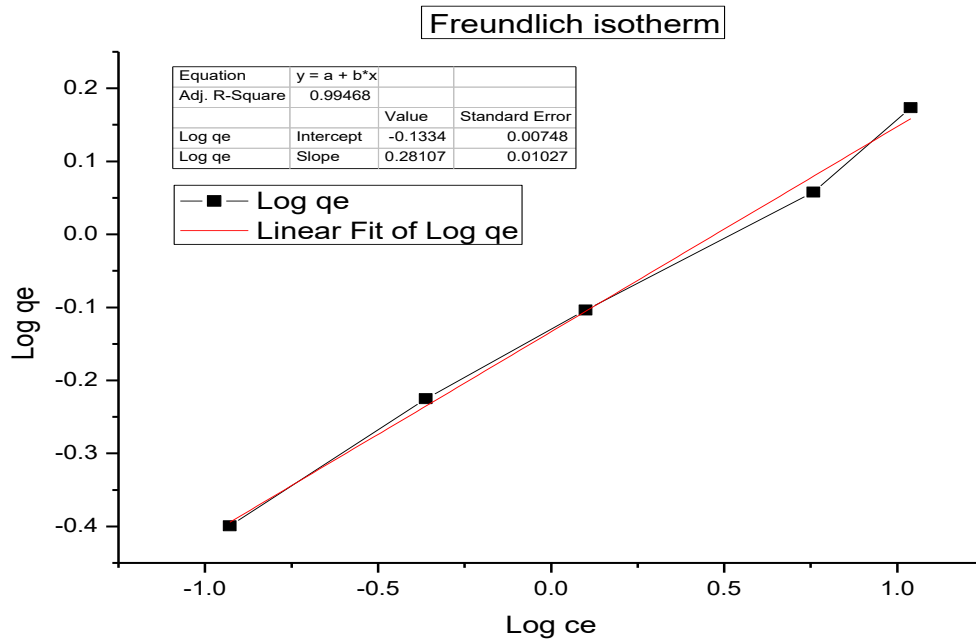


Fig 21. Freundlich isotherm for activated carbon with KOH.

- ✓ Based on these results, the chemical activation of carbon with KOH match with freundlich isotherm model, thus the type of this adsorption is physical.

### 5.3.3- Activated carbon with HNO3:

C	1	2	3	4	6	8
Ads	0,108	0,299	0,483	0,598	1,765	2,004
C <sub>e</sub>	0,394	1,470	2,507	3,155	9,730	11,076
C Ads	19,606	38,53	57,493	76,845	110,27	148,924
X	0,196	0,385	0,574	0,768	1,102	1,489
Q ads	1,960	3,853	5,749	7,684	11,027	14,892
Ads %	98,03	96,325	95,82	96,05	91,98	93,07

Table 7. Study of the ideal concentration of MB for AC with HNO3.

### Langmuir isotherm for activated carbon with HNO<sub>3</sub>:

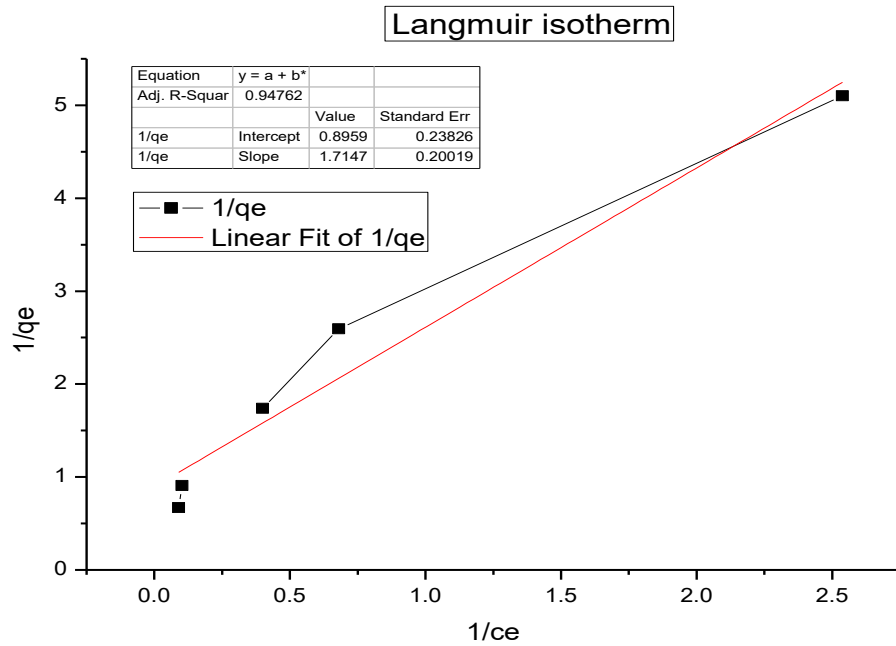


Fig 22. Langmuir isotherm of activated carbon with HNO<sub>3</sub>.

### Freundlich isotherm for activated carbon with HNO<sub>3</sub>:

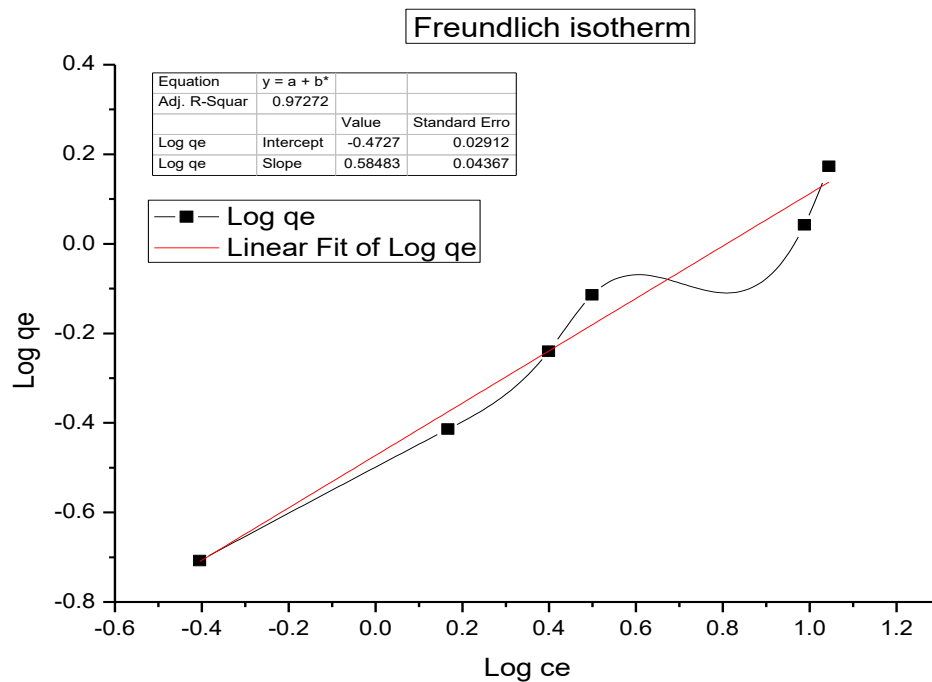


Fig 23. Freundlich isotherm for activated carbon with HNO<sub>3</sub>.

- ✓ In comparison of R square of those two graphs (Langmuir and freundlich isotherms lines), I deduced that this type of adsorption is physical more than its chemical.

## **6- Kinetic study:**

The purpose of this study is to measure the adsorption uptake over time, the concentration of MB and weight of coal are constant, and the amount of time started from 30 min until 3 hours.

Coal weight is 0.1 g in 10 ml of solution, the concentration of MB in the solution is 80 mg/l.

### **6.1- Raw coal:**

Time(MIN)	30	60	90	120	150	180
Ads	0,989	0,757	0,751	0,640	0,678	0,681
$C_e$	5,346	4,042	4,008	3,384	3,598	3,614
C ads	74,654	75,958	75,992	76,616	76,402	76,386
X	0,746	0,759	0,759	0,766	0,764	0,763
Q ads	7,465	7,595	7,599	7,661	7,640	7,638
Ads %	93,31	94,94	94,99	95,77	95,50	95,48

Table 8. Study of the ideal time of adsorption for raw coal.

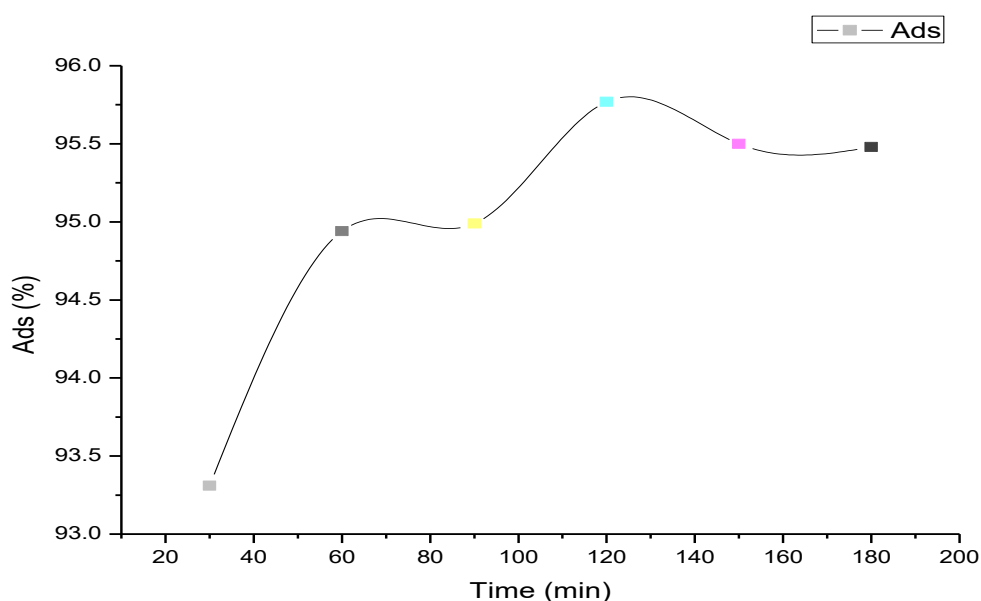


Fig 24. The graph of the percentage of adsorption of raw coal depending on time.

- ✓ Concerning these results the perfect time of adsorption process of coal is 120 min, which is 2 hours.
- ✓ After 2 hours, the adsorption process get reversed and the percentage of adsorption becomes relinquishing, we call this reversed process **desorption**.

## **6.2- Activated carbon with KOH:**

Time(MIN)	30	60	90	120	150	180
Ads	0,621	0,562	0,428	0,203	0,398	0,457
C <sub>e</sub>	3,277	2,946	2,192	0,928	2,024	2,355
C Ads	76,723	77,054	77,808	79,072	77,976	77,645
X	0,767	0,770	0,778	0,790	0,779	0,776
Q ads	7,672	7,705	7,780	7,907	7,797	7,764
Ads %	95,90	96,31	97,26	98,84	97,47	97,05

Table 9. Study of the ideal time of adsorption for AC with KOH.

## **Pseudo first order model for activated carbon with KOH:**

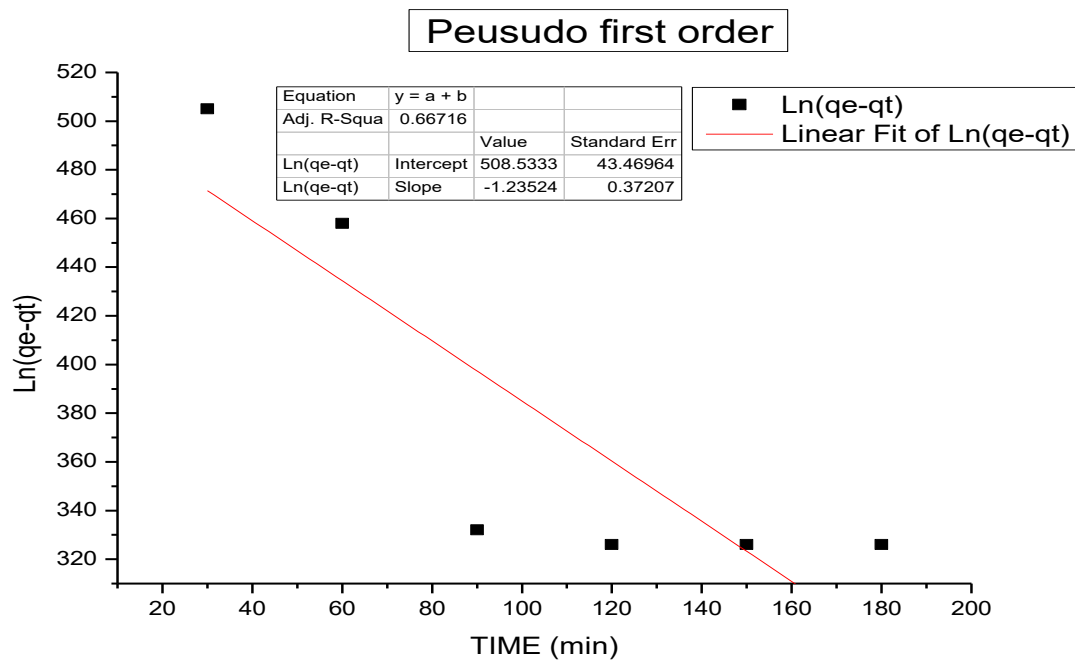


Fig 25. Pseudo first order model for activated carbon with KOH.

### Pseudo second order model of activated carbon with KOH:

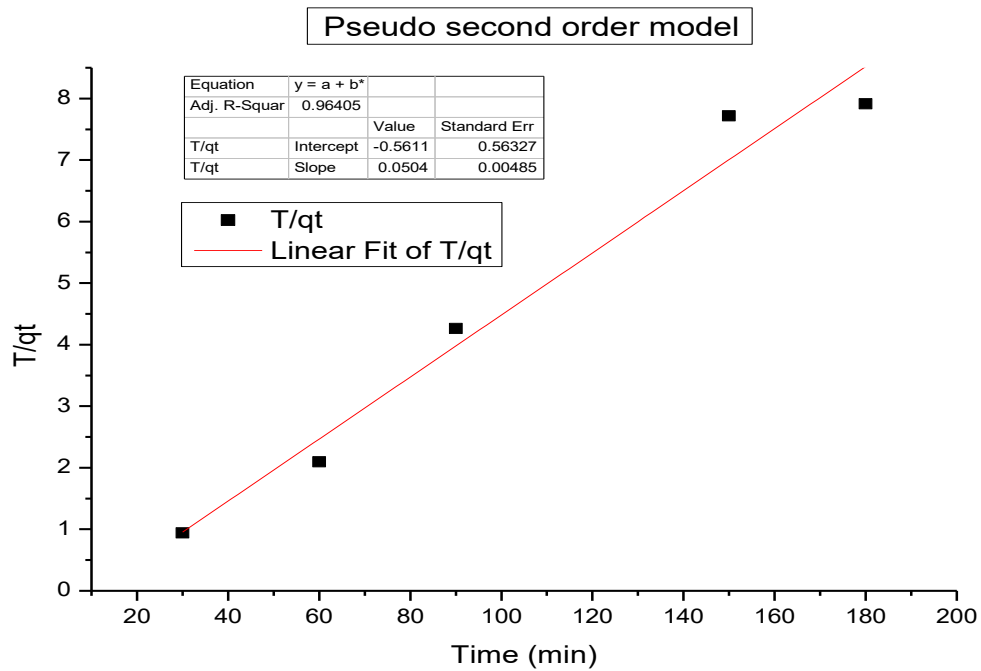


Fig 26. Pseudo second order model of activated carbon with KOH.

### 6.3- Activated carbon with HNO<sub>3</sub>:

Time(MIN)	30	60	90	120	150	180
Ads	1,036	0,993	0,797	0,565	0,730	0,889
C <sub>e</sub>	5,610	5,368	4,267	2,962	3,890	4,784
C Ads	74,39	74,632	75,733	77,038	76,11	75,216
X	0,743	0,746	0,757	0,770	0,761	0,752
Q ads	7,439	7,463	7,573	7,703	7,611	7,521
Ads %	92,98	93,29	94,66	96,29	95,13	94,02

Table 10. Study of the ideal time of adsorption for AC with HNO<sub>3</sub>.



### Pseudo first order model for activated carbon with HNO<sub>3</sub>:

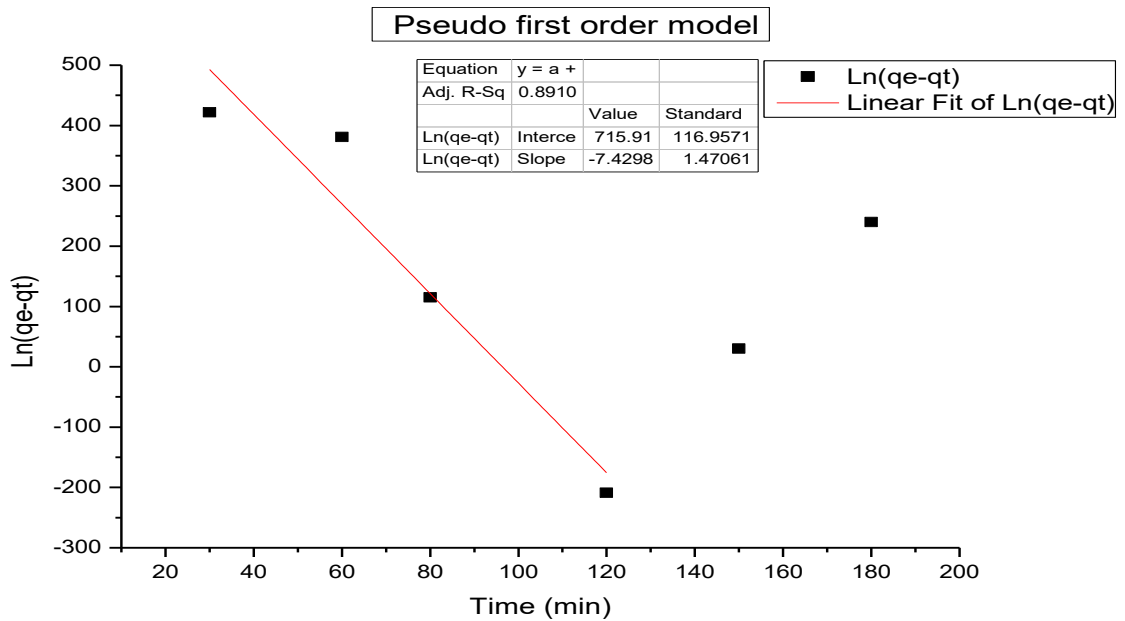


Fig 27. Pseudo first order model for activated carbon with HNO<sub>3</sub>.

### Pseudo second order model for activated carbon with HNO<sub>3</sub>:

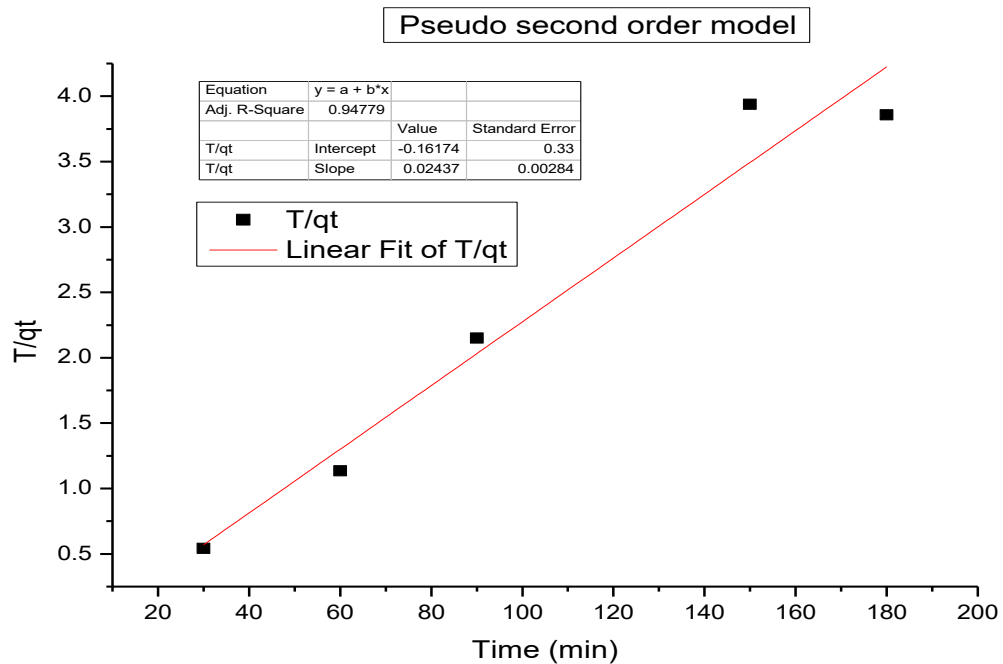


Fig 28. Pseudo second order model for activated carbon with HNO<sub>3</sub>.

**7- Conclusion:**

This study confirmed that potassium hydroxide is better than nitric acid to activate carbon, so the basic products are more effective than acids.

Second, this basic product needs an amount of temperature for good efficacy (80° C).

Finally, a certain quality of activated carbon can adsorb a specific amount of methylene blue in a fixed time that we should respect.

# **General Conclusion**

**General Conclusion:**

The results of this study suggested that different operating conditions for MB adsorption, e.g initial concentration, temperature, and contact time had a significant effect on both adsorption capacity and percent removal, for kinetics and isotherms studies, pseudo-first, pseudo-second-order, and Langmuir, Freundlich isotherms models were in good agreement with a measured data.

The chemical activation we applied in this experiment does enlarge the carbon pores, thus increasing the adsorption capability of this last.

This study confirmed that the activation of coal by a basis is more effective than by an acid according to the isotherms and the modal results.

In addition, the activated coal with acid can give less average adsorption than raw coal itself, so I cannot tell that the phenomena that happened in this case is really adsorption

On the other hand, the coal of bechar mine has a high adsorption capability even in the raw state, thus in order to reduce the cost, we can start using it as its raw.

The chemical activation with an acid shows bad results compared to the activation with a base or even raw form of the coal, This is an indication that the acid makes the pores lose their capability to adsorb somehow.

Hopefully, the future days bring opportunities to do the full experiment and results concerning this inquiry.