Purifying wastewater from phenol and its derivatives before throwing it into rivers.

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Abstract:

Rice husks were treated with inorganic acids such as HCl, HNO_3, H_2SO_4 and organic acids such as acetic acid CH_3COOH to increase the efficiency of adsorption of harmful organic substances, including phenol, from wastewater. The process was monitored The reaction was tracked by UV-vis measurements. The study proved that coal heated to 500 degrees Celsius and treated with sulfuric acid is more capable of adsorption than activated charcoal with other inorganic acids. The study showed that inorganic acids are more dense than organic acids.

Keywords: Rice husk ,Activated carbon, pollutants, wastewater.

تنقية مياه الصرف الصحي من الفينول ومشتقاته قبل رميها في الأنهار

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الملخص:

تمت معالجة قشور الأرز بالأحماض غير العضوية مثل حمض الهيدروكلوريكHCl، HNO_3، H_2SO_4 والأحماض العضوية مثل حمض الخليك CH_3COOH لزيادة كفاءة امتصاص المواد العضوية الضارة، بما في ذلك الفينول، من مياه الصرف الصحي. مت مراقبة العملية وتم تتبع التفاعل بواسطة قياسات الأشعة فوق البنفسجية. وأثبتت الدراسة أن الفحم المسخن إلى 500 درجة مئوية والمعالج بحمض الكبريتيك أكثر قدرة على الامتزاز من الفحم المنشط مع الأحماض غير العضوية الأخرى. وأظهرت الدراسة أن الأحماض غير العضوية أكثر كثافة من الأحماض العضوية.

الكلمات المفتاحية: قشر الأرز، الكربون المنشط، الملوثات، مياه الصرف الصحي.

1.Introduction:

With the increase in the volume and quantity of industrial oily wastewater and and oil spills, and the need to remove or collect oily pollutants emerged From the surfaces of the water, the search began Developing effective and inexpensive ways to remove pollutants and preserve the environment [1] .

In recent years, there are growing concerns among scientists regarding pollution Because of its impact on humans and the environment, especially the aquatic environment. Phenolic compounds are among the major chemicals concern in this regard because its impact on the environment over a long period of time, It accumulates and causes toxic effects on humans and animals[2].

Wastewater and industrial wastes containing phenolic compounds represent a great danger because of their poor biodegradability[3] These are widely present in effluents such as those from coal tar, plastics[4], leather, paint, pharmaceuticals, steel, textiles, timber, pulp, pesticides, and oil refining Exposure to such toxic water pollutants results in damages Impact on human health, aquatic organisms and natural water resources due to production and discharge Untreated liquid water[5,6]. Among the chemically dangerous pollutants 126, phenol is the eleventh pollutant, and the maximum limit for its presence in wastewater is 1 mg / liter limit of maximum total phenols concentration of 0.5 μg L-1 and individual concentration of 0.1 μg L-1 in drinking water[7].

Exposure to phenol as a result of the use of some medicinal products It is extremely irritating to human skin, eyes and mucous membranes. As a result of inhalation or dermal exposure (short-term). Oral phenol is very toxic to humans Its most important symptoms are loss of appetite, gradual weight loss, diarrhea, dizziness, secretion of saliva, dark urine discoloration, Effects on the blood and liver have been reported in chronically (long-term) exposed humans[8].

It was found that adsorption is considered a treatment for wastewater containing organic compounds, where the comb carbon adsorption technique is one of the successful solutions[9]. Carbon has high adsorption feature, it can remove both organic and inorganic compounds either by batch or column methods and can be regenerated For frequent use[10]. Where the reason for the absorption of activated carbon for phenol is its high ability to absorb and expanded its large surface area Therefore, researchers seek to find cheap raw materials that meet the purpose[11]. The rice husk is the outer covering of the rice grain, and it is a by-product of the rice milling process. it's one Waste in all rice producing countries. Usually either dispose of it or burn it In open spaces, causing damage to land and environment pollution. A lot of effort has been made to take advantage of it Including rice husk as an alternative fuel for energy production, production of activated carbon and as a raw material Materials for the manufacture of industrial chemicals based on silica and silicon compounds[12].

It is also necessary to take advantage of rice husks and prevent burning them indiscriminately in order to preserve the environment, as they can be managed and converted into charcoal that, by mixing it with fertilizer, can prevent soil degradation as a result of repeated cultivation of rice, and as a result of the presence of silica, it provides an opportunity to retain nutrients in the soil[13].

Generally, the chemical composition of rice husk includes: 32.24% cellulose, 21.34% hemicellulose, 21.44% lignin, 1.82% extractives, 8.11% water, and 15.05% mineral ash (which is about 96.34% silica content)[14] .Most technologies have disadvantages such as their high cost, low efficiency and the production of associated secondary pollutants. Adsorption can be a very effective procedure due to its low cost Simplicity of design, speed, ease of operation and availability of different absorbent materials without the formation of hazardous substances adsorption process is a superficial phenomenon, the chemical and physical properties of adsorbents and adsorbents can be affected. A suitable sorbent should contain several sorbents[15]. properties such as availability, low cost technology, non-toxicity, High surface ability, high abrasion resistance and stability in various Environmental conditions To date, many low-cost adsorbents including natural materials, Inactive or dead biomass of microorganisms, agricultural waste and Industrial byproducts have been used to remove contaminants. In particular, plant waste and agricultural products such as rice husks as potential absorbent materials[15]. Rice husks can also be important in the adsorption and capture of carbon dioxide coming out of factories and laboratories, thus contributing to reducing global warming[16].

2.Wastewater: The presence of antibiotics in wastewater leads to the emergence of strains of bacteria and superbugs that are resistant to antibiotics [17] Algae was used as an alternative to traditional methods of dealing and treating wastewater and removing its toxicity and its harmful environmental impact, as algae ponds do not need aeration because they provide oxygen and organic acids that bacteria need [18-20].

he generation of wastewater is inevitable in various industries where oil refining for every barrel of oil there are 10 barrels of wastewater [21], The primary treatment eliminates the effect of the substances that cause problems, while the secondary treatment includes the physical, chemical and biological processes that lead to the decomposition of organic materials and the oxidation of materials such as nitrogen to nitrate or phosphorus to orthophosphate. These liquid wastes can be easily dealt with later and do not pose any danger [22]. Heavy metals present in wastewater pose a major threat to human health and can be treated in many ways, the most important of which is adsorption, which is a common method for removing heavy metals from wastewater, where activated carbon is the important material for removing heavy metal ions because of its porous structure [23, 24]. The dyes used, including methylene blue (MB), rhodamine B (RHB), methyl orange (MO), Congo red (CR), dispersed violet, and crystal violet, are the most important pollutants resulting from the textile, leather, cosmetics, pharmaceutical, paint, varnish, and paper industries [24]. There are methods to remove heavy metal ions from wastewater, such as adsorption, chemical and electrical membranes, and photocatalysis [25]. Industries such as electroplating, batteries, pesticides, rayon, tanning, nuclear reactors, and electrolysis all generate heavy metal ions, as these If ions exceed the permissible limit in water, they cause many diseases, including cancer [25]. China has had a leading role in wastewater treatment since the last quarter of the last century, when the problem of water resource shortages worsened, especially in northern China, which led the authorities to address the water shortage through wastewater reclamation [26]. Pollutants threaten the marine ecosystem in addition to their impact on other living species. Traditional sewage plants alone do not succeed in eliminating large pollutants and thus require additional treatments in addition to primary and secondary treatments, as these additional treatments such as adsorption are effective in terms of low cost and effectiveness of treatment[27]. Wastewater is considered one of the pollutants of drinking water, as it includes heavy metals, dyes, pesticides, herbicides, and other aromatic compounds. The accumulation of these materials in the water poses a threat to human health. Liquid industrial waste is treated in several stages according to the physical state of the pollutant, where solid pollutants are initially removed. Then, procedures on liquid wastes such as adsorption, ion exchange, and sedimentation [28] When a person drinks water containing heavy metal ions such as cadmium ions, it affects the metal ions that are beneficial to humans in the digestive system, such as iron and zinc, leading to their decrease and thus increasing cadmium ions, which is a toxic substance to the body [29]. Organic pollutants remain in water for a long time and do not undergo chemical or photodecomposition, breakdown, or biological deterioration,Treating, rehabilitating and renewing wastewater is the best option to reduce the effect of these polluting materials. Among the treatments are adsorption and electrocoagulation (EC)[30]. Hydrogels, which are divided into several types: 1-Hydrogel beads, 2- Hydrogel films, 3- Hydrogel nanocomposites were used to remove traces of pollutants such as nuclear waste, as well as modern agricultural waste and pesticides. The presence of polluting materials, including nitrates, leads to eutrophication of water, a reduction in its quality, and the growth of algae in it. Which requires treating its causes, including nitrates [31].

3.Activated charcoal:

Different adsorbents have been chosen to remove organic materials and dyes from polluted water. These adsorbents include ash and sugar waste (sugar bagasse). Wood pulp, olive stones, walnut shells, sawdust, and clay [32]. The charcoal was activated at a temperature of 750-950 degrees Celsius so that it has a good adsorption capacity for organic and inorganic materials, whether they are solutions or gases. Activated charcoal is divided into three categories:

1- Large porosity (more than 25 nanometers).

2- Medium porosity (less than 25 and greater than 1 nanometer

3- Small in size (its pores are less than 1 nanometer). [33]

Activated charcoal, beta-cyclodextrin, and sodium alginate polymer(SA), Fe_3O_4. How many polymeric materials were obtained in the form of beads consisting of (Fe_3O_4/β-CD/AC/SA).[34]

Activated charcoal is used as an absorbent material due to its high porosity and ability to adsorption, as charcoal is prepared from cheap natural materials, agricultural waste, or peels [35]. Activated carbon is used in some applications such as air and gas purification, as a catalyst, and in electrical energy and drinking water treatment due to its exceptionally high surface area, advanced pore structure, relative chemical stability, and thermal stability [36].

There is activated carbon, which we obtain from local palm oil, which was prepared using the physicochemical method, whereby the palm oil is treated with potassium hydroxide (KOH)and then exposed to carbon dioxide gas (CO_2), treated at 814 degrees Celsius [37].

4. Material and Methods

4.1 Preparation of Adsorbents

The raw material, rice husk (RH) was obtained from a nearby rice mill. The rice husk was washed thoroughly with distilled water to remove adherent soil and clay, and then dried at 105 °C in an oven for 24 h, or it was kept in the sun for a week and burnt at 600 °C for 4 h to form rice husk ash The rice husks were ground and then sieved through different sieves Then the ash are ground, sieved and kept inside the desiccator. Particles with sizes between 500-200 µm were selected and for further processing the coal was activated using inorganic acids such as H_2SO_4, HCl, HNO_3 in high concentrations (3M) and heating more than 100°C with stirring for 3 h.

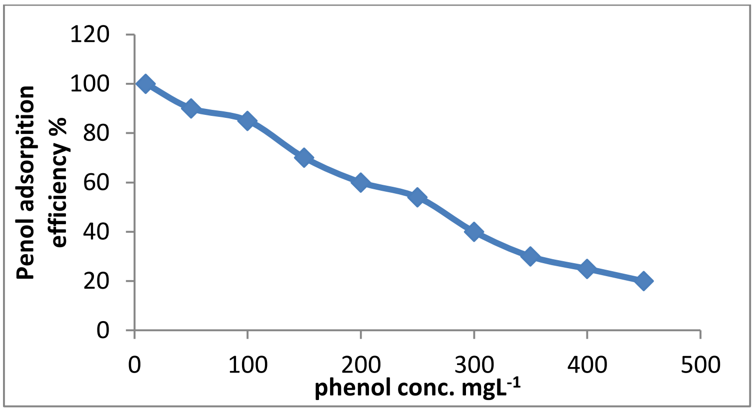
Table 1. Chemical analysis of mineral ash of rice husk

Compounds	The ratio
SiO_2	93
K_2O	4.1
MgO	0.91
$A_{l2}O_3$	0.72
Another	1.3

5. Factors affecting the adsorption of phenol on activated rice huks:

5.1. The effect of the initial concentration of phenol :

The adsorption capacity and capacity increases when the concentration of phenol (5-450) mg L^{-1} increases at(2 gL^{-1} in 200 mL and pH 6 at 30°C). This is due to the ability of activated carbon number to adsorb phenol, The amount begins to decrease as a result of occupying most of the adsorption site as the percentage decreases as the concentration of the adsorbent material increases[38-41].



. Fig.1. The effect of concentration of phenol on adsorption

5.2. The pH effect:

As for the adsorption of phenol from its aqueous solution by rice husks (RHS), and activated charcoal from rice husks (RHAC), when we take (2 gL^{-1} in 200 mL and 4 mg of phenol at 30°C) from the solution, the highest adsorption is between (4-11), and at the lowest From 4 adsorption, the adsorption is slightly due to the H^+ ion that hinders or occupies the coordination sites, but when the pH function rises to more than 12, the phenol molecule turns into a negative ion, and this also corresponds to the ionization of the hydrogen present in the silica, and this leads to repulsion between the phenol and the surface [42-47].

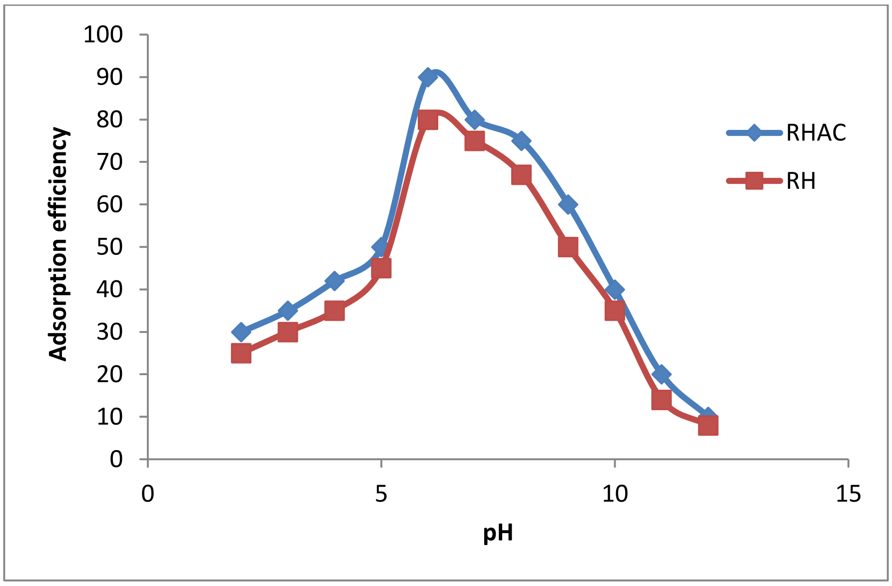


Fig.2. The effect of pH on adsorption

5.3. Time effect on adsorbition:

The adsorption of phenol (2 gL^{-1} in 200 mL and 1mg of phenol at 25°C, and optimal pH6) increases with the increase in time and this is due to the reason that the adsorption processes need time until all the sites of the adsorbent are occupied with the adsorbent, where at first it is fast because the sites of the adsorbent are many up to 120 minutes and then after that the adsorption stabilizes due to the preoccupation of all and equilibrium occurs.[15,42-45,48.49].

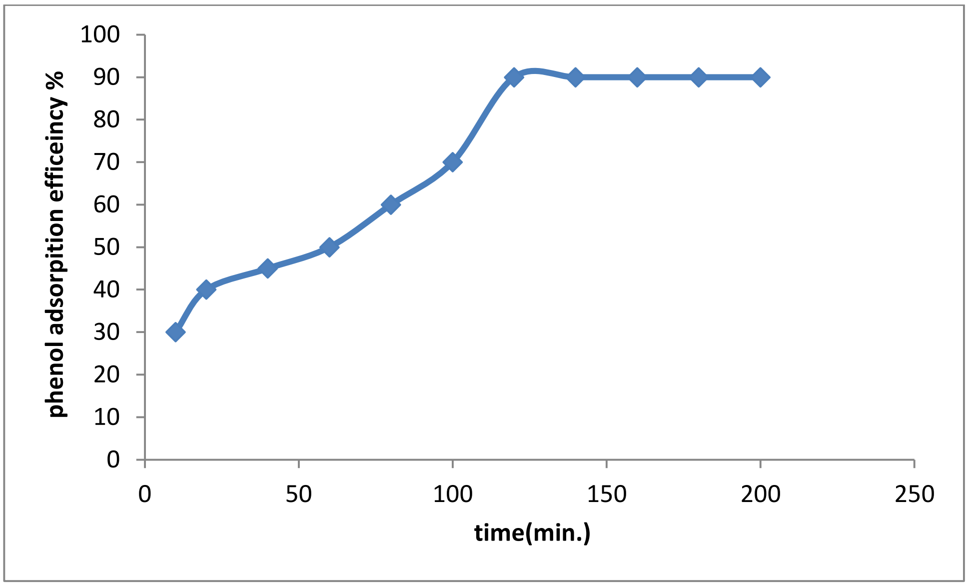


Fig.3. The effect of time on adsorption

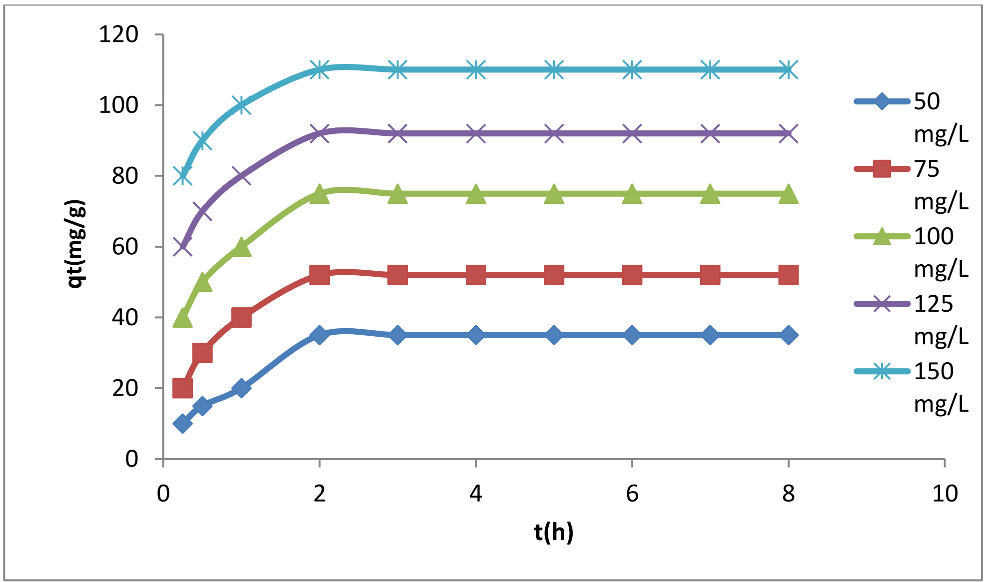


Fig.4. Effect of phenol concentration in solution on adsorption efficiency

When the concentration of phenol increases, the rate of adsorption decreases as the concentration increases (i.e. the ratio of the adsorbed to the non-adsorbed material) Fig3. As for the amount of adsorbed material, it increases, of course, with an increase in the phenol concentration, that is, as the concentration of phenol increases, the amount of adsorbed material increases Fig4

5.4. Effect of Temperature:

The temperature has an important effect on the adsorption process(RH 2 gL^{-1} in 200 mL and 1mg of phenol , and optimal pH6), as the optimum temperature is between 5-50 ºC, but at a low temperature, adsorption is low and the reason is the movement of particles is little because of the lack of kinetic energy, but at high temperature, the adsorption decreases and the reason is the increase in the kinetic energy of the particles The adsorbent reduces the chances of it sticking to the surface and thus the adsorption decreases and decreases more with increasing temperature[49-51].

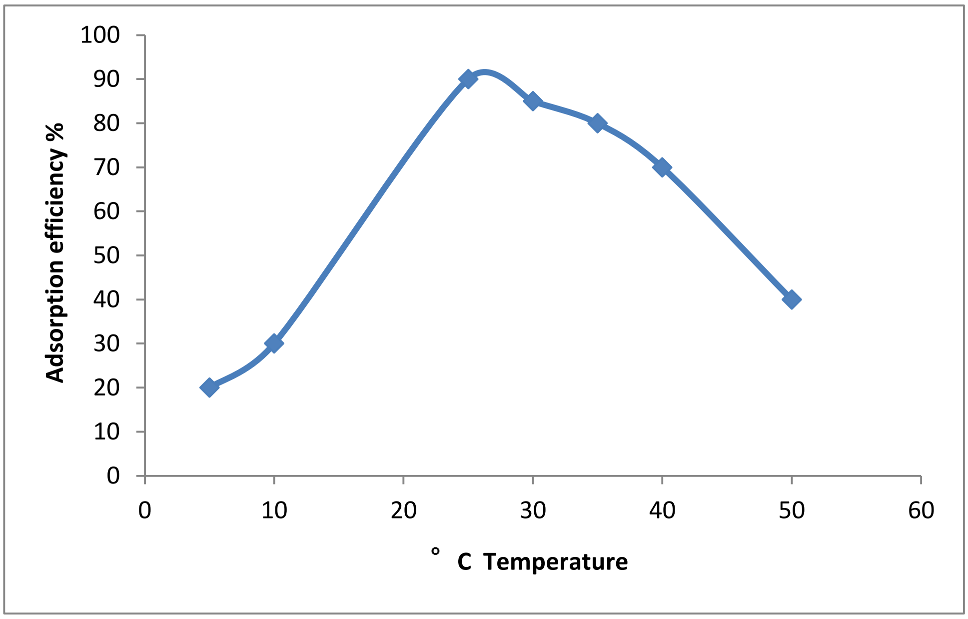


Fig.5. The effect of Temperature on adsorption

5.5. Adsorbent dose:

To find out the amount of adsorbent (rice husks, Activated charcoal) (in 200 mL and 1mg of phenol at 30°C , and optimal pH6), that absorbs the optimum amount of adsorbent material (phenol), we take a range of 0.5-5 g/L of rice husks at the optimal pH 6 and the initial concentration of phenol which is 0.5 mg/L and at the optimum temperature of adsorption 30°C The reason is that the coal ash of rice husks has a greater adsorption capacity than rice husks for the same mass, and the reason is due to the increase in the surface area exposed to adsorption.

. The dose in which we note that the highest adsorption of The jump in weight, which is 2 grams, is the jump in adsorption of phenol to the surface of rice husks and their ash [38-41,52] .

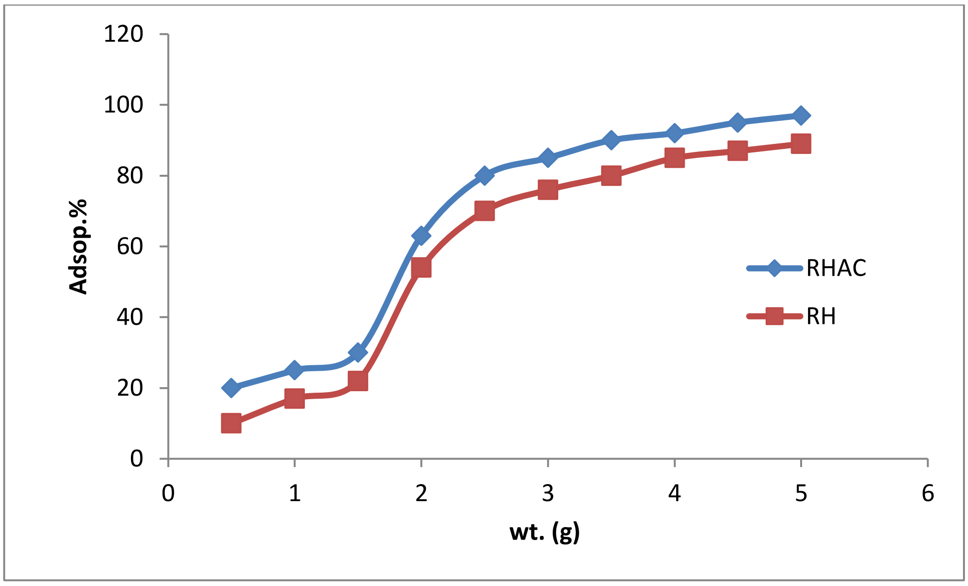


Fig.6. The effect of adsorbent dose on adsorption

5.6. Half the diameter of the rice husk: The surface area has an important role in the adsorption process, as the radius of rice husks ranges between 20-100 µg. The study showed that the smaller the radius, the better the adsorption, because the surface area becomes larger[53-57].

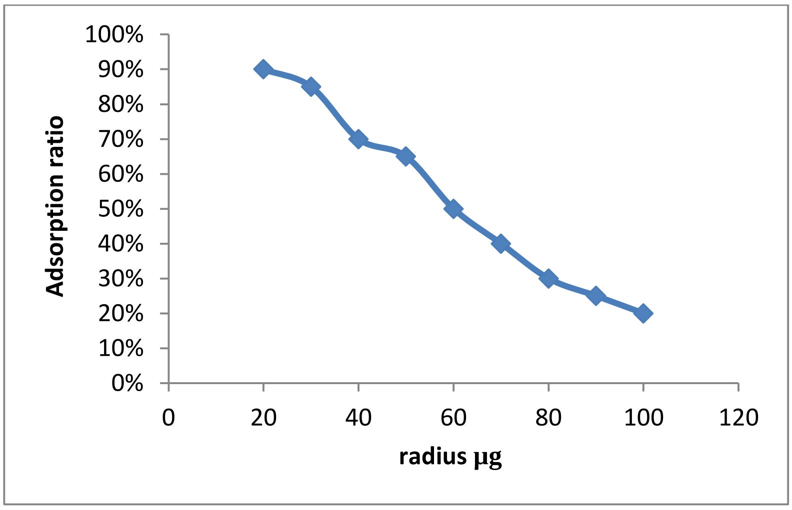


Fig.7. The effect of diameter of the rice husk on adsorption

The study was conducted to evaluate and track the status or efficiency of phenol adsorption from aqueous solutions using rice husks, where the optimal experimental conditions are from the initial concentration of phenol as well as the pH, equilibrium time, and temperature, where 100 mL of phenol solution was taken and placed in a 250 mL vial and added to it Distilled water and the

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Iraqi Journal of Humanitarian, Social and Scientific Research
Print ISSN 2710-0952 Electronic ISSN 2790-1254

amount of rice husks used is 0.4-4 g/L. The solution is placed in a water bath, rocking for a whole night in this vibrator at 120 revolutions per minute. The solution is filtered and the amount of remaining phenol is measured. We conduct several experiments to obtain the rate.

The percentage of phenol removal is derived from Eq.(1).

$$\text{Removal of phenol\%} = \frac{(C_o - C_t)}{C_o} \times 100\% \quad \text{-----------} \quad (1)$$

where C_0 and C_t are phenol concentrations initially and at any given time (mg/L), respectively. The amount of phenol adsorbed per unit quantity of rice husk ash is derived from Eq.(2).

$$q_t = \frac{(C_O - C_e)\,V}{w} \quad \text{----------------} \quad (2)$$

C_O :Inicial Concentration of Phenol.

C_e: Equilibrium Concentration of Phenol.

V: volium of soliution (L) .

W: The mass of dry adsorbent (g) where q_t is phenol quantity adsorbed per unit weight of rice husk ash at any given time (mg/g) and m_s is the amount of rice husk ash added in gram (gm/L).[2,3,16]

6.Thermodynamic Study: Thermodynamic parameters such as the free energy (ΔG° kJ/mol), enthalpy (ΔH° kJ/mol) and entropy (ΔS° J/K.mol) changes during adsorption can be evaluated

$$Kc = \frac{q_e}{C_e} \quad \text{---------------------} \quad (3)$$

$$\Delta G^{\circ} = -RT \ln Kc \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

$$\log K_C = \frac{\Delta S^{\circ}}{2.303R} - \frac{\Delta H^{\circ}}{2.303RT} \quad \text{---------------}(5)$$

Where K_C is the equilibrium constant Ce is the equilibrium concentration.

Table2. Thermodynamic values of adsorption on the surface of rice husk.

H°(kJ/mol)Δ	S°(J/K.mol)Δ	G°(kJ/mol)Δ		
-26.14	-62.23	300K	310K	320K

		-5.432	-4.568	-3.723

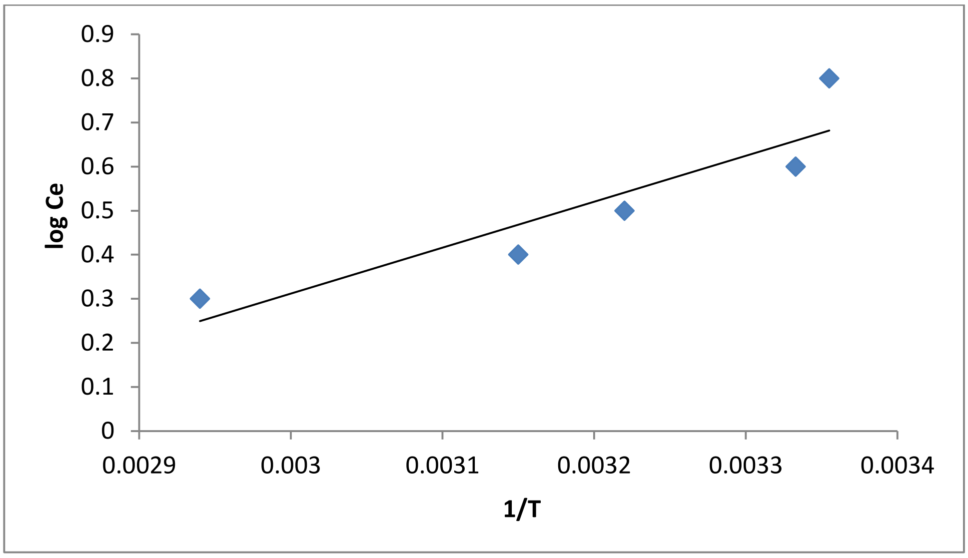

Fig.8.Mximum adsorption amounts of phenol on the surface of rice husks at different temperatures.

7. Adsorption Isotherms:

The isotherm is defined as the relationship between the amount of adsorbate on the surface of the adsorbent and the initial concentration at a constant temperature [58]. The isotherm takes different forms. At the beginning of the adsorption process, the process is fast because the adsorption sites are many, and then it begins to decrease as a result of the sites being occupied little by little[59].

Chemical adsorption is often in one layer that occupies all sites, but physical adsorption consists of several layers The bond between them is weaker than chemical adsorption and is affected by temperature and pressure[60].

Gils classified adsorption isotherms into several classes based on the initial sections of the isotherms such as S, L, H, and C. Where the class S, for example, takes the shape of the adsorption isotherm similar to the letter S, and the adsorbed particles are directed towards the surface in an inclined or vertical manner [60]

As for class L, it is specific to the adsorption isotherm of the Langmuir type, and the orientation of the adsorbed particles is horizontal on the surface, and the adsorption is monolayer. As for class H, it is concerned with high adsorption affinity. This class is observed in very dilute solutions, and when adsorption of large molecules such as polymers. Whereas Class C indicates the presence of a constant partition between the adsorbent material on the one hand and the

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Print ISSN 2710-0952 Electronic ISSN 2790-1254

solution with the adsorbent surface on the other hand, and it indicates a high probability of chemical adsorption [60]

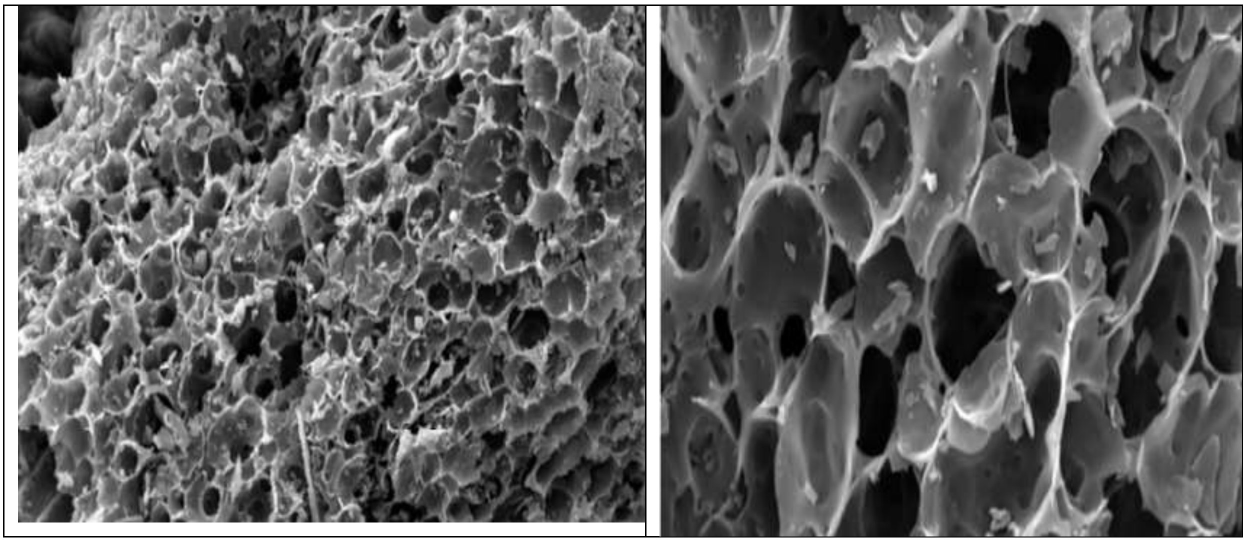

Fig. 9. SEM of Rice Husk Ash

8. Types of Isotherms

8.1.Langmuir adsorption equations

This equation was developed by Irving Langmuir to describe gaseous molecules on flat solid surfaces

He also assumed that adsorption occurs for one layer of molecules on the surface of the homogeneous adsorbent material, where the adsorption is initially rapid after that it begins to gradually stabilize over time as a result of the departure of numbers of molecules equal to the number of adsorbent molecules, and this condition is known as adsorption and is in a state of equilibrium [61]

Langmuir assumed that adsorption of a single molecular layer occurs on the surface of the homogeneous adsorbent, and the amount of adsorbent increases rapidly at the beginning of adsorption, then begins to gradually stabilize due to the separation of some molecules from the surface, leading to what is known as adsorption, and when the adsorption speed is equal to the adsorption speed in a state of equilibrium [62] The Langmuir equation is based on the fact that [62] adsorption occurs on flat surfaces that have a fixed number of Sites that are identical, and these sites are held by one molecular layer that covers the surface, which indicates the maximum adsorption.

The Langmuir equation can be mathematically expressed as follows [63-66]:

$$Ce/Q = 1/K + a/K \cdot Ce$$

Where:

Ce: the concentration of the solute at equilibrium (mg/L).

Q : amount of adsorbent (mg/g)

a, K: Langmuir empirical constants.

When drawing Ce/Q against Ce, the slope is equal to a/K and its intersection is equal to the value 1/K, as in Figure (1-5).

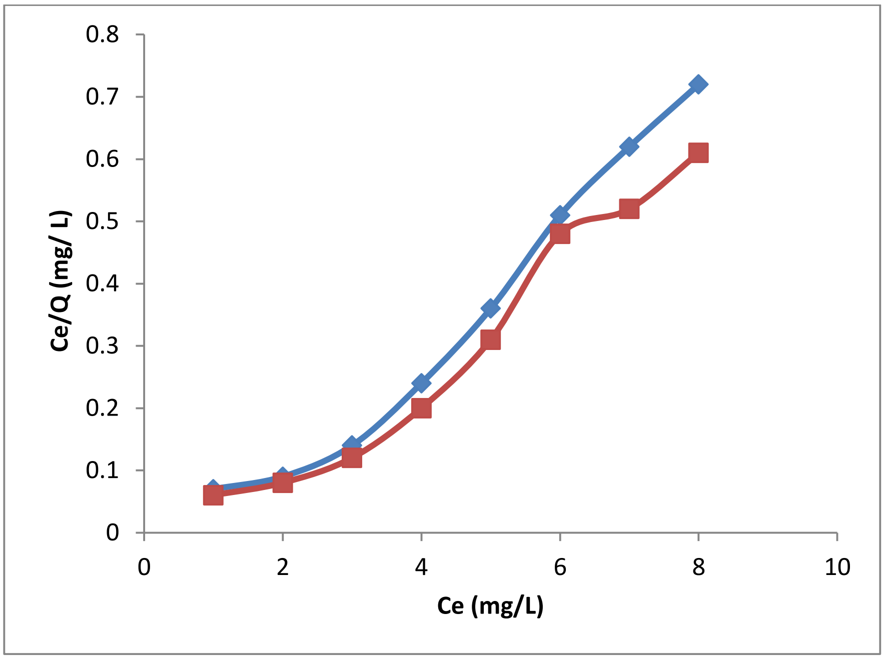

Fig.9. Langmuir isotherm models for the phenol adsorbents.

8.2.Freundlich adsorption equations

This equation was developed by (Freundlich) in the year (1926) [67], as most surfaces are heterogeneous)) meaning that the potential energy changes are irregular and the reason for this is the occurrence of adsorption sites at different levels of energy [68,69] which leads To change the adsorption isotherm, it represents the change in the amount of the adsorbent material per unit area or mass of the adsorbent material with the equilibrium concentration, and the first use of the Freundlich equation is attributed to describing the adsorption of the gas phase, and the adsorption of the solute from the solution. The Freundlich equation can be written as follows [63,64]:

$Q = KF\ Ce^{1/n}$

Where:

Q: the amount of solute adsorbed

Ce: the concentration of the solution at equilibrium n,K_F: Freundlich constants

The linear equation takes the following form:

LogQ = log KF + 1/N log Ce

When drawing log Q against log Ce, we get a straight line whose slope is equal to 1/n, and its intersection is equal to the value of Log KF, as shown in Figure (1-6).

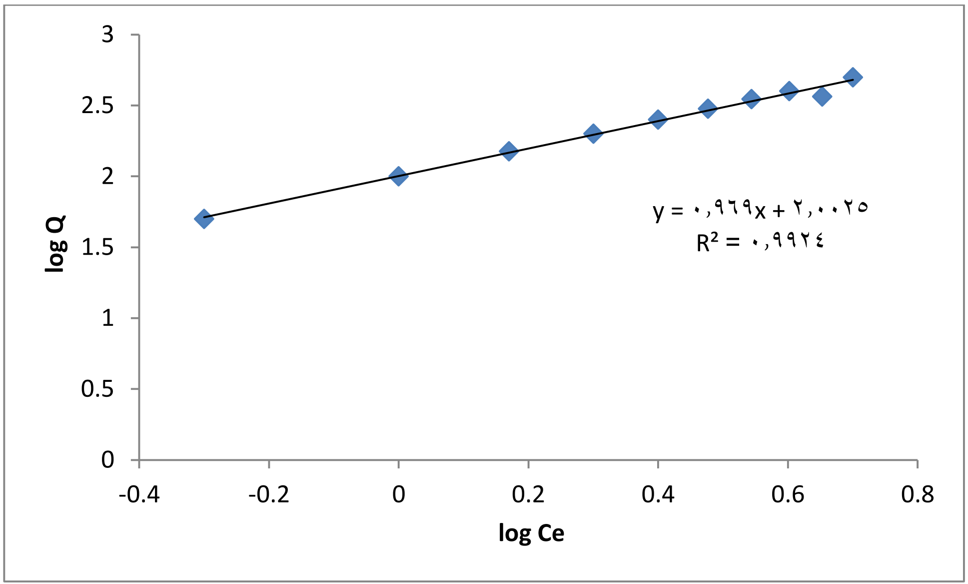

Fig.10. Freundlich isotherm models for the phenol adsorbents .

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Print ISSN 2710-0952 Electronic ISSN 2790-1254

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