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Experimental Modeling for Methylene Blue Active Substances MBAS Adsorption from Water Using Different Sustainable Activated Carbon in Fixed Bed Column

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Abstract

This research includes the effect of activated carbon, the flow rate of the adsorption system, the weight of activated carbon, and contact time between the material to be adsorbed and activated carbon in the treatment of wastewater contaminated with the active substances of methylene blue MBAS from petroleum and petrochemical plants using the adsorption process in a system with a fixed bed and continuous flow. The adsorption process was studied in the presence of two types of activated carbon prepared from local materials available in abundance and at very low prices (wheat husks peganum). The constant bed system was used to conduct the MBAS absorption process on the prepared activated carbon and study the effect of the flow rate, the weight of the activated carbon, and the contact time during the experiments. Activated carbon was prepared by burning (wheat husks) at a temperature of 275 °C for 90 min under the nitrogen gas flow in (4) liters/hour. The same steps were performed for the peganum. The method of chemical activation was also used with phosphoric acid (wheat husks, peganum) and (4) molar solution and leaving the raw materials for (24) hours in the solution for effective activation. They were thoroughly washed with water to enter the oven and incinerated at a temperature of 700°C for wheat husks and 500° C for peganum. SEM's two BET assays investigated the resulting active carbon's surface area and surface morphology. The surface area values were (775) m^2/g for the activated carbon produced from the peganum plant and (615) m^2 / g for the activated carbon produced from wheat husks for both types of carbon. Electron microscopy properties show that activated carbon prepared from peganum has a higher surface porosity than that prepared from wheat husks when using the same activated agent. The isotherms and adsorption kinetics of the dye was investigated at temperatures (30-60)°C for a concentration range of (50 - 250) mg/L.The study results showed that the maximum removal capacity of MBAS using activated carbon prepared from peganum is greater than that prepared from wheat husks. The results showed the first-order rapid increase in the adsorption rate, and the second-order pseudo-model represented the data well. The adsorption system was selected by selecting the best contact time between the material to be adsorbed and the prepared activated carbon, the best solution flow rate, and the activated carbon's best weight. The results indicated that the best absorption time was (2) hours, the best weight of activated carbon was 10 grams, and the best flow rate was 0.1 liter/hour.

"Keywords: Adsorption; sustainable; Methylene-blue; dye; activated carbon; fixed-bed;"

1. Introduction

Wastewater pollution negatively affects the public water supply, leading to health problems such as diarrhea. Environmental pollution monitoring has been interesting in many areas, especially air and water pollution[1]. Saving water is essential to save the future of humans and other living things as the growth in technology is reaching new heights[2]. However, the price we will be paying shortly is very high. One of the problems of this rapid expansion is environmental disturbances and pollution problems[3]. Effluents from the textile and petrochemical industries can be a problem due to dyes and toxic substances in the final effluent. More than a thousand different variants of synthetic colors have been put on the market, saving more than seven thousand tons annually worldwide[4]. The removal of colors from toxic and lethal tissue channels is a big problem due to the difficulties of treating these pigments using typical wastewater purification techniques such as coagulation, osmosis, membrane filtration, chemical oxidation, solvent extraction, chemical precipitation, etc. Since the dyes are resistant to light, oxidants, large operating charges, and other sludge processes, these methods are not highly effective, and surfactants have been used to ensure adsorption of these dyes, including MBAS. This motivated scientists to search for more cost-effective and practical methods and access to activated charcoal adsorption technologies[5, 6]. Adsorption is

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the ideal method for treating textile effluents. Therefore, high-efficiency sorbents play a vital role in the performance of dye adsorption processing[7]. Charcoal has gained great interest as an adsorbent due to its large surface area, high surface reactivity, and favorable pore size distribution[8], which can be activated with various activators such as zinc chloride phosphoric acid, potassium hydroxide, and potassium carbonate[9, 10]. The success of these techniques depends on the development of effective absorbent material. According to the literature, these adsorbents may be natural, agricultural, industrial, household waste, or by-products. The above processes constitute this material for activated carbon with an excellent porous structure with a high surface area ranging from 500 to 2000 m^2/g[11, 12]. The second part is a fixed bed column system designed to absorb MBAS from water. Finally, the experiment calculates the adsorption parameters, including flow rate, adsorption time, and weight of activated carbon. Then a mathematical model is generated using Langmayer, Frendlich, Timken, etc., and the behavioral and absorptive properties are studied. Wastewater pollution negatively affects the public water supply. Charcoal has attracted the attention of adsorbents due to its large surface area, high surface reactivity, and excellent pore size distribution, which can be activated by various activating agents such as potassium hydroxide, zinc chloride, potassium carbonate, phosphoric acid, or their solutions[9, 13, 14]. There are two types of activation: physical and chemical. Physical activation requires a higher activation temperature and a longer time than chemical activation[15]. The study aims to study the adsorption behavior of MBAS on the prepared activated carbon and the effect of changing the parameters (flow rate, carbon weight, contact time between carbon and solution) and finding the appropriate mathematical model.

Experimental Work

1.1. Materials

It was desired to obtain essential information pertinent to interpreting adsorption characteristics in adsorbate-adsorbent systems. Then, using this information to specify the characteristics of the adsorption process for the systems studied. So, it was essential to conduct the experiments with well-defined materials.

1.2. Waste Materials

Wheat husks were collected from mills as they represent the remnants of the rice industry process in Al-Diwaniyah Governorate, and peganum was collected from local markets, whose prices are meager. They were thoroughly washed with distilled water and dried for 72 hours in the sun to evaporate all water and volatile matter. Then, two kg of these materials were ground using an electric grinder (Generic Corporation, JIQI, China) for about 10 min. A sifting analyzer from Gilson Co. was used to test the product for 600 m.
The two materials were kept in separate canvas bags in a desiccator containing activated silica gel.

1.3. Equipment and procedures

The adsorption equipment was made up of a 2.5 litres tank, centrifugal pump, flow meter, and activated carbon tube. The experimental work comprises two steps. The first is preparing the activated carbon from the two types of locally available wastes and the second step examines the adsorption equilibrium and the kinetics of adsorption. Activated carbons were stored in a vacuum oven (Hysic Co., model: VO-64, Korea), operated at 10Kpa pressure and 373K temperature overnight to reduce already adsorbed gases from carbon surfaces.

1.4. Preparation of the activated carbon

Figure 1 shows the process steps of preparing the activated carbon from the two wastes sources, wheat husks, and peganum. The process includes carbonization, impregnation, and activation steps.

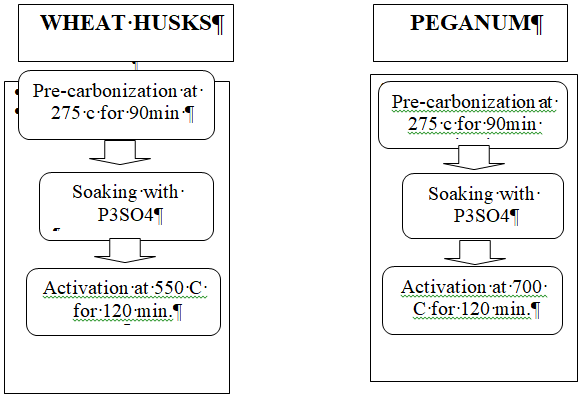

Figure 1. Activated carbon preparation procedure steps.

250 mg of MBAS was dissolved in 1 Liter of distilled water to make dye stock solutions. Five solutions with standard dye concentrations of 50, 100, 150, 200, and 250 mg/L were generated for treatment. These solutions were used to determine the isothermal properties and adsorption kinetics. The adsorption isotherms of methyl blue were tested on two types of activated carbon prepared at 30, 40, 50, 60 degrees Celsius. Experiments were carried out on the adsorption system separately for both prepared activated carbons, according to the variable parameters (carbon weight, adsorption time, and flow rate).
Figure **2** illustrates a diagram of the adsorption process.

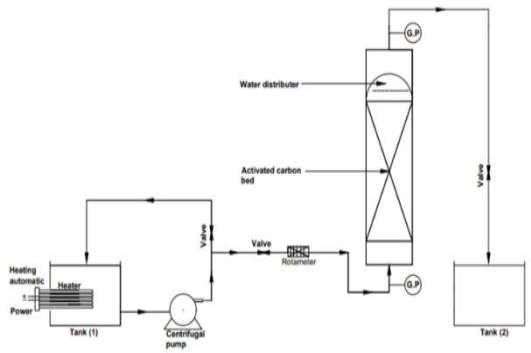

Figure 2. The diagram of the adsorption system.

2. Results and discussions

A comparative study was done for the adsorption of basal dyes on two types of prepared activated carbons. Methyl blue was used as basic dyes. Because adsorption is a surface phenomenon, improving the surface characteristics of activated carbon implies improving adsorption performance. Scanning Electron Microscopy has been utilized to evaluate the surface morphology of the manufactured "activated carbon cells" ("SEM, FEI Co., Model: Inspect S50, Netherlands, Brunner-Taller-Emette (BET) surface area (ASAP2020, Micromeritics, USA)").

2.1. Impact of the carbonization

Tars and low-vapor-pressure substances evaporate, whereas cellulose matter burns off as the carbonization process progresses. As a result, the carbonaceous structure has a greater surface area accessible for adsorption of adsorbable solutes. Figure 3 and Figure 4 show SEM images of carbonized wheat husks and peganum. The carbonization process increases the amorphous and porous properties of the two raw materials, albeit to varying degrees. Charred peganums are highly porous than charred wheat husks, having a random configuration of varied pore diameters. Also, it can be recognized that both carbonized materials contain agglomerates of carbonaceous materials that can be explained into more porosity by physical or chemical activation. The next stage was to treat the carbonized material with a solution of 4 molar concentrations of phosphoric acid. The phosphoric acid was used because previous studies proved its effectiveness in activating carbon.

These solutions promote the charred material's porous structure by melting the uncarbonized material and converting it into two water-soluble produces. The closest explanation was that peganum contains a high percentage of cellulose, and phosphoric acid attacks the lignin content of cellulose at a higher temperature. The treatment thus converts it to a water-soluble substance, which explains the lower weight of samples activated by phosphoric acid after the washing step.

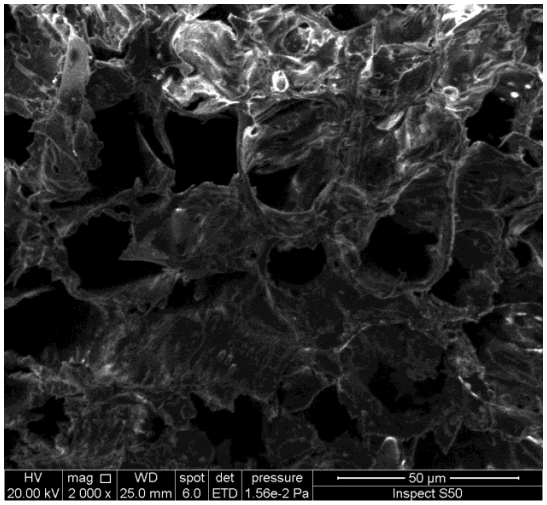

Figure 3. Scanning Electron Microscopy for carbonized peganum.

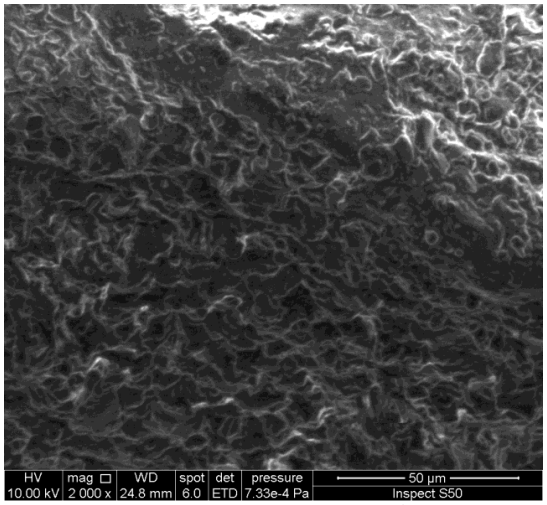

Figure 4. Scanning electron microscopy for carbonized wheat husks.

2.2. Impact of the activation process

During the activation process, elevated heat treatment and the influence of various chemical activating agents resulted in closed pore openings and decreased aggregation of carbon materials.

SEM pictures of activated carbon produced from peganum and wheat husks after phosphoric acid activation are shown in Figure 5 and Figure 6. The activation technique gives these carbonized materials more porous and well developed. However, there are some differences due to the varied raw materials and activating chemicals used.

The images demonstrate that the activated carbon made from the peganum has more uniform surfaces in a homogeneously arranged pattern with high porosity. In contrast, the activated carbon prepared from wheat husk material has a heterogeneous rough surface with random cavities of low porosity. Also, it can be seen that phosphoric acid activating agents produce

"activated carbon" with high density and various pore sizes but with a less regular layout.

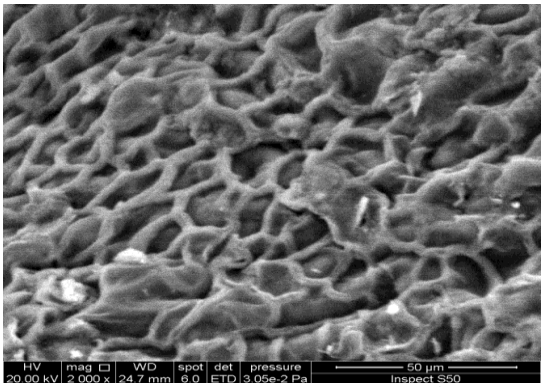

Figure 5. Electron Scanning Microscopy of peganum-based activated carbon activated by phosphoric acid.

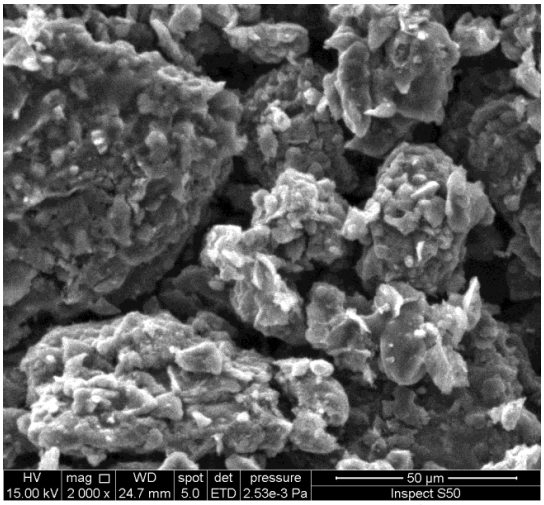

Figure 6. Electron Scanning Microscopy of wheat hust-based activated carbon activated by phosphoric acid.

When activated with phosphoric acid, the results reveal that the activated carbon prepared from peganum outperformed the one prepared from wheat husks. This variation in pores results in activated carbon, which provides peganum with superior absorbency for both basic dyes compared to wheat husks. Table 1 shows the characteristics of the manufactured activated carbon.

Table 1. Characteristic of the activated carbon.

Raw Material	Activating agent	BET surface area m^2/g	Pore type
Peganum	H_3PO_4	625	Meso-pore
Wheat Husks	H_3PO_4	550	Meso-pore

2.3. Effect of Temperature

The temperature impacts the extent of absorption of the MBAS, as shown in Figure 7 and Figure 8. The figures show that the increase in the adsorption temperature is accompanied by a decrease in the concentration of the adsorbed solute on the solid carrier. This finding agrees with previous literature. Therefore, it can be concluded that the gradual transition of the Langmuir equilibrium from the state of strong adsorption to weak adsorption as the temperature increases as a result of decreasing the constant equilibrium KL.

Therefore, adsorption at lower temperatures is preferred for two reasons. The first reason is because the activated carbon absorbs a relatively larger amount of dyes, and the second is because of the stronger adsorption of the activated carbon at low temperatures.

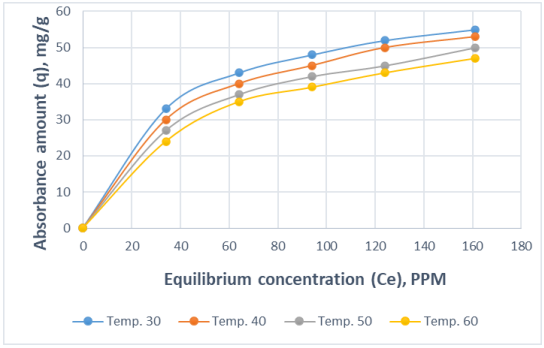

Figure 7. Isothermal adsorption of MBAS on wheat husk-derived activated carbon.

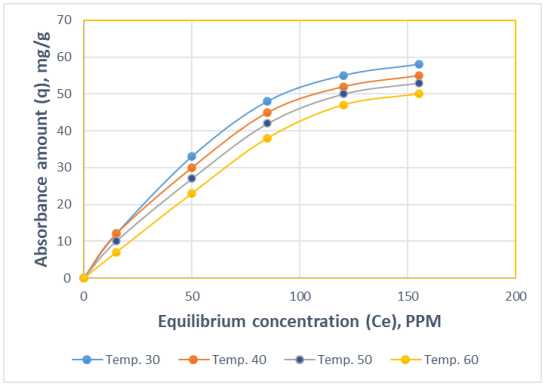

Figure 8. Isothermal adsorption of MBAS on peganum-derived activated carbon.

2.4. Effect of the changes of parameter on the adsorption results

2.4.1 The effect of the weight of activated carbon

The results (A4_A11) indicate that the weight of (10) g of wheat husks and benganum is the best weight for activated carbon because of the sufficient contact and saturation state between the activated carbon particles and the methyl blue dye, assuming the size of the cylinder in which the activated carbon was placed. The possibility of it being (15) gm is better for adsorption if a larger diameter cylinder is adopted.

Table 2. The average values of the experimental conducted to choose the best flowrate (constant adsorption, variable activated carbon weight and flowrate)

CE	ABS	W(g.)	T(hr)	F(l/min)
142.75	1.85	5	2	0.1
147.26	1.91	5	2	0.2
135.91	1.759	5	2	0.3
155.53	2.02	10	2	0.1
150.27	1.95	10	2	0.2
148.76	1.93	10	2	0.3
149.29	1.937	15	2	0.1
148.92	1.932	15	2	0.2
147.04	1.907	15	2	0.3

3.4.2. The effect of the flow rate

The results of the conducted experiments indicate that by increasing the flow velocity, the residence time between the adsorbent material and the methyl blue dye will decrease and thus help in not reaching the saturation state between the dye and the prepared carbon, which leads to a reduction in the adsorption process of the dye.

3.4.3 The effect of the time

The results of the obtained experiments (A4_A11) indicate that the contact time after (2) hours to (3) hours is the best because of the saturation state of the activated carbon molecules.

Table 3. The average values of the experimental conducted to choose the adsorption time (constant flowrate, variable activated carbon weight and adsorption time)

CE	ABS	W(g.)	T(hr)	F(l/min)
138.99	1.8	5	1	0.1
142.75	1.85	5	2	0.1
144.25	1.87	5	3	0.1
149.52	1.94	10	1	0.1
155.53	2.02	10	2	0.1
156.06	2.027	10	3	0.1
146.51	1.9	15	1	0.1
149.29	1.937	15	2	0.1
149.59	1.941	15	3	0.1

Table 4. The average values of the experimental conducted to choose the adsorption time (constant flowrate, variable activated carbon weight and adsorption time)

CE	ABS	W(g.)	T(hr)	F(l/min)
142.75	1.85	5	1	0.2
147.26	1.91	5	2	0.2
148.76	1.93	5	3	0.2
147.26	1.91	10	1	0.2
150.27	1.95	10	2	0.2
151.62	1.968	10	3	0.2
146.89	1.905	15	1	0.2
148.92	1.932	15	2	0.2
149.67	1.942	15	3	0.2

4. Conclusions

The current work demonstrates that activated carbon may be employed as an adsorbent to eliminate basic methyl blue dye from aqueous solutions in a continuous flow system. The porous activated carbon can be made from the peganum plant and wheat husks. The results demonstrated that activated carbon made from peganum and wheat husks activated with phosphoric acid had a significant adsorption capacity, a good porous architecture, and a massive surface area. The flow rate, carbon weight, and adsorption time were the parameter of the flow rate, carbon weight, adsorption time. Studying these parameters revealed that the adsorption data are fitted correctly by Langmuir isotherm for methyl blue dye when using activated carbon from peganum and wheat husks. It shows that the adsorption takes place in a single layer, and the "pseudo-second-order" kinetic model represents the kinetic data significantly. The readings obtained from the adsorption process within the adsorption system indicate that the initial concentration, carbon weight, flow rate, temperature, adsorption time, and the space allocated for carbon in the adsorption tube inside the adsorption system are factors that strongly affect the adsorption properties of the fix bed columns.

3. Acknowledgment

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