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Treatment of Dye-Loaded Wastewater with Activated Carbon from Date Palm Leaf Wastes

Yasamin Majedi,[1] Eman Alhilali,[2] Mariam Al Nehayan,[2] Arwa Rashed,[1] Sarah Shwkat Ali,[1] Nathir al Rawashdeh,[3] Thies Thiemann,[2]* Ahmed Soliman[2]*

[1] Department of Chemical Engineering, Faculty of Engineering, United Arab Emirates University, Al Ain, Abu Dhabi, United Arab Emirates

[2] Department of Chemistry, Faculty of Science, United Arab Emirates University, Al Ain, PO Box 15551, Abu Dhabi, United Arab Emirates

[3] Department of Applied Chemical Sciences, Jordan University of Science & Technology, Irbid 22110, Jordan

E-Mails: thiesthiemann@yahoo.de; thies@uaeu.ac.ae; a.soliman@uaeu.ac.ae

* Author to whom correspondence should be addressed; Tel.: +971-56-692-5943; Fax: +971-3-767-1291

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Abstract: The adsorption of three different dyes on similarly derived carbon materials from date palm leaves was studied. The adsorption kinetics and equilibrium data were investigated based on dyes adsorption tests. The break-through time was noted with a UV-VIS spectrometer to determine the maximum capacity of the date-palm leaf derived carbon material. The types of surface groups present on the carbon surface of the activated date palm leaf derived material were studied. Also, the adsorption will be carried out by dynamic process in a flow-through column and the dynamic adsorption capacity and breakthrough curve were determined.

Keywords: adsorption, dye, activated carbon, agricultural waste, water treatment

1. Introduction

Many industrial wastewaters contain organic pollutants as a result of the used manufacturing processes. Especially, dyestuff from the textile and leather working industries as well as from the paper-making industry poses a problem. Dyes are also used in the plastics, pharmaceutical, food and cosmetics industries [1]. It has been estimated that over 10000 types of dyes are used with an overall annual production of 7 X 10^5 tons [1-4], of which 200.000 tons are discharged into the environment, mostly through the waste-water [4].

Many of the synthetic dyes are difficult to degrade naturally. Thus, they are often resistant towards light, temperature and naturally occurring bacteria [5,6]. Amongst all, reactive azo dyes are most problematic due their excess consumption and high water solubility. The recalcitrance of the dyestuff to biodegradation is apparent from the fact that these compounds escape various stages of wastewater treatment plants and finally enter into the environment. The presence of even a small fraction of dye in water (less than 1 ppm) is highly visible due to the color and affects the aesthetic merit of the streams and other water resources. They also interfere with the penetration of light in water bodies and may affect the aquatic biota. Some of the dyes and/or their degradation products have proved to be toxic, mutagenic and/or carcinogenic in nature [5-7].

Various methods such as adsorption[8], coagulation[9], advanced oxidation[10], and membrane separation[11] are used in the removal of synthetic dyes from wastewater. Adsorption is one of the most effective processes of advanced wastewater treatment [8].

Activated carbon is deemed to be one of the best sorption materials. Because of the expense of carbon sources for activated carbon, studies have been started to investigate the suitability of different agricultural wastes as such a source[12], where admittedly sometimes the uncarbonized agricultural waste itself has been used as the sorbent material. Thus, activated carbon from cassava peels[13], coconut tree sawdust[14], cocoa shells[15], among others, have been used to adsorb dyes.

Date palm (*Phoenix dactylifera* L.) is a major agricultural crop in the UAE and the GCC countries. 3 million tons of palm leaflets, as agricultural waste, are produced annually in the Gulf States. Burning in the field is a common practice that poses environmental air pollution. The purpose of this research was to prepare dehydrated, activated carbon from date palm leaflets as an alternative to commercial activated carbon as a potential, cost effective adsorbent, for the treatment of industrial waste water with the aim of studying the extent to which date palm tree derived materials can adsorb dye-stuff as an organic pollutant as a part of waste water treatment and management.

2. Results and Discussion

2.1 Activated Carbon

The ash content of the dried date palm leaves was found to be around 10% (the ash content was determined from an ashing experiment at 600 ^{o}C). **Table 1** shows the weight loss of the samples after they have been heated for 24h at the given temperatures. **Figure 1** shows two representative infrared spectra, one for a carbon sample activated at 250 ^{o}C and the other for a carbon sample activated at 450 ^{o}C. The infrared of the sample activated at 250 ^{o}C shows a complex pattern, pointing to a complexity of functionalities on the surface and potentially within the material. Indicative for a carbonyl or most likely a carboxyl group is the absorption band at 1720 cm^{-1}, which would signify these functionalities to be present on the surface of the material. Peaks at 2919 and 2850 cm^{-1} suggest C-H, denoting that alkyl functions or an alkyl backbone is still present in the material. The infrared of the sample activated at 450 °C is devoid of the formerly discussed bands. Peaks at 673, 613, 595 cm^{-1} may indicate that aromatic units are still present within the material. This observation is in accord with the significant loss of carbon in the sample activated at 450 °C as compared to the sample activated at 250 °C. The carbon loss would most likely mean a loss of all surface carboxyl groups at 450 °C. The absorption band at 1721 cm^{-1} is less pronounced in carbon samples activated at 300 and 350 °C and is already totally absent with the carbon activated at 400 °C. Carbon activated at 500 °C is very light in color, indicating the samples to consist mostly of ash. **Table 2** shows the acidity/alkalinity of the carbon samples, which was measured upon adding 0.1 g of sample to deionized water (25 mL) and leaving at rest for 24h. It is evident from the table that with increase of activation temperature the alkalinity of the sample increases. This would make sense as the functional groups created by the oxidative sulfuric treatment, as there are carboxylic acid, sulfonic acid and analogous groups would be extruded at the higher temperatures. At the same time it may be that the inorganic components would also partially calcinate so that any carbonates would transform to the more basic oxides or hydroxides.

Figure 1. Infrared spectra for the carbon sample activated at 250 °C (left) and the carbon sample activated at 450°C (right)

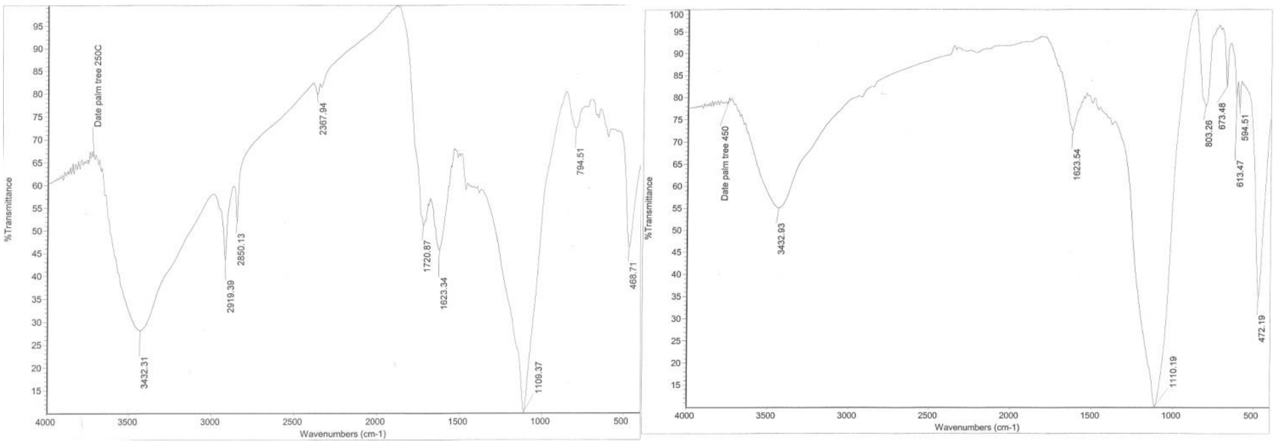


Table 1. The weight loss before and after heating activated carbon (AC) samples

Sample No.	Oven temperature (°C)	Mass of AC before heating (g)	Mass of AC after heating (g)	Loss Percentage (%)
1	250	3.026	2.256	25.4
2	300	3.066	1.696	44.7
3	350	3.866	1.795	53.6
4	400	4.566	2.114	53.7
5	450	4.406	1.215	72.4

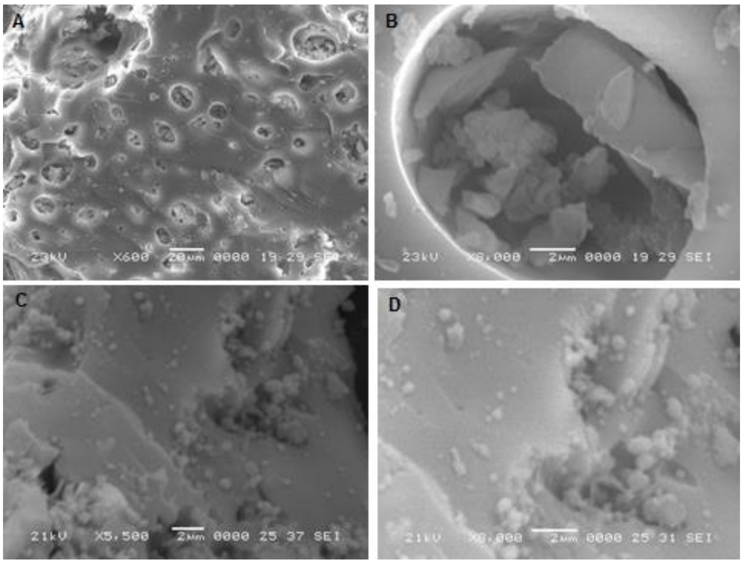
Distilled water (25mL) with 0.1g of different activated carbon, treated at different temperatures, were left in flasks for a day and their corresponding pHs were measured the next day. Results are listed in **Table 2**.

Table 2. pH of AC treated at different temperatures.

Sample No.	**AC treated temperature (°C)**	**pH**
1	200	2.78
2	350	5.21
3	500	8.00

For one sample the surface area of a carbon activated at 250 °C was calculated from an absorption experiment to be 313.5 m^2/g. Also, the texture of the sample prepared at 250 °C was studied using a scanning electron microscope (Figure 2).

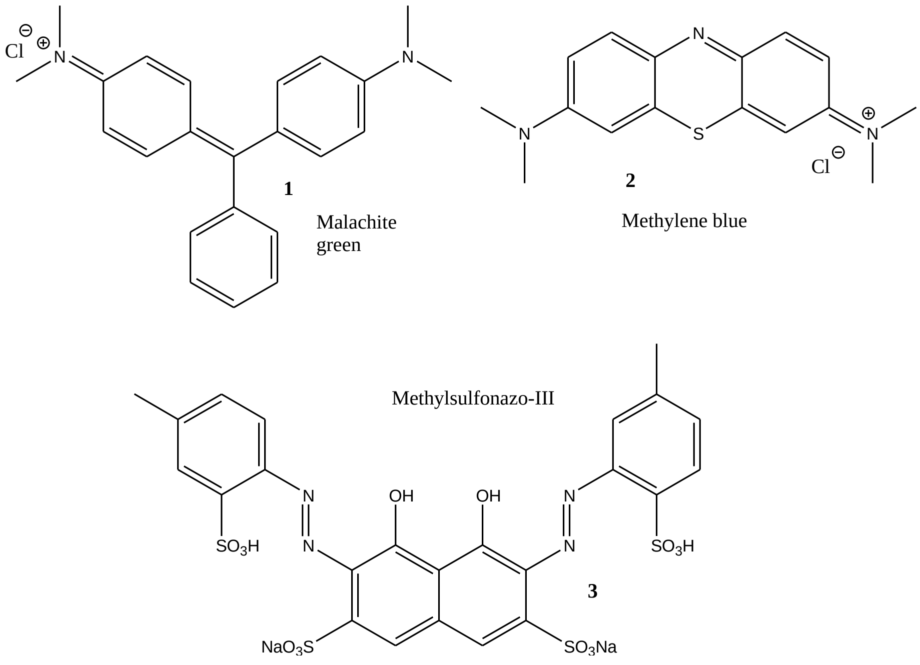
Figure 2. SEM micrographs of unloaded (A and B) and lead(II)-loaded AC (C and D) (A: unloaded AC x600, B: unloaded AC x8000; C: loaded-lead(II) AC x5500, and D: loaded-lead(II) AC x8000).



2.2. Adsorption of dyes on the activated carbon

Three dyes were chosen for this study: malachite green (**1**), methylene blue (**2**), and methylsulfonazo-III (**3**). Malachite green (**1**) is a triphenylmethane based dye, which is used in the textile and leather industry and which has been implicated in water pollution (Figure 4). Methylene blue, 3,7-bis(dimethylamino)phenolthiazin-5-ium chloride (**2**), is used for medical purposes. Methylene blue (**2**) and malachite green (**1**) have some communality in that they are both reasonably large organic cations, sharing an iminiumquinoid unit. Methylsulfonazo-III (**3**), on the other hand is the disodium salt of a tetrasulfonic acid incorporating two azo units and two phenolic units. Importantly, the organic residue is a dianion.

Figure 3. Structures of different dyes.



1 Malachite green

2 Methylene blue

3 Methylsulfonazo-III

2.2.1 Malachite green (MG) dye

An initial calibration graph of absorbance versus concentration was constructed at the absorption maximum at a wavelength of λ = 300 nm through the use of Beer-Lambert law,

$A = \varepsilon bc$ ………………………………………………………………………………………………….......

where A is the absorbance, ε is the molar absorptivity (L mol^{-1} cm^{-1}), b is the path length of the sample (cm), and c is the concentration of the compound in solution (mol L^{-1}).

The adsorption isotherm at 25 ^{o}C has been studied for malachite green to assess the efficiency of the adsorbent to remove methylene blue dye from aqueous solution. Figures 4 and 5 show the effect of dye concentration and time of agitation on the adsorption of the dye on the activated carbon. From these figures, it was noted that the adsorption process reaches an equilibrium at 120 min agitation time. The adsorption capacity of the activated carbon increases with increasing initial dye concentration. The adsorption capacity was calculated according to equation (1), where, C_i and C_e are the initial and equilibrium concentrations of the dye, V is the volume of the aq. dye solution (L), and w is the weight (g) of the palm leaf activated carbon adsorbent.

$$q_e = \frac{(C_i - C_e)V}{w} \qquad (1)$$

After 4 days, we reach a maximum loading of 47 mg malachite green per g carbon (Figure 4).

Figure 4. Adsorption isotherm of MG on activated carbon at 25° C (equilibrium after 4 days).

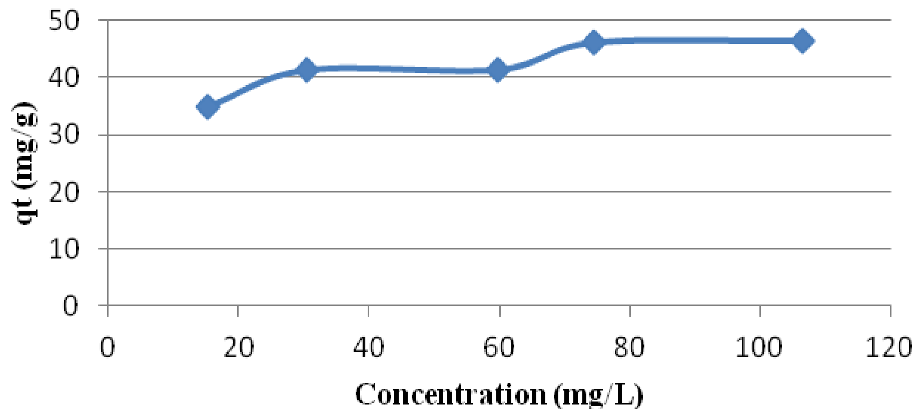
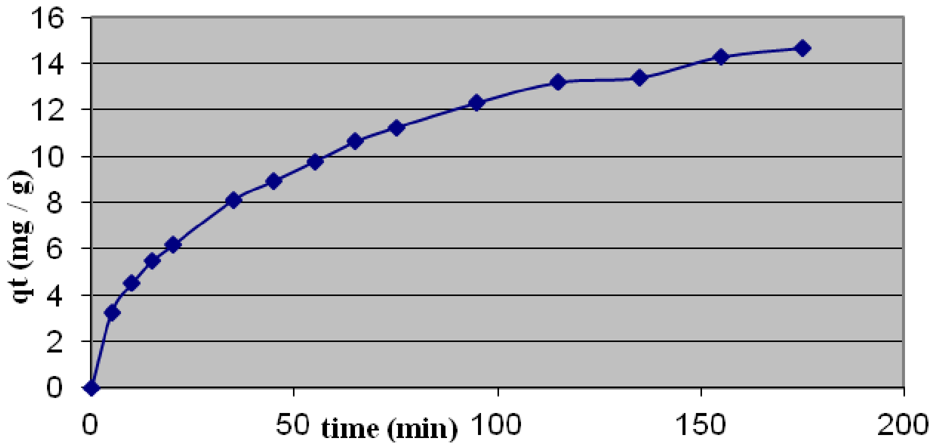


Figure 5. Effect of time on adsorption of MG on date palm leaves.



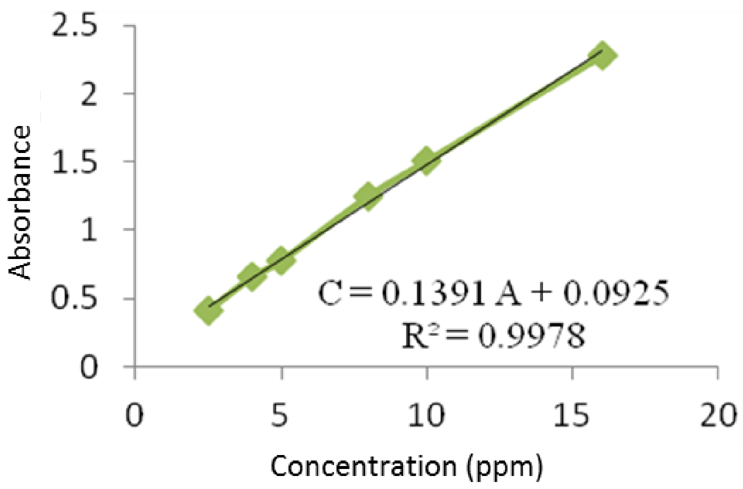
2.2.2. *Methylene blue (MB)*

The adsorption isotherm at 25 °C has been studied for methylene blue to assess the efficiency of the adsorbent to remove methylene blue dye from aqueous solution. An initial calibration graph of absorbance versus concentration was constructed at the absorption maximum at a wavelength of λ = 664 nm through the use of Beer-Lambert law,

$$A = \varepsilon bc \quad \ldots\ldots (1)$$

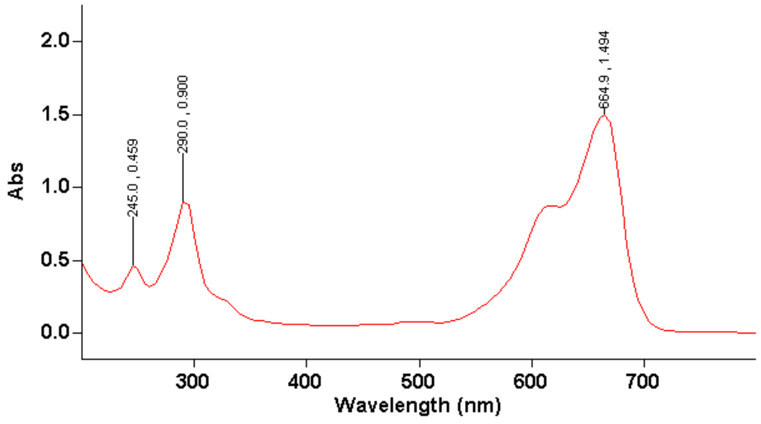
where A is the absorbance, ε is the molar absorptivity (L mol^{-1} cm^{-1}), b is the path length of the sample (cm), and c is the concentration of the compound in solution (mol L^{-1}). Figure 6 shows the calibration curve for methylene blue.

Figure 6. Methylene blue calibration curve.



0.1 g charcoal, treated at 200 °C, was added to aqueous solutions (50 mL) of different concentrations of dye. UV-Vis spectrometry was used to monitor the absorbance spectra of the methylene blue solutions. The absorption spectra of all methylene blue solutions showed an absorption maximum at λ_{max} = 664.9 nm. **Figure 7** shows the adsorption spectra an aqueous solution with 10 ppm methylene blue.

Figure 7. Adsorption spectra of the 10 ppm sample.



The effect of adsorbent mass on the amount of dye adsorbed was determined by using 250 ml of dye solution of an initial dye concentration of 30 ppm with 2 g of adsorbent charcoal in the orbital shaker (250 RPM) at room temperature. The samples were collected every hour and were returned back to the flask on the shaker after analysis. The samples were centrifuged and the supernatant solution was analyzed at a wavelength of 665 nm using a spectrophotometer. **Figure 8** shows the adsorption spectra of the samples collected from the shaker after different time periods of shaking.

Figure 8. Adsorption spectra of the samples collected after different time intervals from the shaker.

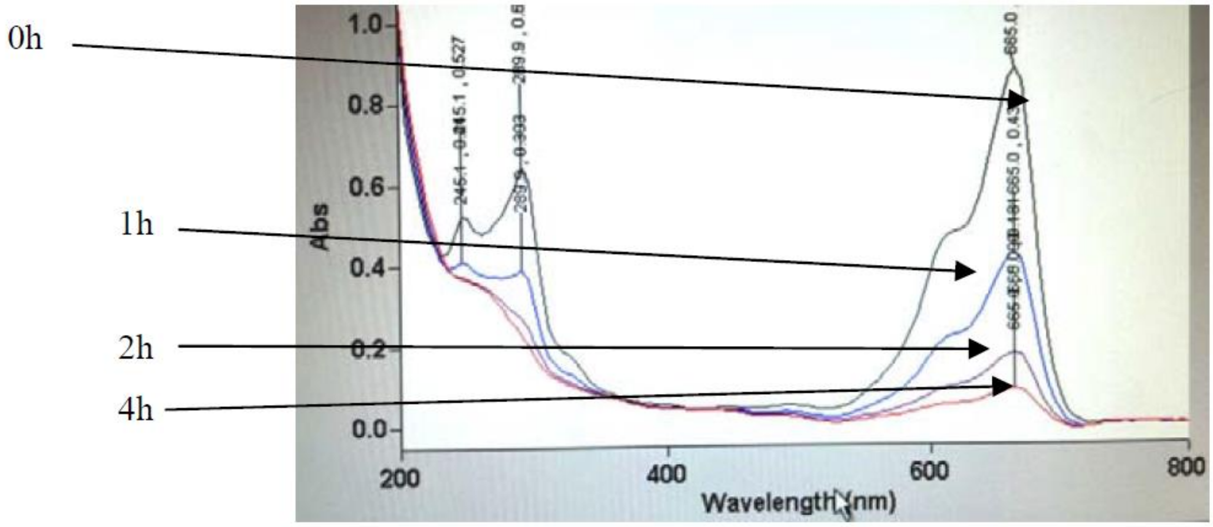


Figure 9. Adsorption isotherm of methylene blue on charcoal

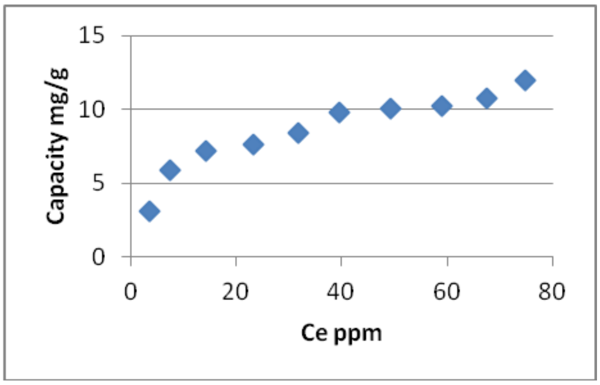
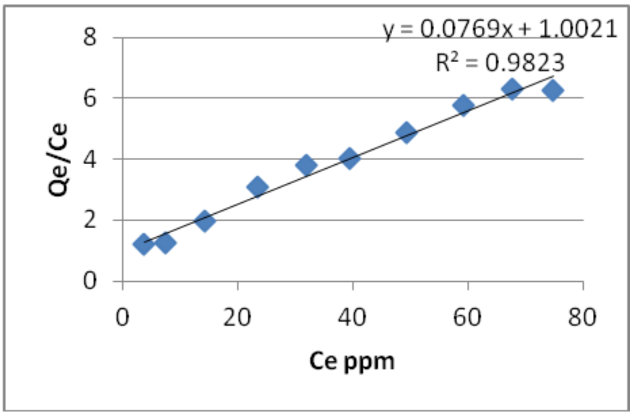


Figure 10. Langmuir Adsorption Isotherm



The equilibrium absorption data was checked by applying the two most common isotherm models – the Freundlich isotherm [16], expressed by eq. (2), and the Langmuir model, expressed by eq. 3 [17]. The obtained results for the adsorption of methylene blue to activated carbons fit best with the Langmuir isotherm, with a correlation coefficient of 0.9823, while the fit of the data with the Freundlich isotherm has a correlation coefficient of 0.91. From this data, we calculated the theoretical adsorption capacity to be 13.2 mg methylene blue / g activated carbon. Nevertheless, the adsorption capacity of the activated carbon for methylene blue is less than for malachite green.

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (2)$$

$$\frac{C_e}{q_e} = \frac{1}{K q_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

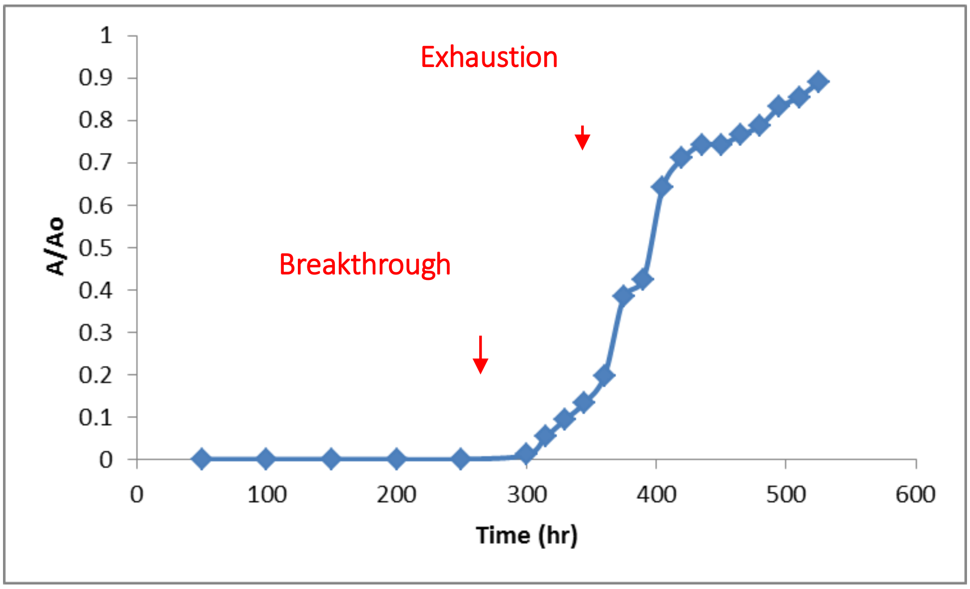
where C_e (mg L^{-1}) is the equilibrium concentration of the adsorbate in solution, q_e (mg g^{-1}) is the amount adsorbed per unit mass of adsorbent at equilibrium, q_{max} (mg g^{-1}) is the Langmuir adsorption constant, representing the maximum adsorption capacity. K_f and n are the Freundlich constants related to the adsorption capacity and adsorption intensity, r. K (L mg^{-1}) is the Langmuir adsorption constant.

2.2.3. Methylsulphonazo (III)

Lastly, the methylsulfonazo-III dye was not adsorbed by the AC, most likely because the dye is anionic and the AC has negative charge on its surface.

2.3. Dynamic experiments and regeneration of the carbon adsorbent in the case of methylene blue.

Figure 11. Flow-through adsorption of methylene blue. Flow rate 0.5 mL/min.



From **Figure 11**, it is noted that the dynamic adsorption capacity is 27.5 mg/g and the break-through time is 315 hours and the exhaustion time is 400 hours. With 4 g of carbon 9.45 L of water contaminated with methylene blue (10 ppm) could be purified.

3. Experimental Section

3.1. Materials and methods

3.1.1. Adsorbent

Naturally collected date palm leaflets from the United Arab Emirates University Campus at Maqam, Al Ain, Abu Dhabi, UAE, were cut into small pieces, washed with deionized water and air-dried for 24 hours. The dried small pieces were soaked in 25% (w/w) H_2SO_4 for 24 hours. The treated leaves were washed carefully with deionized water and dried at room temperature. The black mixture was filtered using a porcelain Buchner funnel under vacuum. Then, the leaf mass was transferred to an oven for carbonization at various temperatures starting at 250°C ± 1°C for 24 hours. The activated carbon was allowed to cool to room temperature and repeatedly washed with deionized water and 1% aq. $NaHCO_3$, respectively, until the pH of supernatants remained constant at around pH 6.0. Then, the obtained activated carbon was dried at different temperatures for 2 hours to remove residual moisture (**Table 1**), ground and sieved by standard steel meshes to select particles between 300 µm and 425 µm in size. The carbon was then stored in dry, clean and well closed polyethylene centrifuge tubes for further use. **Figure 12** shows the palm leaves after activation.

Figure 12. Palm leaves before and after activation

Infrared spectra were taken for the carbons activated at different temperatures. Weight-loss of the carbons was determined. The pH values of the activated carbon in deionized water were measured. The surface area of the activated carbon was estimated from absorption isotherms of methylene blue.

3.1.2. Reagents

All chemicals used in this project were of analytical reagent grade. Deionized water was used in all experiments. A 25% (w/w) H_2SO_4 solution was prepared by diluting appropriate amounts of concentrated H_2SO_4 with water.

3.2 Adsorption experiments

Adsorption experiments were carried in the batch-technique. For this, activated carbon was shaken in a solution of aqueous dye of various concentrations. The agitation rate was 250 rpm. Samples were collected for analysis using a Cary-50Conc-UV-spectrophotometer. Before measurement the sample was centrifuged (3500 rpm, Beckman Model TJ-6) to avoid any residual carbon particles in the UV measurement.

Isotherm studies have been undertaken to assess the efficiency of the adsorbent to remove malachite green (MG) dye from aqueous solution. A stock solution of MG dye (MW =364.9 g/mol) was prepared in deionized water with the concentration of MG dye being 1000 ppm . Standards (20-40-60-80-100 ppm) were made from the stock solution by dilutions using 250 ml volumetric flasks and an appropriate pipette. An initial calibration graph of absorbance versus concentration was constructed at maximum wavelength of λ = 300 nm through the use of Beer-Lambert law. 0.05 g charcoal, treated at 200 °C, was added to 20 mL of different concentrations of dye solutions. UV-Vis spectrometry was used to monitor the absorbance spectra of the MG solutions. The absorption spectra indicated that MG at different concentration exhibited the maximum absorption at the same wavelength, λ = 300 nm.

Also, the adsorption isotherm at 25 ^{o}C has been studied for methylene blue to assess the efficiency of the adsorbent to remove methylene blue dye from aqueous solution. A stock solution of methylene blue dye (MW = 319.65 g/mol) was prepared in deionized water with the concentration of methylene blue being 2000 ppm (1 g of methylene blue with 500 ml of deionized water). Standards (10-100 ppm) were made from the stock solution by dilutions using 500 ml volumetric flasks and an appropriate pipette. An initial calibration graph of absorbance versus concentration was constructed at the absorption maximum at a wavelength of λ = 664 nm

For dynamic experiments, with the help of a peristaltic pump (MasterFlex C/L), we injected a dye solution (methylene blue, 10 ppm) through a steel column (length 10 cm, column inner diameter 0.5 cm) filled with activated carbon (4 g, glass wool or cotton was added on top, weighed down by glass-beads [0.5 g], inflow from the bottom of the column), at a flow-rate of 0.5 mL/min. Dye concentration was measured either by taking samples at given times or by a continuous flow-through UV-cell. For regeneration experiments, an aq. solution of HNO_3 (0.1 – 0.5 M) was injected into the column. The authors recycled the column 5-times for further use.

4. Conclusions

Activated carbons were obtained from date palm leaves after impregnation with sulfuric acid and thermolysis at different temperatures. It could be shown by infrared spectroscopy that the surface of the activated carbons were heavily functionalized. These functional groups were lost upon thermolysis of the material at 400 ^{o}C and above. At the same time inorganic components in the carbons most likely underwent partial calcination.

The sorption of dyes on the palm leaf derived activated carbons seems to be very promising. Malachite green is adsorbed better than methylene blue. The anionic dye methylsulphonazo-III did not show appreciable adsorption.

Conflict of Interest

The authors declare no conflict of interest.

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