Received: 06 February 2022 | Revised: 11 March 2022 | Accepted: 15 March 2022
DOI: 10.22034/ecc.2022.332809.1356
Eurasian Chemical Communications SAMI

FULL PAPER

Preparation and characterization of nano-carbon as an adsorbent for industrial water treatment

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This study included the preparation and characterization of carbon nanoparticles prepared from environmentally friendly plant sources, namely a mixture of walnut shells and date kernels, as diagnosed by atomic force microscopy (AFM) and transmission electron microscopy (TEM), as the results showed that the prepared carbon particles were within nano-size and square in shape, in addition to studying and determining the wavelength of the dye [EBT] under study. It was 516 nm, and the adsorption efficiency of the nano-carbon prepared for the dye was 95.0%. With an ideal weight of 0.5 g, it was found that the equilibrium time was 20 minutes. The results showed that the adsorption efficiency increased at the natural pH of the dye. The thermodynamic functions of adsorption were also calculated, and it was found that the adsorption system was automatic (ΔGº) and less random (ΔS°) and exothermic ((ΔHº) at temperature (Tk).

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KEYWORDS

Nano-carbon; eriochrome; adsorption; nano; pollution.

Introduction

Nanotechnology is a very fast-growing field that has been used almost all over the world in a large number of different economic products through the production of nanoparticles, nano-products with new physical, chemical and size-related properties that are significantly different from bulk [1]. Nanotechnology is an interdisciplinary basic science with its roots in almost all fields of science and technology, dealing with the design and production of objects or structures at the very small level and at the nanometer level by one billionth of a meter [2]. This technology has been used in a wide range of applications such as biomedical devices, medicine, cosmetics, environmental treatment, food, and waste water [3].

The hopes are now set on treating heavy water and sewage water by exploiting the potentials inherent in this technology. The water problem in this case is constantly exacerbating, and the problem of river pollution as a result of mixing with industrial pollutants exacerbates water problems. And that nanotechnology can provide a solution in this vital field through new innovative and unconventional water treatment methods, as well as desalination of salty water using this technology. The American physicist Robert Rudnitsky, the head of a working group concerned with nanotechnology, says: Water purification and desalination have been taking place for decades and using the same methods used today [4]. According to the World Health Organization (WHO), the lack of clean water and sewage water kills 1.6 million children annually [5]. One of these methods is adsorption, which can be defined as the phenomenon of gathering a substance in the form of atoms, molecules or ions on the surface of another substance, and monomolecular adsorption is when adsorption is limited to the formation of one molecular layer on the adsorbing surface or multimolecular when it is limited to the formation of several molecular layers on the adsorption surface [6]. Adsorption is a characteristic feature of many manufactured materials such as zeolite and activated charcoal [7].

Water pollution is one of the problems of the current era due to the difficulty of getting rid of these components due to their different forms dissolved in water for a long time [8]. The adsorption of carbon dioxide (CO2) on activated carbon (AC) prepared from olive trees has been investigated by using a fixed bed adsorption apparatus. The adsorption equilibrium and breakthrough curves were determined at different temperatures 30, 50, 70, and 90°C in order to investigate both kinetic and thermodynamic parameters. There are many different factors that affect adsorption, including the nature of the adsorbent surface, the nature of the adsorbent, the concentration of the adsorbent, temperature, as well as PH [9]. This increasing interest in the adsorption process is due to its high efficiency in the adsorption of toxins and dyes and its low cost [10]. There are many studies in this area [12,11].

The current study involves the synthesis of activated charcoal from dates kernels and walnuts shells. Then, the prepared materials were characterized. The activity of these materials was screened via removing eriochrome dye by applying adsorption phenomenon.

Instruments

The devices in Table 1 below were used to complete this study.

TABLE 1 The devices used in the research

No.	the device name	Device type	The workplace of the device
1.	UV-Vis Spectrophotometer	Shimadzu.PC1650 Duble beam	Research laboratory/ Department of Chemistry/ Samarra University
2.	sensitive electric balance	Sartorius Lab. +0.0001g,BL210S	Research laboratory/ Department of Chemistry/ Samarra University
3.	drying oven	Termaks-S-NO) 104544)	Research laboratory/ Department of Chemistry/ Samarra University
4.	burning oven	Carbolite-England its max 1200C0))	Research laboratory/ Department of Chemistry/ Samarra University
5.	Water bath with temperature controlled agitator	YCW 012S	Research laboratory/ Department of Chemistry/ Samarra University
6.	Atomic force microscopy (AFM)	SPM-AA300 Advanced Angstrom Inc.	Research laboratory/ Department of Chemistry/ Samarra University
7.	pH meter	Hanna -211	Research laboratory/ Department of Chemistry/ Samarra University
8.	transmission electron microscopy (TEM)	Transmission Electron Microscope	Research laboratory/ Department of Chemistry/ Samarra University

The chemicals used in the preparation of activated charcoal from a mixture of date kernels and walnut shells are characterized by high purity. Table 2 shows the chemical formulas of the materials used.

TABLE 2 The chemicals used in the research and some of its properties

No.	Chemicals	Molecular formula	molar mass	supplying company
1.	Hydrochloric acid	HCL	36.5	H.D.B
2.	SODUIM hydroxide	NaOH	40	Merck
3.	Deionized water	H_2O	18	Samarra, Lab pharmaceutical
4.	eriochrome dyes	$C_{20}H_{12}N_3NaO_7S$ PH(7.14)	461	Fluka company

Preparing the raw materials

A quantity of date kernels (Khestawi) and a quantity of walnut shells were taken and washed with warm water for 30 minutes to clean the impurities stuck in them, and then washed with non-ionic distilled water three times and dried in an electric oven (drying oven) at a temperature of (120˚C) for two hours. To get rid of moisture, Figures 1 and 2 show the date kernels and walnut shells used in the research.

FIGURE 1 date kernels

FIGURE 2 Walnut shells

Carbonization and chemical activation processes

100g of date kernels and 100g of walnut shells were weighed after they were completely free of moisture and then placed in the incinerator for two hours at a temperature of (650˚C). After that, it was left to cool, and then it was taken out of the burning oven and crushed well, and 50ml of HCl solution was added to it at a concentration of (0.1) and mixed well and placed in the burning oven again for an hour and a half at a temperature of (550˚C) under N_2 flushing. charcoal mixture was taken out from the charcoal mixture out of the burning oven and it was cooled and then washed several times with non-ionic distilled water and filtered several times with measuring its pH with the addition of (HCl) to it in the form of drops because it is highly alkaline until it became (PH=7). Then it was dried at a temperature of (110C˚) for three hours and then sieved to get a fine powder of nano-activated charcoal [14,13]. The prepared charcoal was characterized using atomic force microscopy and transmission electron microscopy.

Determination of λ_{max} for eriochrome black dye (EBT)

To determine the maximum wavelength for EBTdye, a certain concentration of the dye under study must be prepared for a solution of dye (EBT) that shows highest absorption using a UV-Vis spectrophotometer within the wavelengths (200-800) through a quartz cell that It should be (1cm) thick to find out the maximum wavelength (λ_{max}) of the EBT dye.

Construction of calibration curve for EBT

Eight dilute aqueous solutions were prepared in 10ml volumetric bottles of the standard solution of EBT dye, then the absorbance values of the eight solutions of EBT dye were measured. This process was carried out after zeroing the value of the device using the solvent (water) as a reference (blank) at the greatest wavelength that was drawn as shown in Figure 3 in the results and discussion based on Beer-Lambert law [15].

Adsorption of EBT dye

Adsorption of EBT dye used in industrial applications on the surface of activated charcoal prepared from a mixture of dates kernels and walnut shells was studied by studying the effect of time and the effect of weight of the prepared activated charcoal, and temperature, and after determinin the equilibrium time of dilute solutions prepared from the standard solution of EBT dye.

Effect of Time on adsorption of EBT dye

The equilibrium time was determined by the following steps:

a) A dilute (0.0002M) solution of the standard solution of Eriochrom Black-T was prepared in a 50ml volumetric vial; b) (0.5g) of prepared activated charcoal (adsorbent material) was added to the dilute solution of EBT dye; c) the solution was put in a water bath equipped with a vibrator at laboratory temperature (22˚C) and at a speed of 140 (cycle/min); finally, the solution was filtered at different times, 5,10,15,20,25,30 minutes, respectively, and then the absorbance values of the filtrate were recorded at each of these specific times using a UV-visible spectrophotometer as shown in Table 3.

Effect of the weight of prepared activated charcoal on EBT dye adsorption

The following experiment was conducted to find out the effect of weight on the adsorption process: a) Three volumetric bottles of 50ml capacity were prepared containing dilute solutions of (0.0002M) from the standard solution of EBT dye; b) three different weights of the prepared activated charcoal (adsorbent material) were taken, that were (0.1g), (0.5g) and (0.7g), respectively, and added it to the three dilute solutions of EBT dye; c) the solutions of different weights of activated charcoal were placed in a water bath equipped with a vibrator at a speed of (140 cycles/ min) and at laboratory temperature (22˚C), and when the equilibrium state was reached at (20min); d) all the solutions were filtered and the absorbance was measured for them by a device UV-Vis spectroscopy as shown in Table (4) in the results and discussion. The study was carried out using fixed concentrations of EBT dye and a wavelength of (516nm), and it was found that the optimum surface weight is (0.5g) [16].

The effect of pH on dye removal

Effect of pH on dye adsorption was investigated at a natural pH (pH = 7.1) and the adsorption was then studied, so the adsorption process of the solutions was measured at (pH = 2) and at (pH = 9); pH of solution was adjusted for each case. A solution was added by adding sodium hydroxide (NaOH) at a concentration of (0.1M) and hydrochloric acid at a concentration of (0.1M) using a pH Meter to adjust the required pH, then the solution was shaken by a vibrator after adding (0.5g) of activated charcoal and measuring the absorbance at the wavelength of maximum adsorption of the used dye, considering the greatest percentage.

Effect of temperature on EBT dye adsorption

To find out the nature of the studied system through the effect of temperature, we went through the following steps: a) In a volumetric bottle of 50ml capacity, a dilute solution of (0.0002M) of the standard solution of (EBT) dye was placed; b) (0.5g) of the prepared activated charcoal was added to the diluted solution of EBT dye, and the solution was left in a water bath equipped with a temperature-controlled vibrator until an equilibrium time reached 20 minutes at different temperatures (35˚C, 45˚C, 22˚C, 25˚C); c) then, the solution was filtered at the equilibrium time, that is, every 20 minutes and at each temperature, and the adsorption efficiency was calculated by measuring the absorbance for each temperature [11].

Results and discussion

Diagnosing the activated charcoal surface

The surface of the prepared activated carbon was diagnosed by atomic force microscopy (AFM) and transmission electron microscope (TEM).

Activated carbon can be defined as a porous black solid substance that is tasteless and odorless. It is distinguished from ordinary coal by its ability to remove impurities and purify water, as well as to remove cases of drug poisoning through the adsorption process. This activated charcoal was prepared from environmentally friendly raw materials, namely walnut shells and date kernels together by mixing them, grinding them and burning them. Figure 3 shows the prepared activated charcoal under study compared with the literature.

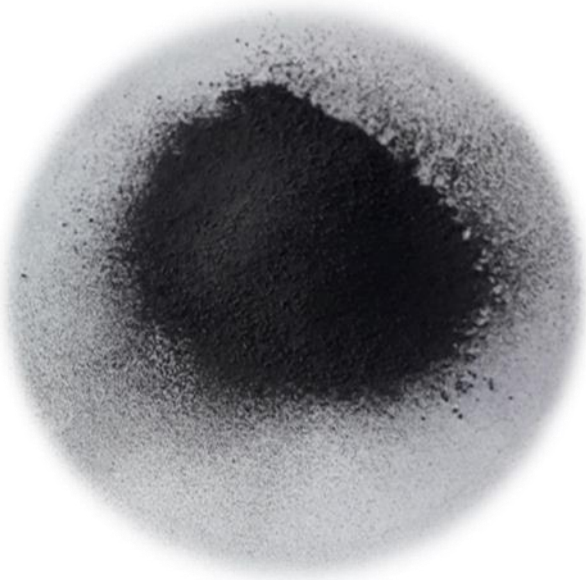

FIGURE 3 Prepared nano carbon

Characterization of activated charcoal with atomic force microscopy (AFM)

The atomic force microscope is an important measuring tool with a superior analytical ability. It is considered one of the most common microscopes for measuring, zooming and moving at the nanoscale [17] because it has a high capacity, as the image appears on the sample surface in a three-dimensional and two-dimensional form, nano and micro and with different magnification power as shown in Figure 4.

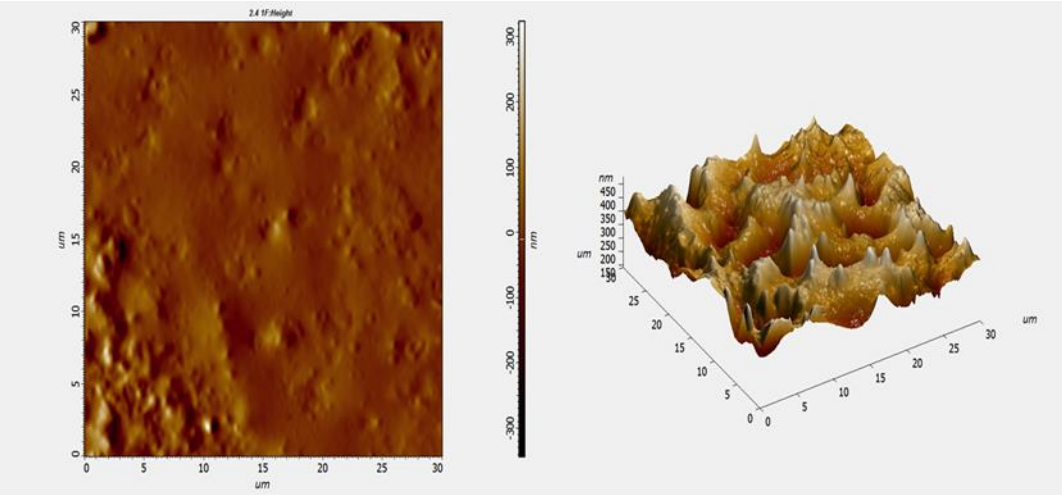

FIGURE 4 Assays of nano-carbon prepared under the atomic force microscope

Characterization of activated charcoal by transmission electron microscope (TEM)

Electron microscopes have a much higher resolution than optical microscopes due to the small wavelength of electrons [18]. The sample shows that the prepared particles are cubic in shape and with different magnification power, as shown in Figure 5.

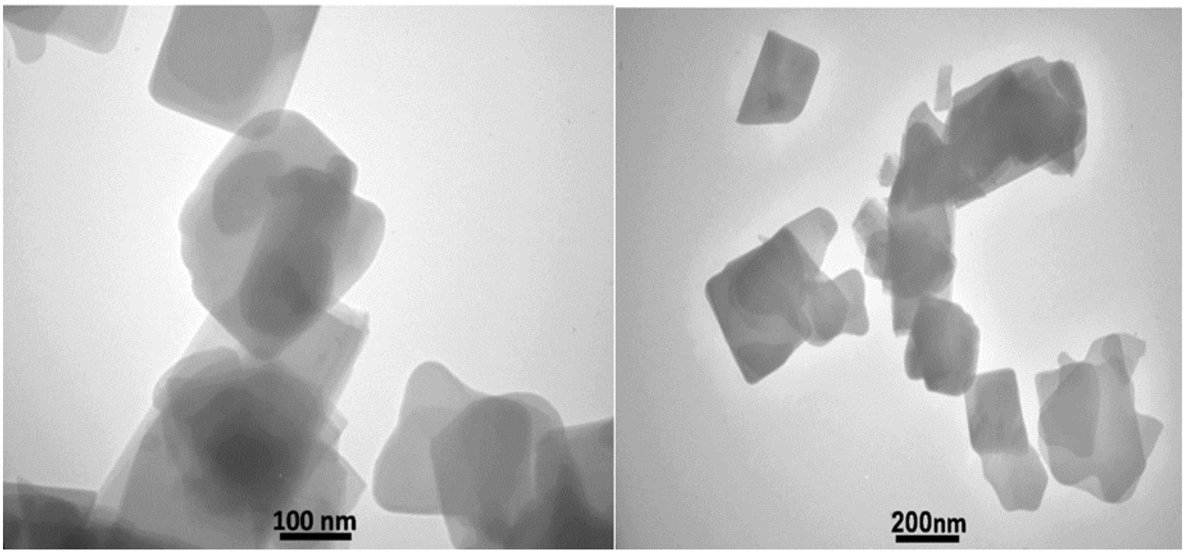

FIGURE 5 TEM images for the prepared nanocarbons

Determining the wavelength and constructing the calibration curve of the EBT dye

The maximum wavelength is prepared by preparing a solution of EBT dye for the purpose of spectral follow-up to take advantage of the ability of this dye to show a clear absorbance in the visible-ultraviolet region. The color of the EBT dye is dark violet to black; it was found that the wavelength of this dye was (516 nm). Also, the calibration curve was built through the following concentrations and 0.00002, 0.00004, 0.00006, 0.00008, 0.0002, 0.0004, 0.0006, 0.0008, respectively, molar to estimate the amount of the outstanding and residual dye in the solution using the spectroscopic method, according to Beer - Lambert's law, and the relationship was drawn between absorbance and concentration as shown in Figure 6. Thus, a linear relationship emerged indicating that it is subject to Beer-Lambert's law.

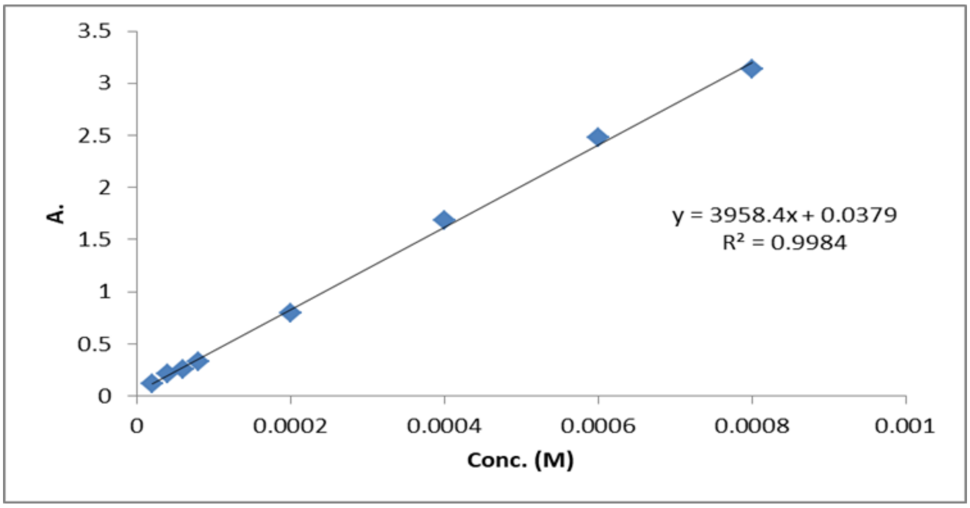

FIGURE 6 The calibration curve of the dye under study

Effect of equilibrium time of EBT dye

To determine the equilibrium time of EBT dye, the concentration of EBT dye was monitored spectrophotometrically with the time for adsorption to reach equilibrium. This experiment was done with the use of a fixed concentration of EBT dye 0.0002M with a fixed weight of 0.5g prepared activated charcoal and a maximum dye wavelength by 516nm, the temperature by 295K and the vibrating speed by 140 rpm as shown in Table 3.

TABLE 3 Effect of time on the adsorption efficiency of the dye on the surface of the prepared nanocarbon

Time (min)	Absorbence	Ce (mg/L)	(mg/g) Qe	Adsoption%
0	0.796	—	—	—
5	0.380	22.389	5.935	57.0
10	0.320	18.484	6.716	64.5
15	0.154	7.549	8.903	85.5
20	0.081	2.603	9.893	95.0
25	0.081	2.603	9.893	95.0
30	0.099	3.905	9.632	92.5

The effect of the weight of the adsorbent material

The effect of the weight of the prepared charcoal (adsorbent material) on the adsorption efficiency of the EBT dye was studied, using three weights of the prepared activated charcoal, which are, respectively, (0.1, 0.5, 0.7) grams, while maintaining the other variables of temperature (295k), vibration speed (140 rpm) and equilibrium time (20 minutes) using the best concentration of (0.0002) molar, and the adsorption was followed up spectroscopically. Most of the adsorption sites are saturated as shown in Table 4.

TABLE 4 The effect of the weight of the prepared adsorbent material on the adsorption efficiency

(Weight of AC(g)	Abs.	Ce (mg/g)	Qe (mg/g)	Adsorption%
	0.218	11.715	8.070	77.5
0.1	0.081	2.603	9.893	95.0
0.5	0.064	1.562	10.101	97.0
0.7	Abs.	Ce (mg/g)	Qe(mg/g)	Adsorption%

Effect of pH

The adsorption efficiency of EBT dye solution was studied under the same conditions of temperature (295K) and dye concentration (0.0002M) with (0.5g) of activated charcoal, and it was found that the best adsorption was at the natural pH of the dye. The results are listed in Table 5.

TABLE 5 Effect of pH on adsorption efficiency

(pH)	Abs.	C_e (mg/g)	Q_e(mg/g)	Adsorption%
Natural	0.081	2.603	9.893	95.0
2	0.069	1.822	10.049	96.5
9	0.140	6.508	9.112	87.5

The effect of temperature

The effect of temperature on the adsorption process of EBT dye on the surface of the prepared activated charcoal was studied at different temperatures (295, 298, 308, 318) K, using the best concentration (0.0002M), as well as using the best weight of activated charcoal (0.5 g) and the speed of the vibrator (140 rpm) and the adsorption process was followed spectroscopically at the equilibrium time (20 minutes) as shown in Table 6.

TABLE 6 Effect of temperature on adsorption efficiency

T(K)	Absorbance	C_e (mg/g)	Q_e(mg/g)	Adsorption%
295	0.081	2.603	9.893	95.0
298	0.163	8.070	8.799	84.5
308	0.166	8.330	8.747	84.0
318	0.178	9.111	8.591	82.5

For the purpose of predicting the automatic of the reaction or the non-automatic of the reaction, the thermodynamic functions of the adsorption process are calculated, which are automatic in conjunction with the decrease in the degrees of freedom of the adsorbent material, expressed thermodynamically by decreasing entropy (ΔSº). This process was therefore carried out in isothermal conditions using the Gibbs equation.

The value of the equilibrium constant can be calculated using the following equation:

$$K_{eq} = \frac{X_{eq}}{a-X_{eq}} \qquad (1)$$

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o} \qquad (2)$$

As. represents

ΔGº = change in standard free energy.

ΔSº = standard (random) entropy change.

T = absolute temperature.

ΔHº = Standard enthalpy.

The value of free energy can be obtained from the following relationship:

$$\Delta G^{o} = -R\,T\,LnKeq \qquad (3)$$

As the adsorption process from the solution either forms one molecular layer and is in contact with the surface of the solid, the other layers that follow are present inside the solution and are weakly connected to the molecular layer, or it forms a layer with the thickness of several molecules as the mutual action between the solute and the solid decreases when exceeding; only one layer thickness.

In order to find out the type of adsorption processes exothermic or endothermic as shown by some research the enthalpy was calculated according to the following relationship:

$$\log Keq = (\Delta H / 2.303\,RT) + C \qquad (4)$$

where it represents:

K is the equilibrium constant for the adsorption process, T is the absolute temperature in Kelvin, R is the general constant for gases. C is the constant of the Vant Hoff equation.

The thermodynamic functions of adsorption were calculated, showing that the negative value of ΔH indicates that the process of adsorption of the dye on the surface of the carbon nanotube is exothermic process. It also indicates that the adsorption is physical because the forces responsible for the adsorption process are weak. We also observed the adsorption process occurs automatically, by calculating the values of the change in free energy (ΔGº) with a negative charge. By obtaining the negative values of (ΔGº) mathematically, we obtained the values of the change in entropy ΔSº through the Gibbs equation from Equation 2 where we noticed that the negative ΔSº values reduce the randomness of the studied system, due to the loss of molecules after adsorption, which is consistent with that of a previous study [11].

TABLE 7 Thermodynamic functions of adsorption

T(k)	1/T (k^{-1})	Keq	lnKeq	ΔG^0 (KJ/mol)	(KJ/mol)ΔH^0	(J/mol.K)ΔS^0
295	0.00338	3.800	1.335	-3.27	-3.5076	**-2.376**
298	0.00335	1.090	0.086	-2.13		**-1.377**
308	0.00324	1.050	0.048	-1.22		**-2.287**
318	0.00314	0.942	-0.059	155.98		**-1.594**

Conclusion

The results of this study confirmed that the prepared carbon contains nanoparticles and this was confirmed by the results and that it contains large pores and a high surface area. Nano-carbon prepared from environmentally friendly plant residues has proven to have a high adsorption capacity in the industrial field, with a high adsorption efficiency equal to 95.0%. The results also showed that the equilibrium time was 20 minutes for the adsorption of EBT dye. The experimental results revealed that the adsorption capacity decreases with increasing temperature with the dye in question, suggesting that the adsorption system is of the exothermic type. These results are in agreement with the adsorption enthalpies (ΔHº) of the adsorbent surface. The calculated values of the thermodynamic functions showed that the enthalpy of adsorption (ºΔH) is negative, which indicates that the adsorption process of the dye is exothermic. Additionally, the negative (ΔS°) values indicate that the occurrence of adsorption reduces the randomness of the system and thus increases the uniformity of the adsorbed dye on the adsorbent surface. The negative (ΔG°) value indicates the automatically of the adsorption system on the adsorbent surface.

Acknowledgments

This research was supported department of Chemistry, College of Education, University of Samarra, and department of Chemistry, College of Education for Pure Sciences, University of Samarra.

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How to cite this article: Mashreq Muhammad Ahmed*, Attallah B. Dekhyl, Liqaa Hussein Alwan. Preparation and characterization of nano-carbon as an adsorbent for industrial water treatment. *Eurasian Chemical Communications*, 2022, 4(9), 852-862. **Link:** http://www.echemcom.com/article_148644.html