



The Removal Of Congo Red Dye (CR) From Wastewater By Used Synthesized Activated Carbon Nanoparticles From Blueberry Seeds: Isotherms, Kinetics, And Thermodynamics Studies

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Article information

Article history:

Received: August, 27, 2022

Accepted: September, 25, 2022

Available online: November, 07, 2022

Keywords:

Pollution,
Blueberry Seeds,
Activated Carbon (AC),
Congo Red Dye (CR),
Anionic Dye,
Adsorption.

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Citation Husain , A. A. , Mahmood , R. S. , Jasim , B. E. , & Samawi , K. A. . (2022). The Removal Of Congo Red Dye (CR) From Wastewater By Used Synthesized Activated Carbon Nanoparticles From Blueberry Seeds: Isotherms, Kinetics, And Thermodynamics Studies. *Journal of Advanced Sciences and Nanotechnology*, 1(4).

Abstract

Activated carbon (AC) was made from blueberry seeds and was found to be nanosized, with a crystal size of 13.48 nm from XRD data and a grain size of 28.93 nm from FESEM. It was then used to remove an anionic dye, Congo red dye (CR), at various temperatures, pH levels, and adsorbent dosages. Langmuir and Freundlich models can be used to predict adsorption data. In terms of regression coefficients, the results show that the Freundlich model fit the data more than the Langmuir model. Free energy G, enthalpy H and adsorption entropy S were all calculated using isotherms to be -48.359 (K), -24.76 (K) and 0.0753 (K) respectively. Furthermore, the pseudo second order rate equation for adsorption was obtained through kinetic studies. Advanced carbon has the same adsorption capacity as other commercially available adsorbents despite its lower price. In contrast, the experimental data was completed by quantum chemical calculations at the B3LYP/6-31G* level of theory using the DFT technique. Theoretical and experimental results are found to agree well.

DOI: [10.55945/joasnt.2022.1.4.147-157](https://doi.org/10.55945/joasnt.2022.1.4.147-157),

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1. Introduction

Industries that use dyes are a significant cause of pollution, and many factories employ dyes in the manufacturing of their products, such as textiles, dyeing droplets, pharmaceuticals, cosmetics, and paper industries, because there are over 1000 different types of dyes that are used according to the influential group and coloring ability [1-3]. Millions of tons of dye leftovers are thrown into bodies of water each year, causing serious environmental issues in certain places [4]. The process of removing impurities from water in order to make it clean is known as adsorption. Adsorbents are the materials substances that are used during the adsorption process. Activated carbon is a very common type of adsorbent because, because activated carbon has a high specific surface area and a uniform pore size distribution, it is frequently utilized for air pollution treatment and water purification [5,6]. Adsorbents with large surface areas can be developed using nanotechnology. It has a large number of active surface sites, a high adsorption capacity, and a high removal rate. Activated carbon is the most commonly used adsorbent as a treatment material [7]. Environmental pollution is one of the most important and most serious problems facing man and threatening his life, especially water pollution, which is one of the most important sources of existence on this planet. In recent years, it has been observed that the pollution of water bodies has increased as a result of technological progress. Perhaps one of the most important sources of water pollution is the dyes used in textile factories and paper factories, and other industries, where these dyes are disposed of by throwing them into the water by factories, and thus the water becomes unhealthy for consumption by living organisms in general and humans in particular.

There are thousands of types of dyes that are used in industry, and they can be classified into anionic, nonionic, and cationic. Perhaps the most important dye that causes pollution is the Congo Red dye, so it has become necessary to shed light on this dye. [8-10]. Congo Red, also called (azo dye) is an anionic dye that is red in the alkaline medium and blue in the acidic medium [11]. It is one of the most important industrial colorants used in industry because of its distinctive properties such as containing chromophore groups and aromatic rings, as the conjugated π bonds are of great importance in making this dye stable [12]. This dye is also characterized by its high solubility in water and, therefore, it remains for very long periods in the environment due to the difficulty of disposal. On this basis, it has been classified as one of the most environmentally polluting dyes [13]. Congo Red (azo dye) is considered one of the most dangerous dyes for the organism because it contains the aromatic amine in its composition, shown in Fig 1, which makes it difficult to damage, as it was observed that when it comes into contact with the eyes and the skin, it causes very severe irritation. Or to an animal, and that continuous exposure to this dye leads to cancer [14,15], so it has become necessary to find a simple and effective way to remove this type of dye, thus reducing environmental pollution and preserving human safety.

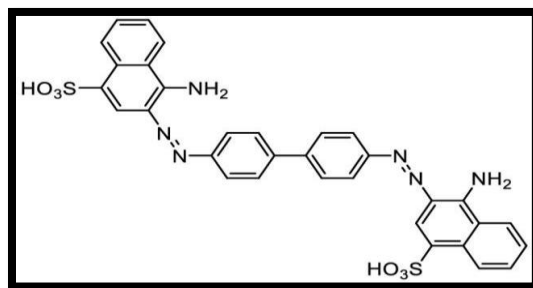


Figure 1. The chemical structure of Congo red dye [8]

2. Experimental

All chemical compounds were obtained from Sigma-Aldrich and used without any purification, Blueberries were also obtained from the supermarket.

2.1 Synthesis activated carbon

(30) g of blueberry seeds was used and dried in the air after adding 3% of hydrochloric acid for (24) hours to remove the oils that were present in the seeds, after which they were washed with deionized water several times to get rid of hydrochloric acid until reaching PH = 7 and then dried with heat at 130 °C for (12) hours. The activating agent used to prepare activated carbon (AC) is nitric acid. 30 g of dried seeds were mixed with 100 ml of nitric acid at a concentration of 5 M and at a temperature of 80 C for two hours with continuous stirring. Then the sample was carbonized at (550) °C for four hours, after which the sample was cooled and washed with deionized water.

2.2 Computational procedures

To understand the relationship between the adsorption molecular structure and its adsorption efficacy, quantum chemical simulations were done. Quantum chemical calculations were carried out using the Gaussian 09 computer package and density functional theory (DFT) using the 6-311G basis set [16-17]. highest occupied molecular orbital (EHOMO), lowest unoccupied molecular orbital (ELUMO), and total molecular dipole moment have all been calculated [18-19].

$$\eta = \frac{\Delta E}{2} = \frac{ELUMO - EHOMO}{2} \dots [1]$$

$$\sigma = \frac{1}{\eta} = \frac{2}{ELUMO - EHOM} \dots [2]$$

$$A = -ELUMO, I = -EHOMO$$

$$\Delta E = ELUMO - EHOMO$$

$$\omega = \frac{\mu^2}{2\eta} \dots [3]$$

where μ^2 is possible electronic chemical, for example ($\mu = -\chi^2$). This score assesses chemical species' proclivity to take electrons. A lower value of denotes a good more reactive nucleophile μ , ω [12].

3. Results and Discussion

In the X-rays pattern for the prepared sample shown in (fig. 2 and Table 1), the appearance of broad peaks 002, 100, and 101 at angles 26, 40, and 44, indicate the formation of activated carbon (AC), The broad peaks show that the activated carbon was in nano size, the average particle size was calculated to be (13.48) nm by a Debye Scherrer equation [16,17]:

$$D = k \lambda \sqrt{\beta \cos \theta} \dots [4]$$

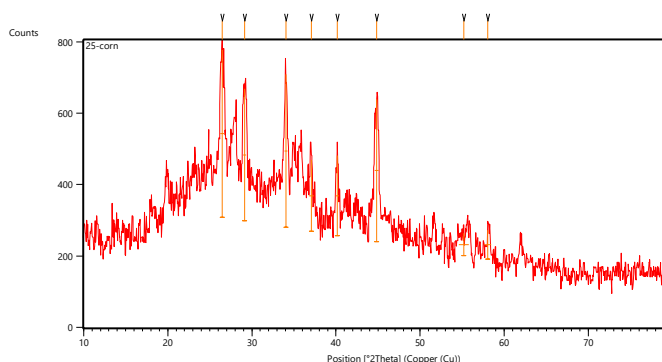
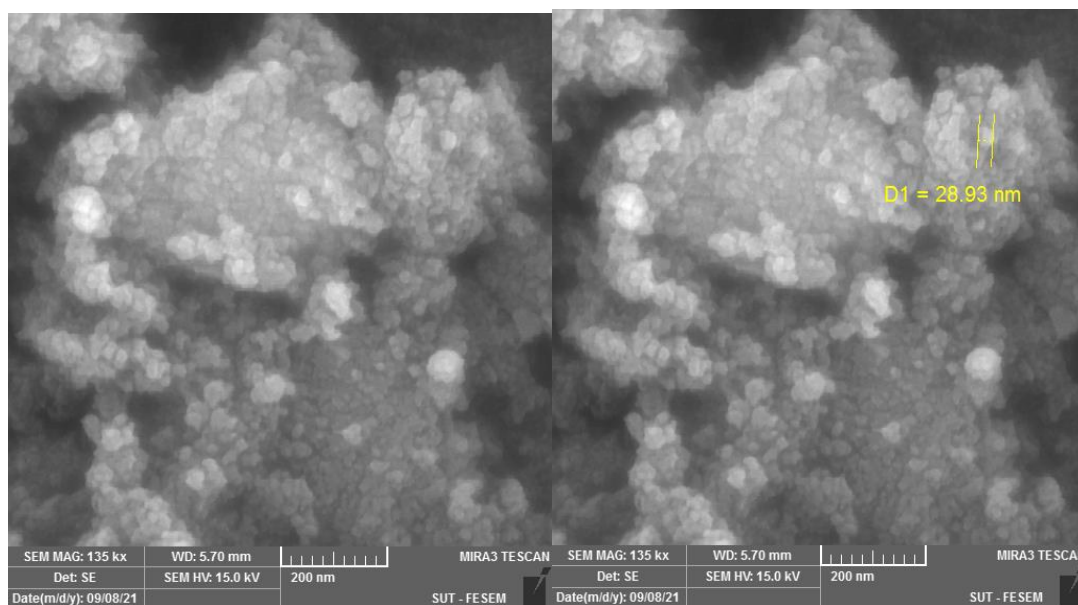


Figure 2. XRD pattern of the (AC) nanoparticles.

Table 1. shows the X-ray diffraction data for (AC).

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]	Tip Width
26.4523	469.62	0.4920	3.36956	100.00	0.5904
29.1456	370.65	0.3936	3.06401	78.92	0.4723
34.0559	429.25	0.3936	2.63264	91.40	0.4723
37.0450	200.00	0.5904	2.42680	42.59	0.7085
40.1228	224.04	0.3936	2.24745	47.71	0.4723
44.8281	399.04	0.4920	2.02188	84.97	0.5904
55.1992	62.78	1.1808	1.66405	13.37	1.4170
58.0497	81.78	0.7872	1.58894	17.41	0.9446

The SEM image of synthesized activated carbon (AC) was given in Fig. 3, it shows the surface morphology, and particle shape, it can be observed that (AC) has a spherical shape, which provides a high surface area, and homogeneous (AC) with a diameter 28.93 nm. which corresponding to the crystal size calculated from XRD pattern.

**Figure 3.** SEM images of activated carbon (AC).

3.1 Adsorption experiment

to study the adsorption of Congo red (CR) dye on activated carbon(AC) NPs; 5-20 mg/L (CR) dissolved in deionized water (0.01g of (AC) were added to 40 ml of (CR) solution at each concentration). The mixture was shaken for 90 min at (293, 298, 303, 308 and 313) K.

3.2 Adsorption isotherm

The concentration of Congo red dye(CR) was set according to the equation:

$$Q_e = (C_e - C_o)V_{sol} / M \dots \dots [5]$$

The isotherm of (CR) adsorption is in accord with the linearized Freundlich isotherms [18] seen in Figure.4. The relationship between the (CR) concentration at equilibrium and activated carbon (AC) is given by this equation:

$$\log Q_e = \log kF + 1/n \log C_e \dots \dots [6]$$

Langmuir isotherm equation:

$$\frac{C_e}{Q_e} = \left(\frac{C_e}{Q_m} \right) + \left(\frac{1}{Q_m} kL \right) \dots \dots [7]$$

From Figure 5 observed that the linear curve of Langmuir isotherm data for (CR) adsorption in its solution did not undertake the Langmuir isotherm according to the low value of R^2 which is 0.6888. So It is not formed single-layer adsorption because activated carbon (AC) is a nanomaterial so we can say is dealing only with Freundlich isotherm [19]

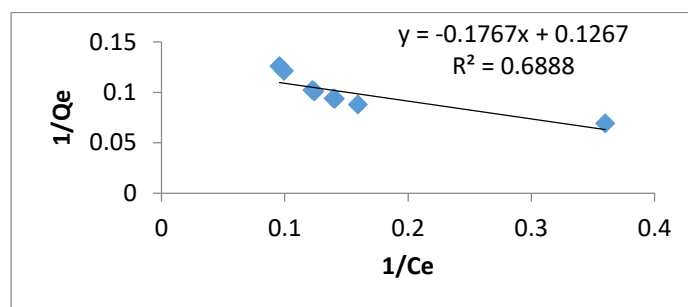


Figure 4. Adsorption equation of Langmuir isotherm.

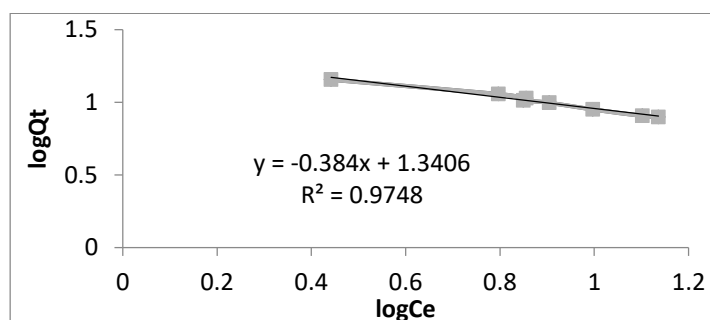


Figure 5. Adsorption equation of Freundlich isotherm.

3.3 The effectiveness of activated carbon (AC) nanoparticles dose

In this study has been used different concentrations of the adsorbent that ranged (0.01, 0.02, 0.03, 0.04, 0.06 g) to study the effectiveness of the adsorbent dose of (AC) nanoparticles on the amount of adsorption of (CR) dye in the solutions, the pH exactly at (7), the temperature at (293 K) and the contact time between the adsorbent surface and the adsorbate at (90min) Note that the initial concentration used for the dye is (10 mg/L), from the Fig.6 observed an increase in the absorption rate of the dye with an increase in the adsorbent concentration, where noticed that when the concentration of (AC) particles (0.01g) the removal rate was reached (30.85 %), while observed that the large absorption rate occurs when reaching Concentration (0.06 g) of (AC), and this is due to the elevation in the number of active sites that be on the surface of adsorbent activated carbon (AC), and thus the removal rate for Congo red (CR) dye becomes greater reached to (97.25%).

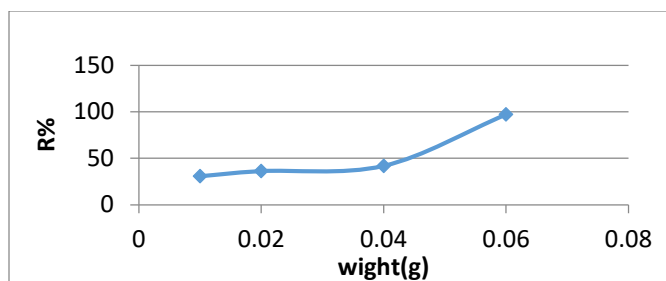


Figure 6. Effectiveness of (AC) nanoparticles dose.

3.4 The effectiveness of Temperature

The effect of the change in temperature on the operation of removing Congo red dye from wastewater by using Activated carbon (AC) was studied by using a temperature domain of (293, 298, 303, 308, 313) K. Noticed that the adsorption operation increased when temperature increased and that case did depending on the type of adsorption so the Our adsorption is a chemical adsorption and its exothermic, this effectiveness shown by Fig.7.

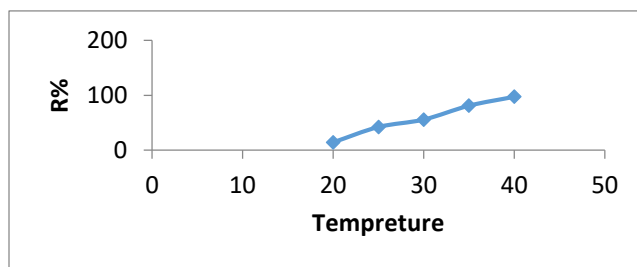


Figure 7. Effectiveness of Temperature.

3.5 The effectiveness of Contact Time

The effectiveness of the contact time between the adsorbent surface activated carbon (AC) nanoparticles with the adsorbent material, Congo red (RC) dye, by variable the contact time, which ranges between (0 - 105) min, where we took the mensuration every (15) min while remaining the concentration of the nanomaterial (AC) at (0.06) gm and the (CR) dye at (15) mg/L at a temperature (313) K and as illustrated in Fig.8, where we noticed the apparition of intense adsorption at the 90 min, and then the adsorption gradually decreases until the equilibrium point is reached at a time (105) min and the reason for this is due to the presence of many of the unfilled sites on the surface of the adsorbent material, which gradually fills up with time, which leads to a decrease in the rate of adsorption.

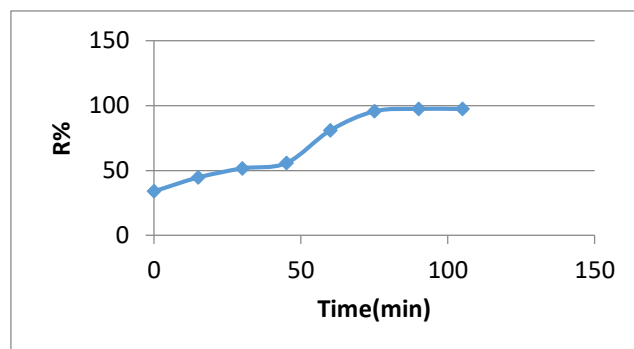


Figure 8. Effectiveness of contact time

3.6 Thermodynamic parameter

Ordinarily, the thermodynamic parameters calculated by using the following equations [20]:

$$\Delta G = \Delta H - T\Delta S \dots [8]$$

$$\log X/m = -\Delta H/2.303R + \Delta S/R \dots [9]$$

ΔH was calculated by the slope of $\log (X/m)$ van Hoff plots versus $1/T$, as shown in Fig.10, and (ΔS) was calculated from the y-intercept. Fig.9. illustrated the relevance for the adsorption between $\log X/m$ and $1/T$ of Congo red (CR) dye and the slope gave the value of ΔH (-24.76) kJ/mol while the ΔS value was taken from the y-intercept (0.0753) KJ/Mol, So from The value of ΔH shows that the adsorption process of (CR) dye by (AC) nanoparticles is exothermic. ΔG for the adsorption was (-48.359) kJ/mol at 293 K and this indicate that the adsorption was spontaneous.

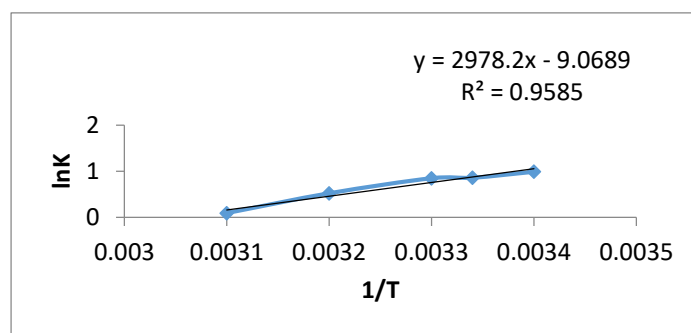


Figure 9. The relationship between $\log X/m$ and $1/T$ for the adsorption of (CR) dye.

4. Theoretical study

4.1 Main Quantum Parameters

Following the experimental research, a theoretical study at the B3LYP/6-311G level was conducted to correlate the experimental results with the molecular structure as well as electrical properties of Congo red dye. As a result, HOMO energy is typically associated with a molecule's proclivity to throw electrons away to an appropriate unoccupied orbital. An increase in EHOMO values thus aids adsorption since it influences the transfer process across the adsorbed layer. The LUMO energy, the other hand, provides information on electron acceptance in the molecule. The lower the ELUMO value, the larger The higher the adsorption efficiency, the greater the ability of the molecule to receive electrons from the surface. It is commonly understood that a good adsorbed molecule is one that can not only give but also accept electrons. Furthermore, the energy gap (Egap) is a significant quantity. When a result, as the energy gap narrows, the adsorption performance of the Congo red (CR) dye on the activated carbon (AC) surface improves. Figure 11 depicts Techniques employed include the Congo red dye's Molecular optimization, electron density distributions of the boundary molecular orbitals, HOMO, and LUMO are all examples of techniques used.

Figure 10 show demonstrates that the HOMO site's electron density resides on the chemical surface of the Congo red (CR) dye. Furthermore, the carbon atom of the phenyl group and the nitrogen atom of Congo red dye are assigned the electron density of the empty molecular orbital (LUMO).

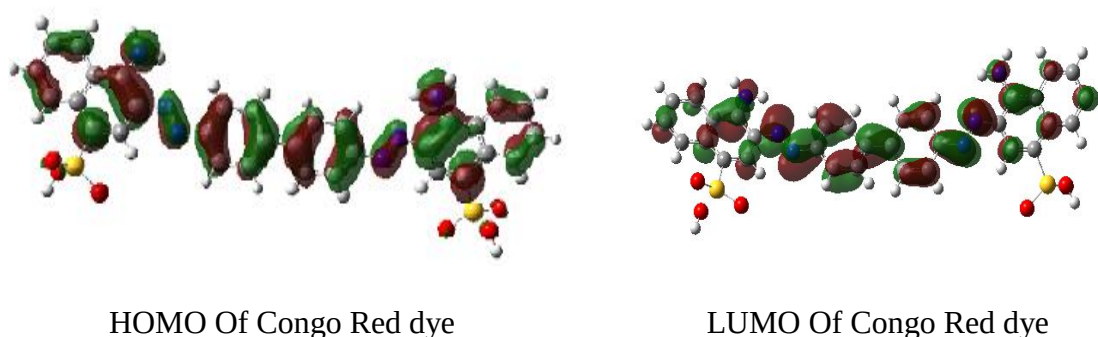


Figure 10. Shows HOMO and LUMO of the Congo red dye

Table 2, summarizes the computed quantum parameters. The energy gap, E_{gap} , is defined by Koopmans' theorem as the difference between HOMO and LUMO energy [13]. The Congo red dye has a high EHOMO energy (-5.9899 eV) and a low ELUMO energy (-3.1710 eV), as well as a low E_{gap} (2.8189 eV) energy difference in comparison to EHOMO and ELUMO, which improves its stability on the activated carbon surface.

Furthermore, the most common is the dipole moment, parameter to describe the polarity of a molecule 44. Molecules with high dipole moments are more reactive, according to the literature. In this study, the dipole moment of Congo red (CR) dye is 13.0146 debyes, which is bigger than the water molecule's value. Furthermore, Chemical hardness, and softness, are important chemical parameters for assessing a molecule's stability and reactivity. As a result, adsorption efficiency rises in proportion to molecule chemical reactivity; in normal conditions, the molecule with the highest adsorption efficiency must have the lowest hardness value. Because of the increase in softness ($= 0.7095 \text{ eV}^{-1}$) and decrease in hardness ($= 1.4095 \text{ eV}$), Congo red (CR) dye exhibits good chemical reactivity with the activated carbon (AC) surface. It may be determined that the Congo Red dye was quickly absorbed by the Activated carbon.

Table 2: shows the CBIPM molecular characteristics determined by DFT from the optimized structure at the B3LYP/6-311G

Method	ELUMO (eV)	EHOMO (eV)	ΔE (eV)	μ (debyes)	η (eV)	σ (eV ⁻¹)	X (eV)	I (eV)	A (eV)	ω (eV)
DFT	-3.1710	-5.9899	2.8189	13.0146	1.4095	0.7095	4.5805	5.9899	3.1710	7.4428
PM3	-1.3816	-8.6874	7.3059	6.8549	3.6529	0.2738	5.0345	8.6874	1.3816	3.4693

4.2 Atomic loads of Mulliken

The higher negative the atomic charges of the adsorbed center, the easier the atom takes away its electrons to the Activated carbon's vacant orbital. Figure 12 depicts the Mulliken charge distribution and polar moment orientation schematically, and the charge distribution data are also gathered in Table 3.

Figure 12 and Table 3 show that the charge densities of oxygen, nitrogen, and some carbon atoms are higher. Electrophiles typically assault the areas with the highest electrical concentrations through 48. Thus, O, N, and specific C atoms have the best ability to bond to the Activated carbon surface.

Furthermore, some carbon atoms have positive charges, which are thought to be the places where nucleophiles attack. As a result, activated carbon (AC) can take electrons via these atoms.

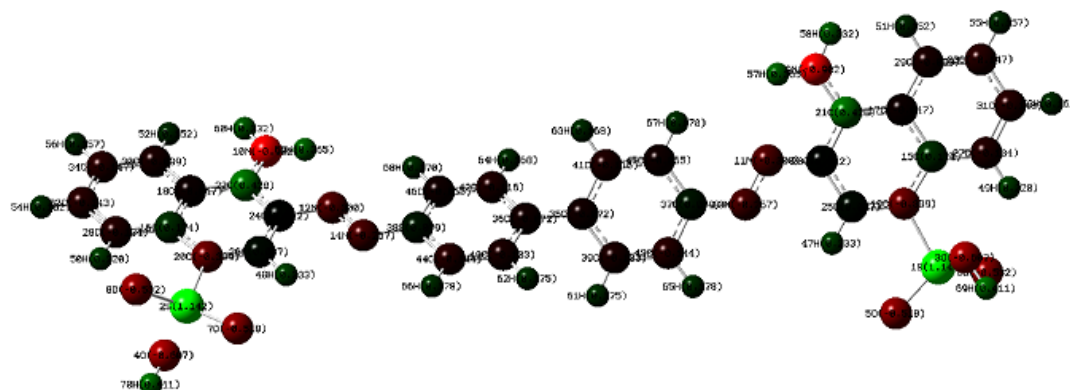


Figure 12. Shows Mulliken charge distribution of the Congo Red dye

Table 3. Calculated of the atomic loads of Mulliken charges

Atom Number	Charge	Atom Number	Charge	Atom Number	Charge
S1	1.141800	C17	-0.047325	C33	0.010300
S2	1.141800	C18	-0.047325	C34	0.010300
O3	-0.196427	C19	-0.399082	C35	-0.072356
O4	-0.196427	C20	-0.399082	C36	-0.072356
O5	-0.518095	C21	0.428065	C37	0.079332
O6	-0.531667	C22	0.428065	C38	0.079332
O7	-0.518095	C23	0.011576	C39	0.072357
O8	-0.531667	C24	0.011576	C40	0.072357
N9	-0.204762	C25	0.269423	C41	0.051850
N10	-0.204762	C26	0.269423	C42	0.051850
N11	-0.299555	C27	0.086125	C43	0.033536
N12	-0.299555	C28	0.086125	C44	0.033536
N13	-0.266729	C29	0.053224	C45	0.105556
N14	-0.266729	C30	0.053224	C46	0.105556
C15	0.173751	C31	0.019101		
C16	0.173751	C32	0.019101		

5. Conclusion

From all the above results, we reached that the activated carbon (AC) nanoparticles that were prepared from blueberry seeds can be considered as one of the nanomaterials that have a high ability to adsorb Congo red (CR) dye because of their high efficiency and low cost of preparation.

(AC) that gave it a range of physical, and chemical applications and the nano size made (AC) has a higher surface area and which made it a good adsorbent under certain experimental conditions, from results were noticed that the maximum adsorption capacity of this dye by (AC) nanoparticles was at Temperature (313) K and at a concentration (0.06 g) of the (AC) nanomaterial with contact time up to (90) minutes.

Theoretical findings were shown to be congruent with experimental findings for the adsorption of Congo Red (CR) dye on the activated carbon (AC), so that a low E_{gap} (2.8189 eV) energy difference in comparison to (EHOMO) and (ELUMO) which increase reactivity of dye according to its value, which improves its stability on the activated carbon surface, this will give good signal to adsorption of this dye on the activated carbon.

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