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Processing *Erucasativa* leaves in the Nanoscale and Studying its Effectiveness for Removing Cibacron Red Dye from their Aqueous Solutions

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Abstract

The discharge of dyes into the water is a significant source of pollution, which is especially concerning given that textile mills are the primary contributor. Nanomaterial-based solutions to this issue have required extensive research and investigation due to their complex nature. In this research, novel nanoparticle were successfully synthesized using the leaves of the Eruca sativa plant. The nano was analyzed using scanning and transmission electron microscopy (SEM and TEM) and it was measurements particle size 28 nm by TEM, 31 nm by SEM and their crystal structure was determined using the X-ray diffraction technique (XRD). The pattern has large peaks at 27.09, 29.90, 39.81 and the crystal size has been calculated to appear around 41nm . The incorporation of NPs resulted in an increase in the uptake of the Cibacron red dye. At a contact time of 35 minutes, observed a faster adsorption onto ES. At a 0.15 gm mass of Erucasativa observed adsorption and remoal 51.7% of dye. In the process of describing the adsorption process, the Freundlich model and the pseudo-second-order model (R2 = 0.9884) were the most appropriate models to use. An investigation into thermodynamics was carried out in order to arrive at the following values for the parameters of ΔG°, ΔH°, and ΔS°: 0.012 kJ/mol, 16.794 kJ/mol. and 56.05J/mol.K. In conclusion, the novel nano that was synthesized is a n excellent adsorbate surface for the Cibacron- red dye.

Keywords: Cibacron red , adsorption, Eruca sativa, Adsorption isothermal, Green synthesis.

1. Introduction

Pollution in the environment and exposure to potential dangers are two of the most significant obstacles a person must conquer in this day and age [1]. This rises is a result of various activities carried out by humans because it was discovered that pollution of the environment has a close connection with the increase in population in the region [2,3]. Water is a component that is considered to be one of the most fundamentalsustaining life. In recent yearsthere has been an increase in the amount of data that has been observed as well as a considerable deterioration as a result of the advancement of technology[4,5], this is due to the fact that tens of thousands of chemicals and compounds are released into the environment on a daily basis, either directly or indirectly, into water sources without subjecting the water to any kind of treatment [6,7] As a result, there has been a lot of focus placed on the problem that the researchers are having with water pollution[8].

Deserving of notice in this day and age Organic components are made up of a wide variety of parts, including materials. Organic components are comprised of many different components. industrial wastewater. There is a significant quantity of organic pollutants present [9]. Risk in terms of the effects they could have in the long run, given that some of them cause diseases that lead to cancer. It is generally accepted that dyes are organic pollutants in aquatic environments, and these pollutants include any and all compounds that are utilized in the coloring of leather,food, as well as other materials [10,11], which pose a myriad of potential dangers to every component of the environment as a direct result of the fact that they have high levels of toxins. In addition, it is generally agreed that dyes are organic pollutants in The reports are produced by the World Health Organization [12].

The majority of the diseases, as stated by the organizations, are infectious to some degree. In developing countries, contamination is the underlying cause of a wide variety of problems. of drinking water. As a result of this, numerous researchers have experimented with many different approaches in order to treating industrial water. There have been a variety of therapies and procedures for getting rid of it that have been tried. organic pollutants that can be found in sewage treatment facilities [13]. Adsorption is one of the methods that can be used on hard porous surfaces. Other methods include photo-oxidation, oxidation through chemical processes, ion exchange, and a method that involves both adsorption and reverse osmosis. It is frequently utilized in cleaning contaminated water from a variety of surfaces, including wood, many surfaces, cellulose, activated carbon, and other materials. The procedures that are described in the reports of the World Health Organization indicate that they are frequently used in cleaning contaminated water[14]. Numerous earlier studies and pieces of research that utilized a variety of adsorbents in order to absorb the dye that was made with cibacron-red can be found here[15,16]. Problems in developing countriesof drinking water Because of this, a number of researchers have utilized a variety of techniques to treat industrial water,and a number of different treatments and elimination strategies have been tried [17]. Organic pollutants found in wastewater treatment plants. To name a few of them: oxidation via chemical processes, photo-oxidation, ion exchange, and a method involving adsorption [18] as well as reverse osmosis Adsorption is one of the methods that can be used on hard porous surfaces. The procedures described in the World Health Organization's reports indicate that it is frequently utilized in cleaning contaminated water, a variety of surfaces including wood, many surfaces, cellulose, activated carbon and other materials were put to use [19-21]. In a number of studies and pieces of research done in the past, a dye made with cibacron-red was absorbed by a number of different adsorbents as **Figure 1**.

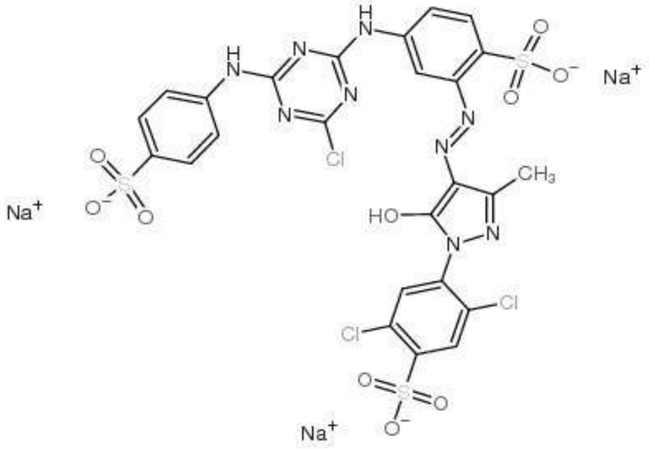

Figure 1. Chemical structure of cibacron-red

2.Experimental

2.1Materials:

All chemicals were analytical grades of reagents and were used from Sigma-Aldrich, without further purification.

2.2 Synthesis Eruca sativa (ES)nanoparticles

The Eruca sativaplant (ES) that was utilized was collected from the farms located in the Wasit Governorate in **Figure2**. After the leaves were picked, they were thoroughly washed and cleaned using deionized water to remove any suspended dirt. Next, the leaves were sun-dried before being ground using an electric grinder. After that, the extract was made by combining 10 grams of watercress powder with 150 milliliters of distilled, deionized water and stirring the mixture constantly with a magnetic stirrer at a temperature of sixty degrees Celsius for thirty minutes. This process was repeated three times. Following that, the material was filtered using filter paper on multiple occasions, and then the filtrate was collected, after which it was stored in the refrigerator.

To prepare the (ES) leaves for use as anadsorption surface, use the ground (ES) after it has been dried and sieved with a 300 µm sieve and then a 75 µm sieve. After this10 grams of ground watercress were added to 100 milliliters of hydrochloric acid (HCl) with a concentration of 0.1 M and the mixture was stirred continuously at a temperature of 30 degrees Celsius for two hours than100 ml of 0.1N sodium hydroxide was added, the mixture was stirred for a total of half an hour. After that, the solution was filtered, washed multiple times with deionized water, dried at 150 degrees Celsius for two hours and then finally burned at 400 degrees Celsius for three hours. A precipitate with a grayish color is producedand it is now prepared for the adsorption process in **Figure 3**.

Figure 2. Eruca sativaplant (ES)

Figure 3. nano Eruca sativa

2.3 The process of preparing the adsorbent

From this solution, dilute solutions of various concentrations (5-50 ppm) were prepared by taking the appropriate volume of the solution and diluting it with deionized water. First, a solution of cibacron- red dye was prepared by dissolving (0.1 g) in 1 liter of deionized water to prepare a concentration of (100 ppm).

3. Results and discussion

3.1 Adsorbents' characterization

3.1.1 X-ray diffraction

Green synthesis compounds were identified using X-ray diffraction. This study was conducted at the University of Tehran in Iran using an X-ray diffraction device with continuous scanning (step size of 2 = 0.05 deq) at a speed of (10deq/min), 40 kV X-ray tube voltage, and 10 deq/min tube speed. The wavelength of 30 mA X-rays was generated using a copper objective. (0.154 nm) and crystal size (D) using the Scherrer-Debye as Equation(1).

$$D = K. \lambda / \beta. COS\theta \quad 1$$

The as-prepared nanoparticles showed diffraction peaks at 2 angles at 27.09˚, 29.90˚, and 39.81˚ and the crystal size was calculated to be 41 nm XRD in **Figure 4**.

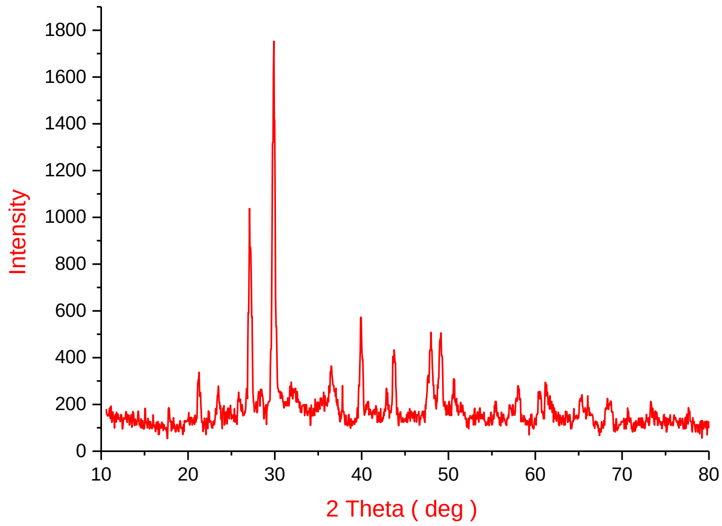

Figure 4. XRD patternEruca sativa nanomaterial

3.1.2 SEM of nanoparticles

The surface of the prepared nanomaterial (Morphology) was studied by a scanning electron microscope at the University of Tehran in Iran to estimate the shape and size of the particles (ES) as can see in **Figure 5**. Images show that the prepared nanoparticles are spherical with some aggregation[23],Randomly scaling 31 nm images yielded nanoparticle sizes.

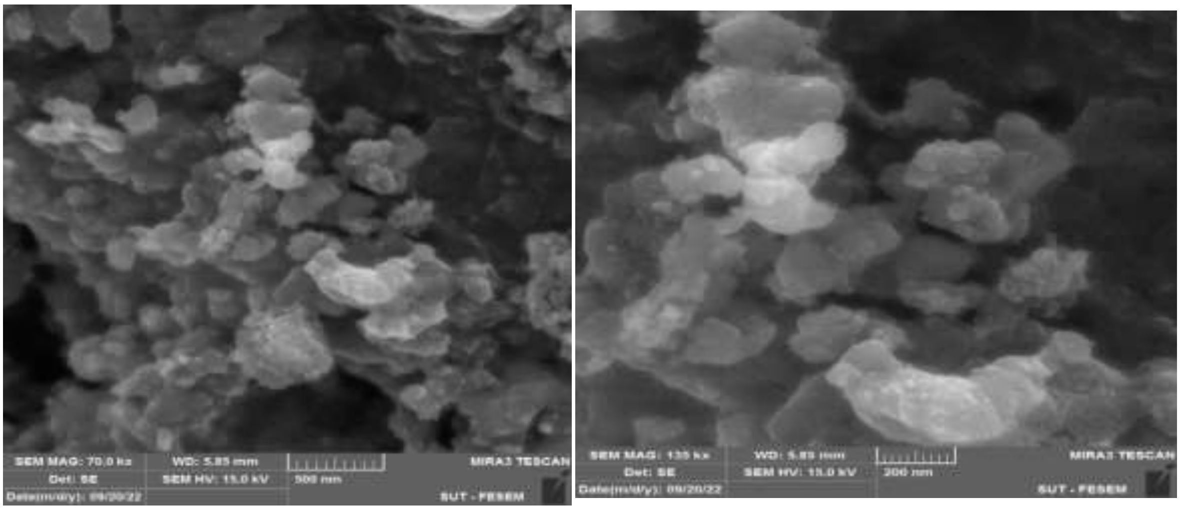

Figure 5.SEM image of ES Nanoparticles

3.1.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy was used to examine nanoparticles at Tehran University. Where diagnostic images indicate nanoparticles at a nanoscale less than 100 nm), it is observed through the images and as shown in **Figure 6** of the ES nanocomposite[24], the spherical shape of the prepared particles, which indicates the formation of zero-dimensional nanoparticles (all dimensions are less than 100 nm), and the size of the as-prepared particles was randomly calculated from the scaling images, which was about 27 nm.

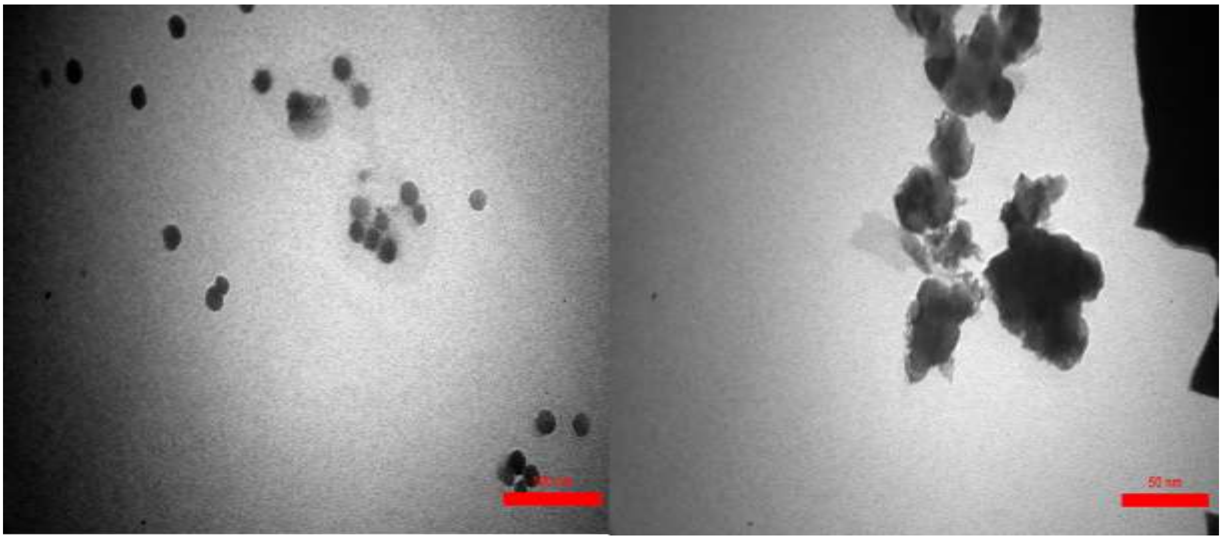

Figure 6.TEM micrographs of the ES NPs

3.2 Adsorption study

The effects of concentration, time and amount of deorbited on cibacron red adsorption on (ES nanoparticles) were examined in this work**.**

3.2.1 Effect of The temperature

Removal of dye adsorption on ES is given in Table (1) as a function of Es Concentrate at at different temperatures 288, 298, 308,318 and 328 K.dye removal and absorption capacity percentage increased from 22% to 30.4% as the adsorption temperature was increased from 288 to 328kof ES concentration. Adsorption fact increases with increasing temperatures indicate an increase in the movement of large metal particles with an increase in temperatures and the running adsorption process is endothermic[25].

Table1. Adsorption values on the surface of Es for removing Cibacron red dye at different temperatures

Temprature	C_0	C_e(ml/L)	Qe(mg/g)	R%
	10	3.3	6.7	67
	20	9	11	55
288	30	17	13	43.3
	40	22	18	45
	50	28.4	21.6	43.2
	10	3.1	6.9	69
	20	8	12	60
298	30	15.2	14.8	49.3
	40	20.4	19.6	49
	50	28	22	44
	10	2	8	80
308	20	7.2	12.8	64
	30	11	19	63.3
	40	18.2	21.8	54.5
	50	24	26	52
	10	1.4	8.6	86
	20	4	16	80
318	30	8.1	21.9	73
	40	15.1	24.9	62.25

	50	20.3	29.7	59.4
	10	1.1	9	89
	20	2.4	17.1	88
328	30	6.9	23.1	77
	40	10.5	29.5	73.75
	50	19.6	30.4	60.8

3.2.2 Effect the time on the adsorption process:

In order to calculate the amount of time necessary for equilibrium to be reached between the adsorbent surface (ES) and the adsorbent (Cibacron red) at a specific temperature, 0.01gm of adsorbent was taken, 10ml of dye with a concentration of 50ppm was added and the mixture was placed in a water bath at a temperature of 298 K with a fast shaking rate. This was done in order to determine the amount of time required for (rpm 400) and at successive time intervals (5,10,15,20,25,30,35) minutes, in order to know the change in concentration with the passage of time in **Figure 7**, and those solutions were placed in a centrifuge, and then the absorbance was measured for them at the greatest wavelength for a dye, which is max = 532 nm), and it was discovered that the best time for obtaining the equilibrium state is thirtyfive minute[26].

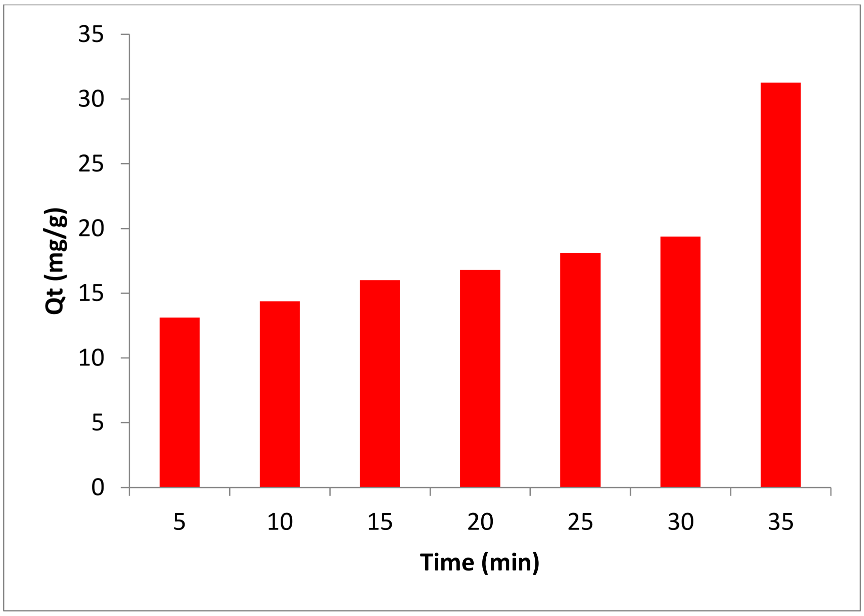

Figure 7. Effect of time on removal of cibacron- red by ES nanoparticles.

3.2.3 Effect the mass on the adsorption process:

The effect of the amount of adsorbent was studied on a dye with different weights(0.005, 0.01,0.05, 0.1,0.15) and a concentration of 50ppm, and it was fixed at a temperature of 298k and at a time of 35 minutes in a water bath containing a vibrator. We note that the dye removal efficiency increases with the increase in the amount of the material, (0.15gm) given as a 51.7% remoal in **Figure 8**.

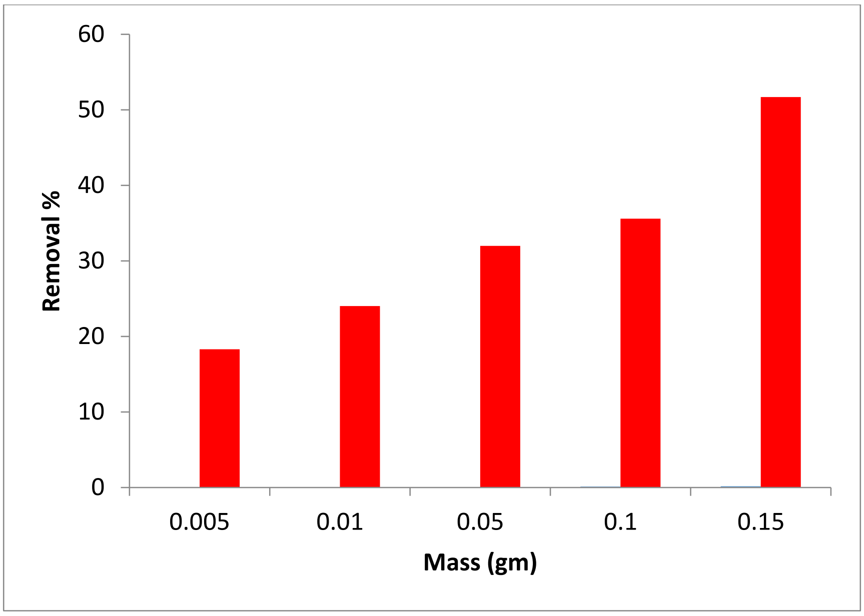

Figure 8. Effect of mass on removal of cibacron- red by ES nanoparticles.

3.2.4 Adsorption isothermal

Experimental isotherms define adsorption capacity, which helps determine the procedure's feasibility for a given application, select the best adsorbent, and estimate dosage requirements. The isotherm plays a key role in the analysis and design of sorption systems.

In **Figure 9,10** Langmuir and Freundlich's equations were used to calculate cibacron-red adsorption onto ES. Isotherm studies were then performed.

The equation that follows shows how well the data fits the Freundlich adsorption isotherm

$$\text{Log } Qe = \log K_f + 1/n \log Ce \qquad 2$$

K_f: Freundlich's constant propagate to adsorption capacitance

n: ameasure of the intensity of the adsorbent surface and depends on the type of adsorbent surface, the temperature and the nature of the adsorbent

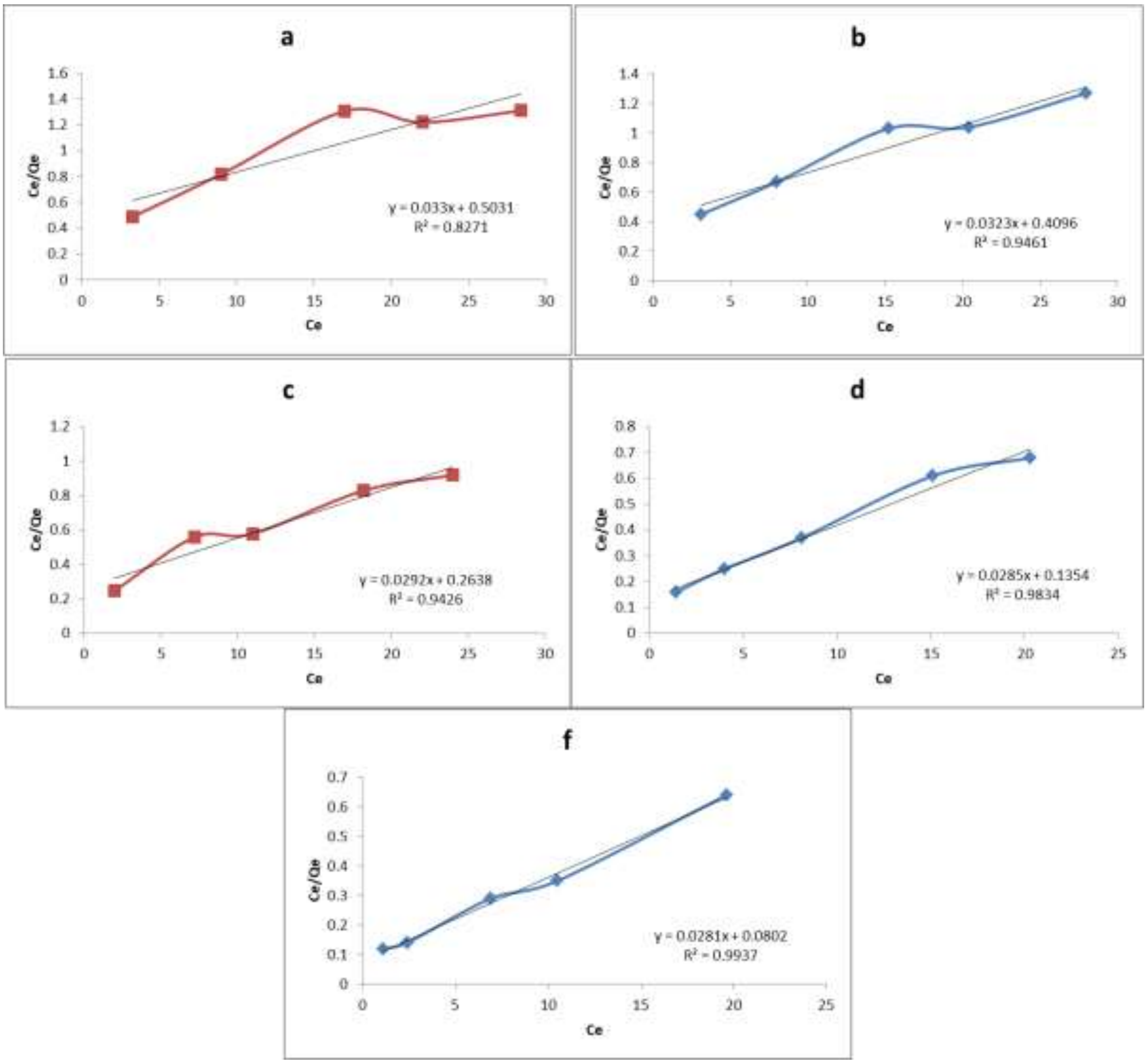

Figure 9. Langmuir models at different temperatures a-288 b-298 c-308 d-318 f-328 K.

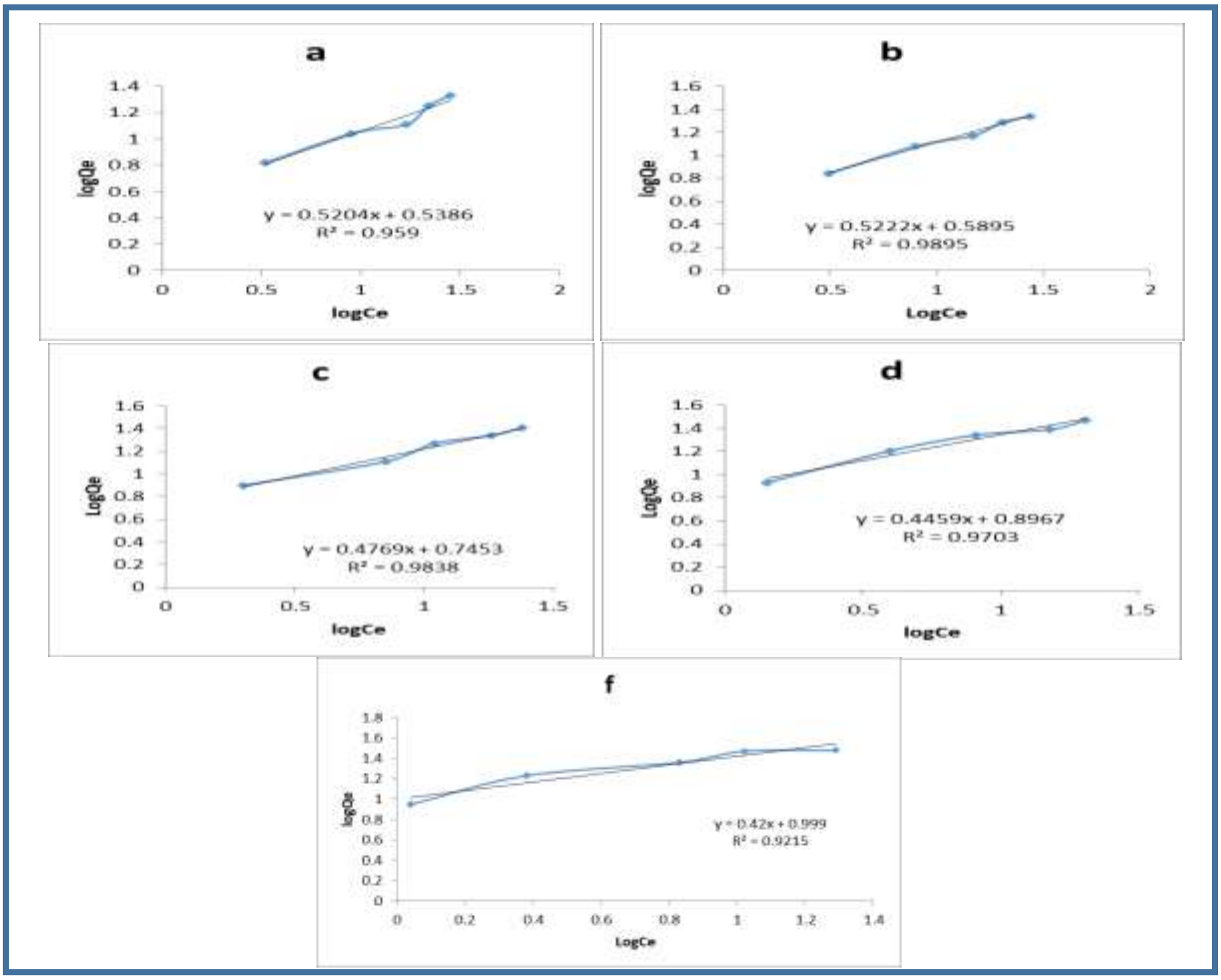

Figure 10. Freundlichmodels at different temperatures a-288 b-298 c-308 d-318 f-328 K

$$C_e/Q_e=1/K_L.q_{max}+(1/q_{max})Ce \quad 3$$

The Langmuir constant is KL (mg/L), but the maximum d Cibacron red dye is q max (mg/g). The separation factor, often known as the dimensionless constant (RL), outlines and illustrates the main features of the Langmuir isotherm:

$$)\ \log(Ce) \quad 4 \log(Qe) = \log(kf) + (\frac{1}{n}$$

While the Temkin adsorbent isometric expression graphically illustrated the interaction between adsorbent and adsorbing particle. This model was applied to the forms shown in Equation below(5):

$$Q_e=B_T\ln K_T+B_T\ln C_e \quad 5$$

By plotting Qe against lnCe, the constants A and B were obtainedwhich are the constants of the Temkin isotherm (L/g) and theTemkin constant associated with adsorption heat (J mol-1),the gas constant, respectively, is 8.314 mol/k. B is a Temkin as well.is the constant isotherm temperature, while is the absolute temperature in Kelvin. Utilizing a spectrophotometer to evaluate adsorption and the preceding relationship, the adsorption Temkin graph to qe against ln Ce is plotted in **Figure 11** and its parameters are calculated.

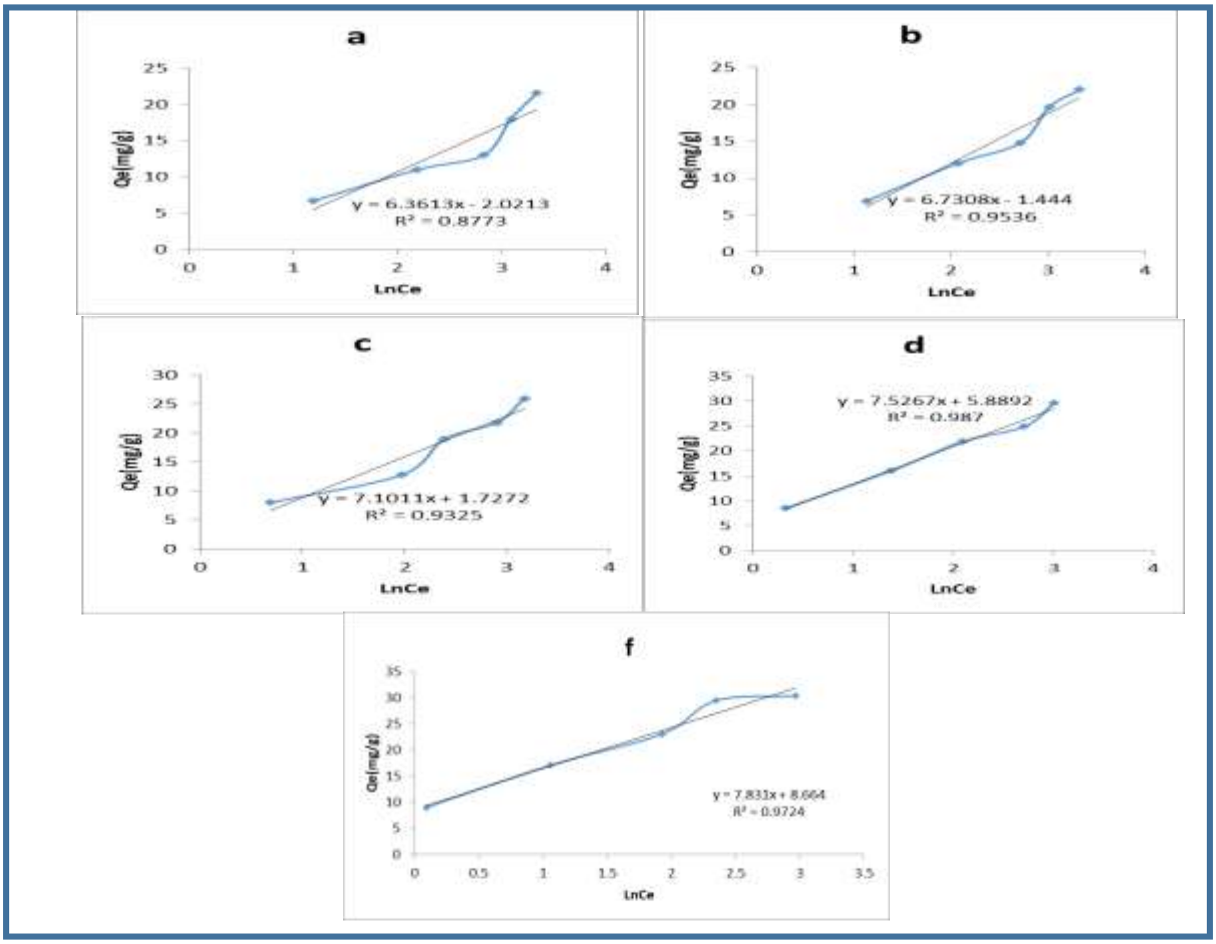

Figure 11. Temkin models at different temperatures a-288 b-298 c-308 d-318 f-328 K.

Table 2. The values of the constants of the linear equations for the adsorption of a dye on the surface of nanoscale (Es) at different temperatures

Tem(k)	Langmuir Constants				Freundlich Constants			Temkin Constants		
	q_{max}	K_L	R_L	R^2	N	K_f	R^2	K_T	B	R^2
288	1.079	0.014	0.98	0.827	1.92	3.45	0.959	0.132	376	0.877
289	1.027	0.0142	0.96	0.946	1.91	3.88	0.989	0.235	368	0.953
308	0.85	0.015	0.9	0.942	2.1	5.56	0.983	5.473	360	0.932
318	0.7	0.017	0.85	0.983	2.24	7.87	0.970	330.2	351	0.987
328	0.648	0.017	0.75	0.993	2.31	9.77	0.921	5790	34.8	0.972

3.2.5 Thermodynamic study

To assess adsorption capability and spontaneity, several thermodynamic parameters were calculated. Using the van't Hoff equations depicted in **Figure 12**, various adsorption parameters, including free energy change, enthalpy change, etc., were estimated. **Table 3** shows the ΔG°, ΔH° and ΔS° values. The negative value of ΔG° indicated that the rate of adsorption was spontaneous and feasible; the positive value of ΔH° (kJ/mol) showed that the adsorption was endothermic; as well as the vastly increased randomness and disorder of the adsorbent surface following the sorption process, which was demonstrated by a positive value of ΔS°.

Table 3.listed the Thermodynamic parametersi .

Surface	C_0 (ppm)	T(K)	ΔH kJ/mol	ΔG kJ/mol	ΔS J/mol.K
Es	10	288	33.4	-1.39	120
		298		-2.59	
		308		-3.79	
		318		-4.99	
		328		-6.19	
	20	288	34.25	-0.31	120
		298		-1.51	
		308		-2.71	
		318		-3.91	
		328		-5.11	
	30	288	32.72	1.04	111
		298		-0.06	
		308		-1.16	
		318		-2.26	
		328		-3.36	
	40	288	24.94	0.542	84.71
		298		-0.298	
		308		-1.14	
		318		-1.99	
		328		-2.83	
	50	288	16.79	0.646	56
		298		0.012	
		308		-0.458	
		318		-1	
		328		-1.57	

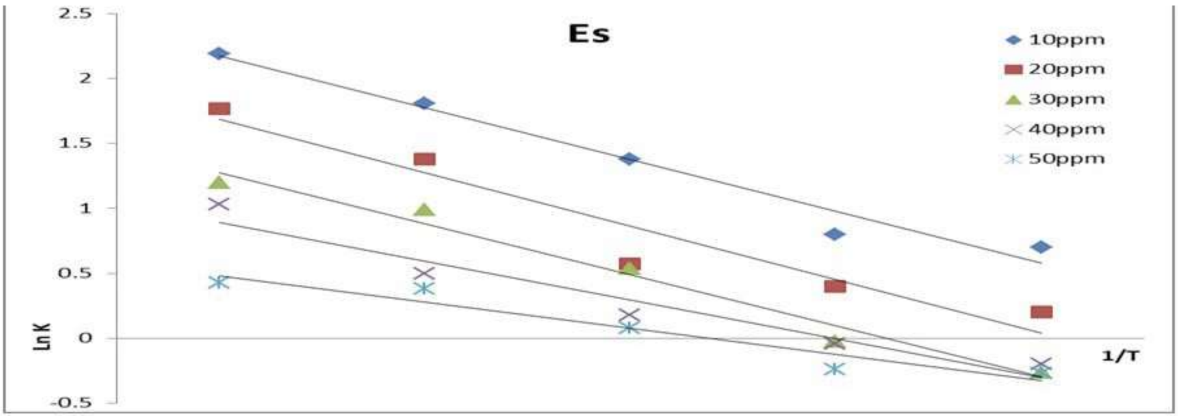

Figure 12. The relation between ln Keq and $^1/_T$ for the adsorption of cibacron- red.

3.2.6 Kinetic models

The behavior of dye during its adsorption on the surfaceadsorbents of NPs are very important in the adsorbent processapplications. According to the findings of the dye study, the adsorption the equilibrium time for 0.01 g of the substance was approximately 30 minutes.
Nanoparticle adsorbentsin addition, both traditional andkinetic models were utilized throughout this investigation to depict the the information regarding adsorption that was mentioned earlier as follows: Pseudo-first-order model(6):

$$\ln (qe - qt) = \ln (qe) - k_1 t \quad 6$$

Where qe (mg g^{-1}) is the adsorption capacity at the equilibrium concentration, at equilibrium, the amount of qt (mg g^{-1}) that has been adsorbed is dye after a certain amount of time, denoted by t (in minutes) and k1 is the pseudo-first-order
Rate constant (min^{-1}), and the results are depicted in **figure 13A** it is possible to use the pseudo-second-order kinetic modelwritten out as

$$t/qe=1/K2qe^2) +(1/qe)t \quad 7$$

In this equation, K_2 represents the pseudo-second-order rate constant.a model of pseudo-second order with a high degree of associationfactor with a high enough R2 value to accurately describe the kinetic information and **Figure 13 B**.

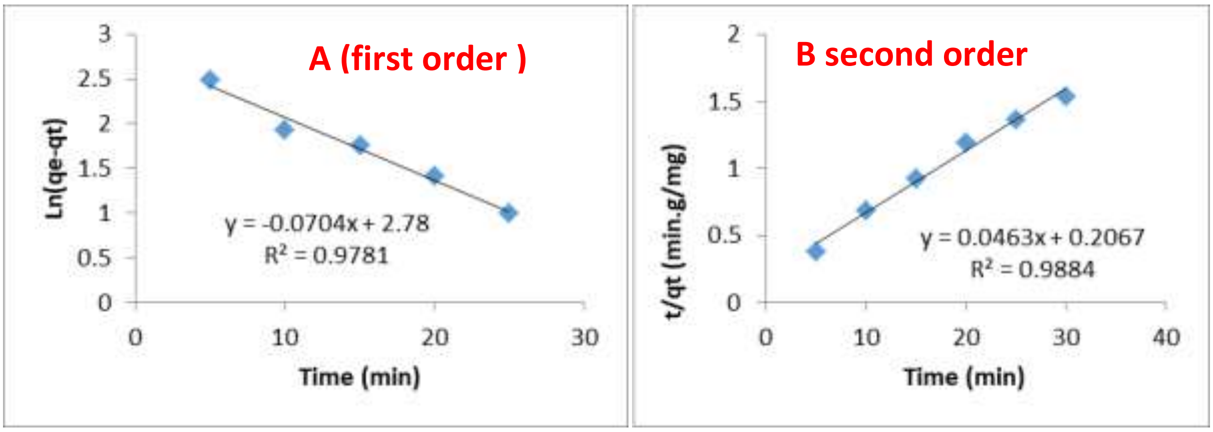

Figure 13 . Parameter kinetics of pseudo first order and pseudo second order

4. Conclusion

This research successfully removed cibacron- red using a low-cost biosorbent made from ES. During nano experiments, a significant degree of elimination was observed. Based on the values of the regression coefficients, the Freundlich model performed better than the Langmuir isotherm due to the value of ΔH (KJ/mol). Frendlich's model was used to simulate the equilibrium of the process, Langmuir and Temkin have been calculated. In order to determine the thermodynamic parameters ΔG°, ΔH° and ΔS°, thermodynamic experimental studies on ES removal by nanotechnology were performed.

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