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Kinetic, Thermodynamic and Equilibrium Studies of Direct Brown-MR Dye Removal by Adsorption on Exfoliated Graphite Oxide

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A B S T R A C T

In this article, the concept of physical adsorption was applied for the removal of Direct Brown-MR (DB) textile dyes from industrial effluents using Exfoliated Graphite Oxide nanoparticles as adsorbent. The Exfoliated Graphite Oxide (EGO) nanoparticles were prepared by the Hummers method. The characterization study revealed the abundance of functional group and nanomaterial features in prepared material. The DB adsorption is increased with rising adsorbent doses, pH, temperature and initial DB solution concentrations. Adsorption through EGO was found to be very effective for the removal of the dye, where the percent dye removal was 99.7%. The equilibrium data were determined experimentally and the equilibrium isotherm was found to be of a favorable type and fit well by Langmuir isotherms. Thermodynamic studies suggest adsorption process's endothermic nature and spontaneity.

Keywords: *Adsorption, dye, exfoliated graphite oxide, isotherms, kinetics*

1. Introduction

A large number of different types of dyes, which are commercially available, are indispensable to the textile, paper, plastics, rubber and leather industries [1]. Many of them are toxic and non-biodegradable in nature and stable to light and oxidation. Dyes are among common synthetic aquatic pollutants of possible environmental concern, because of their extensive, widespread use. These compounds are quite difficult to remove from water since they are resistant to light and oxidizing agents. The presence of these dyes in wastewaters has to be carefully considered, as not even biological degradation was effective in their elimination, the efficiency largely depending on the structure of dye. Biodegradation of dyes is in general not efficient enough, due to the presence of complex and stable aromatic structures.

The chemical methods for the treatment of dyes and dye effluents are precipitation, coagulation, filtration, floatation, electrochemical degradation, and advanced oxidation techniques etc [2, 3]. Adsorption, reverse osmosis, and ultrafiltration are treated as physical methods [4, 5]. Physical methods of treatment of dyes are non-destructive as the dye transfer from water into the adsorbent occurs which generates large amount of residue. Photochemical irradiation of toxic dyes in presence of a photocatalyst is one of the alternative methods developed recently, but the photocatalysts like titanium dioxide and zinc oxide which are semiconductors, they are expensive and inefficient [6]. Disposal of the sludge after dye adsorption/removal is of major concern.

Adsorption is one of the cheapest and simple methods for the removal of dyes. Most common adsorbents are activated charcoal, zeolites, layered materials, metal oxides, and graphite based compounds [7, 8]. Adsorption is most popular due to its advantages of simple operation, low cost, rapid treatment and effectiveness for removing low dye concentration waste streams. Various adsorbents such as clay, perlite, zeolite, and unburned carbon [9] have been developed and used to remove dyes from aqueous solution. However, increasingly stringent standard on the quality of drinking water has stimulated a growing effort on the exploiture of new high efficient adsorbents.

The use of graphene and its composites were recently proposed by several groups for the removal of organic pollutants from aqueous solutions is receiving increased attention. It is due its unique structure, unusual physical and mechanical properties such as high carrier concentration and mobility [10], high thermal conductivity [11], and high mechanical strength [12]. Similar to graphene, GO also has a layered structure and it can be obtained in high yield by controlled chemical oxidation of graphite [13]. GO can be easily functionalized with phenolic, carboxyl, epoxide and other groups by oxidation treatment [14].

The large surface area and the plurality of oxygen functionalities on graphene oxide could play significant roles in the abstraction of oppositely charged organic dyes from aqueous solution [15]. Comparative adsorption studies on the removal of cationic dyes, methylene blue and malachite green, showed that graphene oxide has higher adsorption capacity, and shorter equilibration time compared to pristine graphite [16]. Similar adsorption mechanism was also reported for the adsorption of methyl green using graphene oxide nanosheets [17]. Hence, exfoliated graphene oxide nanosheets are regarded as promising adsorbents for cationic dyes in solution.

The present work focuses on the kinetic and equilibrium conditions for maximum removal of a toxic textile dye, Direct Brown-MR (DB), using dispersed graphite oxide nanoparticles in contaminated water samples and dye solutions of different concentrations. Further, investigation of adsorption characteristics of dye, determination of optimum conditions for the interaction under static conditions, adsorption equilibrium studies, kinetics of

adsorption, and experiments on both synthetic and real effluents for their removal was studied. Starting from experiments on laboratory-prepared synthetic dye solutions, the research was also extended towards the treatment of real industrial effluent samples for the removal of selected dyes. Optimized conditions for Direct Brown-MR described in this work include, Effect of agitation time, Effect of adsorbent dose, Effect of initial concentration and adsorption kinetics studies, Effect of pH, Effect of temperature, Scanning Electron Microscopic studies.

2. Methods and Materials

Experiments were designed by focusing on treatment of real industrial effluent samples with some preliminary experiments. The dye samples and real dye effluent samples were collected from Molaklmuru dye industries and were used for experiments.

2.1 Chemicals and Reagents:

Natural graphite flakes, Mohr's salt, NaCl, NH$_4$OH, NaNO$_3$, KMnO$_4$, H$_2$SO$_4$, HCl, H$_2$O$_2$ (30%), KMnO$_4$, are obtained for SD Fine chemicals, India and the toxic textile dye Direct Brown MR was obtained from Molaklmuru textile dying industry. All the chemicals were of analytical reagent grades and used as received, without further purifications. The aqueous solutions were prepared in double distilled water. The carbon electrodes of > 90% purity were obtained from commercial dry cell, tested for purity and proper surface treatment were given before electrochemical experiments.

2.2 Preparation of graphite oxide:

The graphite oxide was prepared by Hummer's method [18]. The prepared graphite oxide (GO) was characterized by UV-Visible and FT-IR spectroscopy.

2.3. Batch experiments

Dye adsorption experiments were performed by taking 50 ml stock solution of dye (20 to 100 mg l^{-1}) and treated with different dose of adsorbent. The variables studied were agitation time, pH, temperature, adsorbent dose and concentration. After desired time of treatment samples were filtered to remove the adsorbent and progress of adsorption was determined spectro photometrically using Systronics spectrophotometer at the wavelength for maximum absorbance (λ_{max}) which is 520 nm for Direct Brown-MR.

2.4. Effect of agitation time (25, 40, 60, 80 and 100 min)

The experiments were carried out by taking 50 ml samples of dye in separate bottles and treated with dose of adsorbent dose at room temperature and also at variable temperatures.

2.5. Effect of adsorbent dose (0.05, 0.1, 0.2 and 0.4 g)

The study was carried out with different dose of adsorbent with 85 μm average particle size. The concentrations of samples were 10 mg l-1and treated at fixed temperature for 30 minutes.

2.6. Effect of initial concentration and adsorption kinetics studies

The initial concentration provides an important driving force to overcome all mass transfer resistances of the dye between the aqueous and solid phases. The effect of initial DB concentrations on sorption by EGO was investigated in the range of 20-100 mg L^{-1} of the initial dye concentration at an adsorbent dosage of 0.05 g and 0.20 g. In order to determine the controlling mechanism of adsorption process such as mass transfer and chemical reaction, the first order kinetic model is used to test the experimental data.

2.7. Effect of pH (3, 5, 7, 11 and 13)

The effect of pH was studied in the treatment of 50 ml aqueous solution of dyes with 0.2 g dose of adsorbent. All the samples were treated for half an hour at fix temperature (room temperature).

2.8. Effect of temperature (20, 40, 60, 80 and 100 ºC)

The effect of temperature was investigated with 0.2g dose of adsorbent mixing in 50 ml aqueous solution of dyes of concentration 20 mg l-1 and the samples were treated for 30 minutes.

2.9. Scanning Electron Microscopy

The presence of adsorbate on the surface of adsorbent changes the surface morphology of the adsorbent. This can be understood from the scanning electron microscopic studies.

3. Results and Discussions:

3.1. Effect of agitation time

The samples of dye (Direct Brown- MR) of different initial concentrations (20, 40, 80,100mg/L) were taken in separate flasks and treated with different dose of adsorbent (0.05, 0.1, 0.2, 0.4g/50mL). The Figure 1 gives UV-Visible spectra of Direct Brown- MR adsorption onto EGO at $\lambda_{max}=$ 520nm at different contact time and Figure 2 shows a picture of removal of Direct Brown- MR dye by EGO at different time.. From Figure 1 and 2, it is evident that the absorbance value is found to decrease very near to zero in the dye solution after adsorption onto EGO. The variation in percent removal of dyes with the elapsed time has been shown in Table 1. It is evident from the figure that EGO treatment resulted in an increase in removal of Direct Brown- MR, with time and reached up to 99% in 60 min. The optimum time is 60 min for the dye samples at which equilibrium is obtained. The increase in the extent of removal of dyes with increasing time because of the diffusion of more and more dye molecules into the pores of EGO with time. Thus the removal of dyes from aqueous solution is controlled by the rate of transport of the adsorbate species from the outer sites to the interior sites of adsorbent [19].
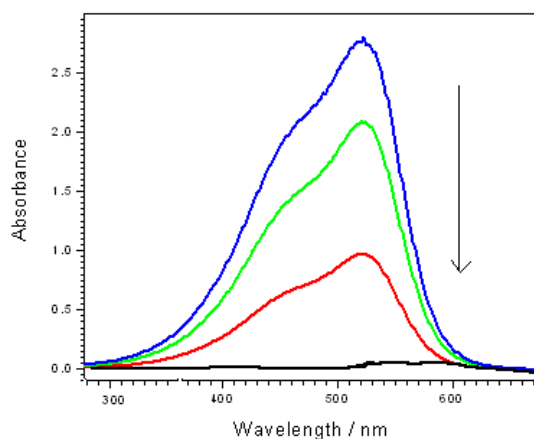

Figure 1: UV-Vis spectra of Direct Brown- MR adsorption on EGO, λ_{max}= 520nm.

Figure 2. The removal of Direct Brown- MR dye with time

The amount of dye adsorbed by the adsorbent was calculated using the following equation,

$$Q_e = \frac{(C_o - C_e)}{m} \times V$$

Where, Q_e = The amount of dye adsorbed by adsorbent (mg/g)

C_o = Initial concentration of dye (mg/L)
C_e = Dye concentration at a given time (or equilibrium time)
V= Volume of the dye solution (L)
m= Weight of adsorbent (g).

The percentage uptake of the dye is calculated by using the following equation,

% uptake of dye $= \dfrac{C_o - C_e}{C_o} \times 100$

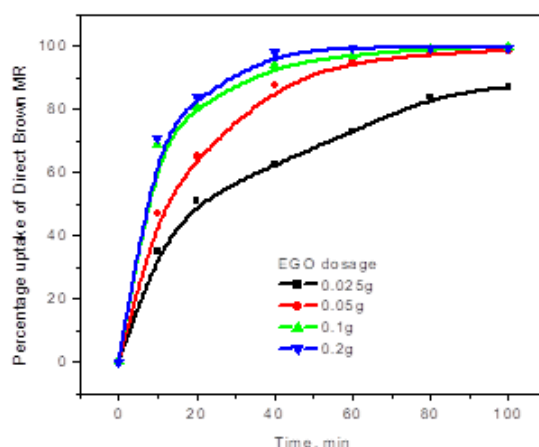Where, C_o = Initial concentration of dye (mg/L)

         C_e = Dye concentration at a given time (or equilibrium time)

Table -1: Percentage uptake of dye (Different initial concentrations of volume 50mL)   at 0.2 g EGO dosage.

Time Min	10ppm % Uptake	20ppm % Uptake	40ppm % Uptake	60ppm % Uptake	80ppm % Uptake	100ppm % Uptake
0	0	0	0	0	0	0
10	80	71	68	68	65	66
20	94	84	81	82	81	80
40	96	98	90	87	89	87
60	99	99.4	97.3	97	96	97
80	99.6	99.6	98.4	98	98	97.2
100	*99.6*	*99.7*	*99.3*	*98*	*97*	*97*

3.2. Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage (adsorbent prepared in different batch) was studied on Direct Brown- MR removal by keeping all other experimental conditions constant. Percentage uptake of Direct Brown- MR on different dosage of EGO is as shown in the Figure 3. The Table -2 gives percentage uptake of dye (20ppm initial concentration of volume 50mL) at various dosage of EGO (g). The results show that as the adsorbent concentration is increased, the percentage of adsorption also increased, but the amount adsorbed per unit mass of the adsorbent decreased relatively. With increasing adsorbent dosage, at fixed contaminant concentrations, more active surface area is available for adsorption and more active adsorption sites are available [20].

Figure 3: Percentage uptake of Direct Brown- MR on different dosage of EGO

Table -2: Percentage uptake of dye (20ppm initial concentration of volume 50mL) at various dosage of EGO (g)

Time	% uptake of dye at various dosage of EGO			
	0.025	0.05	0.1	*0.2*
0	0	0	0	*0*
10	35	47	69	*71*
20	51	65	81	*84*
40	62.5	87.5	94	*98*
60	73	95	97	*99.4*
80	84	97.3	99.2	*99.6*
100	87	98.7	99.6	*99.7*

3.3. Effect of initial concentration and sorption kinetics

The adsorption of Direct Brown- MR for different initial concentration of Direct Brown- MR at room temperature as a function of contact time illustrated in Figure 4, 5 and 6. The curves show rapid initial rate of sorption which reached equilibrium in less than 100 min regardless of initial concentration. Relatively short contact time for the sorption process would indicate that chemisorption is probably important. The fast uptake at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the sorbent, followed by slower sorption due to the intraparticle diffusion. Sorption

kinetic studies can be considered as vital as it provides some important insight about the mechanism of sorption. The modelling of the kinetics of adsorption of Direct Brown- MR onto the EGO were investigated by common model, namely pseudo-first order kinetic models (Langergren, 1898). It may be represented in the following form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 T}{2.303} \text{ (Pseudo-first order)}$$

A plot of the amount of dye adsorbed (mg/g) vs contact time for different dosages is shown in Figure 3. It was observed that the amount of dye uptake, q_e (mg/g), increased with contact time. Further, the amount of dye adsorbed increased with increase in temperature. It follows from the straight line plots of the figure that the dye sorption reaction is of first-order irreversible type and the values of rate constant "K" was calculated from the slope of the plots.
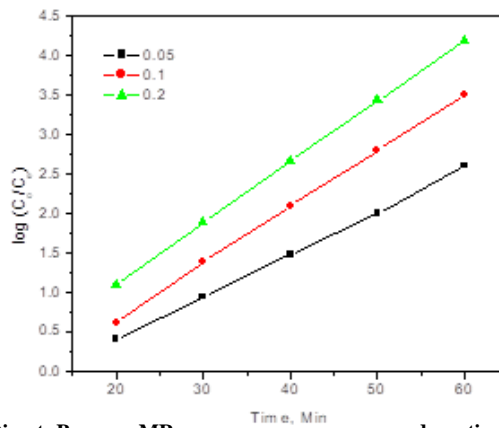

Figure 4: First order kinetic plot of Direct Brown- MR   **adsorption (mass of sorbent = 0.05, 0.1 and 0.2g/50mL of the dye, initial concentration**   **= 20mg/lit, Temperature= 25±2ºC).**
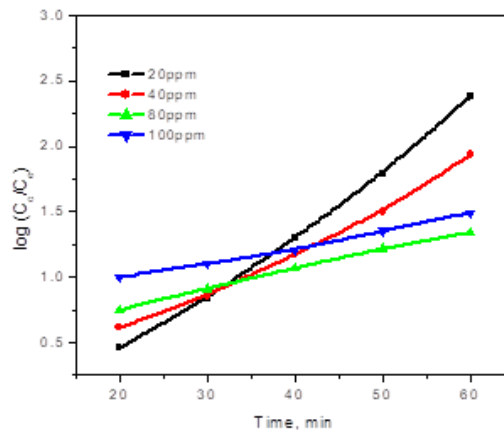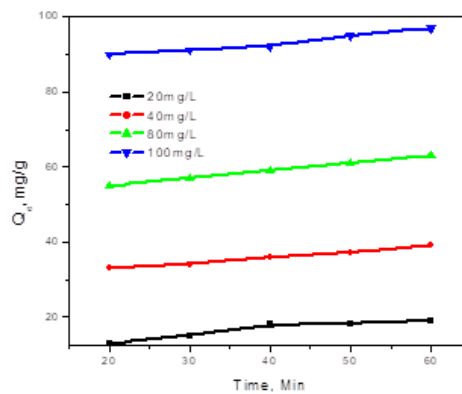

Figure 5: First order kinetic plot of Direct Brown- MR adsorption (mass of sorbent = 0.2g/50mL of the dye, initial concentration = 20, 40, 80 and 100mg/lit, Temperature= 25±2ºC).

Figure 6: First order kinetic plot of Direct Brown- MR adsorption (mass of sorbent = 0.2g/50mL of the dye, initial concentration = 20, 40, 80 and 100mg/lit, Temperature= 25±2ºC).

The initial concentration of solute acts as a driving force for the adsorption process, favoring diffusion and mass transfer processes from the solution (with a higher amount of dye) to the free surface of the adsorbent [21]. As the concentration of the solution increases, the amount of bound material shows a similar trend, then at low initial solution concentration the surface area of the adsorbent and thus the number of adsorption binding sites is high, so the contaminant ions or molecules (in our case dye molecules) can easily bind to the adsorbent surface. At higher initial solution concentrations, the total available adsorption sites are limited, which may result in a reduction in the percentage removal of contaminants. The increase at higher initial concentrations may be attributed to increased driving forces [22]. At low concentrations, the ratio of active sites to dye molecules can be high, allowing all molecules to interact with the adsorbent and be removed from solution almost instantaneously [23].

3.4. Effect of pH

The aqueous solution of dyes having concentration of 20 mg l^{-1} was treated by 0.3 g dose of adsorbent for 30min with pH varying from 3 to 13. The pH was maintained with the help of 0.1 N HCl and 0.1 N NaOH solution. When the aqueous solution of dyes were treated with EGO, it was found that as pH increased from 3 to 7, the % removal of dye increased from 66 to 99.1, as seen in the Figure 7 that the percentage remains almost same in the basic pH, but the adsorption capacity is increased slightly till pH 13. The increased in the removal of dye at higher pH may be attributed to the neutralization of dye.

The presence of carboxyl groups in DB dye can contribute to the adsorption mechanism through the electrostatic interaction between COO$^-$ reactive groups of dye and EGO, but it should be noted that the involvement of strongly dissociated sulfonic groups is much higher than that of partially dissociated carboxyl groups. The strongly acidic sulphonate groups of the dyes were dissociated and converted to anionic dye ions.
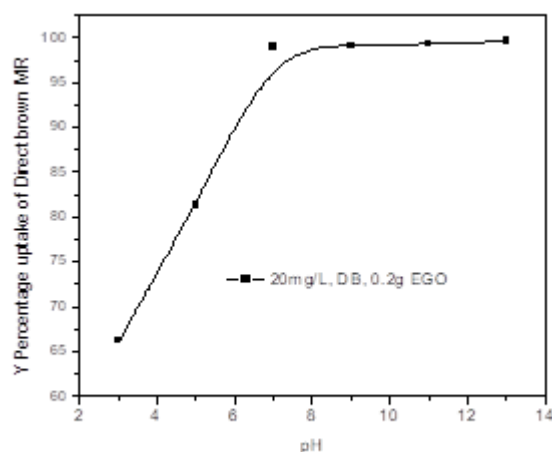
Figure 7: Effect of pH on the removal of Direct Brown- MR by EGO

The pH of the aqueous medium can influence the properties of the adsorbent, the adsorption mechanism, and the dissociation of dye molecules. Not only the adsorbent but also the chemical structure of the dye can be altered by the pH of the solution. The pH changes the surface charge and the degree of ionization of the adsorbed ion [24, 25]. This demonstrates that DB bind more effectively to the adsorbent surface in acidic media.

3.5. Effect of temperature and thermodynamic analysis

Under this parameter, a series of experiments were conducted at different temperatures to investigate the effect of temperature on the sorption of DB dyes onto EGO. As seen from Figure 8, the effect of temperature on the equilibrium dye uptake was observable. An increase in temperature from 20 to 80°C leads to an increase in percentage uptake. When the temperature was further increased to 80°C, equilibrium uptake value was detected to be 98%.

The increase of the dye uptake with increase in temperature suggests that the dye-algal-sorption process may be endothermic in nature. If adsorption is governed only by physical phenomena, an increase in temperature will be followed by a decrease in adsorption capacity [26]. Thermodynamic parameters such as change in free energy ($\Delta G°$) (Jmol^{-1}), enthalpy ($\Delta H°$) (Jmole^{-1}) and entropy ($\Delta S°$) (J K^{-1} mol^{-1}) were determined using following equations

$\Delta G° = RT \ln K°$

$\Delta G° = \Delta H° - T\Delta S°$

$\ln K° = \Delta G°/ RT$

$\ln K° = \Delta S°/R - \Delta H°/RT$

Where K^o is equilibrium constant, C_{solid} is solid phase concentration at equilibrium (mg/l), C_{liquid} is liquid phase concentration at equilibrium (mg/l), T is temperature and R is gas constant.

The ΔG^o values were obtained from equations, ΔH^o and ΔS^o values were obtained from the slope and intercept of plot ln K_o against $1/T$, presented in Table-3. The negative value of ΔG^o indicates the adsorption is favourable and spontaneous. The ΔG^o values increases with increase in temperature and decreases with increase in initial concentration of DB. The low positive values of ΔH^o indicate endothermic nature of adsorption. The positive values of ΔS^o indicates the increased disorder and randomness at the solid solution interface of DB with the adsorbent. The adsorbed water molecules, which were displaced by adsorbate molecules, gain more translational energy than is lost by the adsorbate molecules, thus allowing prevalence of randomness in the system. The increase of adsorption capacity of the adsorbent at higher temperatures was due to enlargement of pore size and activation of adsorbent surface [27].
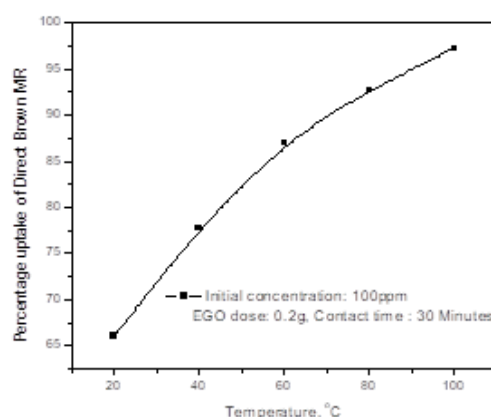

Figure 8: Effect of Temperature on the removal of Direct Brown- MR by EGO

Table 3: Equilibrium constant and thermodynamic parameters for the adsorption of Direct Brown- MR onto EGO.

C_O Mg/L	K_O			ΔG^O (kJ/mol)			ΔH^O (kJ/mol)	ΔS^O (JK^{-1} mol^{-1})
	30°C	40°C	50°C	30°C	40°C	50°C		
20	3.3	4.1	5.8	-1.29	-2.03	-3.17	-7.5	32.1
40	2.4	2.9	4.9	-0.94	-1.53	-2.86	-4.1	21.3
80	1.8	2.6	3.7	-0.63	-1.38	-2.36	-2.2	13.7

3.6. Scanning Electron microscopic studies

SEM image is a powerful tool by which surface morphology of adsorbent can be observed and also size of the particles can be measured. Figure 9 shows the SEM picture of the EGO nanoparticles after the adsorption of dye. It can be seen from the Figure 9 that the layered or fiber type of structure of EGO is not observed. The space is filled with the molecules after adsorption. In the figure it is observed that most of the area on the surface of EGO is covered with adsorbed molecules.

Although some EGO particles are found to be agglomerated, most of the particles, termed as primary particles, can be identified in nanometer scale. A significant change is found for the SEM image of the dye adsorbed sample. From Figure 9, it is observed that most of the mesopores, which are clearly visible, are filled by dye molecules, which is well agreed with previous reports [28, 29].
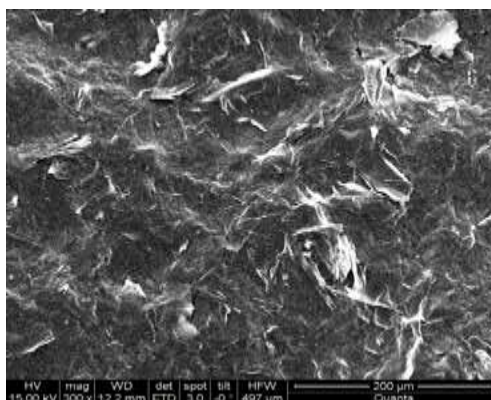

Figure 9: SEM image of EGO after adsorption of DB onto it.

4. Conclusion

Investigations into kinetics and thermodynamic studies of Direct Brown-MR (DB) textile dyes removal in aqueous solution onto Exfoliated graphite oxides have been carried out in this work. The Exfoliated Graphite Oxide (EGO) nanoparticles were prepared by the Hummers method. The DB adsorption was carried out at various parameters like adsorbent doses, pH, temperature and initial DB solution concentrations. At temperature of 298K and pH 7, 99.7% of DB was found to have been removed onto 0.3 mg of EGO at optimized contact time of 100 min, and concentration of 0.6 mg/100mL. The low positive values of ΔH^o indicate physisorption and endothermic nature of adsorption. Experimental data tested against results of the kinetics and adsorption isotherm models showed that the removal of DB was best fitted to pseudo first order. Adsorption through EGO was found to be very effective for the removal of the dye and the thermodynamic studies suggest adsorption process's endothermic nature and spontaneity.

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