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Removal of Ethyl Violet Dye from Aqueous Solution by Graphite Dust and Nano Graphene Oxide Synthesized from Graphite Dust

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Abstract *Nano graphene oxide was synthesized from graphite dust using Hummer's method. The graphite dust and the synthesized nano graphene oxide were used as an adsorbent to remove ethyl violet dye from aqueous solution. The equilibrium amount of dye adsorbed by graphite dust at 303, 313, 323 and 333 K ranged from 5.303 to 37.236, 1.551 to 22.779, 1.058 to 26.026 and from 1.298 to 22.849 mg/g respectively. For nano graphene dust, the equilibrium amount ranged from 1.904 to 41.467, 1.834 to 55.712, 1.058 to 26.023 and from 1.298 to 22.849 mg/g at 303, 313, 323 and 333 K respectively. Nano graphene oxide exhibited better performance than graphite dust except at 333 K. The adsorption of ethyl violet occurred through a physical adsorption mechanism at 303 K but at higher temperature, chemisorption dominated, Langmuir isotherm best described the adsorption of the dye. The theoretical adsorption capacity of the adsorbent increased with temperature. Nano graphene oxide displayed better surface modification properties than graphite dust.*

Key Words: *Decontamination, colour, adsorption, graphite dust, nano graphene oxide*

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1.0 Introduction

Contamination of water due to change in colour could be injurious to aquatic environment because it can affect the intensity of light absorption and hence limits the progress of photosynthesis among marine organisms (Odoemelam *et al*., 2018). Apart from imparting colour to water, some dyes are toxic while others can react with compounds within the environment and lead to the formation of other compounds that may be toxic (Odoemelam *et al*., 2018). There are several industries that use dyes in some of their industrial lines. These include ternary, leather, textile, paint/pigment, drugs and other industries (Zhou *et al.,* 2018). Adsorption is regarded as one of the best methods of decontaminating water because the method is simple to design and less expensive (Kulkarni *et al*., 2013). Some adsorbents can be recycled leading to added advantages (Abbas and Trari, 2015). The basic requirements for a material to be a good adsorbent is to have sufficient binding sites to accommodate the adsorbates (Ahmed and Kumar, 2010). Several adsorbents have been reported for dye but most of them suffer from low adsorption capacity, lack of functionality, reusability and recyclability (Banerjee *et al*., 2017)

According to Hussain (2014), carbon nano materials receive special interest because they can be used as nano adsorbents for liquid and gas-phase adsorption in order to remove environmental pollutants. Also, the adsorption properties of carbon nanomaterials have been reported to be unique than conventional adsorbents, providing more area for adsorption to occurr because of their structures, dimensions, and topologies. Also, additional advantage of carbon nanomaterials has been attributed to the flexibility of being formed on dual-format devices (Sharma *et al*., 2009). Wan *et al*. (2016) reported graphene & carbon-based nanomaterials as efficient adsorbents for oil and organic solvents while Tanian *et al*. (2019) found graphene oxide nano materials as good adsorbents for methylene blue. Studies have shown that nano materials have excellent properties that may not be easily met by the raw counterpart (Sarma *et al.,* 2019; Hussain, 2014; Washawan *et al*., 2019; Sadegh *et al*., 2017). However, literature is scanty on the comparative study of adsorption of ethyl violet on nano graphene oxide. Therefore, the present study is aimed at synthesizing nano graphene oxide from graphite dust and to test the

performance of the nanomaterials on the adsorption of ethyl violet dye compared to the graphite dust.

2.0 Materials and methods

2.1 Chemicals/reagents

All reagents were analar grade and were supplied by the Department of Chemistry, Akwa Ibom State University and were used without further purification. Stock solution of ethyl violet dye was prepared by dissolving 1g of the dye in 1000 ml of double distilled water. Serially concentrations of 10, 20, 30, 40 and 50 mg/L were obtained through dilution.

2.2 Synthesis of nano graphene oxide

This was synthesis using Hummer's method as described by Gupta et al. (2015). The materials used were graphite dust, sodium nitrite, hydrogen peroxide (30%), sulphuric acid (70%), and potassium permanganate (99%). KMnO4 (9 g) was added in portions to a cooled (0 °C) solution of conc. H_2SO_4 (69 ml) containing graphite (3 g) and NaNO3 (1.5 g).

2.3 Batch adsorption process

Batch adsorption process as reported elsewhere was used to study the effect of concentration, contact time, adsorbent dosage and temperature (Odoemelam *et al*. 2018). Amount of dye adsorbed at equilibrium was calculated using the following equation

$$q_e = \frac{C_0 - C_e}{C_0} \times \frac{V}{m}$$

where C_0 is the initial concentration of the dye, C_e is the equilibrium concentration of the dye, V is the volume of solution and m is the mass of the adsorbent.

2.4 Determination of concentration of ethyl violet dye

All spectrophotometric analyses were carried out using 721, P/N: A003 UV-visible spectrophotometer. In spectrophotometric analysis, wave length of maximum absorption of ethyl violet dye was measured. The measured wavelength was used as a reference wave length for all analysis and determination of the concentrations using extrapolation method according to Beer-Lambert's law of spectrophotometry.

3.0 Results and Discussion

3.1 Calibration curve

The calibration curve for ethyl violet dye is presented in Fig. 1. The curve was developed according to Beer-Lambert's law of absorption which reveals a proportional relationship between absorbance and concentration at zero intercept. The equation for the linear plot is y = 0.0709 while R^2 value is 0.9336. These display a high degree of linearity. The developed calibration curve was used for further analytical calculation through extrapolation.

3.2 Effect of concentration at various temperatures

Fig.2 shows plots for the variation of amount of dye adsorbed (by graphite and nano graphene oxide) with initial concentration at various temperature. From Fig. 2, it is evident that the adsorption of the dye unto graphite is concentration and temperature dependent. At all temperatures, the amount of dye adsorbed increase with increase in concentration but decreases with increase in temperature. Increase in the equilibrium amount of dye adsorbed with concentration is due to the increase in the number of the dye molecules that approach the surface of the adsorbent. Adsorption capacity for nano graphene is greater than that of graphite dust in the adsorption of dye.

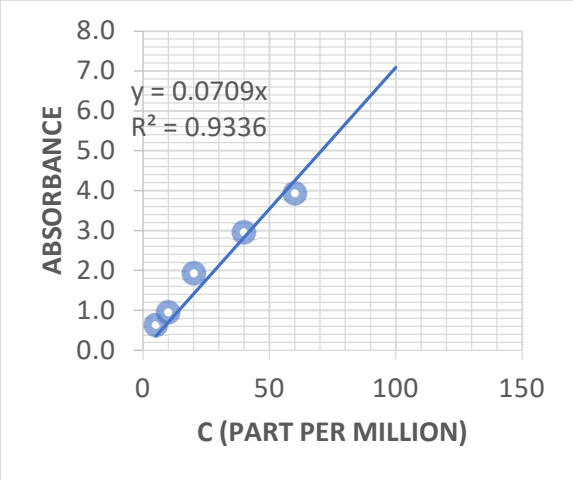

Fig. 1: Calibration curve for ethyl violet dye

According to Odoemelam and Eddy (2009), if the number of adsorption sites in an adsorbent is fixed, the amount of adsorbate adsorbed will increase with concentration because the adsorbate molecules diffusing to the surface will progressively be trapped provided the sticking probability is favourable.

It is also evident from the plots in Fig. 2 that the nano graphene oxide acted as a better adsorbent for the dye than the graphite dust.

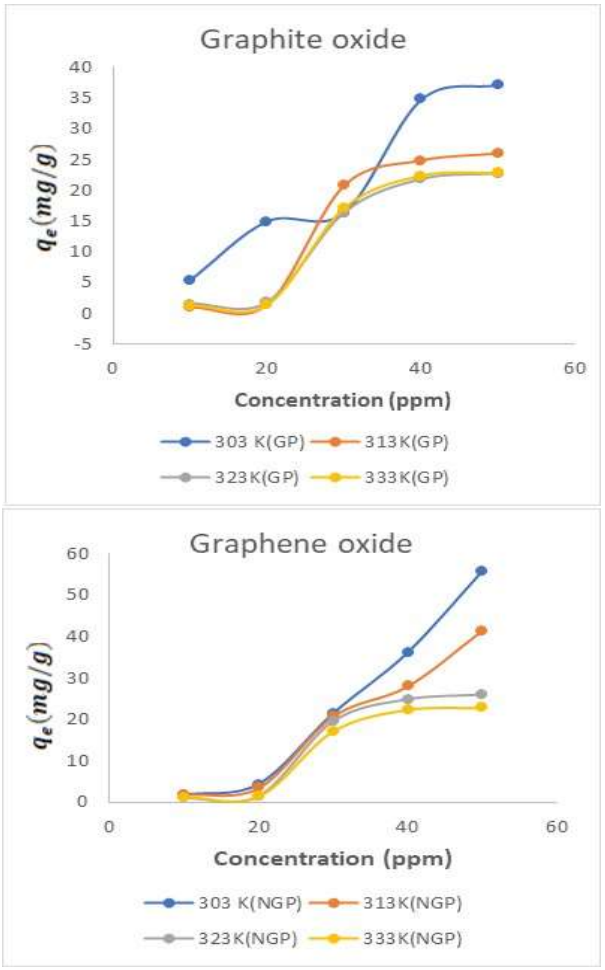

Fig. 2: Variation of amount of dye adsorbed by graphite dust (GP) and nano graphene oxide NGP) with initial concentration at different temperatures

The observed trend in the plots of nano graphene is more ordered than those for the graphite dust. This may be attributed to surface modification during the nano formation stages (ref). Several studies have indicated that nano materials are unique in that they present better surface area than the materials that was used for their formulation. Odiongenyi and Afangide (2019) has reported better.

3.3 Effect of temperature

Fig. 3 presents plots for variation of the amount of different concentrations of dye adsorbed with temperature for graphite dust and nano graphene oxide.

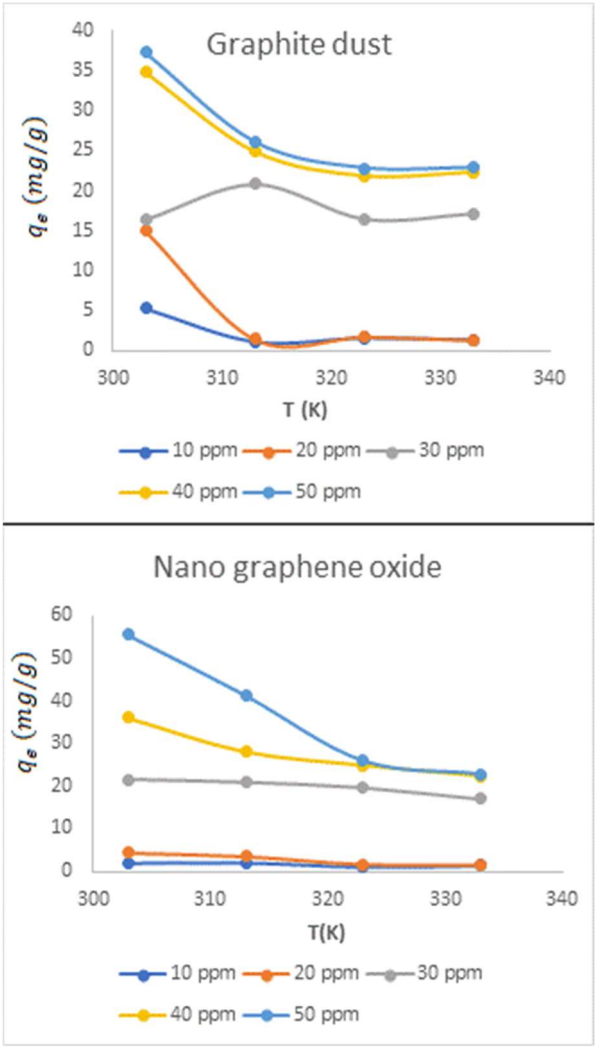

Fig. 3: Variation of amount of dye adsorbed by graphite dust and nano graphene oxide with temperature at various concentrations

The figure indicated that the amount of dye adsorbed decrease with temperature for all concentrations of the dye. However, the observed pattern of decrease was more orderly and unique for nano graphene oxide than for graphite dust. This is attributed to a more orderly and better surface area that

characterized the nano graphene oxide and present it as a better adsorbent than the graphite dust.

3. 4 Thermodynamic and adsorption study

The equilibrium amounts adsorbed(q_e) and equilibrium concentration (C_e) are related to the equilibrium constant according to the following equation (Odoemelam *et al*., 2018),

$$k_c = \frac{q_e}{c_e} \quad (1)$$

Also, from thermodynamics,

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (2)$$

Therefore,

$$-2.303RTlogk_p = \Delta H^* - T\Delta S^* \quad (3)$$

$$-Tlnk_p = \Delta H^* - T\Delta S^* \quad (4)$$

$$lnk_p = \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (5)$$

From equation 5, a plot of $lnk_p\ versus\ \frac{1}{T}$ should be linear with slope and intercept equal to $\frac{\Delta H^*}{R}$ and $\frac{\Delta S^*}{R}$ respectively. These plots are shown in Figs. 4 and 5 for the adsorption of the studied dye unto graphite dust and nano graphene oxide.

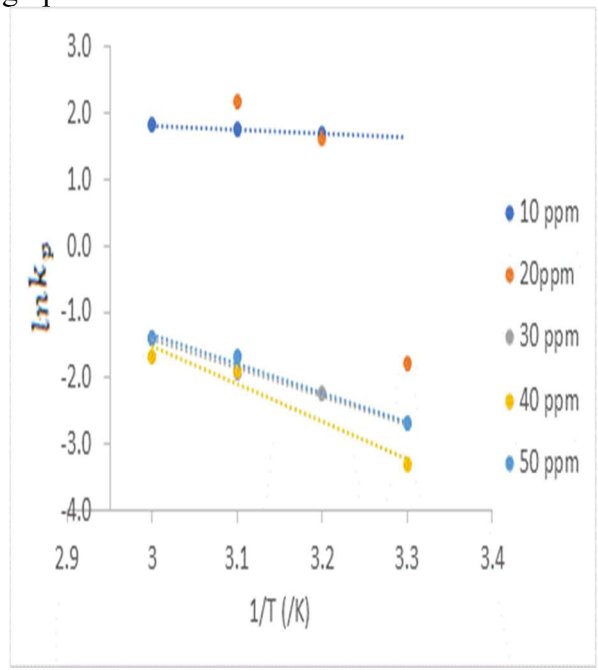

Fig. 4: Variation of lnk_p with 1/T for adsorption of the studied dye unto graphite dust

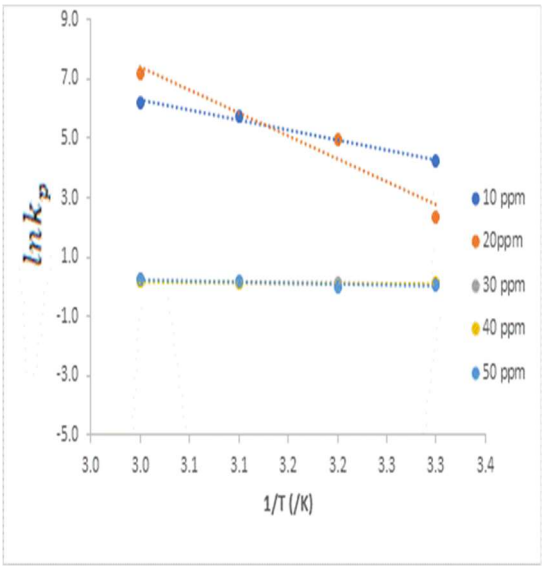

Fig. 5: Variation of lnk_p with 1/T for adsorption of the studied dye unto nano graphene oxide

Thermodynamic parameters deduced from the plots are presented in Table 1. The recorded data indicate high degree of linearity of the plots for both graphite dust and nano graphene oxide adsorbents (R^2 ranged from 0.8146 to 0.9905 and from 0.8544 to 0.9555 for graphite dust and nano graphene oxide respectively.

Data obtained for enthalpy change through the slopes ranged from 5.62 to 36.35 J/mol and from 6.47 to 56.12 J/mol for graphite dust and nano graphene oxide respectively. The enthalpy changes are positive and increases with concentration for graphite dust but decreased with concentration for nano graphene oxide. This indicates that the adsorption of ethyl violet dye on the surface of graphite and nano graphene oxide is endothermic. However, from the trend in variation of amount of dye adsorbed with concentration, the mechanism of adsorption of ethyl violet dye for graphite dust differs from that of nano graphene oxide.

Changes in entropy ranged from 32.04 to 128.00 J/mol and from 8.14 to 220.57 J/mol respectively. This trend is similar to those reported for enthalpy change elsewhere.

Table 1: Thermodynamic parameters for adsorption of the studied dye unto graphite dust and nano graphene oxide surfaces

System	C (ppm)	Slope	Intercept	ΔH^* J/mol)	ΔS^* (J/mol)	R^2
Graphite	10	-0.6759	3.8535	5.62	32.04	0.9875
Graphite	20	-1.853	16.209	15.41	134.76	0.8544
Graphite	30	-4.3098	11.511	35.83	95.70	0.9829
Graphite	40	-5.628	15.396	46.79	128.00	0.9555
Graphite	50	-4.3721	11.776	36.35	97.91	0.9875
Nano graphene oxide	10	-6.7495	26.53	56.12	220.57	0.9905
Nano graphene oxide	20	-1.485	15.87	12.35	131.94	0.9471
Nano graphene oxide	30	-0.3775	1.3723	3.14	11.41	0.8146
Nano graphene oxide	40	-0.265	0.9787	2.20	8.14	0.9849
Nano graphene oxide	50	-0.7787	2.5771	6.47	21.43	0.8496

However, the entropy values were positive, which suggests that the adsorption may not be spontaneous. However, from the Gibb Helmholtz equation, a spontaneous reaction can occur when the enthalpy is less than the product of temperature and entropy change (Eddy *et al*., 2011a). Also, if the enthalpy change is smaller than the product of entropy changes and temperature and the entropy is positive, then the adsorption can be spontaneous. From the results presented in Table 1, the product of the entropy and temperature will always be greater than the change in enthalpy, therefore the adsorption of ethyl violet dye on the adsorbent will always be spontaneous (Eddy *et al*., 2011b).

Adsorption isotherm can furnish information on the adsorption characteristics of the dye. One of the commonest adsorption isotherms is the Langmuir adsorption model, which is applicable to adsorption where there is no interaction between the adsorbed species. The Langmuir isotherm can be represented according to the following equation (Eddy, 2009).

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (6)$$

where Ce is the equilibrium concentration of the adsorbate, q_e is the equilibrium amount of dye adsorbed,

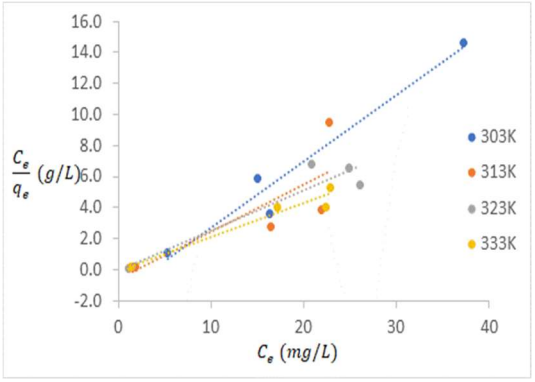

Fig. 6: Langmuir isotherm for the adsorption of the studied dye onto graphite dust

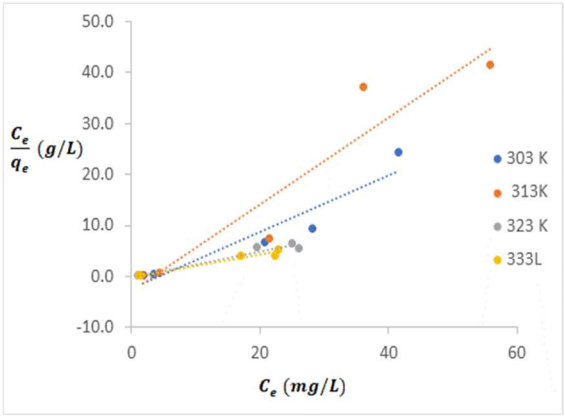

Fig. 7: Langmuir isotherm for the adsorption of the studied dye onto synthesized nano graphene oxide

q_m is the theoretical adsorption capacity while K_L is the adsorption equilibrium constant. This indicates that the Langmuir models is applicable to the adsorption of ethyl violet dye on the surfaces of graphite dust and on nano graphene oxide. Adsorption parameters deduced from the plots are recorded in Table 2. The theoretical adsorption capacity and the equilibrium constant of adsorption is found to increase with increase in temperature. This suggests the appearance of chemisorption adsorption mechanism.

Table 2: Langmuir parameters for the adsorption of the studied dye unto graphite dust and nano graphene oxide

System	T (K)	Slope	Intercept	q_m (mg/g)	K_L	R^2
Graphite oxide	303	0.4252	-1.5413	2.3518	-0.2759	0.9535
Graphite oxide	313	0.3031	-0.6019	3.2992	-0.5036	0.702
Graphite oxide	323	0.2592	-0.0319	3.8580	-8.1254	0.9193
Graphite oxide	333	0.2181	-0.1031	4.5851	-2.1154	0.9629
Nano graphene oxide	303	0.5584	-2.462	1.7908	-0.2268	0.9053
Nano graphene oxide	313	0.8529	-2.9629	1.1725	-0.2879	0.9031
Nano graphene oxide	323	0.2498	-0.0583	4.0032	-4.2847	0.9526
Nano graphene oxide	333	0.2181	-0.1031	4.5851	-2.1154	0.962

4.0 Conclusion

Graphite dust and nano graphene oxide are good adsorbents for the removal of ethyl violet dye from aqueous solution. The nano graphene oxide follows the physisorption mechanism with significant modification of surface properties compared to the graphite dust. The adsorption of the ethyl violet dye obeys the Langmuir adsorption isotherm for both graphite dust and the nano graphene oxide.

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