

## Activation of Soot Carbon Prepared by Paraffin Candle and its Application as Adsorbent Surface of Some Organic Dyes

Hassan Sabeeh Jabr, yasmine salam hassan,

College of Science,  
AL-Muthanna University,  
Samawah, AL-Muthanna, Iraq.  
E-mail: hassansubih87@mu.edu.iq

**Abstract** In this study, locally available and inexpensive materials were used to produce AS<sub>2</sub>, which is widely used in adsorption processes. The AS<sub>2</sub> was prepared from thermally treated of AS<sub>1</sub> at temperature 40 °C for 2 hours. The properties of AS<sub>2</sub> were identified by FTIR, SEM, BET and XRD technique. The AS<sub>2</sub> was used to adsorb the DR and CV dyes from aqueous solutions and the result show that the AS<sub>2</sub> that prepared from AS<sub>1</sub> is good adsorbent. The influence of PH, temperature, Equilibrium time, the adsorbent weight of the adsorption dyes was studied, it was shown that the efficiency of adsorption decreased at PH = 10 and increased at PH=4. The results also showed that the efficiency of adsorption dye on AS<sub>2</sub> decreased by increasing temperature and the optimum contact time of adsorption is 15 min. and the optimum adsorbent weight is 0.08 g.

**Keywords:** Activated soot (AS<sub>2</sub>), Soot (AS<sub>1</sub>), Adsorption, Disperse red.

### 1. Introduction

Many industries, such as plastics, paper, food, cosmetics, textiles, etc., use dyes to color their products. The presence of these dyes in wastewater from these industries, even at very low concentrations, is undesirable, as the color is considered a pollutant that is noticeable by eye, and environmental regulations in most countries have made it necessary to remove the color of wastewater before discharging it [1].

There are several methods to remove these dyes that considered feasible in term of reliability, simplicity, and cost effectiveness. These methods are membranes separation[2], reverse osmosis [3], oxidation[4] , and finally adsorption [5]. However, the adsorption is a common method among the researchers due to its low setup-complexity for the treatment of the dyes solutions.

The typical utilized adsorbent is the active charcoal. Nevertheless, the difficult and the costly process of producing the activated charcoal forced the research for efficient yet inexpensive alternatives[6].

The most frequent difficulty faced in the research for such alternative adsorbents, is the instability of the material prices[7]. Due to this complication, searching for stable, available and

reliable material is one of the factors in researching for alternative adsorbents. On the other hand, the diversity of the properties of the different materials and the expansion of manufacturing makes the selection of ideal material is somewhat a tedious task[8].

The soot created in combustion processes is not uniquely defined. It usually looks black and is mainly made of carbon but it is very different from graphite. Aside from carbon, soot particles also contain up to 10 molecules of hydrogen, and even more when they are small. A great deal of this hydrogen can be extracted in organic solvents as it appears mostly in condensed aromatic ring compounds.

Sometimes, substances are emitted which, when cooled, look like tar or like glassy material, black, brown or even yellow in color. Such materials may be the quenched intermediates of the soot formation process. Sometimes they result as a condensation product of the heavy hydrocarbons formed during combustion; or they may be fuel droplets which have passed through the combustion zone more or less untouched. Finally, they may be normal soot particles on which heavy hydrocarbons have condensed, as is the case with diesel smoke.[9]

In this research, two adsorbents are studied which are the DR and CV on soot. The paper organized as follow: in Section 2, the materials as well as the instruments that are used is stated. Section 3 describe the process of preparing the DR and CV solutions. The factors that affect the adsorption are stated in Section 4. The results are detailed in Section 6. And finally, the findings of the research are concluded in the Section 7.

## **2. Experiment setup**

The chemical materials that utilized in this research have been supplied by the companies Sigma Aldrich and BDH. Moreover, the Fourier transform infrared spectrophotometer from Shimadzu is used with the model number FT-IR-8000 to measure the FTIR spectrum in the range  $(4000-400) \text{ cm}^{-1}$ . On the other hand, an UV-Visible Spectrophotometer from the same company is used to measure the Ultraviolet-Visible spectrum by the device with model number UV-1800PC. The XRD analysis conducted on the System D 6000 X-Ray Diffractometer. The setup for measuring the Cu K $\alpha$  radiation diffraction intensity was 40 Kv monitored in at  $2\theta$  range when the temperature between  $10^\circ - 80^\circ$ . Finally, the FEI Nova Nano SEM 450 is used for the scanning electron microscope (SEM) of the activated soot surface morphology. In SEM, the voltage acceleration is in range 15-20 Kv and the images of the surface morphology are taken at different

magnification.

### 3. The preparation of CV and DR solutions

An 0.05 gram of CV and DR dyes are dissolved in 500 milliliters of distilled water. The concentration of a stock aqueous solution of these dyes is 100 ppm. The range of the absorbance spectrum is 200-800 nm measured by the UV-Visible spectrophotometer. The calibration curve is prepared by choosing dye concentration from 10 ppm to 100 ppm.

Figure 1 show the chemical structure of the used dyes.

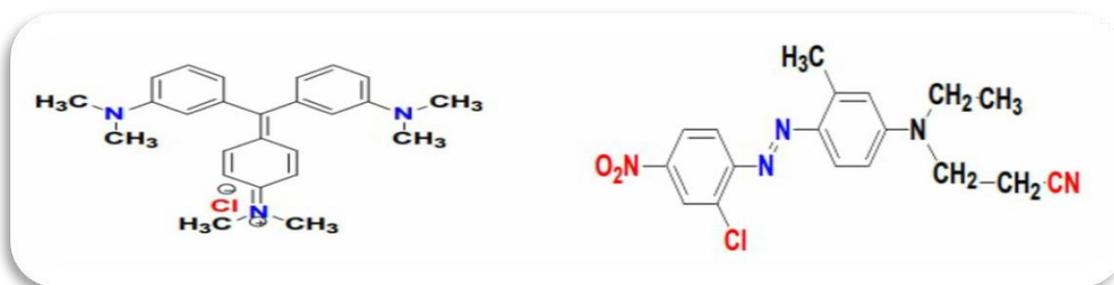


Figure 1: The chemical structures of CV and DR dyes.

### 4. Preparation of AS<sub>2</sub> from the AS<sub>1</sub>

The AS<sub>1</sub> was prepared from candle paraffine and was collected in clean and dry beaker. Later, the collected AS<sub>1</sub> is dried by using oven at 80 °C and for a period of 24 hours. Afterward, this dried AS<sub>1</sub> is grinded and sieved then was activated to produce AS<sub>2</sub> with particle size of 125 μm.

### 5. The Study factors that affect the adsorption process

There are several study factors that affect the process of adsorption. These factors are: Equilibrium time of the adsorption, pH, temperature, and the adsorbent weight. A detailed description of effect of these factors on the absorption process is stated in this section.

#### 5.1 The adsorbent weight influence measurement

The second study factor is the weight of the adsorbent on the process of absorption. During this test, the temperature is 25 °C, the dye solution volume is 25 ml, the pH = 7, and the equilibrium time is 15 min while the adsorbent weight changed between (0.02, 0.04, 0.06, 0.08,

and 0.1g). identical to the studying of the other factors, the test tubes are also placed in water bath in shaker that rotate at the speed of 180 rpm. The dye solution is measured at 515 and 536 nm.

## **5.2 The effect of Equilibrium time measurement**

To study the effect of the equilibrium time on the adsorbed quantity of dye, the time has been varied while the other factors have been fixed. The duration of time that are considered are 5, 10, 15, 20, 25, 30 and 60 minutes. The concentration of the dye is fixed on 50 ppm, the temperature fixed on 25° Celsius, the volume of the dye solution is 25 ml, the AS<sub>2</sub> weight is 0.08 g, and lastly, the pH of the dye solution kept the same without modification.

In this setup, the test tubes are set in water bath and shaker that run at 180 rpm. Then, the sample was filtration by micro filter paper. After that, the dye solution absorbance is measured with UV in range 515 and 536 nm.

## **5.3 The influence of pH on adsorption process measurement**

Similar to the setup of the previous sub-section, the study of the pH is also including measurement of samples in different Ph, the dye concentration is 50 ppm. The temperature is 25° Celsius. the equilibrium time is 15 minutes and the weight of the adsorbent is 0.08g. for the same volume of the dye solution, the pH level is varied from 4 to 7 and to 10. The adjustment of the pH conducted using NaOH or 1M HCl solutions. Finally, the test tubes set in the water bath in shaker that rotate at the speed of 180 rpm. After 15 minutes the solution separated and the dye absorbance is measured with UV in range 515 and 536 nm

## **5.4 The temperature influence measurement**

In the setup for measuring the effect of the temperature on the adsorption process, the temperature is changed from 25°C to 35°C to 45°C. The pH is kept at 7 and the concentration of the dye is 50 ppm in 25 ml solution. The dyes contact time is set to 15 minutes during this test.

# **6. Results and discussion**

## **6.1 Characterization of AS<sub>2</sub>**

The FT-IR (KBr disc, cm<sup>-1</sup>) spectra of AS<sub>2</sub> showed the presence of a absorption bands is aromatic (C-H) at 3153 cm<sup>-1</sup>, FT-IR spectra also showed the presence of strong bands at 2985 (-

CH), 2360 (C N),. Moreover, 1558  $\text{cm}^{-1}$  is imputed for C=O and C=C group respectively. Lastly, the bands at 1427.37 and 1377.22  $\text{cm}^{-1}$  are caused by the bending of C-H group.

The SEM analysis shows the surface morphology of  $\text{AS}_2$  before and after activation were examined by scanning electron microscopy, as presented in Figure 2. S image shows regular particle shapes with large scale of pores and surface were smooth. After activation, the surface area of  $\text{AS}_2$  was wide and had no sharp edges.

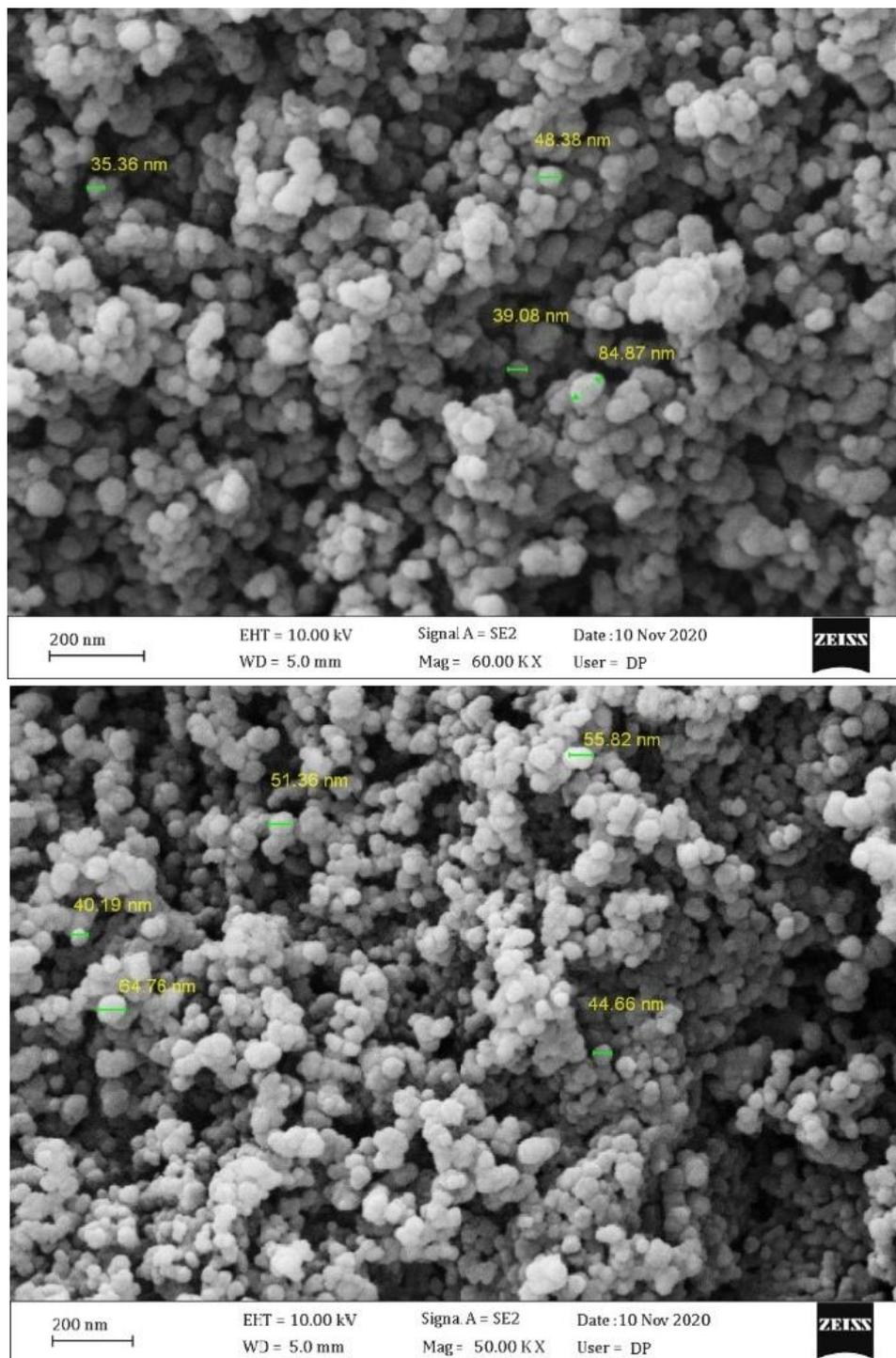


Figure 2: SEM micrograph of the AS<sub>2</sub> (upper part before activation, lower part after activation)

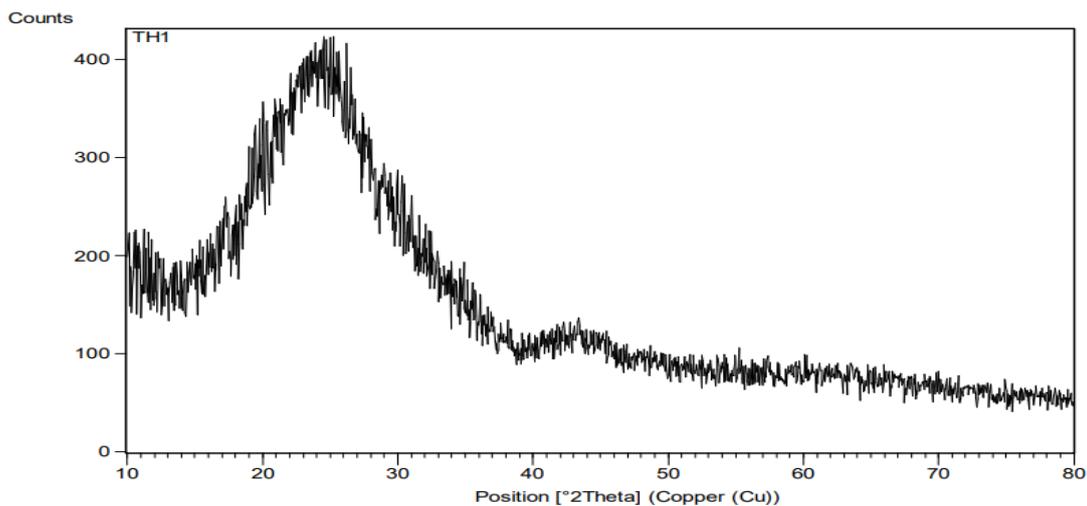


Figure 4: the XRD of AS<sub>2</sub> particles

The XRD pattern of AS<sub>2</sub> is illustrated a peak at  $2\theta = 43.5^\circ$ , and  $25^\circ$  the peak at  $2\theta = 29.00^\circ$  return to the non-crystalline structure of AS<sub>2</sub> so it is smooth. After demonstrating the Characterization of AS<sub>2</sub> in the next sub-sections the study factor results are presented.

## 6.2 The Effect of equilibrium Time on the Adsorption process

The results of the testing setup for the effect of the equilibrium Time in Sub-section 5.2 are demonstrated in **Error! Reference source not found.**. The result indicate that the equilibrium time is 15 min.

where the sites available for adsorption saturation with the increase of time until the time when the sites are fully saturated<sup>17</sup>, that depending on the chemical and physical nature for dye and saturation of active sites on the surface.

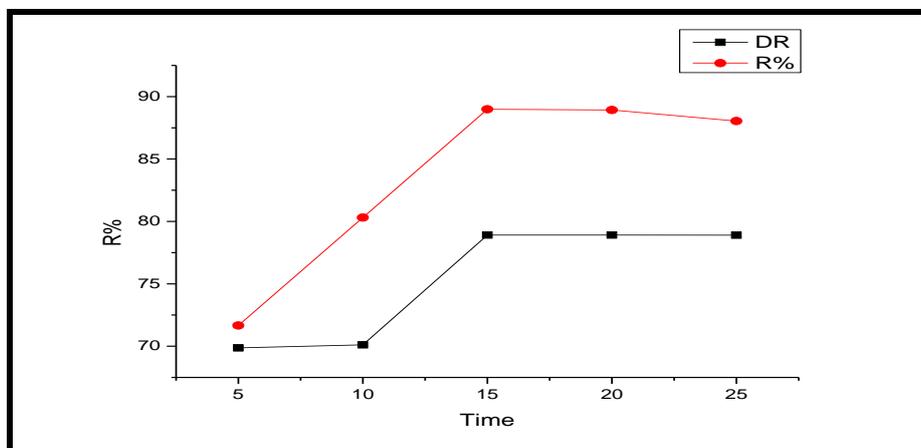


Figure 5: The effect of contact time on the adsorption of the two dyes onto AS<sub>2</sub>

### 6.3 The result changing the pH on the adsorption process

The results of the testing setup of the pH value on the adsorption process in Sub-section 5.3 are stated in **Error! Reference source not found.**. From the figure, it's clear that the maximum percentage of CV and DR dyes removal occurred when the pH value is 4, while pH value of 10 yielded the least performance in the adsorption process.

The pH solution can be arranged as follows: -

$$(4 > 7 > 11)$$

The result can be reasoned by that the CV and DR dyes consist of amino group. When these dye dissolve in water, its ionized produce ions. These positive-charged ions are attracted to the negative-charged AS<sub>2</sub> particles due the phenomena of electrostatic attraction forces. Another explanation is that the presence of (N-N) double bond group on the ring. This group convert to ion which has the negative charge. When these ions interact with the oxygen atom, a hydrogen bonds are formed which result in reduction of the ability to drive the electrons towards the ring. Hence, reduction in the adsorption capacity at basic medium[10]

The Eq. 1 calculate the quantity of the adsorbed while Eq. 2 measure the percentage of the dye removal.

$$q_e = \frac{v}{m} \times (C_0 - C) \quad (1)$$

$$E = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

Where C<sub>0</sub> is the concentrations in mg/L of initial dye in the solution while C is the concentrations in mg/L of the remaining dye in solution. v is the volume of the dye solution in liters, q<sub>e</sub> is the rate of dye to the adsorbent mg/g, m is the mass of adsorbent in grams and finally E is the percentage of dye removal.

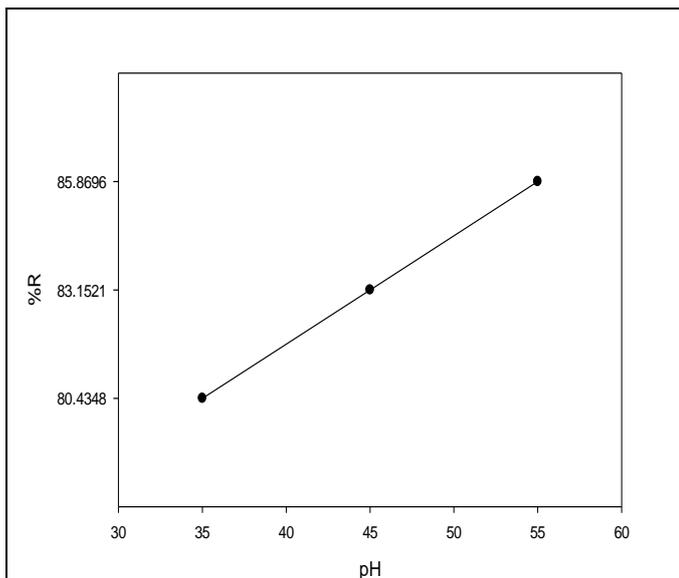


Figure 6: Effect of pH on the absorbance of DR on AS

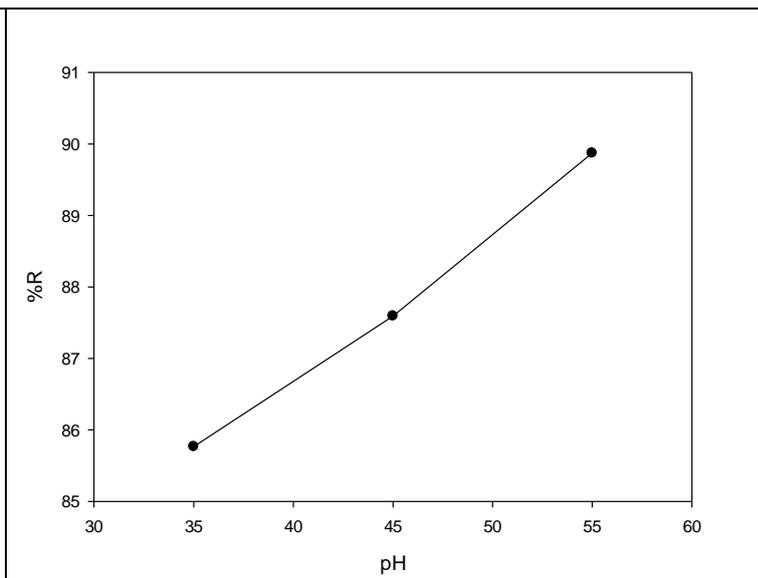


Figure 7: Effect of pH on the absorbance of CV on AS

### 6.4 The result of varying the Temperature on the absorbance

The effect of temperature on the absorbance is presented in **Error! Reference source not found.** and 9. The result show that the absorbance efficiency decrease when the temperature increase. The result also shows that the preferred working temperature for adsorption is 25°C. The behavioral of the dye adsorption by the AS<sub>2</sub> can be concluded to be typically exothermic[11].

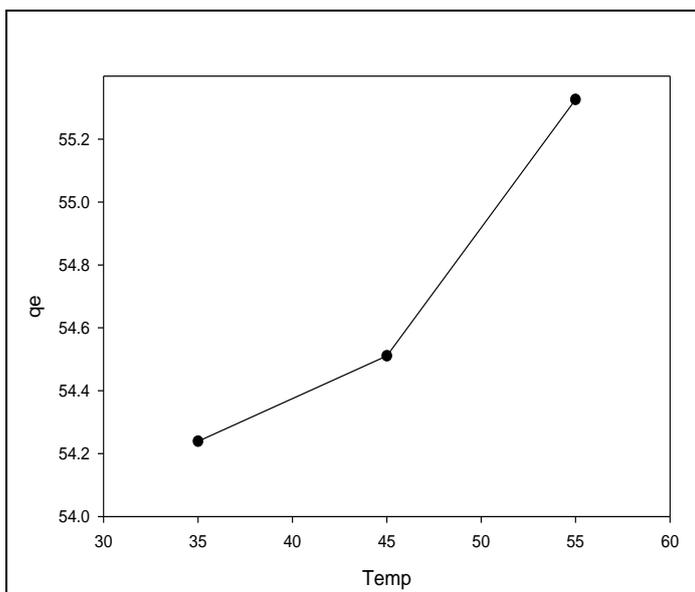


Figure 8: Effect of temperature on the absorbance

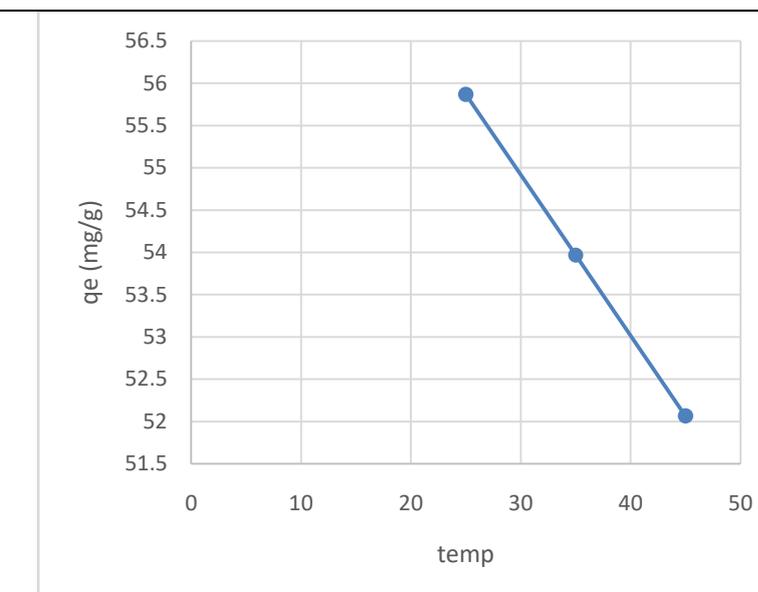
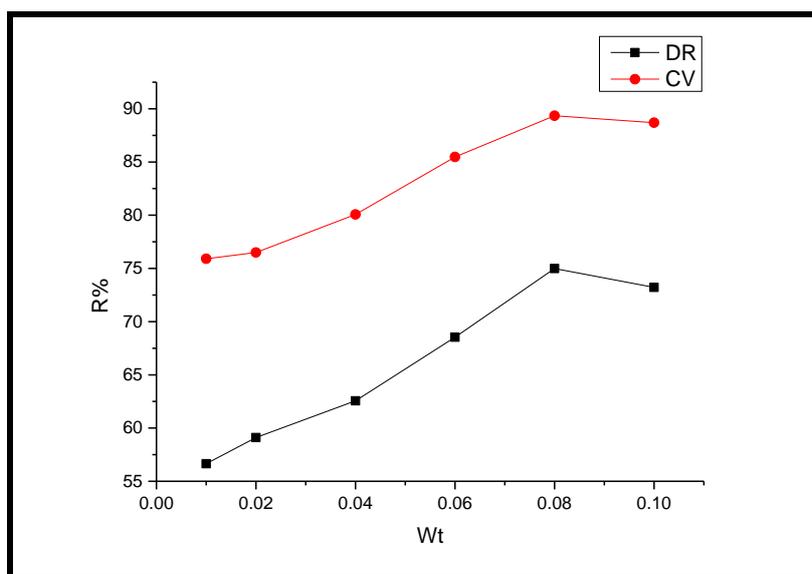


Figure 9: Effect of temperature on the absorbance

## 6.5 Effect of adsorbent weight

The **Error! Reference source not found.** show the effect of various quantity of adsorbent on the absorbance. From the figure two point can be highlighted, first, the increase of the quantity of the adsorbent increases the efficiency of the DR and CV absorbance and second, the optimal weight of adsorbent is 0.08 g. The result can be attributed to the increase of the number of the active sites on the AS<sub>2</sub> surface and hence increase of the surface area that are capable of the adsorption[12] which result in better adsorption performance.



**Figure 10:** Effect of adsorbent dosage on removal of the two dyes onto AS<sub>2</sub>

## 6.6 Adsorption isotherm

The analysis of the isotherm provide insight about the process of the capacity of the absorbance centration. The isotherm analysis was conducted by applying the Langmuir and Freundlich equations of adsorption to the experimental data.

The Freundlich isotherm model describe the solutes adsorption from light to a solid surface. Furthermore, Freundlich isotherm model also state that various sites with numerous adsorption energies are entangled[13].

Figure illustrate the linear isotherm relation of the Freundlich equation when various concentrations of dye solutions with the adsorption of the AS surface. While Figure show the linear isotherm relation of the Langmuir equation on the same AS.

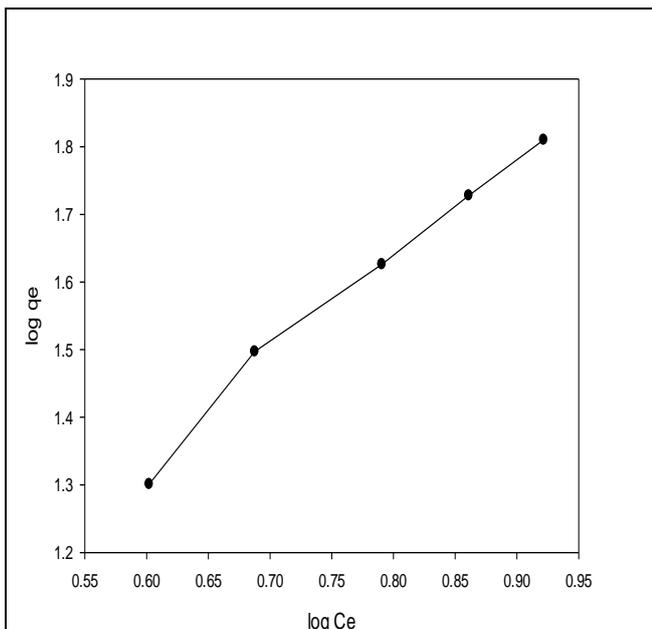


Figure 11: Freundlich isotherm for adsorption of DR onto AS<sub>2</sub>

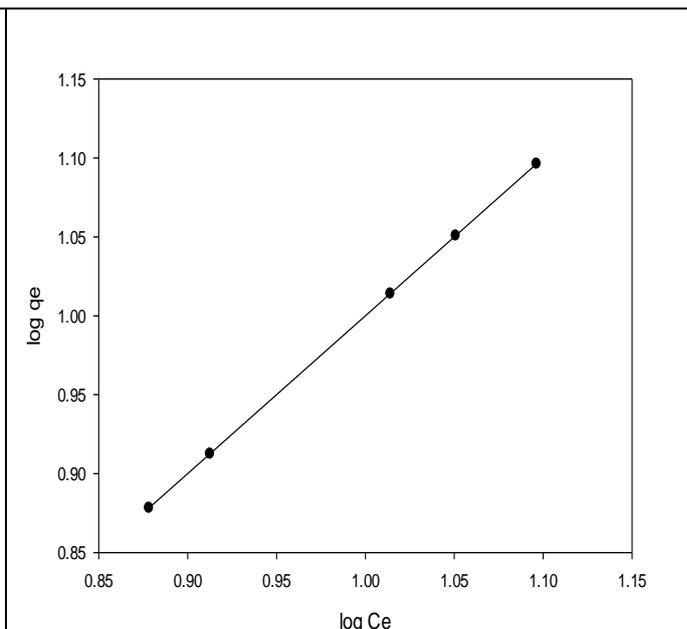


Figure 12: Freundlich isotherm for adsorption of CV onto AS<sub>2</sub>

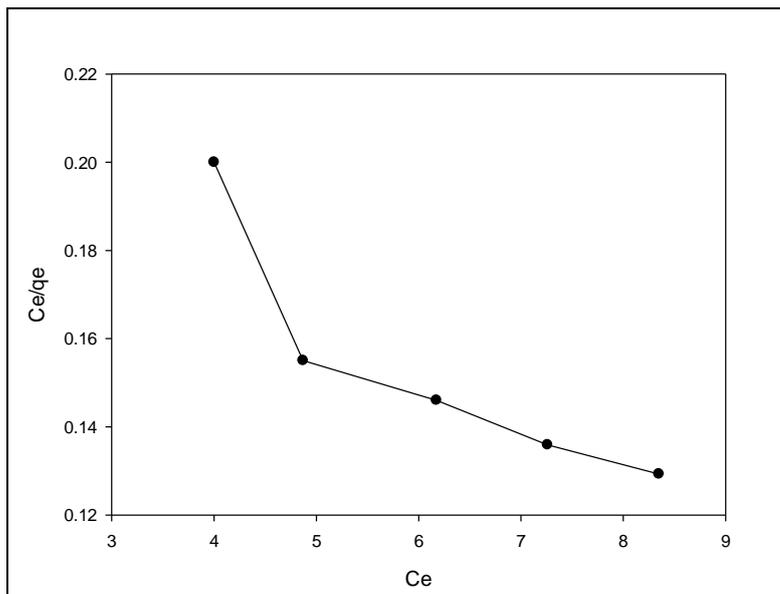


Figure 13: Langmuir isotherm for adsorption of DR onto AS<sub>2</sub>

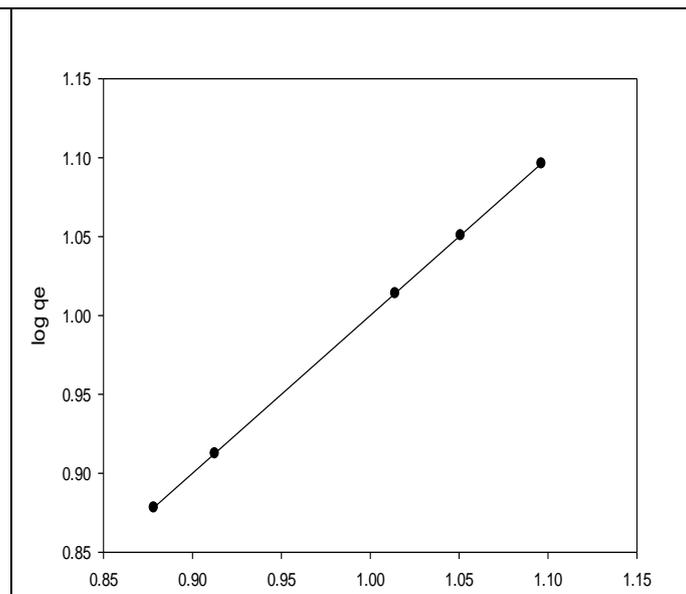


Figure 14: Langmuir isotherm for adsorption of CV onto AS<sub>2</sub>

The linear Freundlich equation is:

$$\log q_e = \log K_f + 1/n \log C_e$$

K<sub>f</sub> is the Freundlich constants. The K<sub>f</sub> and n give an information about the adsorption degree

as well as the nature of the surface whether a heterogeneous or homogenous. Whereas the adsorption capacity ( $Q_m$ ) and the Langmuir constant ( $b$ ) are determined using the equation:

The Langmuir equation:  $\frac{C_e}{q_e} = \frac{1}{Q_m} + b \frac{C_e}{Q_m}$

Table 1: Freundlich and Langmuir equations parameters of DR

Isotherm constant	Freundlich			Langmuir		
The constants and coefficient of correlation values	$K_f$	$n$	$R^2$	$Q_m$	$b$	$R^2$
	<b>0.636</b>	<b>0.100</b>	<b>0.8747</b>	2.399	4.730	0.9495

Table 2: Freundlich and Langmuir equations parameters of CV

Isotherm constant	Freundlich			Langmuir		
The constants and coefficient of correlation values	$K_f$	$n$	$R^2$	$Q_m$	$b$	$R^2$
	<b>0.030</b>	<b>0.376</b>	<b>0.9718</b>	2.940	0.057	0.3997

From Table 1, it can be seen that the value of  $n$  is less than one which indicate the surface is a heterogeneous. If the values of the correlation coefficient  $R^2$  from Langmuir isotherm are compared to the Freundlich isotherm  $R^2$  values, it is clear that values in the later is greater than that in the Langmuir. Hence, Freundlich equation is more suited for the adsorption of CV and DR dyes presented in aqueous solutions when AS is used which also indicate that the adsorption is a multilayer[14].

### 6.7 Adsorption process thermodynamic

Traditionally, the analysis of Thermodynamics were applied to the adsorption processes solely to estimate kind of the adsorption reaction. However, its of utmost importance to study the Thermodynamics in the range 298 - 318 K which involve change in standard enthalpy ( $\Delta H^0$ ), entropy ( $\Delta S^0$ ) and Gibbs free energy ( $\Delta G^0$ ). The determination of these values can be started by calculating the Gibbs free energy change by using the equation:

$$\Delta G^0 = - R T \ln k$$

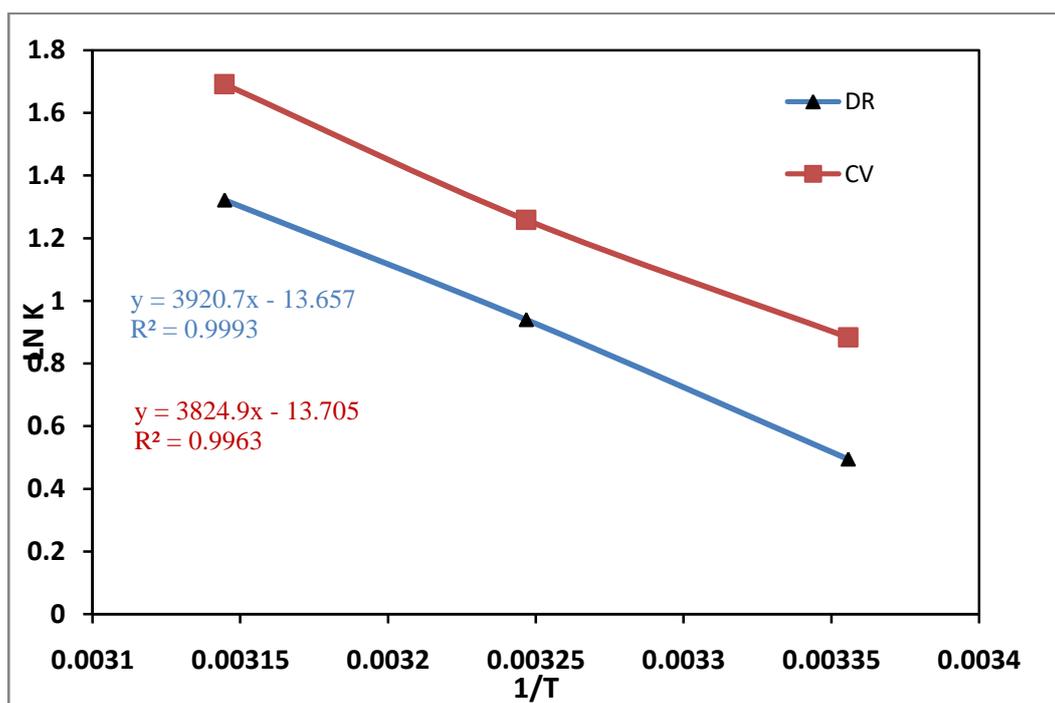
the  $\Delta G^0$  is the Gibbs free energy change which measured in  $\text{KJ.mol}^{-1}$ , while R is the universal gas constant which equal to  $8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ , while T is the absolute solution temperature which measured in Kelvin and finally K represent the constant of thermodynamic equilibrium for the adsorption which was calculated using the equation:

$$K = (q_e m) / (C_e V)$$

the standard enthalpy ( $\Delta H^0$ ) change is calculated by first using Van't Hoff - Arrhenius equation to calculate  $\ln K$ :

$$\ln K = (\Delta S^0) / R - (\Delta H^0) / RT$$

and then by plotting the values of  $\ln k$  against  $1/T$ . The values of the  $-\Delta H/R$  and  $\Delta S/R$  are both calculated from the slope and intercept of the linear plots as in **Error! Reference source not found.**



The Table show the thermodynamic parameters of CV and DR dyes adsorption with AS. From the table, by observing the  $\Delta G$  and  $\Delta H$ , it can be seen that the adsorption was exothermic and spontaneous i.e. physical adsorption.

Table 3: thermodynamic parameters of adsorption DR dye onto active carbon

$-\Delta H^0$ ( $\text{K.J.mol}^{-1}$ )	$-\Delta G^0$ ( $\text{J.mol}^{-1}$ )	$-\Delta S^0$ ( $\text{J.mol}^{-1}.\text{K}^{-1}$ )
5438.27	15210.80	152.645

Table 4: thermodynamic parameters of adsorption CV dye onto active carbon

$-\Delta H^\circ$ (K.J.mol <sup>-1</sup> )	$-\Delta G^\circ$ (J.mol <sup>-1</sup> )	$-\Delta S^\circ$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )
4938.64	12539.98	125.026

## 7. Conclusion

The main points that can be concluded from this research are: first, the process of adsorption is an effective method for dye removal from water. Second, the used adsorbent is commercially available in affordable prices which make the reproduce\ this research on large scale for dye contaminates removal is cost effective. Third, the best results achieved when the value of pH = 4. Fourth, the increase of quantity of adsorbent also increase its effectiveness of adsorption. Fifth, the use Freundlich isotherm to highlight the linear relation of the adsorption data is favorable compared to the Langmuir isotherm. Finally, the process of adsorption of the DR and CV dyes by the AS<sub>2</sub> was exothermic and spontaneous which can be seen in the thermodynamic analysis by obtaining the  $\Delta H^\circ$  and the  $\Delta G^\circ$ .

## References

- [1] S. Pal and P. L. Meena, “□ Green Materials for Removal of Dyes Present in Wastewater,” vol. 5, no. 12, pp. 5–8, 2014.
- [2] M. A. H. Johir, M. Pradhan, P. Loganathan, J. Kandasamy, and S. Vigneswaran, “Phosphate adsorption from wastewater using zirconium ( IV ) hydroxide : Kinetics , thermodynamics and membrane fi ltration adsorption hybrid system studies,” *J. Environ. Manage.*, vol. 167, no. 3, pp. 167–174, 2016, doi: 10.1016/j.jenvman.2015.11.048.
- [3] P. Liang, K. Xiao, Y. Zhou, X. Zhang, and B. E. Logan, “A New Method for Water Desalination Using Microbial Desalination Cells,” vol. 43, no. 18, pp. 7148–7152, 2009.
- [4] M. Idrissi, J. Lamonier, D. Chlala, J. Giraudon, and M. Chaouch, “Traitement du toluène présent à l ’ état de traces dans l ’ air , en présence de catalyseurs Cu-Bentonite ( Treatment of toluene present in trace amounts in air , in the presence of Cu-catalysts Bentonite ),” vol. 5, pp. 2303–2308, 2014.
- [5] Y. Miyah, A. Lahrichi, and M. Idrissi, “Removal of cationic dye – Methylene bleu – from

- aqueous solution by adsorption onto corn cob powder calcined .,” vol. 7, no. 1, pp. 96–104, 2016.
- [6] K. K. H. Choy, G. McKay, and J. F. Porter, “Sorption of acid dyes from effluents using activated carbon,” vol. 27, pp. 57–71, 1999.
- [7] D. Noureddine, “Adsorption des inhibiteurs à base d ’ extraits de plante sur une surface d ’ acier doux.”
- [8] E. A. S. Al-hyali and M. T. H. Al-neemy, “Thermodynamic Study of The Adsorption of Some Azo Dyes on Activated Carbon,” no. April 2018, pp. 201–218, 2017.
- [9] P. Chemic and W. German, “C24H , 2 / . J,” vol. 7, 1981.
- [10] R. T. M. Dharmendirakumar, G. Vijayakumar, G. Vijayakumar, R. Tamilarasan, and M. Dharmendirakumar, “Adsorption , Kinetic , Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from ...,” *Journal of Materials and Environmental Science*, vol. 3, no. June. pp. 157–170, 2015.
- [11] Ü. Geçgel, O. Üner, G. Gökara, and Y. Bayrak, “Adsorption of cationic dyes on activated carbon obtained from waste Elaeagnus stone,” *Adsorpt. Sci. Technol.*, vol. 34, no. 9–10, pp. 512–525, 2016, doi: 10.1177/0263617416669727.
- [12] M. S. E. Abdo, S. A. Nosier, Y. A. El-Tawil, S. M. Fadl, and M. I. El-Khaiary, “Removal of Phenol from Aqueous Solutions by Mixed Adsorbents: Maghara Coal and Activated Carbon,” *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.*, vol. 32, no. 4, pp. 1159–1169, 1997, doi: 10.1080/10934529709376602.
- [13] J. Zhou, C. Tang, B. Cheng, J. Yu, and M. Jaroniec, “Rattle-type carbon-alumina core-shell spheres: Synthesis and application for adsorption of organic dyes,” *ACS Appl. Mater. Interfaces*, vol. 4, no. 4, pp. 2174–2179, 2012, doi: 10.1021/am300176k.
- [14] F. Güzel, H. Saygılı, G. A. Saygılı, and F. Koyuncu, “Elimination of anionic dye by using nanoporous carbon prepared from an industrial biowaste,” *Journal of Molecular Liquids*, vol. 194. pp. 130–140, 2014, doi: 10.1016/j.molliq.2014.01.018.