Adsorption Study of Basic Fuchsin Dye on The Astragalus Root Surface In Al-Muthanna Province

Sahar Ismail Naji *College of Science, AL-Muthanna University, Samawah, Iraq.*

Khawla. K. Jasim, College of Science, AL-Muthanna University, Samawah, Iraq. E-mail: khawla.kani@mu.edu.iq*

Abstract

The objective of this research is to study the removal of Basic Fuchsin (FU) dye frome its aqueous solution, by the AS surface which prepared from locally available and inexpensive material (Astragalus plant root). The properties of the adsorbent surface was investigated by SEM, FT-IR, TGA, XRD, and BET techniques. The effect of PH, temperature, equilibrium time, and the adsorbent dosage on the FU dye adsorption was studied. The result showed that the contact time was 90 minutes. The adsorption isotherm of the FU dye was of the (S-type) according to the Giles classification, and is more fit to the Freundlich equation. The negative values of (ΔG°) and (ΔH°), showed that the adsorption process of FU dye was spontaneous and exothermic respectively. The kinetic result indicates that the adsorption process obeys with pseudo second order.

Keywords: Adsorption; Astragalus plant; Basic Fuchsin; Isotherm; Kinetic.

1. Introduction

Dyes are colorful materials designed to give any colorable substance a color, such as fabrics, and papers [1] Many industries such as, plastics, textiles, leather, food, and cosmetics, etc, all these industries use pigments or dyes to color their products, this present problems in the form of colored wastewaters that require pretreatment [2]. Dyes could be toxic, damage to human beings, and considered threat to environment [3], which could be treated by physical or chemical methods, but are expensive and ineffective in treating a wide range of wastewaters. Adsorption on activated carbon found to be effective for dye removal, but it is costly. Therefore low cost alternatives have been proposed. For example china clay [4] wood [5], banana peel [6], orange peels [7], pineapple peels [8], soil [9], waste coir pith [10], and bagasse pith [11] are being evaluated as alternatives to remove dyes from the colored wastewater. The adsorption with agricultural products has been used as an economical procedure for the removal of the different pollutants, and has proved to be efficient in remove many species of pollutants such heavy metals, phenol, dyes, and gasses [12].

The focus of this study was to evaluate the adsorption potential of the crude Astragulas root in removing Basic Fuchsin (FU) dye from its aqueous solutions using batch method. Different adsorption isotherms such as Temkin ,Langmuir, and Freundlich models have been applied to adsorption data. The thermodynamics and kinetics studies the removal of this dye onto the Astragulas root have been investigated.

2. The Instrumentation

The FTIR spectrum in the range (4000-400cm^{-1}) were recorded by FT-IR-8000, Shimadzu Fourier transform infrared spectrophotometer. The Ultraviolet-Visible spectrum were measured using UV-1800PC Shimadzu, UV-Visible Spectrophotometer in range 200-800 .The analysis of XRD was performed with Xpert Phillips Holland Diffractometer. The intensity of Cu Ka radiation is generated at 40 Kv was recorded in the 2θ range between (10°- 80°).

The morphology of the AS surface was tested using the (SEM) scanning electron microscopy of (Fesem Tescan Mira3 France) at an accelerating voltage in the range between (15-20Kv). The morphology images of the Astragulas root (AS) surface were taken at various magnifications. The curve of the TGA was measured using (Perkin Elmer-TGA 4000) instrument.

3. Preparation of Basic Fuchsine solutions

The stock solution (500ppm) of Basic Fuchsine dye was prepared by dissolving (0.25g) of Basic Fuchsin dye **Fig. 1** in distilled water (500ml), the maximum absorbance wavelength (λ_{max}) of Basic Fuchsine dye determined using absorbance spectrum ranged from (200-800nm) by the UV-Visible spectrophotometer. Calibration curve was obtained by using series of dye solutions prepared at concentrations ranging (0.3-100 ppm).

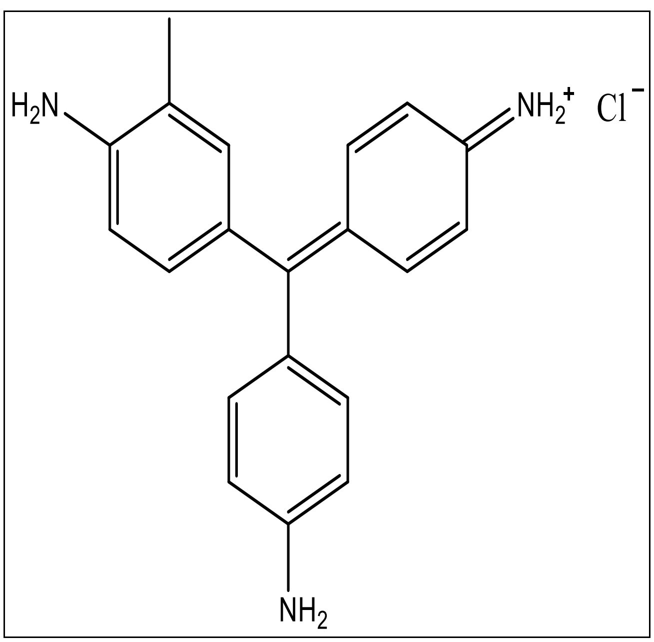

Fig. 1. Chemical structure of Basic Fuchsin.

4. Preparation of AS surface from the Astragulas root

The samples of the root of Astragalus plant were collected from the desert of Al-Salman district in Al-Muthanna Governorate. Then washed by using the distilled water, and then the Astragulas root was dried in the oven at (53ºC) for (5h). Thereafter, the root was grinded and sieved to a particle size (125µm).

5. Studying the factors effecting on adsorption process

5.1 Effect of the Equilibrium time

To determine equilibrium time between adsorbed amount of the FU dye by adsorbent, Basic Fuchsine dye concentration (50ppm) was taken at different times (10-300) min, the volume of Basic Fuchsine solution (25ml) was held constant, and the weight of the AS surface (0.5g) constant. With the natural pH of the dye solutions. Volumetric flasks were placed in water-bath shaker at 25°C and 125rpm. Then in a centrifuge (10min). After separation, the absorbance of the Basic Fuchsine solution was measured at (545 nm).

5.2 The effect of the pH

For studying the effect of pH on adsorption. The dye concentration (50ppm), with constant volume of the dye solution (25ml) at different values (4, 7, 10) of pH. The pH value was adjusted by using the desired amount of dilute solutions of HCl and NaOH. The temperature and the absorbent weight were (25℃) and (0.5g) respectively, and the equilibrium time (50min). Then the test tubes putt in a water bath-shaker at 125 rpm. placed in a centrifuge (10min), and the absorbance of the solutions was determined at 545 nm.

5.3 The effect of temperature

For determining effect of temperature on the adsorption process of Basic Fuchsine (FU). Various solutions (10-80ppm) were prepared. Also (0.5g / 25mL) was added in the flasks. They were shaked in a water-bath shaker at 125rpm for 90 minutes, at three different temperatures (25-35-45°C), using the natural pH of the solutions (not changed).

5.4 The effect of adsorbent dosage

Different weights have been taken (0.02, 0.05, 0.1, 0.2 and 0.5g) at 25°C. The volume and concentration for the dye solutions were (25ml, 50ppm) respectively. The equilibrium time (90min) and the pH were not changed. The test tubes putted in a water bath-shaker at 125 rpm, then the tubes were put in a centrifuge (10min), and measure the absorbance of the solutions.

6. Results and discussion

6.1 Characterization of AS surface

The FTIR spectrum of AS surface **Fig. 2** shows three broad and overlapping beams at wave numbers (3419.9, 3406.49, 3389.04 cm^{-1}) due to the vibration stretching of the hydroxyl group (H-O), the band at 2924.18 cm^{-1} is caused by the C-H stretching vibration, and the bands at 1741.78 and 1637.62 cm^{-1} are refer to C=O and C=C groups. The stretch band at 1244.13cm^{-1} is refer to the ester C-O group.

The results of the TGA analysis for the AS surface **Fig. 3** showed that the percentage of the remaining weight is 0.00% of the original weight, and three characteristic decomposition stages were shown. The first step of weight loss (5.39%) was observed between 40-182°C, this loss is due to the removal water molecules. The highest amount of mass loss was found during the second stage (63.2 %) occurred between 182–439ºC, assigned to the breakage of the bonds of some groups onto the AS surface such as carbonyl and hydroxyl groups. The third mass loss (31 %) between 439–840°C, where the total weight loss for AS sample was 100%.

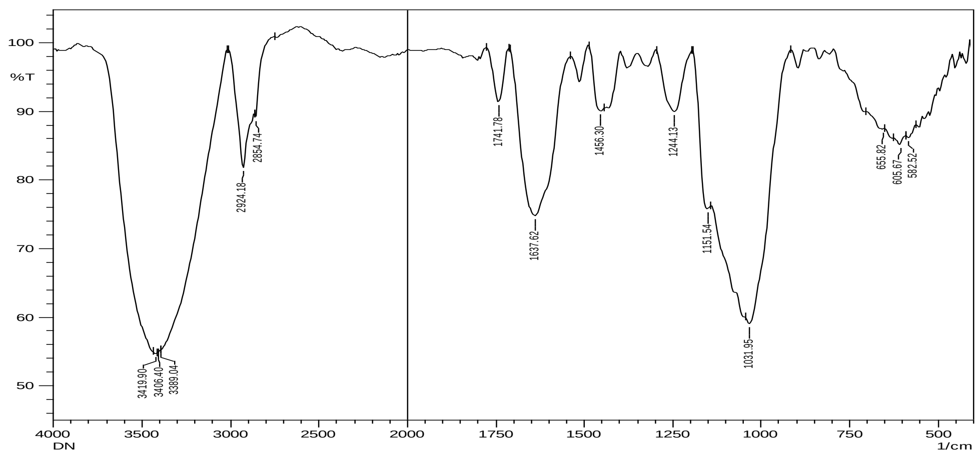

Fig. 2. The FT-IR Spectra of AS surface.

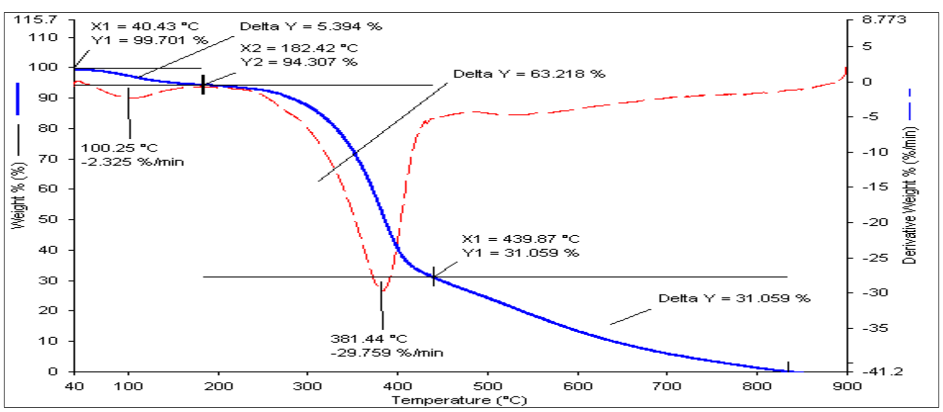

Fig. 3. The TGA analysis of AS surface.

The morphology of the Astragalus root powder (AS) surface was investigate. **Fig. 4** shows the SEM micrographs of AS, careful observation of the images at different levels of magnifications, **Fig. 4. (a)** revealed the presence of a very rough surface made up of granular particles. In addition, the shape of the particles is rocky, irregular, and with different sizes. At high magnification shown in **Fig. 4. (b),** the average particle size ranges between (52-14 nm).

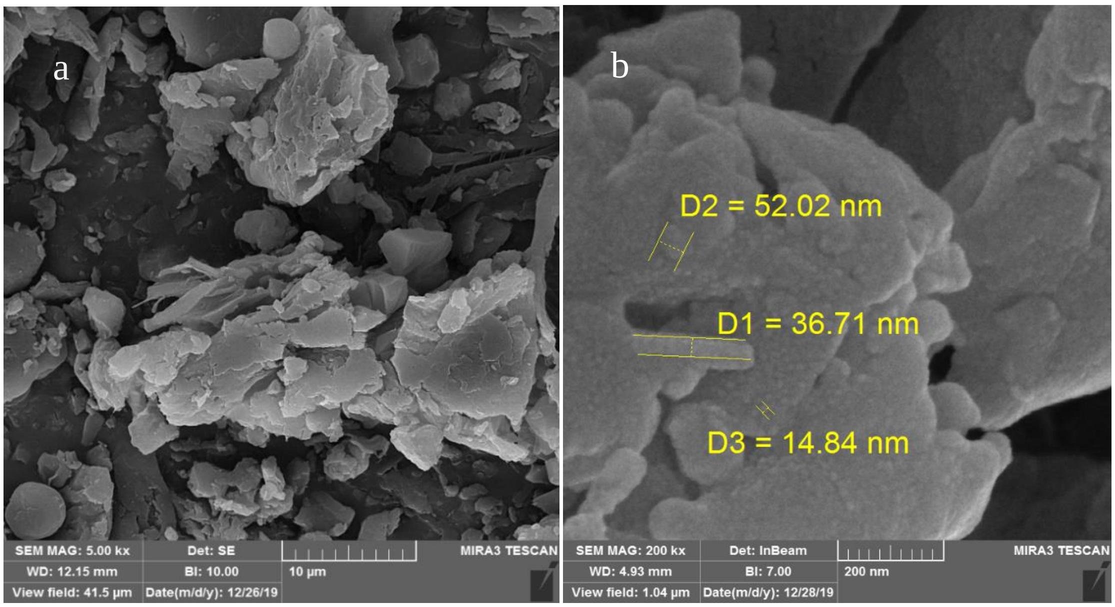

Fig. 4. SEM micrographs of AS at magnifications of (a) 5000 mag, (b) 200000 mag.

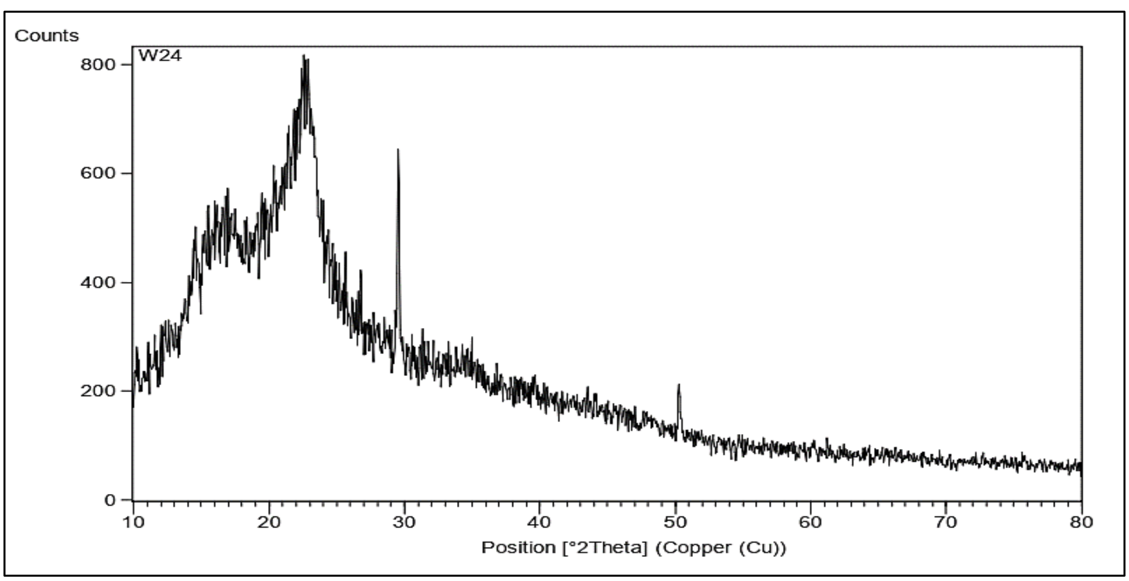

Fig. 5. The X-ray diffraction pattern for AS surface.

The XRD diffraction pattern of AS **Fig. 5** showed two types of diffractions that indicate the presence of two phases, a broad diffraction band at 2θ angle of ca. 22° confirming the amorphous nature of the sample [13]. In addition, it can be observed that there are two sharp diffraction peaks appeared at 2θ = 29.5° and 50.2° indicate the presence of the second, crystalline phase. The mixture of amorphous and crystalline peaks reveals that the (AS) has semi-crystalline structure [14] [15].

6.2 The effect of equilibrium Time

Different periods of time (10, 30, 40, 50, 60, 90 and 300) min were taken to determine the equilibrium time of the adsorption into the AS surface, with temperature 25℃, the volume of dye solution (25 ml) and weight of AS (0.5 g) were held constant. **Fig. 6** shows that the time required to reach the equilibrium was (90 min). The percentage removal of the dyes increases with time because initially unoccupied active sites are available more for the adsorption of the dye and as the time increase, the active sites are used up and a stable state is resulted, an equilibrium state. Where the sites are reached fully saturated [16].

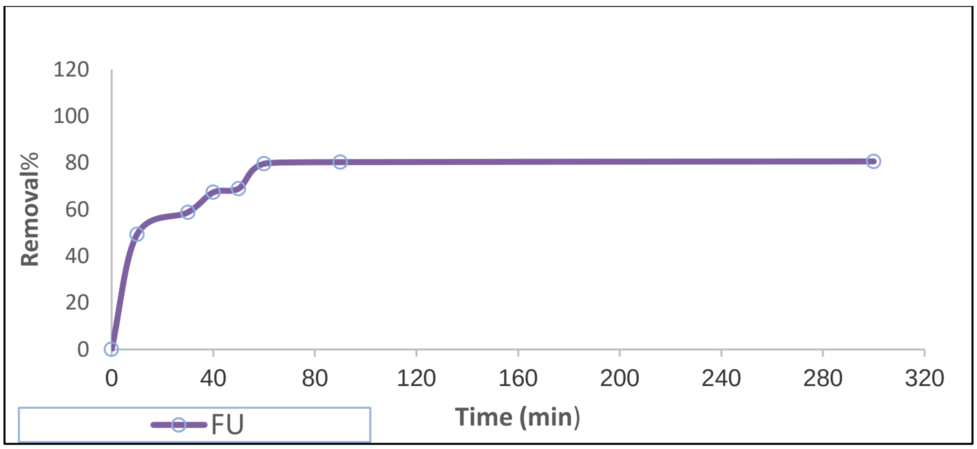

Fig. 6. Effect of equilibrium time.

6.3 The effect of pH

The obtained results pointed that the removal percentage (R%) for Basic Fuchsine on AS surface was increased with increasing the pH solution. The adsorbed amount increases with the change of the solution pH in the following order: 10 > 7 > 4

As shown in **Fig. 7** At lower pH, H^+ may competing with the cationic dye (FU dye) for the adsorption sites of the AS surface, therefore inhibiting the adsorption of the FU dye, and thus restricts the approach of ions FU (positively charged) toward the AS surface [17].

The adsorbed amount of the dye **(equ.1)**, and dye removal (R%) **(equ.2)** are calculated as following:

$$qe = \frac{V(C_0 - C_e)}{M} \quad (1)$$

$$R\% = \frac{C_0 - C_e}{C_0} * 100 \quad (2)$$

Where

C_0, C_e are initial and remaining dye concentrations in the solution (mg/L). qe is the adsorbed amount of the dye (mg/g). And v is dye solution volume (L). m is the mass of adsorbent (g) and R is percentage dye removal (%).

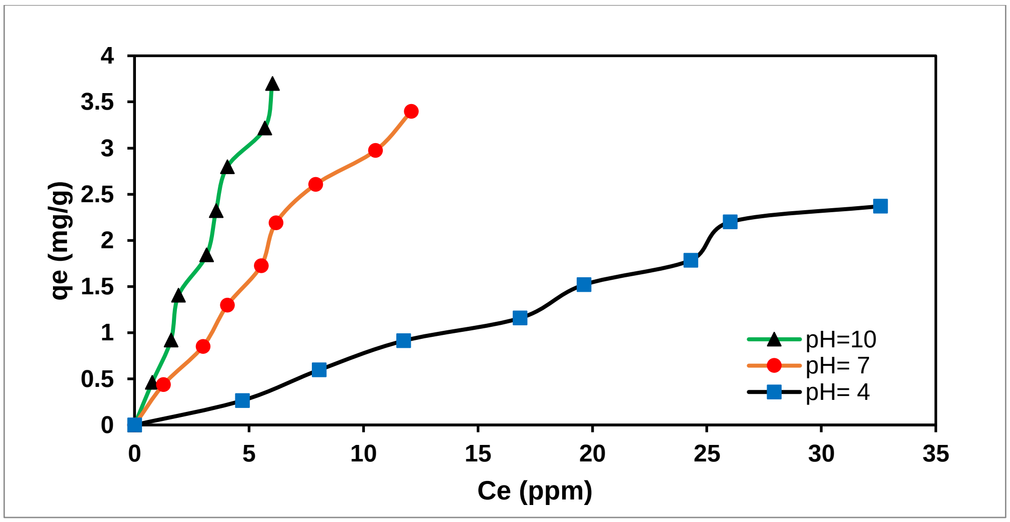

Fig. 7. Effect of pH on the adsorption f FU into AS.

6.4 Effect of Temperature

various temperatures were taken (25, 35 , 45)°C, with volume (25 ml) of Basic Fuchsine solution. Various solutions (10, 20, 30, 40, 50, 60, 70, and 80ppm) were used. With the natural pH of the solutions (not changed). The results **Fig. 8** showed that the efficiency of the adsorption of FU on AS decreased with increase temperature, which indicates that the adsorption by AS is an exothermic in nature [18], therefore, the most favorable temperature was 25°C.

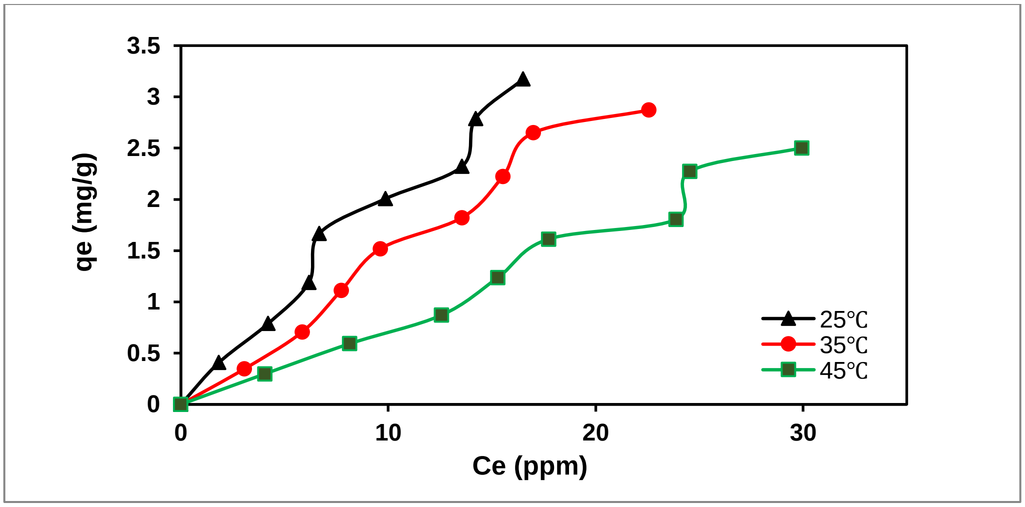

Fig. 8. Effect of temperature on the adsorption capacity of FU dye for AS.

6.5 The effect of adsorbent dosage

Fig. 9 shows, the convenient weight of adsorbent is 0.5 g, the percentage of FU dye removal into the AS surface increases with increasing the dosage of the adsorbent, which is due to the increase in the number of active sites on the AS surface that are available to adsorb the FU dye [19].

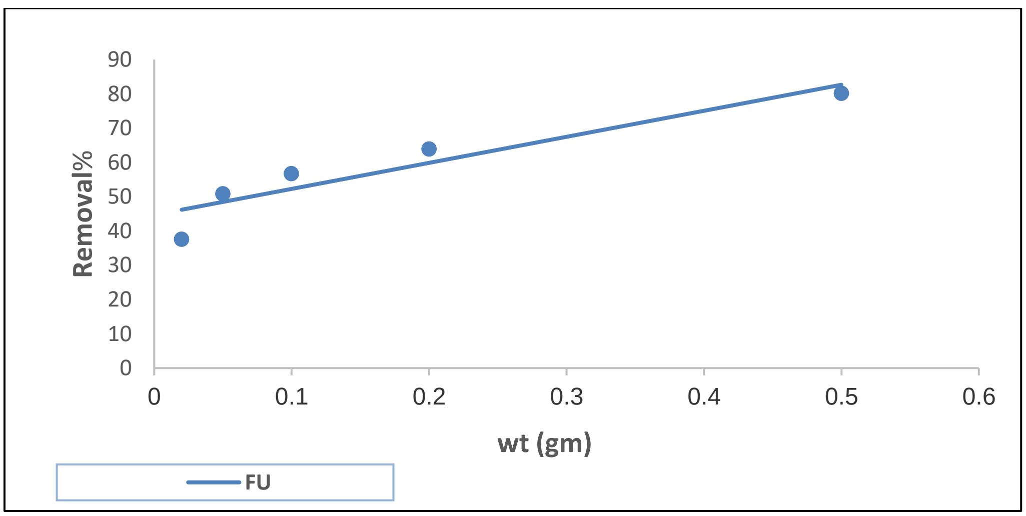

Fig. 9. Effect of adsorbent dosage.

Adsorption isotherm

Studying adsorption isotherm afford important knowledge about the adsorption procedure and the adsorption capacity. The data applied to Langmuir, Freundlich, and Temkin models. The Freundlich isotherm describe the adsorption from the liquid to the solid surface, and considers that different sites with multiple adsorption energies are engaged [20]. Fig. 10 shows the

Freundlich equation adsorption on AS surface in several concentrations, by plotting the linear equation of Freundlich isotherm, The constants of Freundlich (K_f, n) were calculated, and give knowledge about the adsorption amount and the quality of surfaces (heterogeneous or homogenous). In addition, the Langmuir constant (b) and (Qm) the maximum adsorption capacity were calculated by the linear equations as following:

The Langmuir equation: $\frac{Ce}{qe} = 1\backslash Qm * b + Ce/Qm$

The Freundlich equation : $\log q_{eq} = \log K_f + 1/n \log C_{eq}$

The Temkin equation: $q_e = B_1 \ln K_T + B_1 \ln C_e$

Table1: Values of the parameters for Langmuir, Freundlich, Temkin equations.

Langmuir			Freundlich			Temkin		
qm	be	R^2	K_f	n	R^2	K_T	B_1	R^2
20.242	0.0108	0.218	1.073	0.230	0.978	0.266	1.245	0.907

When compare the coefficient of correlation (R^2) values for Langmuir, Freundlich, and Temkin isotherms, the Freundlich's R^2 values is greater than the other values. Therefore, the Freundlich model is more fitted for the adsorption procedure of the Basic Fuchsine in the aqueous solution onto the AS surface. Therefore, it is a multilayer adsorption (more than one layer) [21].

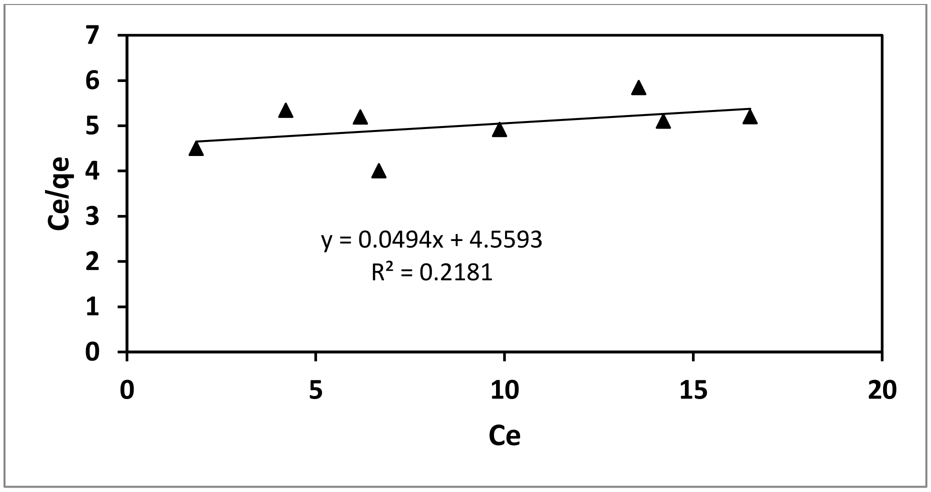

Fig. 8. Langmuir isotherm for adsorption of dye on AS.

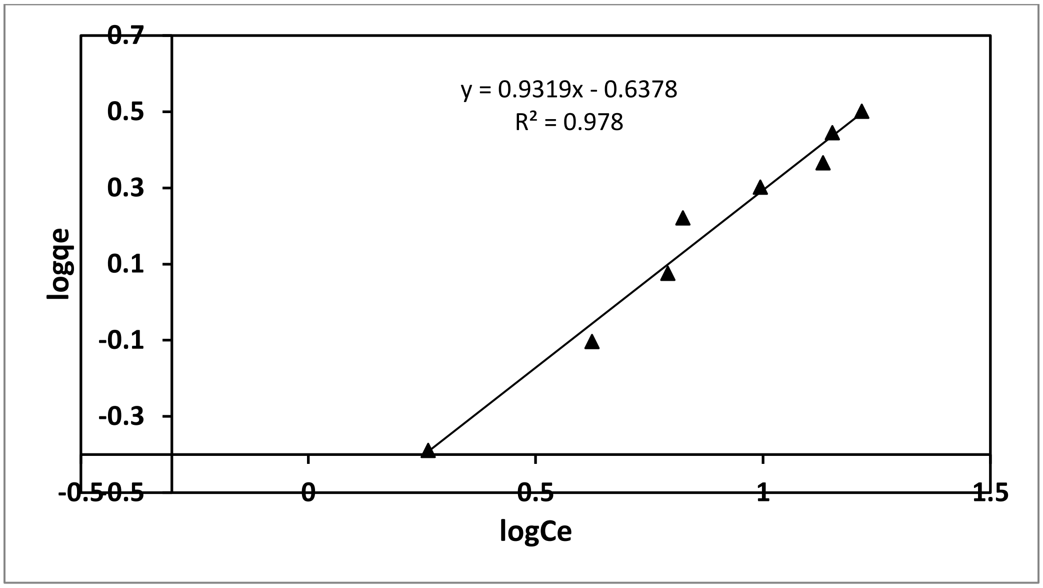

Fig. 9. Freundlich isotherm for adsorption of dye on AS.

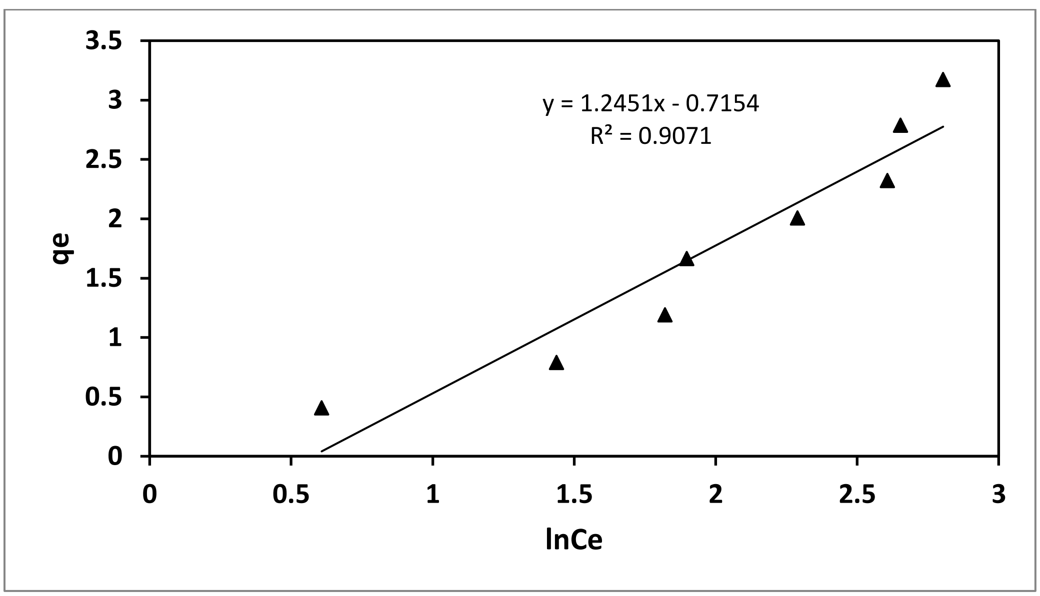

Fig. 10. Temkin isotherm for adsorption of dye on AS.

Thermodynamics of adsorption process

Thermodynamics study were performed only to the adsorption procedure for estimate the type of the adsorption reaction. Therefore, it is significant to study the Thermodynamics parameters at (298 to 318) K of the adsorption entropy (ΔS^0), and Gibbs free energy (ΔG^0), and the change in the standard enthalpy (ΔH^0), Gibbs free energy change can be calculated from the as:

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

The ΔG^0 is the change in Gibbs free energy ($KJ.mol^{-1}$), and T is absolute solution temperature (in Kelvin, R is the universal gas constant (8.314 $J.mol^{-1}.K^{-1}$),) and K is thermodynamic equilibrium constant to the adsorption. The value of (k) has been calculated by on the equation:

$$K = (qe\ m)/(Ce\ v)$$

Where the standard enthalpy change (ΔH^0) were calculated by using the values of lnk against 1/T according to Van't Hoff - Arrhenius equation:

$$\ln k = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT}$$

From the intercept and slope of the linear plots the values of ($\Delta S/R$) and ($-\Delta H/R$) have been calculated. The results from Table 2 of thermodynamic analysis shows that the adsorption of Basic Fuchsin onto the AS surface was spontaneous and exothermic (physical adsorption), that obtained from $\Delta G°$ and ΔH.

Table 2: Thermodynamic Parameters of the Adsorption Basic Fuchsin Dye onto AS.

- ΔH ($K.J.mol^{-1}$)	**-Δ*G*°** ($J.mol^{-1}$)	**-Δ*S*°** ($J.mol^{-1}.K^{-1}$)
31.229	2524.393	93.249

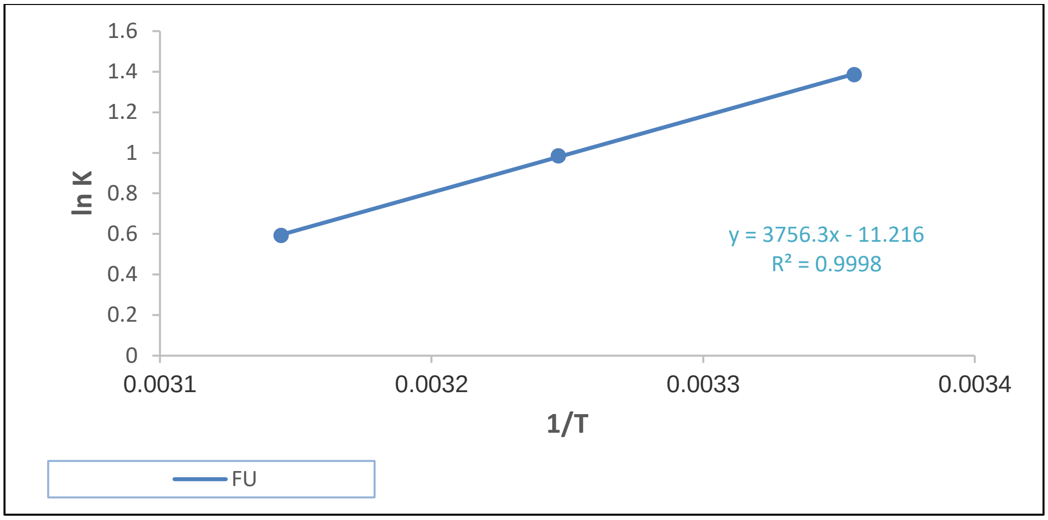

Fig. 11. Values of lnK versus 1/T of adsorption for the three dyes onto AS.

Conclusion

1. The procedure of adsorption is a favorable method for the water dyes removal.

2. The AS adsorbent is low cost and widely available.

3. Adsorption procedure is favorable at the pH=10 for the dye removal.

4. The capacity of adsorption increases with an increase in the adsorbent amount.

5. The Freundlich isotherm is more suitable for the adsorption processes.

6. The results of the thermodynamic analysis shows the adsorption of Basic Fuchsin onto the AS surface is spontaneous and exothermic, that obtained from $\Delta G°$ and ΔH.

References

[1] V. Katheresan, J. Kansedo, and S. Y. Lau, "Efficiency of various recent wastewater dye removal methods: A review," J. Environ. Chem. Eng., vol. 6, no. 4, pp. 4676–4697, 2018.

[2] K. Ramakrishna and T. Viraraghavan, "Dye Removal Using Low Cost Adsorbents," War. Sci. Tech., vol. 36, no. 2, pp. 189–196, 1997.

[3] S. Sadri Moghaddam, M. R. Alavi Moghaddam, and M. Arami, "Coagulation/flocculation process for dye removal using sludge from water treatment plant: Optimization through response surface methodology," J. Hazard. Mater., vol. 175, no. 1–3, pp. 651–657, 2010.

[4] V. K. Garg, R. Gupta, A. B. Yadav, and R. Kumar, "Dye removal from aqueous solution by adsorption on treated sawdust," Bioresour. Technol., vol. 89, no. 2, pp. 121–124, 2003.

[5] P. K. Malik, "Dye removal from wastewater using activated carbon developed from sawdust: Adsorption equilibrium and kinetics," J. Hazard. Mater., vol. 113, no. 1–3, pp. 81–88, 2004.

[6] M. A. Hossain, H. H. Ngo, W. S. Guo, and T. V. Nguyen, "Removal of copper from water by adsorption onto banana peel as bioadsorbent," Int. J. GEOMATE, vol. 2, no. 2, pp. 227–234, 2012.

[7] G. Annadurai, R. S. Juang, and D. J. Lee, "Adsorption of heavy metals from water using banana and orange peels," Water Sci. Technol., vol. 47, no. 1, pp. 185–190, 2003.

[8] M. M. A., "Batch Removal of Hazardous Safranin-O in Wastewater Using Pineapple Peels as an Agricultural Waste Based Adsorbent," Int. J. Environ. Monit. Anal., vol. 2, no. 3, p. 128, 2014.

[9] T. A. Albanis, D. G. Hela, T. M. Sakellarides, and T. G. Danis, "Removal of dyes from aqueous solutions by adsortion on mixtures of fly ash in batch and column techniques," Glob. NEST JournalGlobal NEST Int. J., vol. 2, no. 3, pp. 237–244, 2018.

[10] C. Namasivayam and D. Kavitha, "Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste," vol. 54, no 1, pp. 47–58, 2002.

[11] N. K. Amin, "Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith," Desalination, vol. 223, no. 1–3, pp. 152–161, 2008.

[12] M. A. M. Salleh, D. K. Mahmoud, W. A. W. A. Karim, and A. Idris, "Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review," Desalination, vol. 280, no. 1–3, pp. 1–13, 2011.

[13] N. C. Das et al., "Correlation between local structure and refractive index of e-beam evaporated (HfO_2-SiO_2) composite thin films," J. Appl. Phys., vol. 108, no. 2, pp. 1–5, 2010.

[14] M. A. Ramlli, M. A. Maksud, and M. I. N. Isa, "Characterization of polyethylene glycol plasticized carboxymethyl cellulose-ammonium fluoride solid biopolymer electrolytes,"

AIP Conf. Proc., vol. 1826, no. 1, pp. 020001-6, 2017.

[15] F. Adam, K. M. Hello, and S. J. Chai, “The heterogenization of l-phenylalanine-Ru(III) complex and its application as catalyst in esterification of ethyl alcohol with acetic acid,” Chem. Eng. Res. Des., vol. 90, no. 5, pp. 633–642, 2012.

[16] M. Suneetha and K. Ravindhranath, “Removal of nitrites from waste waters using adsorbents derived from Phyllanthus Neruri plant,” Indian J. Chem. Technol., vol. 25, no. 4, pp. 345–352, 2018.

[17] G. Annadurai, R. S. Juang, and D. J. Lee, “Use of cellulose-based wastes for adsorption of dyes from aqueous solutions,” J. Hazard. Mater., vol. 92, no. 3, pp. 263–274, 2002.

[18] S. D. Khattri and M. K. Singh, “Removal of malachite green from dye wastewater using neem sawdust by adsorption,” J. Hazard. Mater., vol. 167, no. 1–3, pp. 1089–1094, 2009.

[19] N. Shimizu, C. Ogino, M. F. Dadjour, and T. Murata, “Sonocatalytic degradation of methylene blue with TiO2 pellets in water,” Ultrason. Sonochem., vol. 14, no. 2, pp. 184–190, 2007.

[20] 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,” vol. 4, no. 4, pp. 2174–2179, 2012.

[21] C. A. Coles and R. N. Yong, “Use of equilibrium and initial metal concentrations in determining Freundlich isotherms for soils and sediments,” Eng. Geol., vol. 85, no. 1–2, pp. 19–25, 2006.