RESEARCH ARTICLE

Removal of Safranine-O Dye from Aqueous Solution using Prepared Activated Carbon from Apple Seed Coat: Kinetic, Thermodynamic, and Isothermal Studies

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Received: 24th July, 2021; Revised: 17th August, 2021; Accepted: 05th September, 2021; Available Online: 25th September, 2021

ABSTRACT

In this study, to prepare the activated carbon, the shell of apple seeds was used to get rid of the dye safranine-O present in the wastewater. Several important factors were studied, including equilibrium time, pH solution, temperature, dye concentration, and weight of activated carbon, where it was observed that the percentage of removal increases with increasing weight of the surface AC and decreases with increasing dye concentration. Also, the percentage of removal increases with the increase in the equilibrium time, and the temperature has a very important effect on the adsorption process, as it was observed that with the increase in temperature, the percentage of removal of dye increased. The adsorption isotherms are described by the Langmuir isotherm and the Freundlich isotherm. The Langmuir isotherm was found to give the best efficiency compared to the Freundlich isotherm. Where the best adsorption efficiency at different temperatures was (291, 300, 309 K) 27.55, 33.33, 36.66 mg/g, in the same order. The adsorption kinetics of safranine-O dye was also studied using first-order reaction and second-order reaction. Kinetic studies have shown that the reaction obeys a second-order reaction. Thermodynamic parameters were calculated including (ΔG°), (ΔH°), and (ΔS°) changes, to predict the nature of adsorption. The estimated values for ΔG° were -1.75, -2.58, and -2.95 kJ/mol at 291, 300, and 309 K, at the same order.

Keywords: Activated carbon, Adsorption capacity, Apple seed coat, Safranine-O.

International Journal of Pharmaceutical Quality Assurance (2021); DOI: 10.25258/ijpqa.12.3.9

How to cite this article: Aljeboree AM, Algubury HY, Bennecer A, Kmal RQ, Alkaim AF. Removal of Safranine-O Dye from Aqueous Solution using Prepared Activated Carbon from Apple Seed Coat: Kinetic, Thermodynamic, and Isothermal Studies. International Journal of Pharmaceutical Quality Assurance. 2021;12(3):211-216.

Source of support: Nil.

Conflict of interest: None

INTRODUCTION

Many types of dye are employed in industrial factories like paper, carpets, paper, rubbers, cosmetics, plastics, and textiles in order to color their products. There are many types of pollutants released to the water sources during dye production. The textile industries released high amount of color wastewater, which are mainly poisonous water sources.[1] The colored wastewater of these factories containing high concentration of organic compounds, which are difficult to remove from aqueous solution, these types of dye can be careful as one of the utmost dangerous pollutants, due to they have mutagenic, teratogenicity, and carcinogenic influence and cause several disorders health to human beings like dysfunction of the kidney, concentrations reproductive method, brain, liver, and central nervous method even present at low.[2,3] Numerous techniques, including chemical, physical, and biological systems, have been employed to remove the dye wastewater. These methods can remove dyes from wastewater. At the present time, the researcher's interest has increased in the adsorption technology, which depends on the purification of polluted water resulting from dye factories and industrial factories.[4-6] Also, the adsorption technology is considered an easy, available, simple, high-efficiency, and high-capacity technique in the treatment of dyes with very high concentrations.[7] Activated carbon is very widely used in the removal of pollutants, especially dyes, because of its high ability to absorb pollutants and organic compounds. Activated carbon (AC) has been utilized for safranine-O dye adsorption because of its great specific surface area and great number of surface-active adsorption sites.[8-10] In recent years, conversion of the low cost materials available in large quantities like fly ash, coal, wool wastes, silica gel, agricultural wastes, and clay

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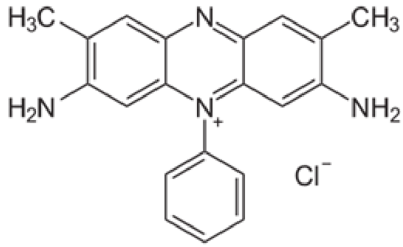

Figure 1: Chemical structure of Safranine-O dye

materials into activated carbon can be utilized as adsorbents for the treatment of wastewaters having dyes, pigments, and other colorants.[11] The objective of this work is to study and describe different factors like the effects of equlibrum time, safranine-O dye conce, primary pH, adsorbent mass, and temperature on dye adsorption rate. Adsorption isotherms, kinetics, and Thermodynamic studies have to be performed to understand how the removal of the selected dyes on activated carbon was too calculated. Safranine-O dye: Safranine-O dye (Figure 1) is a reddish-brown powder that can dissolve in water, and it is commonly used in dyeing fabrics, paper, leather, cotton, silk, and wool. It also has wide uses for biological laboratory purposes. The presence of safranin dye has a negative effect on human health, as it causes pain in the stomach, mouth, tongue, and lips, which leads to nausea and diarrhea, such as irritation of the mouth, tongue, throat, lips, and stomach pain, which may lead to vomiting, nausea, and diarrhea.

MATERIALS AND METHODS

Materials and Chemicals

The apple seed coat was collected from ASDA supermarket (Northampton, UK). The pH was adjusted by adding 0.1 M, Hydrochloric acid (HCl), and sodium hydroxide (NaOH) w Deionized water was utilized to prepare wholly of the solutions. A standard solution of 100 mg/L safranine-O dye was prepared via dissolving 0.01 g of safranine-O dye in 100 mL deionized water. Wholly of the several concentration solutions were prepared by appropriately diluting the standard solution. The chemicals utilized in the investigation are being used without further purification.

Preparation of Activated Carbon

Preparation of activated carbon from raw materials (apple seed coat) that were collected from ASDA super market (Northampton, UK). The samples were washing by DW at different times to remove dust and other contaminations. Later they peel seeds off. After that the sample was dry at 120°C for 2 hours. This method that materials heating at 200°C in furnace graphite of 1h in an inert atmosphere via flushing nitrogen prior to and during the heating time. After that, the sample result was cooled to room temp. And washing by DW at several time to adjusted the pH samples about the pH7 and final products were dry at 110°C for 2 hours to give powder activated carbon.[12]

Adsorption Experiments

In this work the adsorption investigates was carry out to calculate the effect of several factors (adsorbent mass, pH solution, equilibrium time, and primary concentration of dye) for the percentage removal of safranine-O dye on the surface of activated carbon. Batch adsorption investigates was performed by utilizing a sample having a known dosage of activated carbon and 100 mL of safranine-O dye solutions of known initial concentration in 250 mL Erlenmeyer flasks and shaking on a shaker water bath controlling temperature operated at a constant speed of 120 rpm. Next, stirring on a shaker for pre-determined time intervals to reach the adsorption equilibrium isotherms and the optimum adsorption amount of safranine-O dye, then the mixture was treated by centrifugation of solid-liquid separation.[13] Stirring on a shaker of pre-determined time intervals, 3 mL were withdrawn with a clinical syringe of the clear solution and analyzed using a UV-vis spectrometer to determine the dye concentration. The quantity of dye adsorbed onto the adsorbent at equilibrium, adsorption capacity q_e (mg/g), was calculated utilizing the following (Eq. 1):

$$q_e = \frac{(C_o - C_e)\, V_{(L)}}{W} \quad (1)$$

The removal percentage of safranine-O dye (R%) via the AC in the aqueous solution was estimation utilizing in (Eq. 2):

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Adsorption Isotherm

The adsorption isotherm is an important factor in improving the utilization of the activated carbon. It can be utilized to estimate the removal percentage of the AC and refer to the interaction between the activated carbon and the safranine-O dye. There are two types of the adsorption process. The first is called physical adsorption via weak van der Waals forces. The second is called chemical adsorption via chemical bonding, depending on the interaction between the adsorbate and the adsorbent. The linear forms of the isotherm Langmuir (Eq. 3) and isotherm Freundleich (Eq. 4) :

$$\frac{1}{q_e} = \frac{1}{q_{max}\, K_L\, C_e} + \frac{1}{q_{max}} \quad (3)$$

q_{max} is the maximum adsorption efficiency (mg/g), and K_L is the Langmuir constant (L/mg), which reflects the adsorption rate.

$$q_e = K_f\, C_e^{1/n} \quad (4)$$

Adsorption Kinetics

A series of investigations was crying out for studying two types of Kinetic models, which can be utilized to study the rate-controlling step of adsorption and the mechanism adsorption. Two models kinetic were considered: the first model and second model. The linear forms of the first model (Eq. 5), and the second model (Eq. 6), can be calculated:

$$\log q_e - q_t = \log (qe) - \frac{K_1}{2.303} t \quad (5)$$

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Thermodynamics

The most important thermodynamic factors like (ΔG°), (ΔH°), and (ΔS°) for adsorption of safranine-O dye onto AC were tested. These parameters were estimated utilizing the following (Eq. 7)

$$\Delta G° = - RT \ In \ Ks \quad (7)$$

The (ΔH°) of adsorption and entropy (ΔS°) of adsorption were estimated from adsorption result at several temperatures (291,300,309 K) utilizing the Van't Hoff (Eq. 8)

$$In \ k_s = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \quad (8)$$

RESULTS AND DISCUSSION

Effect of Contact Time

The influence of equilibrium time is a significant factor in determining the contact time in which best safranine-O dye is removed. A series of investigates were performed for investigated the percentage removal of dye as a function of time using 40 ppm of safranine-O dye with 0.09 g/100 mL at difference temperatures (291, 300, and 309 K). The percentage removal dye gradually increases with time, then start to level off at 50–60 minutes. As shown in Figure 2. During the first 30 minutes, the removal rate of safranine-O dye is very fast due to a great number of active adsorption sites.[14] Later the removal percentage rate slows down until it reach to the equilibrium state because of the slow diffusion of dye particles in to the tine holes of the AC.

Effect of Temperature

A series of investigations were performed to study the percentage removal of safranine-O dye from aqueous solution, using 40 ppm of safranine-O dye with 0.09 g/100 mL of AC at different temperatures (291, 300, and 309 K) (Figure 2). The adsorption capacity rises by increasing temperature, indicating an endothermic reaction.

Effect of pH Solution

The effect of initial PH solution on the removal of safranine-O dye by activated carbon was investigated in pH range (2–9) with the known concentration of safranine-O dye 40 ppm and 0.09 g/100 mL of activated carbon. The solution pH of the aqueous solution was adjusted utilizing 0.1 M HCl and 0.1 M NaOH. The removal rate of safranine-O dye as a function of pH is shown in Figure 3. The adsorption efficiency increases by rising pH value. It was observed from Figure 3 that the (Qe) rises from (2.74 to 55.55) mg/g when the initial pH increases from pH (2 to 9). This behavior can be explained dependence on the presence of a large number of active sites on the AC. The activated carbon surface can be divided into two parts depending on the medium. When the acidic medium the activated carbon surface will be positive charge, the electrostatic repulsion takes place among the AC and the positive charge of safranine-O dye, leading to decrease adsorptive removal of the dye. But when the initial pH values increase (basic medium), the AC has a negative charge. Therefore, the electrostatic attraction between the negatively charged sites of the adsorbent and the positively charged safranine-O dye molecules occurs. Depending on this feature, the adsorptive removal of the dye on the activated carbon rises by increasing solution pH.[15]

Effect of Activated Carbon Content

Is a significant parameter for effective safranine-O dye removal because it estemation the sorbent/sorbate equilibrium of the method. A series of experiments were performed to conduct the removal percentage of safranine-O dye, using 40 ppm of safranine-O dye with varying activated carbon dosage rang (0.04–0.09) g/100 mL. As shown in Figure 4. with increasing activated carbon content from 0.04 to 0.09 g/100 mL, the removal capacity of safranine-O dye almost linearly increases 25 to 97.5 % and then starts to level off because of rises

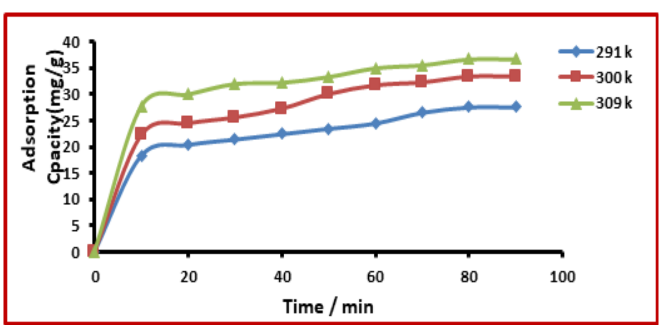

Figure 2: Effect of equilibrium time on the adsorption of safranine-O dye onto activated carbon at severalure temperatures.

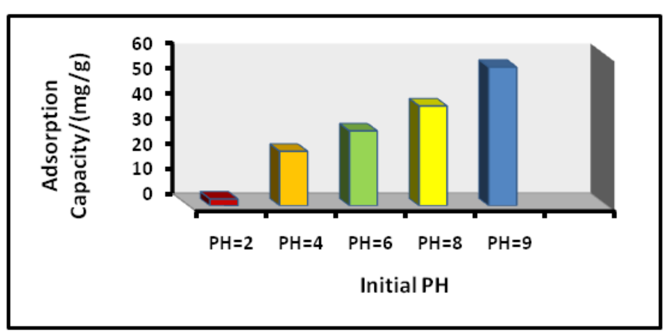

Figure 3: The adsorption process of Safranine-O dye onto activated carbon at initial Safranine-O dye concentrations = 40 ppm, amount of activated carbon = 0.09 gm/100 mlusing several pH range (2-9).

of active sites. The best percentage %removal is 97.5% at 0.09 g/100mL.[16,17]

Effect of Initial Dye Concentration

A series of experiments were performed for tested the influence of the varying in the dye conc. of safranine-O dye rang (40–90) ppm on the percentage removal efficiency using constant activated carbon dosage (0.09 g/100 mL). It could be observed from Figure 5. that the adsorption efficiency raised via increasing of the concentration of safranine-O dye then start to be flat since the primary dye concentration raised. To explain this behavior, increasing the initial dye concentration leads to an increase in collusion and consequent increase adsorption process. Moreover, in the first stage of adsorption, there are many adsorption sites, so It was found that the rate of safranine-O's adsorption process was reached in the first 20 minutes of adsorption very greatly. After that, the remaining adsorption sites were decreased when the initial dye concentration increased, which means activated carbon's exterior surface reached saturation. The removal of adsorption decreased by a rise in the primary conc, of safranine-O dye. The maximum removal efficiency is 94.68% at 40 ppm.[18]

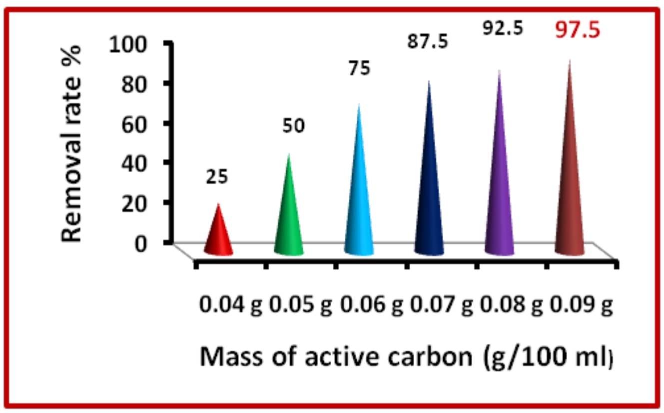

Figure 4: Effect of adsorbent dosage on the adsorption of Safranine-O dye onto activated carbon (initial Safranine-O dye concentration = 40 ppm, T = 309 K).

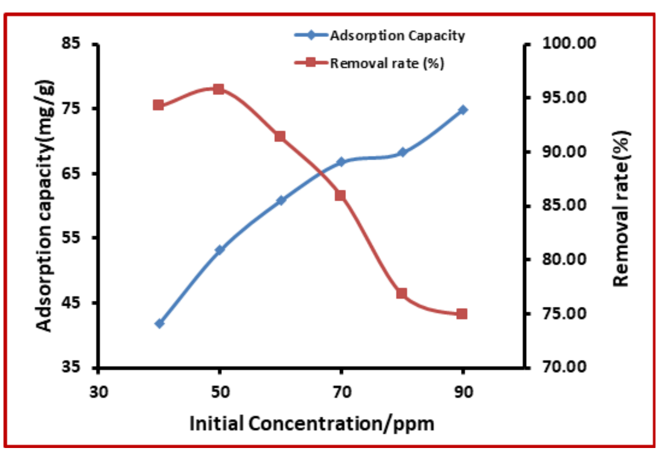

Figure 5: Effect of initial concentration on adsorption process on the surface of activated carbon using 0.09 g/100 mL.

Adsorption Isotherm

In this project, the adsorption isotherm was tested to refer to adsorption mechanism and reach the optimum adsorption efficiency. Two adsorption models, Langmuir and Freundlich equation, were utilized to study the adsorption model. As we know the isotherm, Langmuir is describing the monolayer adsorption onto a surface with a finite number of sites. The liner of model Langmuir calculates from (Eq. 6). The regression coefficients and isotherm factors for Freundlich and Langmuir isotherms are shown in Figures 6 and 7, respectively, and tabulated in Table 1.

The regression coefficients indicated that the result is best fitted vi the Langmuir isotherm Figure 6. The isotherm Langmuir adsorption has the best R^2 value =0.9984. Thus, the investigational result is well fitted via the isotherm Langmuir adsorption, which assumes monolayer sorption on a surface by a finite number of identical sites.[19]

Table 1: The factors of isotherm Langmuir and isotherm Freundlich at 309 K for adsorption of Safranine-O dye on to AC.

	Langmuir			*Freundlich*		
Adsorbent	q_{max}	K_L	R^2	K_f	n	R^2
Activated carbon	50.76	0.32	0.9984	12.12	2.11	0.9848

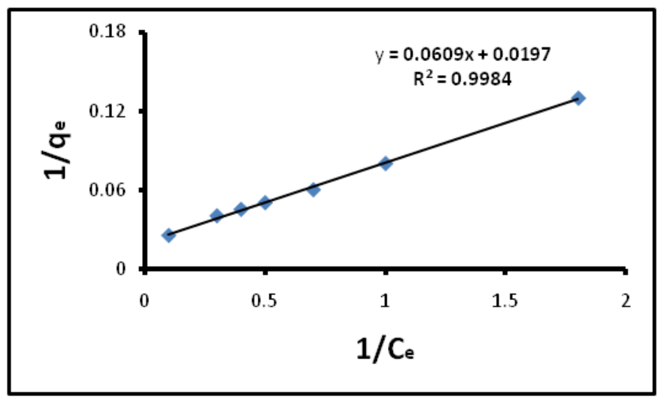

Figure 6: The linear Isotherm Langmuir adsorption for Safranine-O dye adsorption by the activated carbon.

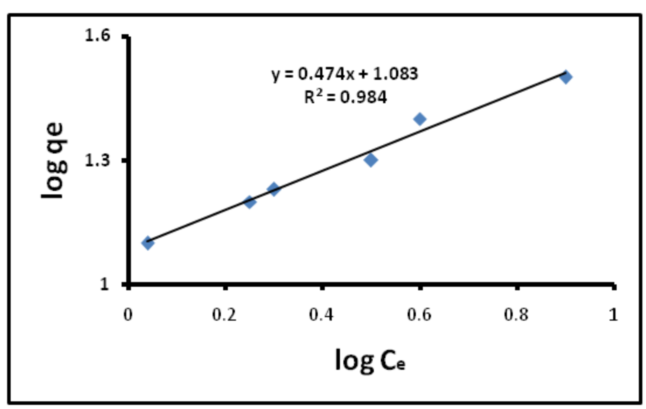

Figure 7: The linear isotherm Freundlich adsorption s for dye safranine

Kinetics Studies

A series of experiments have been performed to estimate model the kinetic; the data was evaluated via (Eq. 5), and (Eq. 6) connected to the first and second kinetics models, in the same order. The equation first model assumes that the solute uptake rate is directly proportional to the saturation concentration—the uptake quantity of dye through time.

From Table 2, it can be noted that the model first model provided a poor fit ($R^2 = 0.8499$) for the investigational result found (Figure 8). These data represent the adsorption result are not following via the first-order kinetic model.

As shown in Figure 9, the investigational result was flawlessly fitting to the kinetic model second order, by great values $R^2= 0.9963$. These data indicate that the activated carbon adsorption of safranine-O dye followed the model kinetic order rather than the first order.[20]

Estimation of Thermodynamic Parameters

The thermodynamic factors like (ΔG°, ΔH°, and ΔS°) were investigated to deduce the adsorption mechanism. These parameters can be estimated using (Eq. 7), and (Eq. 8).

Table 2 Comparison of the model first and second-order adsorption rate constants.

	First-order		*Second-order*	
Adsorbent	*K1*	R^2	*K2*	R^2
Activated carbon	0.071	0.8499	0.0037	0.9963

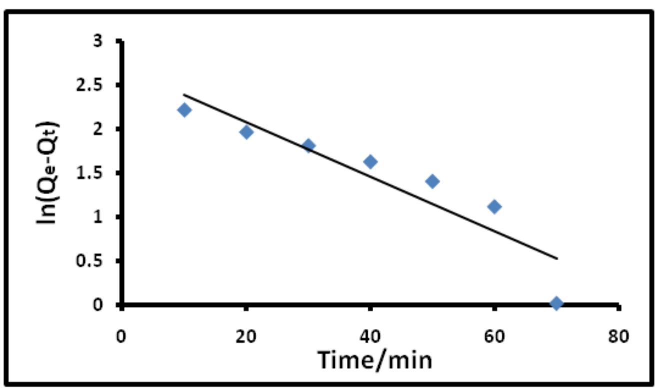

Figure 8: The fitting result of adsorption procedure via first model equation at 309K.

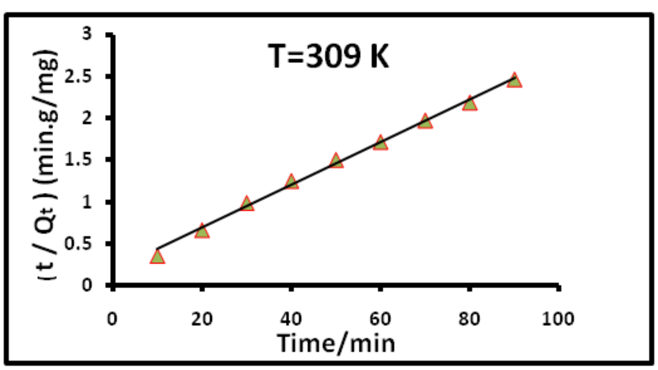

Figure 9: The fitting result of adsorption procedure via second model equation at 309K.

The value of the thermodynamic equilibrium constant (K_s) for the adsorption of safranine-O dye onto AC can determine by plotting ln (q_e/C_e) versus C_e as appear in Figure 10 and the data are listed in Table 3.

The thermodynamic factors (ΔH°) and (ΔS°) was estimated from the slope and intercept of the Van't Hoff plot (Eq. 8) by plotting ln(Ks) versus (1000/T), respectively, as shown in Figure 11, where the slope represent standard enthalpy changes and intercepts represent (ΔH°). All data is shown in Table 4.

From the Figure 11 and Table 4. The values of ΔG° for safranine-O dye adsorption onto activated carbon equal (-1.75, -2.58, and -2.95) kJ/mol , at 291, 300, and 309 K at the same order. These results indicate that a spontaneous adsorption process occurred. The changes of enthalpy (ΔH°) and entropy (ΔS^0) of adsorption were 17.37 kJ/mol and 66.19 kJ/mol, respectively. The positive value of ΔH° indicates that the adsorptions process of safranine-O dye onto activated carbon endothermic adsorption in nature.

CONCLUSION

In this research, the activated carbon was successfully prepared from apple seed coat could be utilized as charge

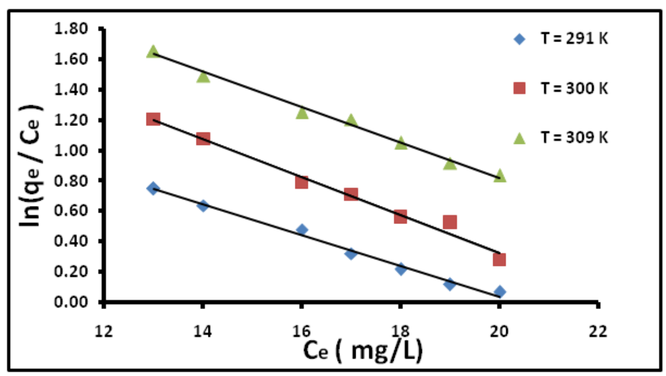

Figure 10: Linear plots for determination of equilibrium constant value at different temperatures.

Table 3: Thermodynamic equilibrium constant at different temperatures.

Temperature/K	*Ks*	R^2
291	2.066	0.9933
300	2.8189	0.9878
309	3.1616	0.9934

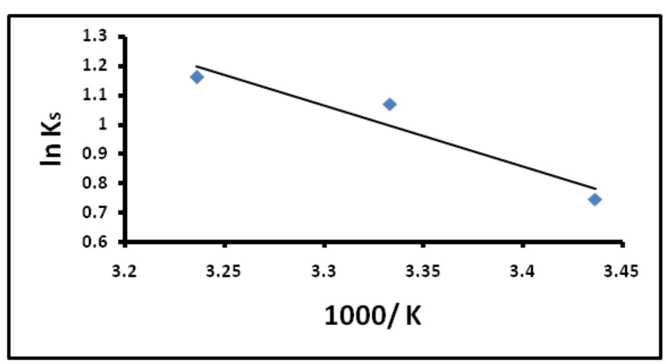

Figure 11: Plot of ln Ks versus 1000/T for Safranine-O dye adsorption.

Table 4: Thermodynamic factors ΔG°, ΔH°, and ΔS° for activated carbon's Safranine-O dye adsorption process.

Temperature/K	*ΔG°/KJ.mol^{-1}*	*ΔH°/ KJ.mol^{-1}*	*ΔS°/ KJ.mol^{-1}*
291	-1.75	17.37	66.19
300	-2.58		
309	-2.95		

and abundantly available AC for the percentage %removal of hazardous safranine-O from aqueous solution. The adsorption capacity was dependent on the operational parameters, including equilibrium time, the quantity of initial safranine-O dye adsorbed, adsorbent dosage, initial pH, and temperature. The removal percentage (%) of the dye rises depending on the increase in equilibrium time and reaches the contact after about 60 minutes. The optimum amount (0.09) g/100 mL of the activated carbon used to remove safranine-O dye. The equilibrium adsorption efficiency of the adsorbent for safranine-O dye increased with increasing conc, and the optimum concentration of safranin dye (40 ppm) in which highest E% of safranine-O. The adsorption of safranine-O dye onto AC was dependent on the one of the utmost significant parameter the initial pH, which affects on the adsorption capacity. The safranine-O was optimally adsorbed at pH 9. The amount of safranine-O dye adsorbed increased with the temperature rise, indicating that the adsorption method is endo-thermic. The adsorption kinetics of safranine-O dye onto the surface of activated carbon obey the second-order model. The adsorption isotherm was investigated using both Langmuir and Freundlich isotherm. The data indicate that Langmuir model could well describe the adsorption data. The calculated thermodynamic factors ΔG°,ΔH°, and ΔS° showed the adsorption process's spontaneity, endothermic nature, and irreversibility.

REFERENCES

1. Bulut Y, Aydın H. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells, Desalination. 2006;194:259-267.
2. Wang Y, Liu Q, Shu L, Miao M, Liu Y, Kong Q. Removal of Cr(VI) from aqueous solution using Fe modified activated carbon prepared from luffa sponge: kinetic, thermodynamic, and isotherm studies, Desalination and Water Treatment. 2016: 1–12.
3. Halim HA, Abdel A. Adsorption of Heavy Metals from Industrial Wastewater using Palm Date Pits as Low Cost Adsorbent, International Journal of Engineering and Advanced Technology. 2014;3:71-76.
4. Aljeboree AM, Alkaim AF. Removal of Antibiotic Tetracycline (TCs) from aqueous solutions by using Titanium dioxide (TiO2) nanoparticles as an alternative material, Journal of Physics: Conf. Series. 2019;1294: 052059.
5. Pham T, Lee B, Kim J, Lee C. Improved removal of Cd(II) from aqueous solution by synthesized nanozeolite, Desalination and Water Treatment. 2016;3:1-10.
6. Azmia NH, Alia UF, Ridwana FM, Isaa KM, Zulkurnaia NZ, Aroua KM. Preparation of activated carbon using sea mango (Cerbera odollam) with microwave-assisted technique for the removal of methyl orange from textile wastewater, Desalination and Water Treatment. 2016;2:1-10.
7. Jin L, Sun Q, Xu Q, Xu Y. Adsorptive removal of anionic dyes from aqueous solutions using microgel based on nanocellulose and polyvinylamine, Bioresource Technology. 2015;197:348-355.
8. Yaqo EA, Anaee RA, Abdulmajeed MH, Tomi IHR, Kadhim MM. Electrochemical, morphological and theoretical studies of an oxadiazole derivative as an anti-corrosive agent for kerosene reservoirs in Iraqi refineries ;Chemical Papers. 2020;74(6); 1739-1757.
9. Al-Jbouri AMS, Abood FM, Hindi NKK, Alkaim AF. Evaluation of antimicrobial activity of the aquatic extract against bacterial isolates from periodontitis in Babylon Province, Iraq. Biochemical and Cellular Archives. 2018;18:1345-1350.
10. Aljeboree AM, Alshirfi AN, Alkaim AF. Removal of Pharmaceutical Amoxicillin drug by using (CNT) decorated Clay/ Fe2O3 Micro/Nanocomposite as effective adsorbent: Process optimization for ultrasound-assisted adsorption, International Journal of Pharmaceutical Research. 2020;11:80-86.
11. Hakim T, Kandila EA, Saad AA, Abdel A, Aboelhasan AE. Study on adsorption behavior and separation efficiency of naturally occurring clay for some elements by batch experiments, European Journal of Chemistry. 2012;3:99-105.
12. Li Q, Yuea Q, Suc Y, Gaoa B, Sunb H. Equilibrium, thermodynamics and process design to minimize adsorbent amount for the adsorption of acid dyes onto cationic polymer-loaded bentonite, Chemical Engineering Journal. 2010;158:489-497.
13. Aljeboree AM, Alkaim AF, Abdulrazzak FH, Abbas AS, Alshirifi AN. Spectrophotometric Determination of Pharmaceutical by Oxidative Coupling of 4-Aminoantipyrine: A Short Review, Journal of Engineering and Applied Sciences. 2019;14:5561-5569.
14. Malik R, Ramteke DS, Wate RS. Adsorption of malachite green on groundnut shell waste based powdered activated carbon, Waste Management. 2007;27:1129-1138.
15. Aljeboree A M, Alshirifi AN, Alkaim AF. Ultrasound-assisted adsorption of pharmaceuticals onto clay decorated carbon Nano composites as a novel adsorbent: As a Applicable for environmental studies, Journal of Physics: Conference Series. 2020;1664:012098.
16. Aljeboree AM, Abbas AS. Removal of Pharmaceutical (Paracetamol) by using CNT/TiO2 Nanoparticles, Journal of Global Pharma Technology. 2019;11:199-205.
17. Nasr JB, Hamdi N, Elhalouani F. Characterization of activated carbon Prepared from sludge paper for methylene blue adsorption Journal of Materials and Environmental Sciences. 2017;8:1960-1967.
18. Hazim Y. Al, Qasim YM . Prepared coupled ZnO-Co_2O_3 then study the photocatalytic activities using crystal violet dye, Journal of Chemical and Pharmaceutical Sciences. 2016;9(3):1161-1165.
19. Aljeboree AM, Alkaim AF. Role of plant wastes as an ecofriendly for pollutants (Crystal Violet dye) removal from Aqueous Solutions, Plant Archives. 2019;19: 902-905.
20. Aljeboree AM. Adsorption and removal of pharmaceutical riboflavin (RF) by rice husks activated carbon, International Journal of Pharmaceutical Research. 2019;11:255-261.