Removal of Textile dye by Using Activated Carbon in Aqueous Solution

Wilaiporn Insuwan*, Khattiya Moonchaisook and Benjamaporn Junkrin

Rajamangala University of Technology Isan Surin Campus, Faculty of Agriculture and Technology, Surin 32000, Thailand

* Corresponding author. E-mail address: wi_insuwan@hotmail.com

Received: 1 July 2019; Revised: 23 January 2020; Accepted: 28 January 2020; Available online: 5 June 2020

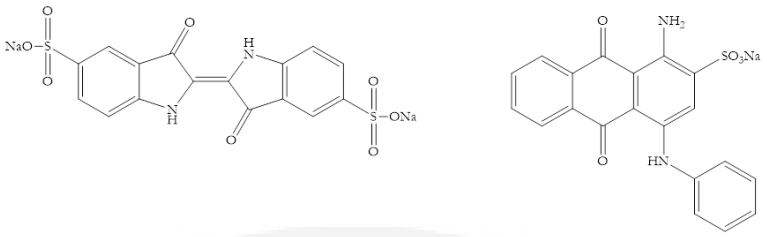
Abstract

Two textile dye (indigo carmine and acid blue 25) were removed using activated carbon (AC) as solid adsorbent. Effects of various parameters such as adsorbent dosage, contact time, kinetics and thermodynamic properties were investigated by batch adsorption technique. The results shown that the adsorption kinetics of textile dye was determined by the pseudo-second order model and adsorption isotherms fitted very well with Langmuir model. In addition, thermodynamic properties indicated that the adsorption of both textile dye on AC were endothermic and spontaneous process. The maximum adsorption capacities (qm) of indigo carmine and acid blue 25 onto AC was 89.29-104.17 mg/g and 1,428.00-2,000.00 mg/g, respectively. This results could be explained by stronger interaction between acid blue 25 and AC. This work indicated that AC can be used as an alternative adsorbent for removal of textile dye especially acid blue 25, due to the low cost and high efficiency of adsorption capacity.

Keywords: textile dye, adsorption, kinetics, activated carbon

Introduction

Surin is one of the northeastern province of Thailand, famous for the so much known Thailand silk. Therefore, textile is one of the important sectors in Thailand. Although, the textile dye has many benefits, one of the main drawbacks is its wastewater from bleaching and dyeing process which was not suitable treated and discharged into the environment. How to remove the contamination of dye in wastewater was very important before flow in drains and rivers. Various methods for remove textile dye in wastewater such as electrochemical processes (Stergiopoulos, Dermentzis, Giannakoudakis, & Sotiropoulos, 2014), electrocoagulation (Adeogun & Balakrishnan, 2016), biosorption (Kumari & Abraham, 2007), ion exchange (Karcher, Kornmüller, & Jekel, 2002; Pathania, Sharma, & Singh, 2017; Liu, Wu, Chiu, Suen, & Chu, 2007) and adsorption (Tangsathitkulchai et al., 2012; Elizalde□González & Peláez□cid, 2003; Wasti & Ali Awan, 2016; Al-Ghouti, Khraisheh, Allen, & Ahmad, 2003) were reported. However, due to complex structure compound, high thermal and chemical stability and toxic of textile dye is very hard to treat by conventional method. The adsorption is alternative method for dye removal because it is effective separation process, low cost and easy to perform. Activated carbon is very potential for as an adsorbent used in textile dye removal that have been reported in the literature (Razi, Hishammudin, & Hamdan, 2017). This review presented about factor affecting textile dye removal by activated carbon. Indigo carmine and acid blue 25 (shown in Figure 1) were used in textile industries that is a dark blue dye (Mall, Taneja, & Thakur, 2013; Badii, Ardejani, Saberi, Limaee, & Shafaei, 2010). Both of dye were highly toxic dye that may lead to negative effects on human health and environment. In this study, the adsorption of indigo carmine and acid blue 25 by activated carbon as an adsorbent were reported. In this work, physiochemical parameters such as, adsorbent dosage, contact time, kinetics and thermodynamic parameters investigated in a batch adsorption technique. The equilibrium data evaluated using Langmuir and Freundlich isotherms.



Indigo carmine Acid blue 25

Figure1 Structure of textile dye (a) Indigo carmine (b) Acid blue 25

Methods and Materials

Materials and chemicals

Activated carbon (AC) was supplied by Merck, Germany. Acid blue 25 and indigo carmine were obtained from Sigma Aldrich. A stock solution was prepared by dissolved 1.0 g of textile dye in 1000 mL distilled water to make of 1000 ppm (mg/L).

Adsorption studies

The adsorption were proceed to study adsorbent dosage, kinetics and adsorption isotherm. Adsorbent dosage were carried out by 25 mL of dye solution, 200 ppm that obtained by diluting the dye stock solution and mixed with amount of the AC (0.0025-0.0500 g) in 125 mL Erlenmeyer flask. The mixture was shaken for 12 hour in shaker bath at 303 K. The adsorbent was removed by centrifuged 5000 rpm for 5 min. Then, the residual dye concentration was determined by UV-Visible spectrophotometer by measuring the absorbance at a wavelength of maximum at 610 nm and 600 nm for indigo carmine and acid blue 25, respectively.

Kinetic experiments were performed by 100 mL of dye solution 10, 30 and 60 ppm mixed with 0.01 g AC in 125 Erlenmeyer flask. The mixture was shaken in shaker bath at 303 K with specific period in range 30-360 minute. After that the procedure was also performed following the similar adsorbent dosage.

Adsorption isotherm were carried out by 25 mL of dye solution that mixed with 0.01 g AC. The mixture was shaken for 360 minute for ensure equilibrium. Then the procedure was also performed following the similar adsorbent dosage.

The amount of dye adsorbed at equilibrium (q_e, mg/g) were calculated by Eq. 1

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

Where V (L) is the volume of the solution, and m (g) is the mass of the AC. C_0 (mg/L) and C_e (mg/L) are concentrations of dye in solution at initial and equilibrium, respectively. Case of kinetic data the amount of dye adsorbed at any time, q_t was calculated by Eq. 2, where C_t (mg/L) is concentrations of dye in solution at any time.

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

Results and discussion

Effect of adsorbent dosage

Figure 2 shown the effect of AC dosage on the adsorption of textile dyes at 303 K. The results show that percentage of adsorption for both the indigo carmine and acid blue 25 was increased with increasing mass of AC. However, percentage adsorption was remained at AC dosage of 0.01–0.05 g. Thus, 0.01g of AC was suitable for the contact time and kinetic study of textile dyes adsorption. This results can be explained by increased AC dosage should be increasing number of active sites for adsorption process. On the other hand, percentage adsorption was remained constant after AC dosage 0.01g indicating that the adsorbent was already saturated and cannot be uptake the amount of textile dye into active sites (Badii et al., 2010).

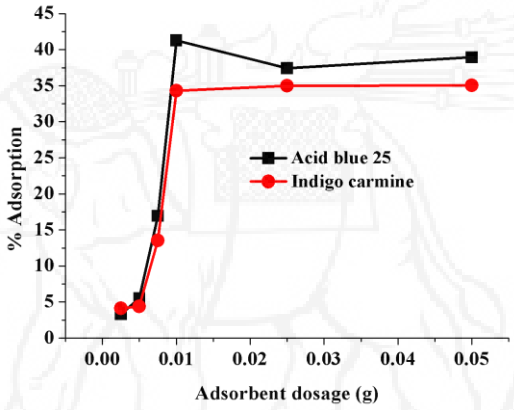


Figure 2 The effect of adsorbent dosage on the dye adsorbed on AC.

Effect of contact time

To find out the best period for adsorption process was achieved. The contact time for dye adsorbed onto AC was vary in range 30–360 min. Figure 3 shows the effect of contact time on the adsorption of indigo carmine (a) and acid blue 25 (b) onto AC at different initial concentrations ranging from 10 to 60 ppm.

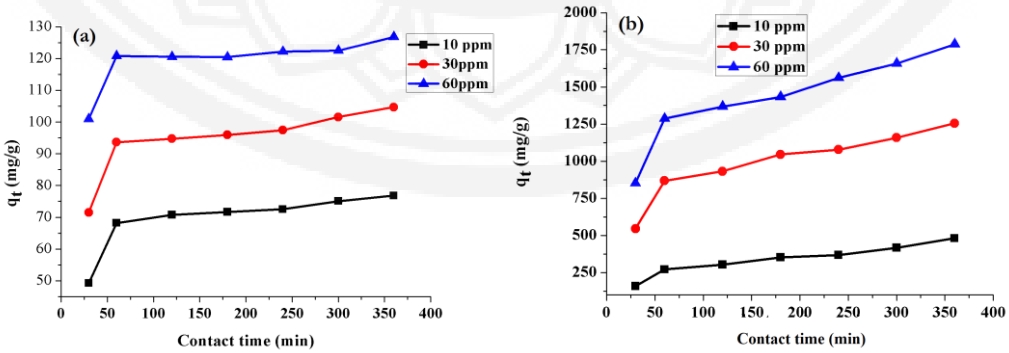


Figure 3 The effect of contact time on the adsorption of indigo carmine (a) and acid blue 25 (b) onto AC, at different initial concentrations, adsorbent dosage = 0.01 g, Temperature = 303 K

The results shows similar trend both of indigo carmine and acid blue 25 that at the first 60 minute, the adsorption was rapidly occur and then after 60 minute the adsorption was slower and remained constant until 360 minute. This indicates that the dye uptake increase with increasing of time until equilibrium was reached at 60 minute. After that the active sites of AC was occupied by dye molecules, the rate of adsorption was negligible (Badii et al., 2010). In addition, the amount of dye adsorbed at any time (qt) was increased with increasing initial dye concentrations from 10 ppm-60 ppm. This is may be because of the higher initial concentrations of dye make high possibility of collision between dye and AC.

Adsorption kinetics

In order to investigate the mechanism of adsorption kinetic models are generally used to test experimental data. Pseudo first order and pseudo second order equations can be used assuming that the measured concentrations are equal to surface concentrations (Vijayakumar, Tamilarasan, & Dharmendirakumar, 2012; Rinku, Shripal, & Hemant, 2015).

The pseudo first order and pseudo second order equation are given by Eq. 3 and 4, respectively (Rinku et al., 2015).

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (3)$$

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where qe (mg/g) and qt (mg/g) are the amount of dye adsorbed at equilibrium and the amount of dye adsorbed at any time, respectively. k_1 (min^{-1}) and k_2 (g/mg/min) are the rate constant of the pseudo first order and pseudo second order adsorption, respectively.

The kinetic data in table 1 and 2 were obtained by plot between ln(qe-qt) versus t (pseudo first order) and t/qt versus t (pseudo second order) that shown in Figure 4 and 5 A straight line of ln (qe - q) versus t suggests that process followed first order kinetics and the plot t/q versus t should give a straight line if second order kinetic model is applicable.

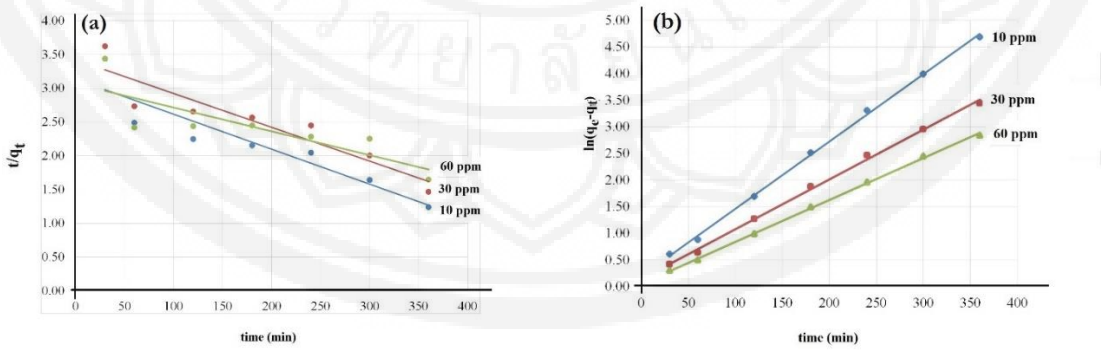


Figure 4 Pseudo first order (a) and Pseudo second order (b) adsorption kinetics of indigo carmine adsorbed on AC, at different initial concentrations, adsorbent dosage = 0.01 g, time= 360 minute

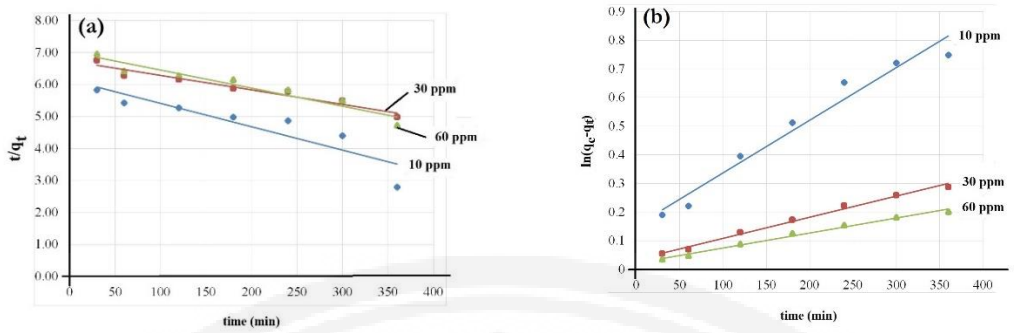


Figure 5 Pseudo first order (a) and Pseudo second order (b) adsorption kinetics of acid blue 25 adsorbed on AC, at different initial concentrations, adsorbent dosage = 0.01 g, time= 360 minute

Table 1 and 2 were show the values of kinetic parameters that the pseudo-second order chemical reaction kinetics provide the best correlation coefficients (R^2) and the experimental value of qe agree with qe in calculation. The results indicates that the adsorption mechanism was chemisorption. In this mechanism, the kinetics of adsorption should be correspond to a reversible second order. Therefore, the adsorption kinetics can be very satisfactorily approximated by a pseudo second order model for all the indigo carmine and acid blue 25 that finding was also in good agreement with adsorption of phenol onto activated carbons (Fierro, Torne´-Ferna´ndez, Montane´, & Celzard, 2008).

Table 1 Kinetic parameters for indigo carmine adsorbed on AC at different initial concentrations

Parameters			Pseudo first order model			Pseudo second order model		
Temp. K	C_0 (mg/L)	q_e (exp.) (mg/g)	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg/min)	R^2
303	10	80	23.04	$5.20x10^{-3}$	0.8535	79.36	$0.80x10^{-3}$	0.9987
303	30	109	30.66	$5.00x10^{-3}$	0.8540	106.38	$0.60x10^{-3}$	0.9978
303	60	132	21.53	$3.50x10^{-3}$	0.6758	127.58	$1.10x10^{-3}$	0.9990

Table 2 Kinetic parameters for acid blue 25 adsorbed on AC different initial concentrations

Parameters			Pseudo first order model			Pseudo second order model		
Temp. K	C_0 (mg/L)	q_e (exp.) (mg/g)	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg/min)	R^2
303	10	497	462.29	$7.30x10^{-3}$	0.8219	556.00	$2.12x10^{-5}$	0.9643
303	30	1,400	838.82	$4.50x10^{-3}$	0.9455	1,429.00	$1.39x10^{-5}$	0.9907
303	60	1,900	1,111.3	$5.60x10^{-3}$	0.9273	2,000.00	$1.12x10^{-5}$	0.9892

Adsorption isotherm

The Langmuir and Freundlich models were commonly applied in wastewater treatment. The Langmuir isotherm is based on the assumption that the surface of the adsorbent is uniform, adsorbed molecules do not interact and only monolayer is formed. Langmuir adsorption isotherm can be expressed as Eq. 5 (Insuwan & Rangsriwatananon, 2014).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

q_m (mg/g) is the maximum amount of dye adsorbed on AC. K_L (L/mg) is the Langmuir constant that related to the affinity of adsorption. C_0 (mg/L) and Ce (mg/L) are concentrations of dye in solution at initial and equilibrium, respectively.

The Freudlich adsorption isotherm is used to describe a heterogeneous adsorption surface that expressed as Eq. 6

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

K_F is the Freudlich constant. n is an empirical constant and 1/n indicated that intensity of adsorption.

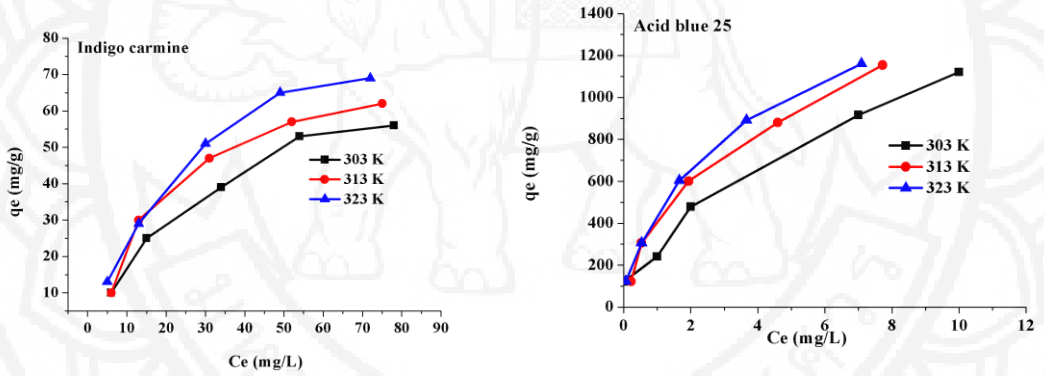


Figure 6 Adsorption isotherm of textile dye adsorbed on AC, adsorbent dosage = 0.01 g, time= 360 minute

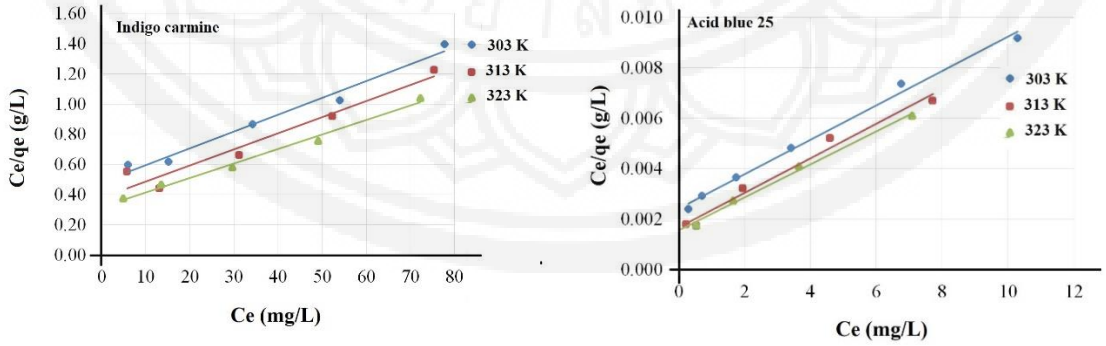


Figure 7 Langmuir isotherm of textile dye adsorbed on AC, adsorbent dosage = 0.01 g, time= 360 minute

The adsorption isotherm of indigo carmine and acid blue 25 onto AC were shown in figure 6. Both indigo carmine and acid blue 25 have shown consistent results that the adsorption was increased by increase of

adsorption temperature 303, 313 and 323, respectively. This results indicated that at higher temperature, the increased rate of diffusion of dye molecules into pores of AC may take place. In addition, increasing temperature decrease viscosity of solution, mobility of molecules increased that can cause passed through the pore of AC (Li, Zhong, Wang, Xue, & Zhang, 2015; Ramesh & Sreenivasa, 2015). The adsorption data for textile dye was analysed by the Langmuir model (see figure 7) and Freundlich model (figure not shown). Table 3 and 4 shows the parameters of the isotherm models. The equilibrium data fitted reasonably to the Langmuir models by considering the values of R^2 (>0.9). Both the maximum amount of acid blue 25 adsorbed on AC (q_m, mg/g) and K_L were higher than that indigo carmine adsorbed on AC.

In the present study, the interaction between dye molecules and AC were composed of (i) electrostatic interaction between anion (SO^-_3 group) of dye molecule and positively charged activated carbon (ii) H-bonding between oxygen or nitrogen atom dye molecule and hydrogen atom of AC (iii) pi-pi interaction between pi electrons of AC and pi electrons of benzene ring of dye molecule. However, the adsorption capacity of acid blue 25 is higher than that of indigo carmine at all temperature. This may be due to electron donating group of acid blue 25 molecule, it causes stronger interaction between adsorbate and adsorbent (Zaidan & Freitas, 2015).

Table 3 Parameters of adsorption isotherms of indigo carmine onto AC

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F ($mg^{1-1/n}/L^{1/n}g$)	n	R^2
303	0.02	89.29	0.9782	3.35	1.47	0.9686
313	0.03	93.46	0.9420	4.08	1.50	0.9172
323	0.03	104.17	0.9899	5.07	1.55	0.9758

Table 4 Parameters of adsorption isotherms of acid blue 25 onto AC

Temperature (K)	Langmuir isotherm			Freundlich isotherm		
	K_L (L/mg)	q_m (mg/g)	R^2	K_F ($mg^{1-1/n}/L^{1/n}g$)	n	R^2
303	0.29	1,428.00	0.9782	293.13	1.61	0.9686
313	0.41	1,428.00	0.9420	332.65	1.37	0.9172
323	0.48	2,000.00	0.9899	224.46	4.07	0.9758

Adsorption Thermodynamics

Thermodynamic parameters such as change in Gibbs free energy ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) was calculated by the following equation 7 and 8 (Insuwan & Rangsriwatananon, 2014).

$$\Delta G^{\circ} = -RT\ln K_L \quad (7)$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

Where R is ideal gas constant (8.314 $JK^{-1}mol^{-1}$), T is temperature (K) and K_L is Langmuir constant.

Table 5 Themodynamic parameters for textile dye adsorption on AC.

Adsorbent	Textile dye	Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol/K)
AC	Indigo carmine	303	-9.50	10.86	9.45
		313	-9.15		9.40
		323	-9.42		9.36
	Acid blue 25	303	-3.10	21.71	3.12
		313	-2.31		2.51
		323	-3.98		1.90

Table 5 lists the thermodynamic parameters that negative Gibbs free energy value indicated a spontaneous adsorption process. The positive value of enthalpy change (ΔH° = 10.86 and 21.71kJ/mol) was confirmed that the endothermic nature of dye adsorbed by AC and physical adsorption process between dye molecule and AC (Nwodika & Onukwuli, 2017). In addition the positive value of entropy change (ΔS°) indicate an increase in randomness at the solid-solution interface.

Conclusion

In the present study, textile dyes were removed by activated carbon (AC) as an adsorbent. Various parameters such as adsorbent dosage, contact time, kinetics and thermodynamic properties were investigated. The results was found that suitable conditions for adsorption was 0.01 g of adsorbent, contact time 360 minute. The adsorption kinetics for both dye was good agreement with the pseudo second-order model that the dye adsorption process was chemisorption. Adsorption data was well- fitted with Langmuir isotherm equation and the thermodynamic parameters were shown adsorption to be endothermic process (ΔH° = 10.86 and 21.71 $kJmol^{-1}$ for indigo carmine and acid blue 25, respectively), negative value of change in Gibbs free energy indicated spontaneous process. Moreover, the higher maximum adsorption capacities of acid blue 25 (1,428.00-2,000.00 mg/g) more than that indigo carmine (89.29-104.17 mg/g) was explained by strong interaction of acid blue 25 with AC.

Acknowledgments

The financial support to enable this research work from Rajamangala University of Technology, Isan Campus is gratefully acknowledged.

References

Adeogun, A. I. & Balakrishnan, R. B. (2016). Electrocoagulation removal of anthraquinone dye Alizarin Red S from aqueous solution using aluminum electrodes: kinetics, isothermal and thermodynamics studies. *Journal of Electrochemical Science and Engineering, 6*(2), 199-213.

Al-Ghouti, M. A., Khraisheh, M. A. M., Allen, S. J., & Ahmad, M. N. (2003). The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth. *Journal of Environmental Management, 69*(3), 229-238.

Badii, K., Ardejani, F. D., Saberi, M. A., Limaee, N. Y., & Shafaei, S. Z. (2010). Adsorption of Acid blue 25 dye on diatomite in aqueous solutions. *Indian journal of technology*, *17,* 7-16.

Elizalde□González, M. P., & Peláez□cid, A. A. (2003). Removal of textile dyes from aqueous solutions by adsorption on biodegradable wastes. *Environmental Technology, 24*(7), 821-829.

Fierro, V., Torne´-Ferna´ndez, V., Montane´, D., & Celzard, A. (2008). Adsorption of phenol onto activated carbons having different textural and surface properties. *Microporous and Mesoporous Materials*, *111,* 276-284.

Insuwan, W., & Rangsriwatananon, K. (2014). Evaluation of adsorption of cationic dyes on H-LTL and K-LTL zeolite. *Journal of Porous Materials, 21,* 345-354.

Karcher, S., Kornmüller, A., & Jekel, M. (2002). Anion exchange resins for removal of reactive dyes from textile wastewaters. *Water Research, 36*(19), 4717-4724.

Kumari, K., & Abraham, T. E. (2007). Biosorption of anionic textile dyes by nonviable biomass of fungi and yeast. *Bioresource Technology, 98*(9), 1704-1710.

Li, C., Zhong, H., Wang, S., Xue, J., & Zhang, Z. (2015). Removal of basic dye (methylene blue) from aqueous solution using zeolite synthesized from electrolytic manganese residue. *Journal of Industrial and Engineering Chemistry, 23*(25), 344-352.

Liu, C. H., Wu, J. S., Chiu, H. C., Suen, S. Y., & Chu, K. H. (2007). Removal of anionic reactive dyes from water using anion exchange membrane as adsorbent. *Water Research, 41,* 1491-1500.

Mall, I. D., Taneja, N., & Thakur, C. K. (2013). Treatment of Indigo Carmine Dye Bearing Wastewater by Electrocoagulation. In *2nd International Conference on Environment, Agriculture and Food Sciences, August, 25-26 2013* (pp. 86-90). Malaysia: Kuala Lumpur.

Nwodika, C., & Onukwuli, O. D. (2017). Adsorption Study of Kinetics and Equilibrium of Basic Dye on Kola Nut Pod Carbon. *Gazi University Journal of Science, 30*(4), 86-102.

Pathania, D., Sharma, S., & Singh, P. (2017). Removal of methylene blue by adsorption onto activated carbon developed from Ficus carica bast. *Arabian Journal of Chemistry, 10,* 1445-1451.

Ramesh, T. N., & Sreenivasa, V. P. (2015). Removal of indigo carmine dye from aqueous solution using magnesium hydroxide as an adsorbent. *Journal of Materials, 2015,* 10.

Razi, M. A. M., Hishammudin, M. N. A. M ., & Hamdan, R. (2017). Factor Affecting Textile Dye Removal Using Adsorbent From Activated Carbon: A Review. *MATEC Web of Conferences*, *103,* 06016.

Rinku, J., Shripal, S., & Hemant, P. (2015). Removal of Malachite green dye from aqueous solution using magnetic activated carbon. *Research Journal of Chemical Sciences, 5*(12), 38-43.

Stergiopoulos, D., Dermentzis, K., Giannakoudakis, P., & Sotiropoulos, S. (2014). Electrochemical decolorization and removal of indigo carmine textile dye from wastewater. *Global NEST Journal, 16*(3), 499-506.

Vijayakumar, G., Tamilarasan, R., & Dharmendirakumar, M. (2012). Adsorption, Kinetic, Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite. *Journal of Materials and Environmental Science, 3*(1), 157-170.

Wasti, A., & Ali Awan, M. (2016). Adsorption of textile dye onto modified immobilized activated alumina. *Association of Arab Universities for Basic and Applied Sciences, 20,* 26-31.

Zaidan, F., & Freitas, P. A. M. (2015). Flow Injection Analysis of Indigo Carmine Using Green Coconut,(Cocos Nucifera L.) Fiber as a Bioadsorbent. *International Journal of Engineering Research & Science (IJOER), 1*(8), 39-46.