Bulgarian Chemical Communications, Volume 50, Special Issue L (pp. 290– 300) 2018

Decolourisation of the colored textile industries using a new combination of activated carbon and fiber; kinetic, thermodynamic and isotherm studies

M. Khazravi[a], M. Bahmaei[a,*], M. Ebrahim Olya[b], S. Masoud Etezad[b]

[a] *Department of Chemistry,Tehran North Branch, Islamic Azad University ,Tehran, Iran*

[b] *Department of Environmental Research, Institute for Color Science and Technology, P.O. Box 16765-654, Tehran, Iran*

Submitted March 24, 2016; Accepted August 8, 2016

The objective of this work is the simultaneous application of activated carbon powder and synthesized fibers as appropriate adsorbents for dye removal of the colored wastewaters. In addition, the effect of different key operating parameters such as time, pH, adsorbent dosage, initial dye concentration, column height and solution flow rate were investigated for optimization of the adsorption conditions. According to kinetic studies results, pseudo second order model was found to be well compatible with the kinetic data. Furthermore, study of the absorption isotherms (Langmuir, Freundlich and Temkin) indicated the compatibility of the process with Langmuir isotherm (R2=0.9775). The investigation of the effects of thermodynamic parameters including Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) in the adsorption of Reactive Blue 19 dye using activated carbon powder and fibers simultaneously indicated a spontaneous reaction and an endothermic process.

Keywords: Adsorption, Carbon fibers, dye, Decolourisation

INTRODUCTION

The increasing water consumption in the industries and application of organic dyes have considerably increased the production of the industrial colored wastewaters in recent years [1]. Synthetic dyes are an important group of the environmental pollutants widely used in textile, dyeing, paper and leather industries due to their low price and high resistance against temperature and light [2,3]. Textile industry wastes generally consist of pollutants such as acids, bases, toxic compounds and organic dyes including substituted and heterocyclic aromatics, polyazo, reactive dispersive azo, diazo, anthraquinonoid and metal complex based compounds [4,5]. Reactive dyes are a large group of the dyes widely used in the industry due to their luster and good and easy dyeing properties [6]. Half of the reactive dyes used in the textile industry directly enter the plant sewages [7]. Dye contamination of water sources causes kidney, liver and neurological disorders and leads to mutation and carcinogenicity in living organisms as a result of aromatic groups, chloride and heavy metals [8]. Many of these dyes are toxic and cause death of aquatic life and microorganisms [9]. Therefore, these industrial wastewaters must be treated prior to being released to the environment. Great attention is currently being paid to dye removal in industrial wastewaters because of the significance of water quality. Different treatment techniques including physical methods such as adsorption, ion exchange and membrane filtration are effective in dye removal without production of undesirable by-products [10].

Chemical methods such as coagulation and advanced oxidation such as ozonization method are not cost effective in terms of efficiency [11, 12]. Biological methods used for dye removal are time consuming and require expensive instruments and special, high energy equipment [13]. In addition, since these dyes are water soluble, they form large quantities of complicated by-products the removal of which from wastewaters is extremely difficult [14]. The application of carbon active adsorbents, applied for dyes and heavy metals, and many other novel adsorbents such as coke and ashes from thermal power plants may be preferred over other chemical and physical treatment methods [15,16].

Carbon fibers are one of the most effective and important adsorbents compared with other adsorbents. Carbon fibers possess numerous small pores of minimum mesoporosity. These fibers have high densities and specific surface areas, excellent adsorption rates and small footprints [17, 18].

Carbon fibers could be used in heavy metal removal [19], medical applications [20], steam sensors [21], catalysis [22], electrochemical applications [23] and storage of natural gas and biogas [24].

The simultaneous application of activated carbon powder and fibers as appropriate adsorbents for Reactive Blue 19 dye from aqueous solutions was

* To whom all correspondence should be sent:
E-mail: *mbahmaei@gmail.com*

investigated in order to find optimal experimental conditions and environmental factors such as pH, temperature, and time, stirring rate, adsorbent dosage and initial dye concentration in the wastewater in this work.

MATERIALS AND METHODS

Materials

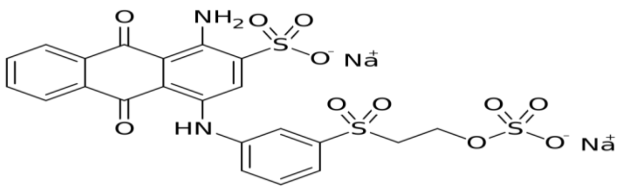
Reactive Blue 19 (RB19) dye was obtained from Alvan Sabet Co. Table 1 shows the specifications of RB19 dye. The adsorbent was purchased from JACOBI Co. (Sweden).pH of the solution was adjusted with HCl and NaOH (Merck).

Methods

In order to find the optimal experimental conditions, environmental factors such as pH, temperature, time, adsorbent dosage and initial dye concentration in the wastewater were investigated.

According to the conventional textile industries condition, the primary environmental conditions were initial concentration of 20 mg/L, adsorbent dosage of 0.3 g of and adsorption time of 30 minutes. The adsorption experiments were carried out using a jar test instrument (Aqualatic, Germany). The samples were then transferred into falcons and the suspended particles were separated by a centrifuge. The light absorption by the samples, which is an indication of the dye concentration in the solution, was determined using a spectrophotometer.

Table 1. Charactrization of the dye(Reactive blue 19)

Name	Reactive blue 19
Symbol	RB19
Type color	Anionic
Molecular Formula:	C22H16N2Na2O11S3
Molecular weight (g/mol)	626.54
Wavelength of maximum absorption (nm)	568
Chemical structure of color	

Dye removal and the time required to reach equilibrium was measured prior to and after the process and the efficiency of dye removal was calculated using the following equation:

$$R = \frac{A_0 - A_t}{A_0} * 100 \qquad (1)$$

where Ao is the light absorbance by the dye at the characteristic λ_{max} at time zero and At is the light absorbance after time t.

A batch system and a fixed bed reactor were used in the experiments. A system consisting of a vertical, cylindrical reactor with a 10 cm length and internal diameter of 5 cm was used for this purpose. The column interior was filled with activated carbon powder and fibers. The optimal values of pH, temperature, adsorbent dosage, dye initial concentration, bed height and the solution flow rate were obtained from the continuous process in order to increase the dye removal efficiency. A prepared wastewater sample containing 20 mg/L of Reactive Blue 19 dye was added to the reactor containing activated carbon powder and fibers and the amount of the reduced dye concentration leaving the reactor at a certain time was measured using UV/Vis spectrophotometry method.

LABORATORY APPARATUS AND EQUIPMENT

A JENWAY 6300 visible spectrophotometer was used to measure the light absorbance by the liquids. This instrument was used to measure and evaluate the dye removal in the experiments. A GTK10768 centrifuge was used to separate the suspended particles and eliminate the interference of suspended particles in reading the light absorbance values. 1 M

NaOH and HCl were used to control the pH of the prepared wastewater in the 3-11 pH range. A digital Mettler Toledo pH meter was used for pH measurements.

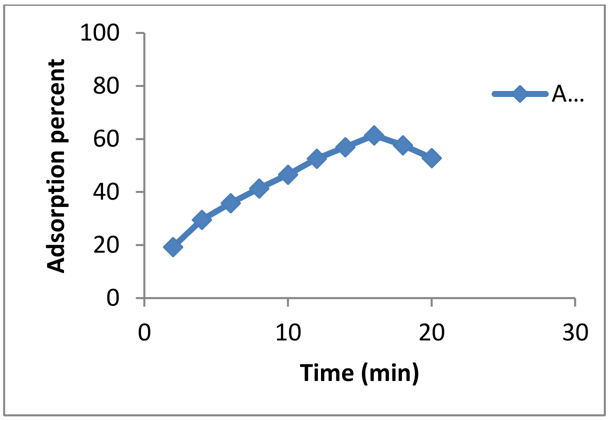
RESULTS AND DISCUSSION

The effective parameters in the removal of Reactive Blue 19 dye from an industrial wastewater using activated carbon adsorbent alone and combination of activated carbon powder and fibers, including pH, temperature, and time, stirring rate, adsorbent dosage and dye initial concentration were investigated. The optimal values in dye removal using activated carbon (t=50 min., pH=5, adsorbent dosage=0.55 g/L, stirring rate=60 rpm and initial dye concentration=10 mg/L) indicated the higher and more appropriate efficiency of the combination of activated carbon powder and fibers compared with carbon fire alone in the adsorption of Reactive Blue 19 dye.

4.1. Effect of time on removing of dyes

In order to study the influence of carbon fiber and carbon active contact time on removing of reactive blue 19, tests were performed in conditions of pH=4.5, initial dye concentration of 20 mg/L, and adsorbent amount of 0.25 gr.

The results showed the absorbance increased gradually and reached the maximum level because of Van der Waals forces then decreased. Finally, due to saturation of adsorbent pores and reduction of energy between adsorbent and adsorbed substances, collision forces were overcome Van der Waals forces and hence desorption effect occurred. The recovery of reactive blue 19 removing by carbon fibers and carbon active powder was 61.40% in 16 minutes (Figure1).



4 **Figure 1.** Effect of time on Reactive Blue 19 dye removal efficiency by activated carbon powder and fibers

4.2. pH effect

In order to study the effect of pH and determine its optimal value, five 20 mg/L samples of the dye and appropriate amounts of activated carbon powder and fibers with pH values of 3, 5, 7, 9 and 11 were prepared in 500 mL Erlenmeyer flasks. The solution pHs were adjusted by adding 1 M NaOH and HCl. The effect of pH on the removal efficiency is shown in Figure 2 . According to the Figure, at a fixed initial concentration of the dye, the adsorption capacity of the dye by the combination of carbon active powder and fibers significantly increases in acidic pHs, the highest removal occurring in 16 minutes. The protons available in the acidic media can provide positive charges on the carbon surface and thus adsorb anionic dye molecules, increasing the adsorption rate. Furthermore, no good adsorption is observed at high pHs, which is probably due to the tendency of the hydroxyl group to compete with the anionic dye molecules for adsorption on the positive sites on the carbon active powder and fibers [25,26]. The oxidation of oxygen containing compounds on the surface can also transfer positive charge to the carbon active powder and fiber surface [27,28]. Therefore, the best removal efficiency was observed at pH=4.5

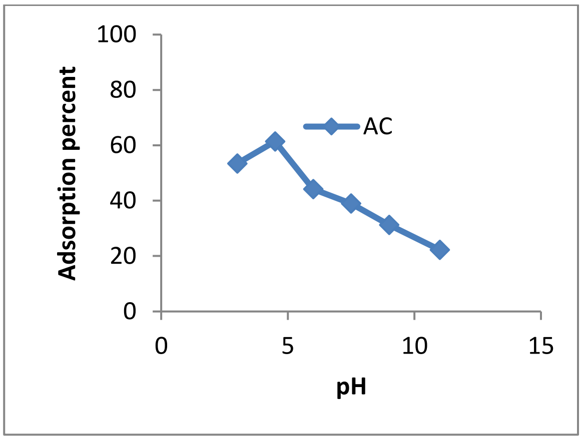


Figure 2. Effect of initial pH on Reactive Blue 19 dye removal efficiency by activated carbon powder and fibers.

4.3. Effect of the adsorbent dosage on dye removal efficiency

Adsorbent dosage is an important parameter in adsorption studies since it determines the adsorption capacity. In order to study the effect of adsorbent dosage on the Reactive Blue 19 dye removal process by carbon powder and fibers, different doses of the adsorbent in the 0.05-0.35 g/L range at pH=4.5 and initial dye concentration of 20 mg/L were used. 20 minutes through the process, as observed in Figure 3, the efficiency of dye removal increases by increasing the adsorbent dosage, the minimum and maximum dye removal efficiencies being 0.05 and

0.35 g/L, respectively. The increased adsorption efficiency is due to the increased adsorption sites available to the dye, which enhances the probability of the entrapment of the dye in the combination sites of activated carbon powder and fibers, leading to the adsorption of the dye in the inner layers of the adsorbent and preventing its accumulation on the outer surfaces [29]. As observed in Figure 3, the adsorption efficiency increases at first. However, no further increases are observed at higher doses. Therefore, 0.3 g was selected as the optimal adsorbent dosage.

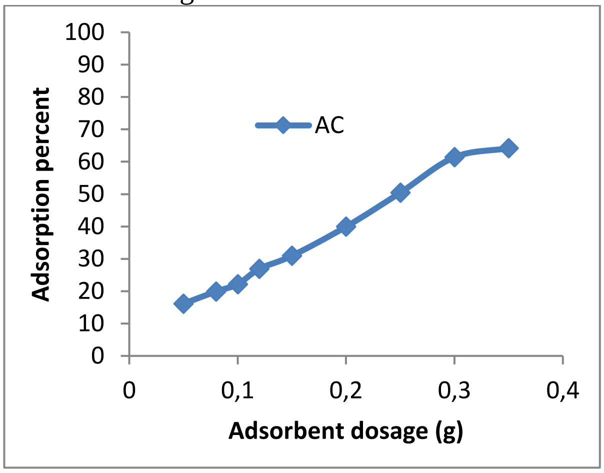


Figure 3. Effect of adsorbent dosage on Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers.

4.4. Effect of initial dye concentration

The effect of initial dye concentration on the process efficiency and the amount of the dye removed per unit mass of the adsorbent was investigated. To study the effect of initial dye concentration on the removal efficiency and determine the optimal value, the experiment was carried out in three 500 mL Erlenmeyer flasks containing 10, 20 and 30 mg/L of the dye at pH=4.5 using 0.3 g of the adsorbent during 20 minutes. Dye removal is obviously dependent on the initial dye concentration since the number of adsorption active sites remains constant decreasing the initial dye concentration for a given quantity of the adsorbent. However, upon increasing the initial dye concentration, the number of ions, which must be adsorbed in the adsorption active sites increases causing decreased adsorption percentage [29]. Based on the results obtained, the optimal initial dye concentration under the experimental conditions is 20 mg/L. (Figure 4)

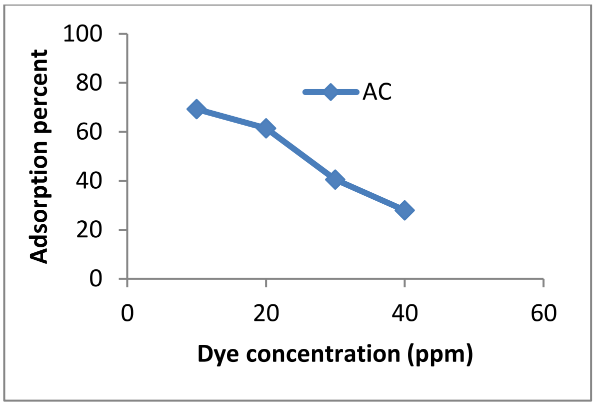


Figure 4. Effect of initial dye concentration on Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers.

4-5- Effect of solution flow rate

Solution flow rate is one of the effective parameters on the design of a fixed bed system. The adsorption efficiency of 20 mg/L of the adsorbent was studied using a bed height of 100 mm and solution flow rates of 10, 20 and 30 mL/min in order to obtain the optimal solution flow rate at pH=4.5 using 0.3 g of the adsorbent during 20 minutes. As observed in the Figure, at higher solution flow rates, the system reaches equilibrium more quickly. However, at lower solution flow rates, the dye requires more time to contact the adsorbent, which results in further adsorption of dye ions by the adsorbent in the column [30]. Considering the changes in the curve slope and adsorption capacity, mass transfer rate is observed to have an ascending trend at higher solution flow rates. This causes faster saturation in the bed height unit (mass transfer zone) and thus less opportunity of dye penetration in ten adsorbent pores. Dye leaves the column before establishment of the equilibrium. The results obtained are justifiable according to mass transfer principles [31]. Based on the results obtained, the optimal Solution flow rate under the experimental conditions is 10 mL/min.

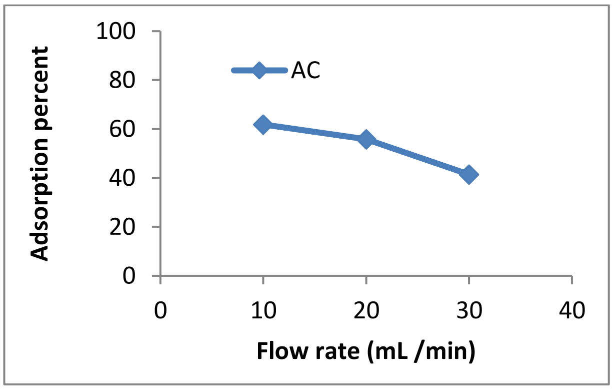


Figure 5. Effect of solution flow rate on Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers.

4-6- Effect of bed height

The adsorption efficiency of a certain amount of the adsorbent was studied using different bed height of 30, 70 and 100 mm in order to obtain the optimal bed height in a fixed bed system at pH=4.5 using 0.3 g of the adsorbent during 20 minutes. Dye removal clearly depends on the optimal bed height in a fixed bed system. As the bed height increases, the dye will have more time to contact with the adsorbent, which causes increased efficiency of dye removal. As observed in the curve, the curve slope decreases increasing bed height, which broadens the mass transfer area leading to the possibilities of further bonding between the dye and absorbent [32,33]. Based on the results obtained, the optimal Solution flow rate under the experimental conditions is 100 mm..

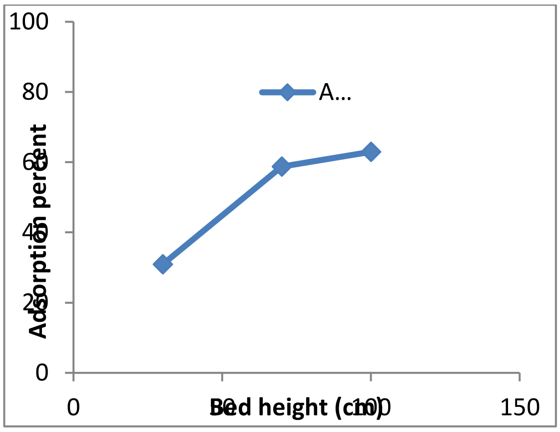
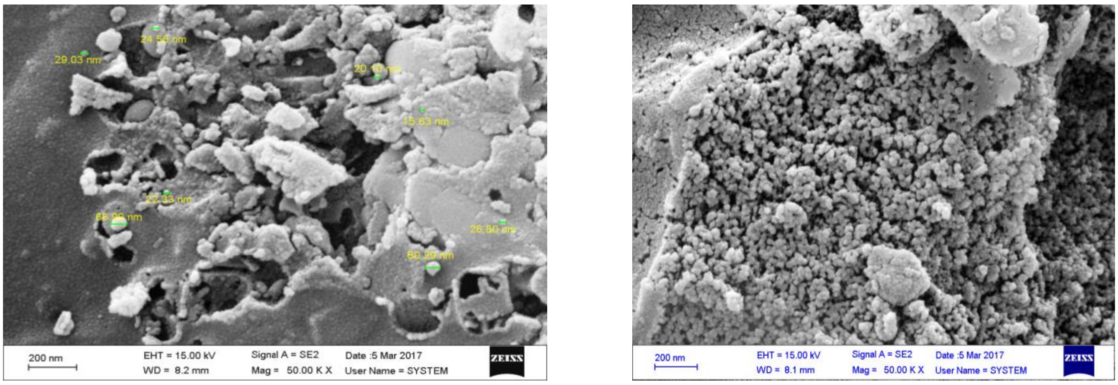


Figure 6. Effect of bed height on Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers.

4-7-SEM analysis

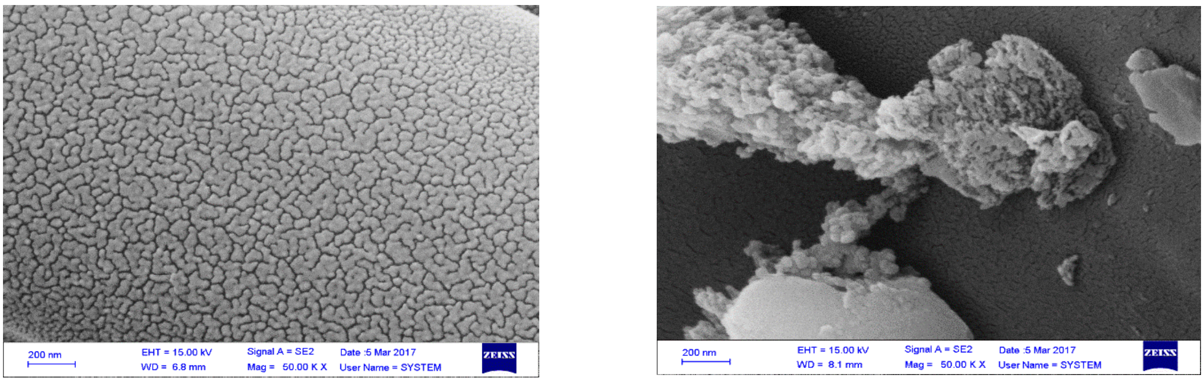
SEM analysis is used to determine the surface morphology and the main physical characteristics of the adsorbent surface. SEM is also used to determine the particle shape, porosity and proper distribution in terms of size. Figures A and B show the SEM images of the adsorbent and adsorbed dye. As observed in the Figure A, the adsorbent is composed of hollow pores of different sizes and unformed parts. Figure B shows white spots characteristic of effective adsorption of dye molecules in the adsorbent pores.



A:before adsorption of RB19 dye

B:after adsorption of RB19 dye

Figure 7: SEM imaging of activated carbon powder



A:before adsorption of RB19 dye

B:after adsorption of RB19 dye

Figure 8: SEM imaging of activated carbon fibers.

4-8- FTIR analysis

FTIR spectroscopy is used to study the vibrations of the surface functional groups and the bonds responsible for dye adsorption. The main peaks for activated carbon fiber surface are observed at 3430 cm-1 [48]. The bands associated with sulfate and secondary Carboxyl are observed in 1380 cm-1 and 2900 cm-1 ranges, respectively [34]. In addition, the band observed in the region of 1450 cm-1 corresponds to the Reactive Blue 19 aromatic ring carbon. broadened and its intensity has decreased. The comparison of the FTIR spectra of the adsorbent and dye indicates good adsorption of the dye [35].

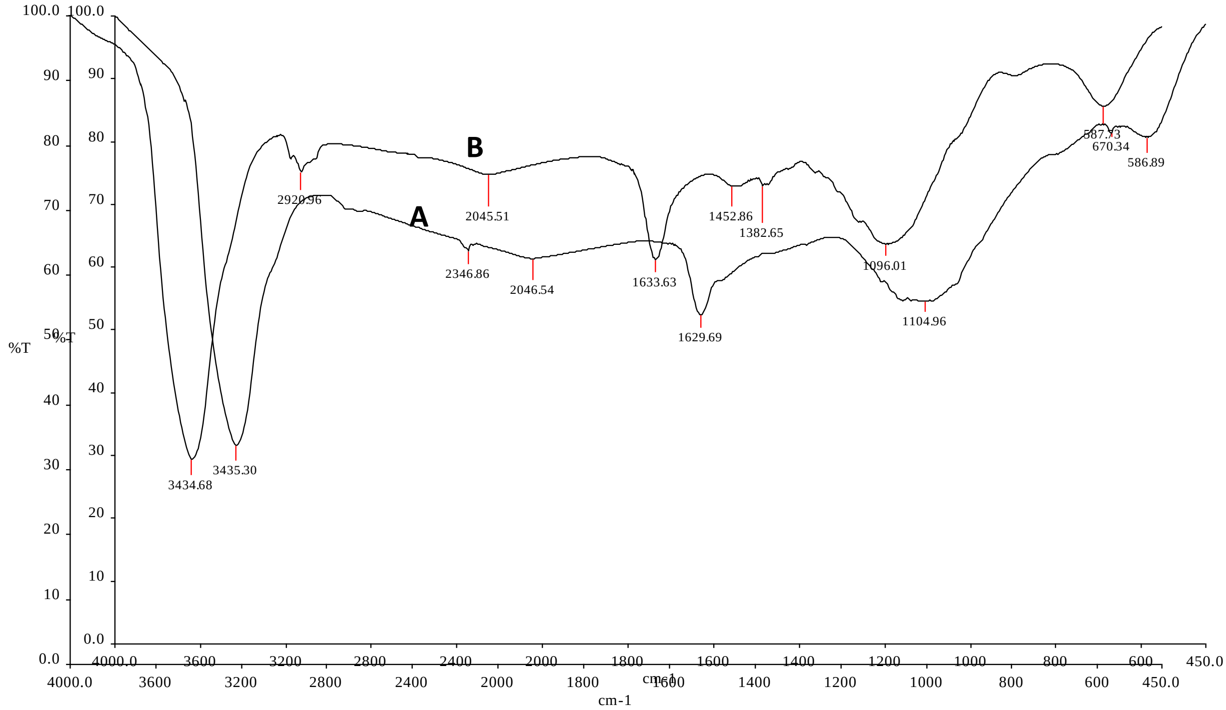


Figure 9: FT-IR spectrum of (A) before (B) after absorbing the color

REACTION KINETICS

The prediction of the adsorption process rate and the dimensions of the reactor designed are of the most important factors in an adsorption system. Dye adsorption kinetics has been studied using pseudo first order [36], pseudo second order [37] and intrinsic particle adsorption models [38]. Equation 2 is a linear form of pseudo first order model [36]:

$$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)\,t \qquad (2)$$

Where qe is the amount of dye adsorbed at equilibrium in mg/g, qt is the amount of dye adsorbed in time t (mg/g) and k1 is the first order kinetic equilibrium rate (L/min).

The linear form of pseudo second order model could be shown by Equation 3 [37]:

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \qquad (3)$$

Where k2 is the pseudo second order equilibrium rate (g/mg.min).

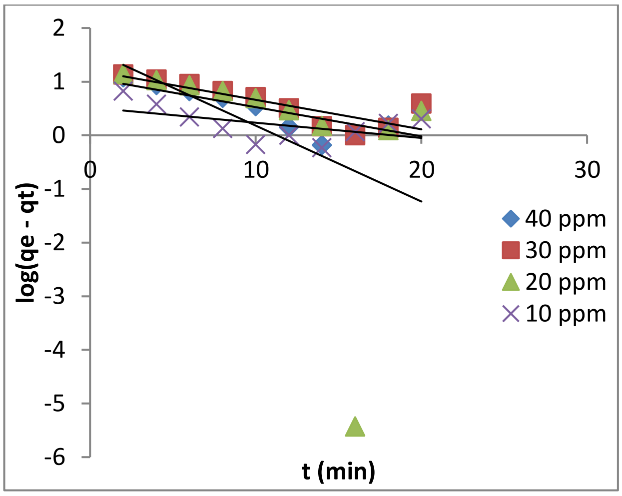


Figure 10- Pseudo first order kinetic for Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers

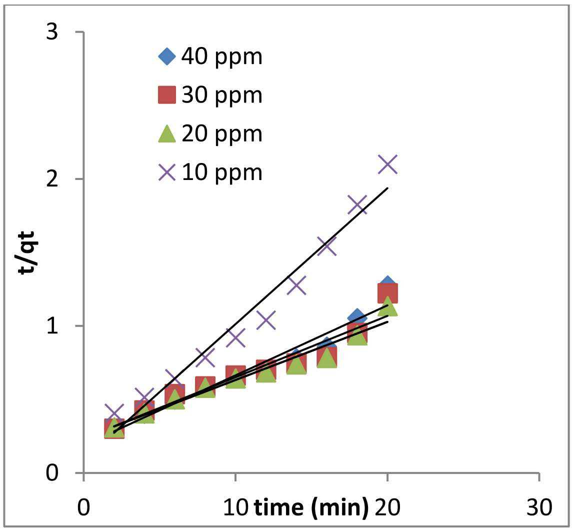


Figure 11.- Pseudo second order kinetic for Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers.

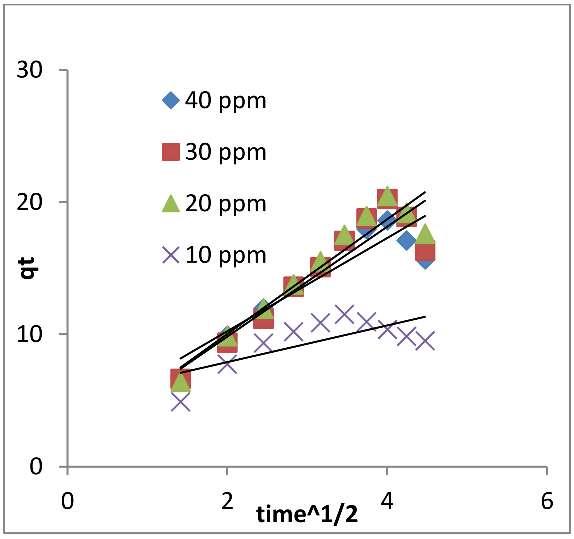


Figure 12. Intrinsic particle adsorption kinetics for Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers.

To study the effect of the resistance against intrinsic particle penetration on the adsorption process, the intrinsic particle model can be used by the following Equation [38]:

$$qt = kpt1/2 + I \qquad (4)$$

Where kp is the intrinsic penetration rate constant and I is the boundary layer thickness constant.

Pseudo first order, pseudo second order and intrinsic particle adsorption models were used to investigate the different amounts of carbon active fiber adsorption in the dye removal system.

Log (qe − qt) vs. t (Figure 10), t/q vs. t and qt vs. t1/2 were plotted for pseudo first order, pseudo second order and intrinsic particle adsorption models, respectively. R2, I, kp, k2 and k1 values were then calculated. Considering the kinetic data shown in Table 2, the pseudo second order model is the predominant mechanism compared with the pseudo first order and intrinsic particle adsorption models since it has the highest regression coefficient (R2=0.9997). In addition, the calculated value of qe ((qe)Cal.) is compatible with the experimental qe ((qe)Exp.).

Table.2 Kinetic coefficients for Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers

Adsorbents	dye concentration (ppm)	(qe)Exp	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
			(qe)Cal	K1	R2	(qe)Cal	K2	R2	I	KP	R2
combined active carbon powder and fibers	10	11.5449	3.3006	0.0654	0.2813	10.8225	1326.464	0.9659	5.1361	1.3854	0.5156
	20	20.4678	39.3912	0.3258	0.1927	25.3164	0.0065	0.9545	1.3684	4.3334	0.905
	30	20.2531	16.2442	0.1266	0.6946	23.9808	0.0074	0.9231	1.5251	4.1544	0.8655
	40	18.6274	11.7057	0.1252	0.6072	21.0084	0.0120	0.9515	13.1986	3.5221	0.8315

ADSORPTION ISOTHERMS

Equilibrium isotherm equations are used for investigation of the surface properties and adsorbent tendency and better description of the parameters and the results of adsorption experiments. Adsorption isotherms are important in the optimization of adsorption [39].

Three important, conventional isotherm models including Langmuir, Freundlich and Temkin have been used in this research [40,41].

6-1- Langmuir isotherm

Langmuir equation, developed by Langmuir in 1951, is associated with the interaction between the adsorbent and adsorbed as a single-layer, reversible and linear chemical reaction. This equation is a relatively simple model, which assumes that the adsorbent surface is completely uniform and each adsorbent site can surround at least one adsorbed molecule and there are no interactions between the adsorbed molecules. This isotherm is based on the assumption that there are adsorption sites on the adsorbent surface, each being capable of adsorbing one molecule. Therefore, the adsorbed layers will have a thickness of one molecule. In addition, it is presumed that all the adsorbent sites have identical tendencies toward adsorbed molecules and the presence of the adsorbed molecules on one site does not affect the adsorption of the molecules on the adjacent site [42- 45]. Langmuir equation can be expressed as follows:

Ce/qe= 1/KLQ0 + Ce/Q0 (5)

Where Ce is the equilibrium concentration in mg/L, qe is the adsorbed amount in equilibrium (mg/g), KL is the Langmuir coefficient and Qo is the maximum adsorption capacity(mg/g).

6-2- Freundlich isotherm

Freundlich equation experimentally uses the logarithmic model obtained and investigates the effects of the different energy levels of adsorption. This equation is based on the assumption that the adsorbent has a non-uniform surface consisting of different levels of adsorption sites and adsorption on each level of the site follows Langmuir isotherm. This model assumes that the number of participating sites with specific absorption energy exponentially decreases with increased free energy level [46].

Freundlich adsorption model can be expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{6}$$

In which qe is the equilibrium load on absorbent (mg/g), KF is the adsorption capacity per concentration unit (mg/g)(L/mg)1/n, l/n is the adsorption intensity experimentally measured and sometimes reported as β (dimensionless) and Ce is the equilibrium concentration in wastewater stream (mg/L).

When the equation is plotted based on log-log, it follows a straight line. Freundlich equation can be expressed in the following form:

log qe = log KF + (1/n) log Ce (7)

Freundlich equation is used by environmental engineers for experimental data and quick preparation of some general information regarding the tendency of a compound for being adsorbed. For irreversible adsorbed chemical compounds, l/n (curve slope) is zero. l/n is between zero and one for properly adsorbed chemicals, greater than one for improperly adsorbed chemicals and infinite (or very large) for chemicals not adsorbed [47].

6-3- Temkin isotherm

This isotherm consists of a factor used for calculation of adsorbent-adsorbate interactions. The adsorption heat, which is the temperature function of all the molecules in one layer, is assumed to decrease linearly, rather than logarithmically, with the adsorbent covering area [48-50].

qe=B1lnKT+B1lnCe (8)

qe is plotted vs. lnce. A straight line is obtained by B1lnKT and KT from the slope and width from the origin, respectively. B1 constant is associated with the heat of adsorption and KT is the equilibrium coefficient (l/mg).

Table 3- Isotherm linear coefficients for Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers

Adsorbents	Langmuir			Freundlich			Tempkin		
	Q0 (mg/g)	KL (L/mg)	R2	KF (L/mg)	n	R2	KT (L/mg)	B1	R2
combined active carbon powder and fibers	20.2429	0.5482	0.9775	141.1237	4.0048	0.6165	3.2358	12.343	0.8589

THERMODYNAMIC ADSORPTION

Thermodynamic properties depend on the changes of Gibbs free energy, enthalpy and entropy must be investigated in order to better understand the effect of temperature on the adsorption process. Thermodynamic properties are obtained carrying out adsorption experiments of Reactive Blue 19 dye with a concentration of 20 ppm using enzyme stabilized on activated carbon adsorbent (powder and fibers) at temperatures of 25, 35 and 45 oC.

ΔG is calculated using the following equation:

$$\Delta G = -RT \ln KC \quad (9)$$

In which KC is the adsorption equilibrium constant (from Langmuir model). T is the absolute temperature and R is the universal gas constant.

The relationship between KC and ΔS and ΔH thermodynamic parameters is given by Van't Hoff equation.

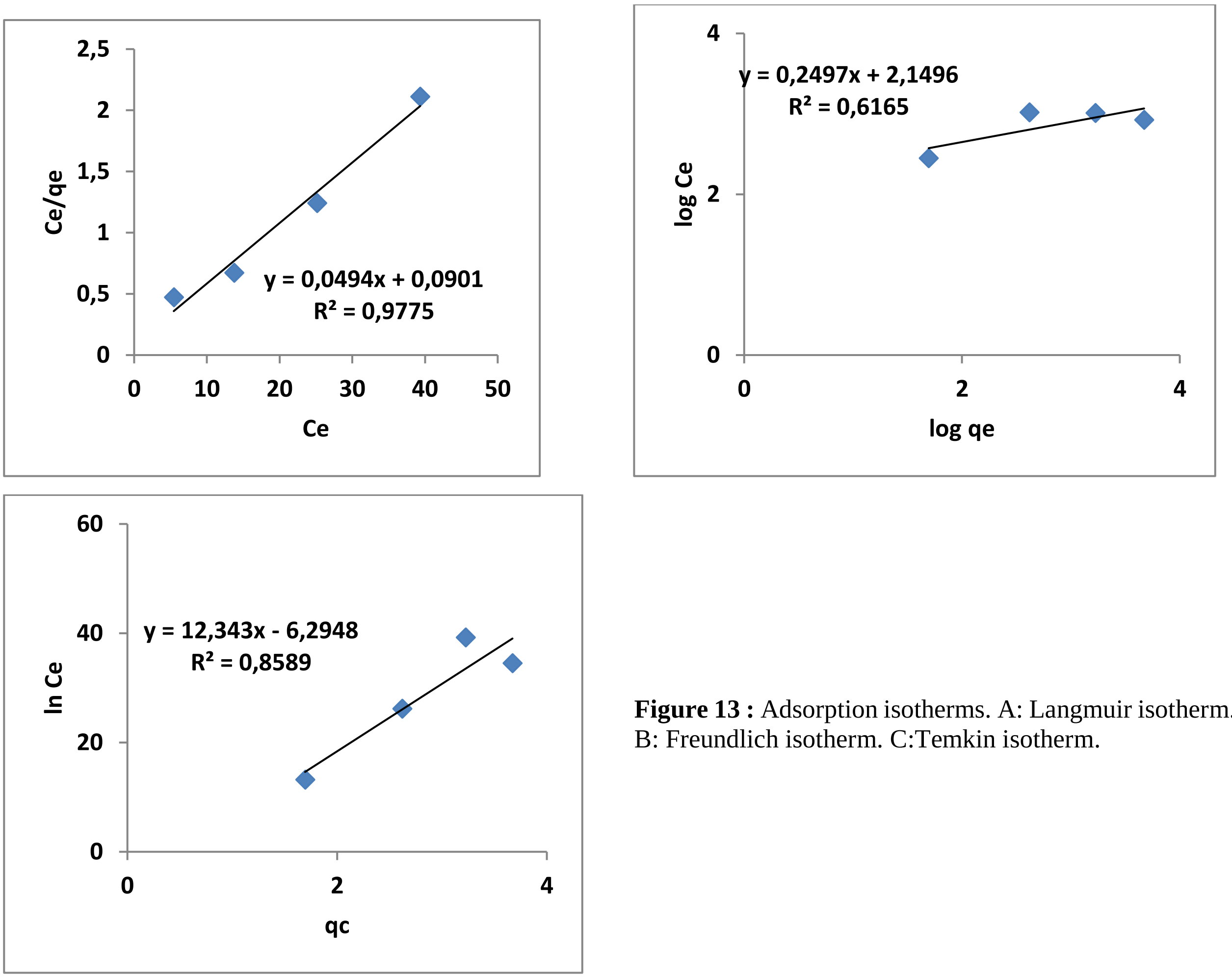


Figure 13 : Adsorption isotherms. A: Langmuir isotherm. B: Freundlich isotherm. C:Temkin isotherm.

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

$$\log K_c = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (11)$$

If logarithm KC is plotted vs. 1/T, ΔH and ΔS are obtained from the slope and width from the origin, respectively. As observed in Table 4, increasing temperature from 25 to 35 and 45 oC changes ΔG values from -1.1503 to -1.4158 and -1.6063, respectively, the more negative ΔG indicating the spontaneity of the adsorption process. In addition, positive ΔH indicates the endothermic nature of the adsorption process while negative ΔH signifies the exothermic nature of this process. Positive ΔS shows increased entropy in the encounter of the two solid/liquid phases during the adsorption process [51].

Table 4- Thermodynamic parameters

Adsorbents	Temperature (K)	Δ G (kJ/mol)	Δ H (kJ/mol)	Δ S (kJ/mol)	R2
combined active carbon powder and fibers	298	-1.1503	7.2623	0.02826	0.9943
	303	-1.4158			
	318	-1.6063			

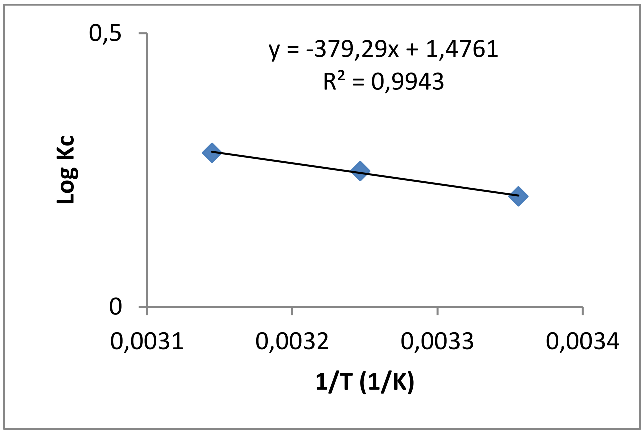


Figure 14. Adsorption thermodynamics of Reactive Blue 19 dye removal efficiency by combined activated carbon powder and fibers

CONCLUSION

According to the results, a combination of activated carbon and fiber was an effective process for dye removal of colored wastewater. Kinetic studies showed a pseudo first order kinetic for decolourisation using the combination process. Also, ΔG, ΔH of the adsorption were calculated and study of the absorption isotherms (Langmuir, Freundlich and Temkin) indicated the compatibility of the process with Langmuir isotherm.

REFERENCES

1. P. Bahmani, A. Maleki, A. Ghahremani, S. Kohzadi, *J Heal. Hyg*. **4,** 57 (2013).
2. I. Anastopoulos, G. Z. Kyzas, *J. Mol. Liq*. **200,** 381 (2014).
3. O. Gök, A. S. Özcan, A. Özcan, *Appl. Surf. Sci.*, **256**, 5439 (2010).
4. M. Anousha, M.T. Samadi, M. Samarghandi, N. Hossani, Eleventh National Conference on Environmental Health, (2008).
5. A. H. Mahvi, B. Heibati, *J. Heal. Hyg.*, **1,** 7(2010).
6. X.Y. Yang, B. Al-Duri, *Chem. Eng. J.*, **83**, 15 (2001).
7. R. Campos, A. Kandelbauer, K. H. Robra, C.P. Artur and G.M. Gubitz, *J. Biotechnol.*, **8**, 131 (2001).
8. J. Fu, Z. Chen, M. Wang, S. Liu, J. Zhang, R. Han, Q. Xu, *Chem. Eng. J.* **259**, 53 (2015).
9. A.A. El-Bindary, A. Z. El-Sonbati, A.A. Al-Sarawy, K. S. Mohamed, M.A. Farid, *J. Mater. Environ. Sci.* **6,** 1, (2015).
10. P. Vandevivere, R. Bianchi and W. Verstraete, *J. Chem. Tech. Biotech.*, **72**, 289, (1998).
11. M. Bayramoglu, M. Kobya, O.T. Can, M. Sozbir, *Sep. Purif. Technol.*, **37**, 117, (2004).
12. O.T. Can, M. Kobya, E. Demirbas, M. Bayramoglu, *Chemosph.*, **6**, 181, (2006).
13. T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresour. Technol*, **77**, 247 (2001).
14. T.T. Ma, P.R. Chang, P.W. Zheng, F. Zhao, X.F. Ma, *Chem. Eng. J.*, **240,** 595 (2014).
15. E. Demirbas, N. Dizge, M. T.Sulak, M Kobya, *Chem. Eng. J.*, **148**, 480 (2009).
16. T. Y. Kim, H. J. Jin, S. S. Park, S. J. Kim, S Y. Cho, *J. Indust. Eng. Chem.*, **14**, 714 (2008).
17. M.C. Venceslau, S. Tom, J.J. Simon, *Environ. Technol.*, **15,** 917 (1994).
18. M. Bielska, J. Szymanowski, *Water Res.*, **40**, 1027 (2006).
19. J.P.A. Dhas, *M.Sc. Thesis, University Science Malaysia, Malaysia*, (2006).
20. Y. Sudaryanto, S.B. Hartono, W. Irawaty, H. Hindarso, S. Ismadji, *Bioresour. Technol.*, **97,** 734 (2006).
21. K. Aleksandra, E.L. Grabowska, G. Gryglewicz, *Bioresour. Technol.*, **99,** 7208 (2008).
22. A. Bacaoui, A. Yaacoubi, A. Dahbi, C. Bennouna, R.P.T. Luu, F.J. Maldonado-Hodar, J. Rivera-Utrilla, C. Moreno-Castilla, *Carbon*, **39** 425 (2001).
23. 23. F.C. Wu, R.L. Tseng, *J. Coll. Interf. Sci.*, **294,** 21 (2006).
24. A.A. Ahmad, B.H. Hameed, A.L. Ahmad, *J. Hazard. Mater.*, **170,** 612 (2009).
25. S. Brunauer., P.H. Emmett, E. Teller, *J. Am. Chem. Soc.*, **60,** 309 (2002).
26. M. Alkan, O. Demirbas, S. Celikcapa, M. Dogan, *J. Hazard. Mater.*, **116,** 135 (2004).
27. S.V. Mohan, N. Chandrasekhar Rao, J. Karthikeyan, J., *J. Hazard. Mat.*, **90**, 189 (2002).
28. S. Sadaf, H.N. Bhatti, M. Arif, M. Amin, F. Nazar, *Chem. Ecol.*, **31,** 252 (2015).
29. A.A. El-Bindary, M.A. Abd El-Kawi, A.M. Hafez, I.G.A. Rashed, E.E. Aboelnaga, *J. Mater. Environ. Sci.*, **7**, 1023 (2016).
30. D.C.K. Ko, J.F. Porter, G. McKay, *Chem. Eng. Sci.*, **55,** 5819 (2000).
31. V.C. Taty-Costodes, H. Fauduet, C. Porte, Y.S. Ho, *J. Hazard. Mater. B*, **123,** 135 (2005).
32. Z. Zulfadhly, M.D. Mashitah, S. Bhatia, *Environ. Pollut*, **112,** 463 (2001).

33. K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, *J. Hazard. Mater.*, **113B,** 223 (2004).
34. E.Elkhattabi, M. Lakraimi, M. Badreddine, A. Legrouri, O. Cherkaoui, M. Berraho, *Appl. Water Sci.*, **33,** 431 (2013).
35. N. Dizge, C. Aydiner, E. Demirbas, M. Kobya, S. Kara, *J. Hazard. Meter.*, **150,** 737 (2008).
36. S. Lagergren and K. Sven, *Vetenskapsakad. Handl.*, **24**, 1, (1898).
37. H. Mahabadipour (2017). Second Law Analysis of Dual Fuel Low Temperature Combustion in a Single Cylinder Research Engine (Mississippi State University).
38. W. J. Weber and J. C. Morris, *J. Sanitary Eng. Div. Am. Soc. Civ. Eng.*, **89**, 31, (1963).
39. A. Y. Nobakht, Y. A. Gandomi, J. Wang, M. H. Bowman, D. C. Marable, B. E. Garrison, D. Kim, and S. Shin, *Carbon*. **132**, 565 (2018).
40. M. Uğurlu, *Micropor. Mesopor. Mater.*, **119**, 276 (2009).
41. E. Demirbas, M. Kobya, S. Oncel, and S. Sencan, *Bioresource Technol.*, **84**, 291 (2002).
42. N. K. Amin, *Desalin.*, **223**, 152 (2008).
43. A. Hamidi, S. Jedari, *Sharif Civil Engineering Journal*. **29**, 29 (2011).
44. A. Y. Nobakht, S. Shin, K. D. Kihm, D. C. Marable, W. Lee, *Carbon*. **123**, 45 (2017).
45. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
46. H. M. F. Freundlich, Z. *Phys. Chem. (Leipzig)*, **57**, 385 (1906).
47. K. Fytianos, E. Voudrias, and E. Kokkalis, *Chemosph.*, **40**, 3 (2000).
48. M.I. Tempkin, V. Pyzhev, *Acta. Phys. Chim. USSR*, **12**, 327 (1940).
49. C. Aharoni, M. Ungarish, *J. Chem. Soc. Faraday Trans.*, **73,** 456 (1977).
50. M. J. Tempkin V. Pyzhev, *Acta Physiochim. USSR*, **12**, 217 (1940).
51. V.Gokmen, A.Serpen, *J. Food Eng.*, **53,** 221 (2002).