Journal of Materials and
Environmental Science
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2021, Volume 12, Issue 6, Page 887-898

http://www.jmaterenvironsci.com

Synthesis of activated carbon by chemical activation of apricot stone with adsorption kinetics

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Received 09 Feb 2021,
Revised 29 June 2021,
Accepted 03 July 2021

Keywords
- ✓ *activated carbon*
- ✓ *adsorption*
- ✓ *apricot stone*
- ✓ *dyes removal*
- ✓ *adsorbent*

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Abstract

Apricot stones were evaluated as raw material in the production of an adsorbent for the basic dye (Reactive Blue 222) from aqueous solutions at various concentration (35-100 mg/l) and temperatures. Phosphoric acid was using as the activating agent in chemical activation method. The synthesized activated carbon was characterized by BET surface area analysis. FTIR, and laser particles size analysis. Data is presented for the adsorption of reactive blue dye onto activated carbon from aqueous solution in a batch system. Two adsorption isotherm models were employed to correlate two sets of experimental adsorption isotherm data, which were obtained by batch tests. The kinetics of adsorption of RB have been discussed using two kinetic models, i.e., the pseudo-first-order model and the pseudo-second-order model. Thermodynamic parameters, such as ΔG, ΔH and ΔS, have been calculated using the thermodynamic equilibrium coefficient obtained at different temperatures and concentrations. The thermodynamics of RB dyes adsorption indicates endothermic process, activated carbon from the hard shells of apricot stones have the best adsorption properties and the highest surface area. The results are analyzed within the context of three common adsorption models; the Langmuir, Freundlich, and Intra-particle diffusion adsorption isotherms. The equilibrium data were best fit by Langmuir isotherm model.

1. Introduction

Dyes are used extensively in various industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., and also in production of colored products. It is estimated that about 2% of many dyes are produced annually in the global market are discharged into the water system with most of the sources generated from textile industries.

There are many studies in the literature relating to the production and characterization of activated carbon from agricultural wastes [1-8]. Activated carbon (AC) is widely used as an adsorbent on an industrial scale mainly in the purification/separation of liquids and gases and also as a catalyst and catalyst support [9]. Activated carbons may be used for purification of wastewater, in which the content of metal ions often exceeds the admissible sanitary standards [13-14]. In Iraq, most of the activated carbons used by industries are imported from various countries such as South Korea, China, Iran, and Turkey. However, there is a possibility to reduce the imported cost by producing activated carbon using sources of local raw material such as, canning industry, residues from agriculture and food industries are the non-product outputs obtained from the growing and processing of raw agricultural products.

The present work deals with the investigation of the characteristic's properties of prepared carbon adsorbents from apricot stones, the effect of the treatment conditions and the choice of precursors on the properties of the activated carbons, effect of various parameters such as pH, adsorbent dosage, contact time, and adsorbate concentration on removal capacity of methylene blue. Also, kinetics of adsorption isotherms were studied.

2. Methodology

2.1 preparation of activated carbon

Chemical activation technique was used to produce the activated carbon from apricot stones and coconut shells [10,11,12]. The stones and shells were washed with distilled water to remove undesirable impurities and dried in an oven at 110°C for 12 h, then crushed to particle size ranges from 1 to 2 mm. The samples were impregnated with the 50 vol. % H_3PO_4 solution at room temperature by weight ratio of 1.5:1 for 24 h, after impregnated, solution was filtered to take the impregnated samples, then dried at room temperature for 3 days, after drying the samples containing at least 15% H_3PO_4. To produce activated carbon, acid impregnated samples were heated at rate of 10 0C /min to a final carbonization temperature of 600 ^{0}C for 2-3 hours, the carbonization was achieved in a muffle furnace. The activated carbon products were crushed to obtain small particles (30-70 mesh or 0.595-0.212mm) and rinsed with boiling distilled water to decrease the pH value, then drying for 24 h in an oven at 80°C. The operation conditions, density and yield of the different samples prepared by the method of chemical activation are summarized in Table 1.

Table 1 preparation conditions and yields of the activated carbon obtained at temperature 700 ^{o}C

Carbon name	H3PO4 (vol.%)	Carbonization temperature (°C)	Weight after impregnation (g)	Weight after carbonization (g)	Weight after washing/drying (g)	Bulk density (g/cm^3)	Yield (wt%)
Apricot	50	700	250	110	90	0.84	36

2.2 Experiments

The adsorption of reactive blue dye onto activated carbon surface to adsorb dye solution with different initial concentrations was studied, to prepare a stock solution, 0.1g of reactive blue was dissolved in 1000 ml of distilled water where 100 ml of reactive blue solution with various initial concentrations (35-100 mg/l) were added to six flasks. Equal mass of 0.1 g of the prepared activated carbon was added to each flask. The flasks were agitated on a mechanical shaker for 30 min at 50 °C to reach equilibrium state, then the solutions were filtrated and analysed by taking amount of dye remaining in solution. The dye concentration was measured by spectrophotometry at 600 nm due to Agilent UV–Vis Cary 60 PC scan double beam recording spectrophotometer using 1cm glass cells.

The amount of dye adsorbed at equilibrium, q_e (mg/g), was calculated by [15]:

$$q_e = \frac{V}{m}(C_0 - C_e) \qquad \text{Eqn. 1}$$

where C0 and Ce (mg /l) are the initial and equilibrium dye concentrations, respectively, V (l) is the volume of the solution and m (g) is the mass of the adsorbent.

The removal efficiency of reactive blue was estimated by [16]:

$$E\% = \frac{C_0 - C_t}{C_0} \times 100 \qquad \text{Eqn. 2}$$

2.3 pH adjustment

The standard method ASTMD 3838-80 was used to determined pH value, a sample of 1g activated carbon added to 100 ml of deionised water and stirred for 1 hour. pH meter was used to reading PH value, the solutions with a pH greater than 7 are basic or alkaline in nature.

2.4 Adsorbate

In this study a reactive blue 222 dye $C_{37}H_{24}N_{10}$ $Na_6O_{22}S_7$ (Mwt 1323 g/mol) was used as adsorbate. Its water soluble dye has absorption maximum at about 602 nm. The chemical structure of reactive blue is shown in Figure 1.

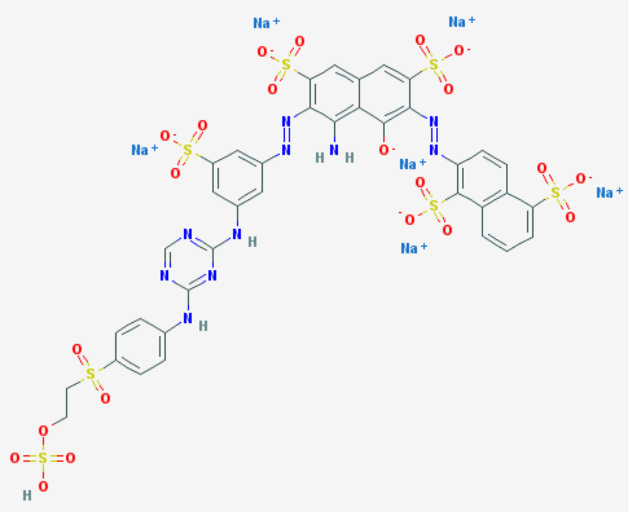


Figure 1: Chemical structure of reactive blue

3. Adsorbent characterisation

Synthesized activated carbon of plant base was analyzed with the N_2 adsorption desorption test based on the Brunauer-Emmett-Teller (BET) principle, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and particle size analysis.

3.1 BET surface area analysis

BET surface area, average pore diameter and pore volume of the activated carbon were determined by most usual standard procedure of The Brunauer Emmett Teller (BET) [13]. The BET surface area (SBET) was determined with the standard BET equation applied in a relative pressure range from 0.06 to 0.3. The total pore volume was calculated at a relative pressure of approximately 0.91, and at this relative pressure, all pores were completely filled with nitrogen gas. The average pore diameter can be estimated by [14]. The BET surface areas and total pore volumes of the carbons produced at 50 vol.% concentration of H_3PO_4 are 1115 m^2/g and 0.91 cm^3/g, respectively, these parameters may be effected due to duration time of carbonisation and acid concentration.

3.2 FTIR analysis

The prepared adsorbents were tested with Nicolet iS10 FTIR spectrometer from Thermo Scientific with a spectral range from 4000 to 400 $cm^{-1}$was used to determine the functional groups of the activated carbon. Peak occurring at 1320/cm is characteristics C=C stretching vibration of aromatic ring. The peak observed at 1700/cm is due to C=O stretching n the ketone aldehydes, or carboxyl group. The FTIR analysis as shown in Figure 2.

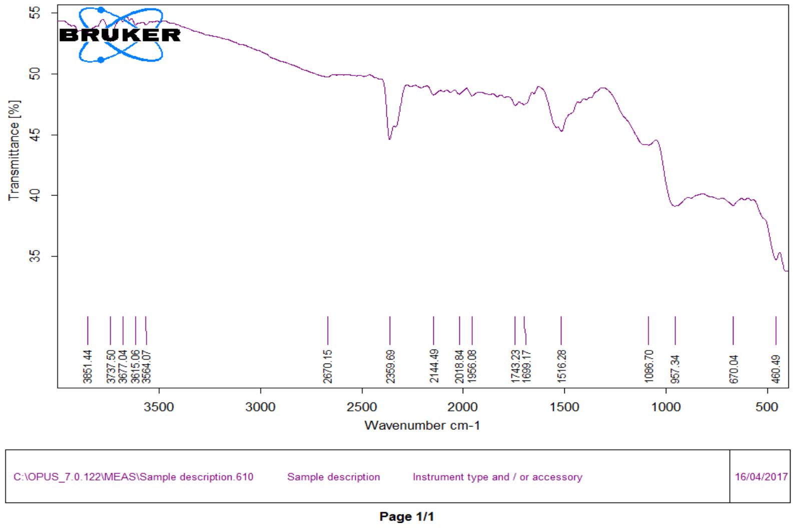


Figure 2 FTIR spectroscopy spectrum of the activated carbon synthesized from apricot stone.

3.3 SEM analysis

Scanning Electron Microscopy (SEM, Phenom proX, Phenom-World BV, Netherlands) was used to study the surface morphology of the particles of the AC, the acceleration voltage of the microscope was set to 15 kV. The appropriate SEM image of carbonized apricot stone with magnifications 500x, and averaged diameters about 50 µm was shown in Figure 3, as can be observed from Figure After the activation process, a significant amount of pores were developed on the surfaces of the bio chars, which were circular in shape. However, the temperature and pyrolyzed cycles play an important role in creation of sufficient porosity.

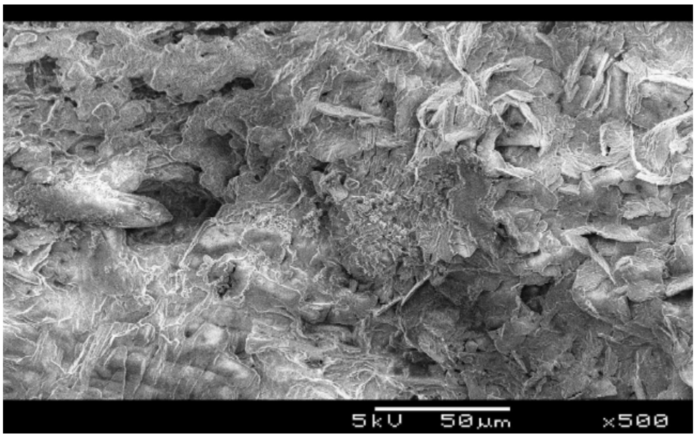


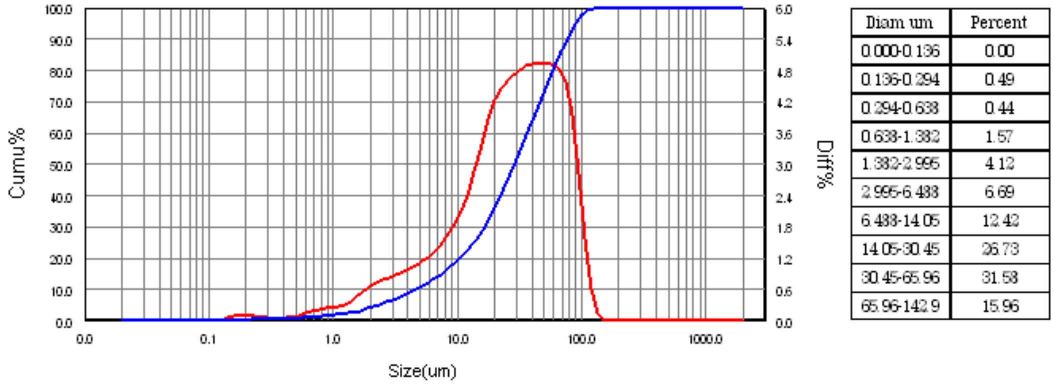
Figure 3. SEM images of apricot activated carbon under process temperature at 700 °C for 30 min.

3.4 Iodine Number

This test method covers the determination of the relative activation level of unused or reactivated carbons by adsorption of iodine from aqueous solution. The amount of iodine absorbed (in milligrams) by 1g of carbon from a 0.1N iodine solution when the equilibrium iodine concentration is exactly 0.02N is called the iodine number. Standard test method for determination of iodine number of activated carbon was described in ASTM Designation: D4607-94. Iodine number is a measure micro-pore content of the activated carbon, a higher iodine number indicates higher micro porosity of the sample. Iodine number of activated carbon of apricot stone and coconut shells will be found is 895 and 780 respectively.

3.5 Particle size analysis

Particle size analysis for samples of prepared activated carbon from apricot stones, coconut shells and industrial activated carbon were carried out using Bettersize 2000 laser particle size analyser range (0.02 -2000 µm) the results shown in Figure 4.



Diam um	Percent
0.000-0.136	0.00
0.136-0.294	0.49
0.294-0.638	0.44
0.638-1.382	1.57
1.382-2.995	4.12
2.995-6.488	6.69
6.488-14.05	12.42
14.05-30.45	26.73
30.45-65.96	31.58
65.96-142.9	15.96

Figure 4 Particle size analysis of activated carbon synthesized from apricot stone.

4. Adsorption isotherms and kinetics

The Freundlich isotherm is used to show the surface heterogeneity, which shows the multilayer adsorption properties of the adsorbent. The empirical equation is based on the hypothesis that the reactive sites over the adsorbate are distributed exponentially with the heat of the sorption process [17]. This is represented non-linear expression of Freundlich isotherm model by Eqn.3 :

$$qe \;=\; k\,C_e^{1/n} \qquad \text{Eqn.3}$$

where qe and Ce represent the amount of dye adsorbed at equilibrium, the concentration of dye in the bulk fluid at equilibrium respectively, k and 1/n are the adsorption capacity and adsorption intensity, respectively.

Eqn. 3 can be linearized and the temperature dependent constants k and $1/n$ found by linear regression:

$$lnqe \;= ln\,k\; + \frac{1}{n}\ln Ce \qquad \text{Eqn.4}$$

The Langmuir isotherm assumes a uniform surface, which is reasonable with many fabrics. The isotherm is represented by the Eqn.

$$q_e = \frac{Q_0 b C_e}{1+bC_e} \qquad \text{Eqn.5}$$

The constant Q_0 represents the maximum adsorbate that can be adsorbed onto the surface, and b is the isotherm constant. If b is large, and the quantity $Q_0\ b$ is much larger than one, the linear form of this adsorption isotherm is.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e} \qquad \text{Eqn.6}$$

In order to predict the adsorption behaviour of the activated carbon, Lagergren-first-order [18], pseudo-second-order [19] and Weber and Morris intra-particle diffusion reaction models [20] were used to determine the kinetics of the adsorption of reactive blue from an aqueous solution.

A pseudo first order model the Lagergren first order kinetic model can be used [21,22].

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad \text{Eqn.7}$$

where q_e and q_t represent the amounts of reactive blue adsorbed (mg/g) at equilibrium and at time *t*, respectively. *k1* (min–1) is the Lagergren rate constant. The linear form of the pseudo-first-order model for adsorption of dyes from aqueous solution is described in Eqn.8.

$$\ln(q_e - q_t) = lnq_e - k_1t \qquad \text{Eqn.8}$$

Equilibrium kinetics data were analyzed using the linear form of the pseudo second order equation and are expressed by the following Eqns. [23,24,25].

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \qquad \text{Eqn.9}$$

where k_2 represents the rate constant of second order adsorption (g/mg·min^{-1}).

Intra-particle diffusion reaction model in order to gain insight into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic experimental results were analyzed by the intra-particle diffusion model to elucidate the diffusion mechanism. According to intra-particle diffusion, the uptake varies almost proportionally with the half power of time. The prediction of the rate-limiting step is essential to have insight into the adsorption mechanism. The intraparticle diffusion coefficient kid can be calculated by Eqn. (10), the linear form of the intra-particle diffusion reaction model is represented by the following formula [Kalavathy et al. 2005] (26) .

$$q_t = k_{id}t^{1/2} + c \qquad \text{Eqn.10}$$

, where *c* is the intercept which reflects the boundary layer effect, k_{id} is the intra particle diffusion reaction model. Figure 10 shows the plot of *qt versus* $t_{1/2}$. The values for k_{id} *and c* were calculated, respectively, from the slope and intercept and are presented in Table 2

5. Results and discussion.

The calibration curve of AC for removal of reactive blue at wave length of 600 nm was obtained due to spectrophotometer technique shown in Figure 5.

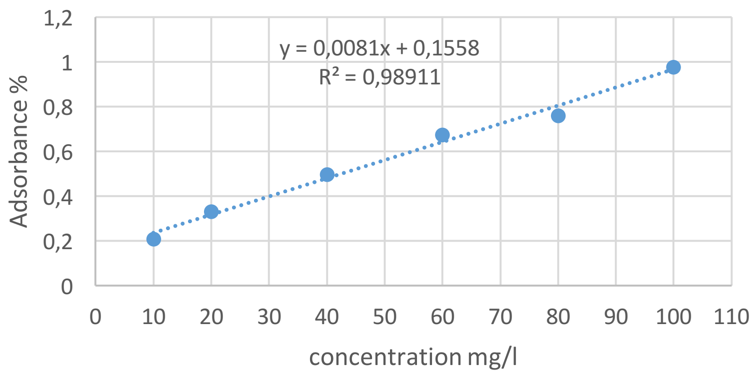


Figure 5 Caibration curve of reactive blue pigment adsorbance at wave length of 600 nm.

From the graph the slope was found to be 0.0081. Thus, the equilibrium concentration at time t is Ce = (absorbance)/(0.0081)

5.1. Effect of initial RB concentration.

Figure 6 show that the effect of initial concentration of basic dye (RB) solution on Adsorption for various contact time at 25^0 C, the reaction of adsorbate almost increased linearly with contact time until to reach its equilibrium value, the adsorption capacity increased with high level of initial pigment concentration and at equilibrium (qe) increased from 0.6 to 1.5 mg/g with an increase in the initial dye concentrations from 35 to 100 mg/L.

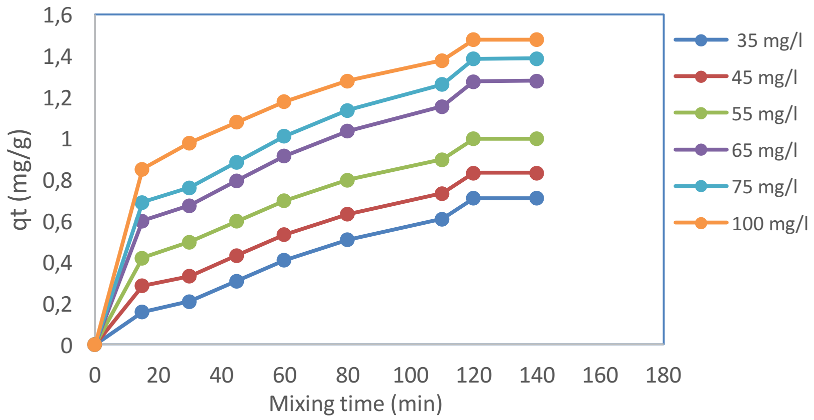


Figure 6 Adsorption capacity vs. adsorption time at various initial RB concentrations at 25^0C

5.2 Effect of pH

The relation of initial pH of solution and the percentage dye removal was shown in Figure 7. The removal efficiency has a maximum value at pH range 4 to 6 say in acid media. This behaviour attributed to the availability of a senior number of active site on the adsorbent surface and related to the solute uptake to the active sites and as well to the chemistry from the solute in the solution.

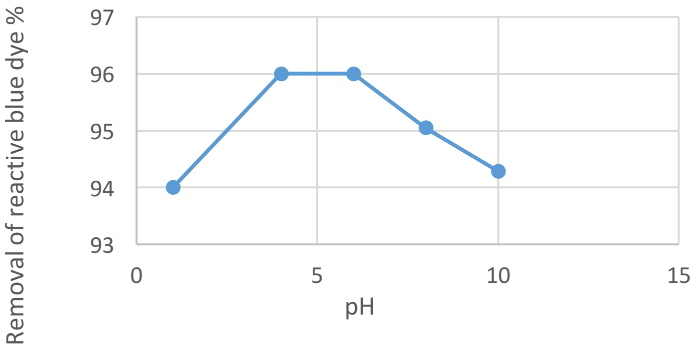


Figure 7 Effect of pH value on removal percent of reactive blue.

5.3 Effect of temperature

Figure 8 shows the effect of temperature adsorption RB dye. It be observed that the equilibrium of adsorption increases with temperature at initial RB concentrations 100 ppm, so the sorption process was endothermic. It had been show the amount of adsorbed dye increases with rising of temperature from 25 to 50 ^{0}C in the other hand some cases the solubility of the dye molecules is affected with the increase of the temperature which finally has a significant impact on the removal efficiency.

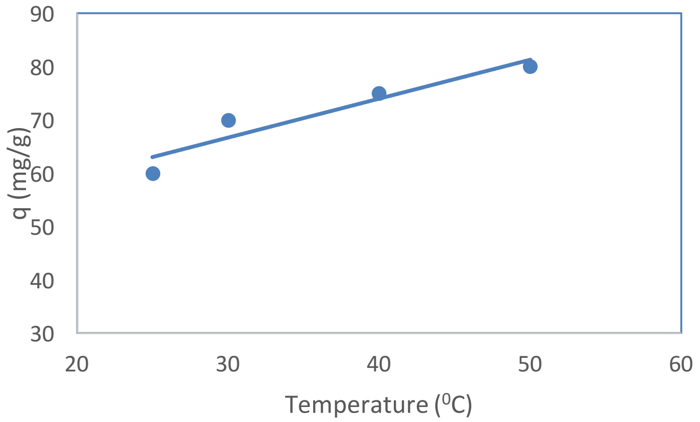


Figure 8 influence of temperature on adsorption equilibriume of RB dye.

5.4 Equilibrium isotherms

In this work, the Langmuir and Freundlich models were used to describe the relation between the amount of dye adsorbed and its equilibrium concentration. The experimental data was fitted to the linear form of Langmuir isotherm Eqn. 5 with a slope of 49.7 as shown in Figure 9

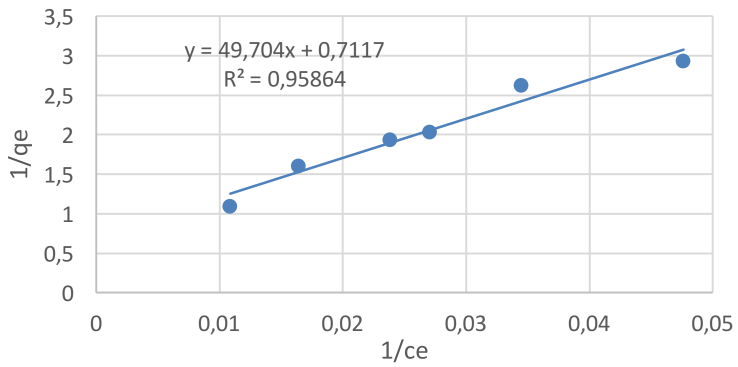


Figure 9 The Langmuir adsorption isotherm for RB dye adsorption onto AC .

The amount of RB dye adsorbed q_e has been plotted against the equilibrium concentration (c_e) as shown in Figure 10. We can show that the equilibrium adsorption density, qe increased with the increase in dye concentration. It can be observed that the correlation coefficient R^2 is 0.95 and the values of k and n are 1.03 and 0.04, respectively the adsorption is chemical due to the value of n ($n<1$).

5.5. Adsorption kinetics

The kinetic adsorption studies predict the progress of dyes adsorption during the sorption to reach the equilibrium. In addition, the estimate of the adsorption mechanism is important for design purposes. To analyze the adsorption mechanism, pseudo-first order, pseudo-second order, and intra-particle diffusion models were used.

5.5.1. Pseudo first order model.

Linear regression analysis of $\ln(q_e - q_t)$ versus t (min) were carried out for experimental data shown in Figure11. Lagergren first order kinetic model, the values of *qe* and *k1* are determined from the slope and intercept point of the graph.

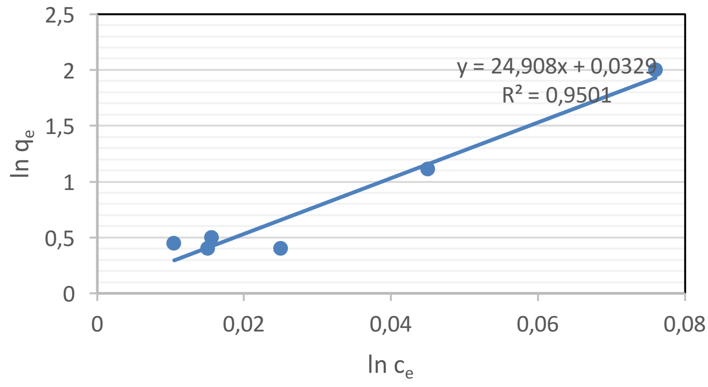


Figure 10 Coconut ac Freundlich isotherm.

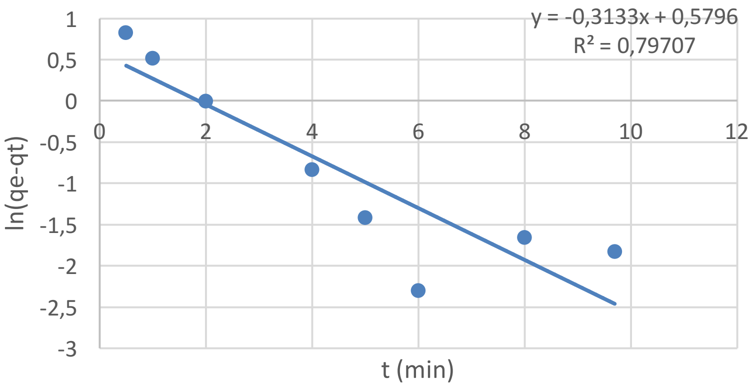


Figure 11 Pseudo first order kinetics fit for dye adsorption onto apricot AC.

5.5.2 Pseudo second order model.

Another model can be used to explain the sorption process is pseudo-second-order model, Figure 12 shows the linear plots of t/q_t versus t. Values for k_2 and q_e were calculated, respectively, from the slope and intercept point of the graph. The slope and intercept values are 0.29 and 0.38, respectively.

5.6 Thermodynamic parameters

The thermodynamics of the adsorption process were studied at three different temperatures. Thermodynamic parameters such as the Gibbs free energy change (ΔG), enthalpy changes (ΔH) and entropy change (ΔS) can be used for the characterization of temperature effect on the adsorption process. These parameters were calculated using Van't Hoffs Eqn.s:

$$\Delta G = -RT\ln K \qquad \text{Eqn. 11}$$

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad \text{Eqn. 12}$$

where K the equilibrium constant of the adsorption process as a function of temperature, which is calculated from equilibrium adsorption [27].

$$K = \frac{q_e}{C_e}$$

R is the molar gas constant (8.314 J/mol K) and T is the absolute temperature. K is the equilibrium constant obtained for each temperature from the Langmuir model. ΔH and ΔS were obtained from the slopes and intercepts of the linear plots of InK against 1/T as shown in Figure13. The values of the thermodynamic parameters are listed in Table 4.

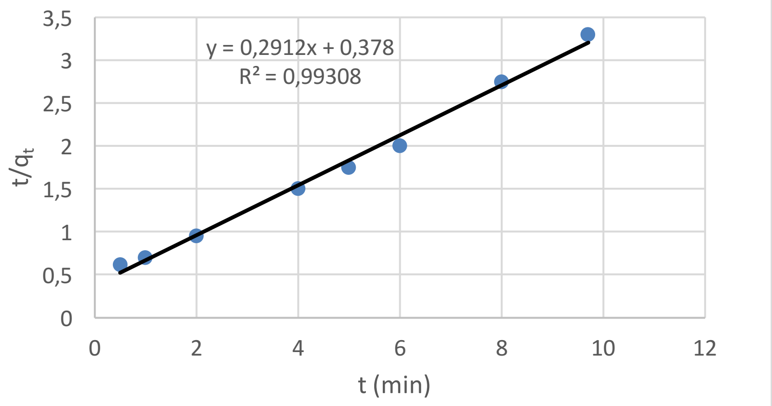


Figure 12 Linear regression of pseudo second order kinetics fit for dye adsorption onto apricot AC.

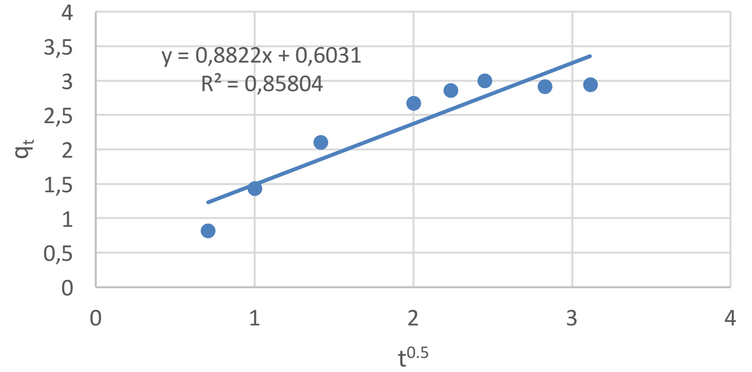


Figure 13 Intra particle diffusion kinetics fit for dye adsorption onto apricot AC.

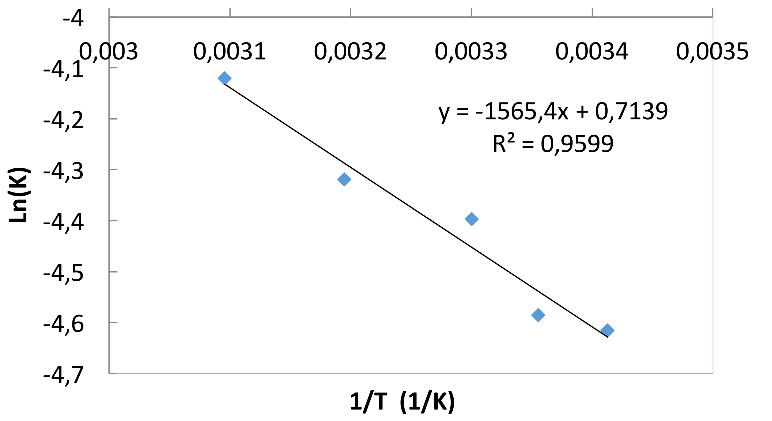


Figure 14 Van't Hoff plot for adsorption of RB.

Table 4 Thermodynamics parameters for the adsorption of RB dye.

ΔS (J/mol)	ΔH (kJ/mol)	ΔG (kJ/mol)	R^2
5.936	13.14	11.2	0.96

Conclusions

Activated carbon was successfully synthesized from apricot stones with the phosphoric acid activation process. The prepared AC is an effective adsorbent for the removal of reactive blue from an aqueous solution. The adsorbent was characterized by BET, particle size and FTIR.

The present of adsorption decreases with increases in the initial reactive blue concentration, but the actual amount of reactive blue adsorbed per unit mass of carbon increased with increase in reactive blue concentration. The Langmuir equation gives an accurate description of the experimental data. A kinetic study showed that the adsorption behaviour of the activated carbon followed the pseudo-second-order kinetic model. In addition, the experimental result showed that 100% dye removal was obtained by the adsorption process in 12 min.

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(2021) ; http://www.jmaterenvironsci.com