

Obtaining activated carbon from grape pulp and removing of reactive blue 19 from the aqueous solution

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Abstract

As an adsorbent for the removal of reactive blue 19 (RM 19) from the aqueous solution, grape pulp carbon (GMC), an agriculture allow cost by product, was used. Activated carbon was obtained by chemical activation of a grape meal with zincchloride. The surface area of the grape pulp carbon was calculated as 1542.71 m²/g surface area using the BET method. The experiment data showed that adsorption was extremely pH dependent and optimal pH was decisived as 3.0. The maximum dye adsorption capacity was 587.7 mg/g at 45 °C. Freundlich and Langmuira adsorption models were used for a mathematical definition of adsorption equilibrium. According to the experimental data, the Freundlich model was a very good fit. Mass transfer and kinetic models were applied to experimental data to investigate the mechanisms of adsorption and potential rate steps. The mass transfer and intraparticle diffusion were found to play an significant role in the adsorption mechanisms of paint and adsorption kinetics in the first-class kinetic model. The adsorption test results were found to be important in terms of environmental friendliness, economical and easy availability by the activated carbon obtained from the reactive blue 19 textile dye grape pulp.

Key words: Grape pulp, chemical activation, activated carbon, adsorption, reactive blue 19

Introduction

Paints used in the textile industry are widely used in many sectors such as textile, rubber, plastic, leather tanning, paper production, food technology, photo electrochemistry cells, etc. (Baseri et al., 2012; Clarke et al., 1980). It has been determined that discharging the paints used in the industry into environmental waters causes significant environmental and health problems. As a result of the effect of photosynthetic activity in the water due to the reduced light penetration due to the lime-dissolving nature of various non-decomposed dyes (Bharathi et al., 2013). They have a toxic effect on some aquatic organisms and pose a serious health risk to humans (Lee et al., 2006). Since reactive dyes cause major nature problems compared to other dyes, they must be removed completely from wastewater. Many synthetic dyes resist biodegradation due to their complex aromatic molecular structure. Color removal is difficult with traditional biological

processes (Clarke et al., 1980; Farah et al., 2007; Akar et al., 2010).

Since agriculture and other wastes are cheaper, the trend towards different alternative materials for adsorbents has been developed. Such inexpensive adsorbents (Hamaaed and Daud, 2008) provided laboratory-scale investigations of color wastes at diverse grades. For a long time, exploratory has been conducted to advance cheaper and more influential adsorbents. Many non-traditional low price adsorbents have been recommended from natural materials, biosorbents and waste materials such as industry and agriculture. These materials can be used to remove the sorbets from the paint solution. ne of the agricultural industry by-products that cannot be utilized properly in our country is grape pulp.

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The grape pulp is obtained as a result of squeezing and squeezing the grape with its garbage and stems as it is, or after separating from the garbage while making wine. Our fresh grape production is around 3.5 million tons every year. Approximately 3% of the grapes produced in our country are considered as wine grapes. Considering that 15-25% pulp is obtained from the processed wine grapes, the production of grape pulp is not to be underestimated. As the growers can not benefit from the grape pulp obtained during the winemaking, it may cause significant accumulation at the production points and discarded because they cannot be evaluated, and in this context, considerable environmental pollution (Özdüven et al., 2005).

Activated carbons are generally produced from materials with major quantity carbon content and have started to be preferred due to their high porosity and wide surface area. The adsorption properties of the activated carbons increase depending on the porosity structure. The chemical structure also affects the adsorption capacity of activated carbons. Activated carbons contain two types of impurities. The first of these are the elements that are chemically bound to activated carbon. Oxygen and hydrogen, which are derived from the starting materials and remain in the structure of the activated carbon as a result of incomplete carbonization or chemically bound to the surface during activation, are among these impurities. The second is the ash part of the product, which is not an organic part and contains inorganic components (Robinson et al., 2001). These materials are influential adsorbents for many organic compounds in water and wastewater treatment (Faria et al., 2004; Ali and Gupta, 2007). The activated carbons obtained from the elements are very expensive because they are economically expensive. More recently, efforts have been made to develop highly economical adsorbents that are an alternative to them. The raw materials to be used in the production of activated carbon are selected according to the area intended to use activated carbon, the structure of the process, the properties of the substance to be adsorbed and the cost. Some of the different adsorbent materials used in the production of activated carbon are sawdust, rice husk, rice shells, sugar beet pulp (Gezer, 2019), carop powder (Gezer et al., 2019, Gezer and Ersoy, 2018), peanut shell, cotton kernel shell, myrobalan, rubber core-sheath, cashew nut sheath, palm kernel sheath, palm tree rowler, pongam kernel sheath, cherry kernel, apricot stone, almond bark, oak wood waste, corn husk, corn stove and cotton stalks (Ramakrishna et al., 1997; Gupta et al., 2007).

Coagulation in the treatment of wastewater containing dyestuffs, methods such as flocculation, electrochemical treatment, and adsorption are used. It is known as the most used method in dye removal because it can be applied easily and inexpensively among the mentioned methods and is one of the most effective treatment methods. Although these techniques have proven to be influential in the literature, in recent years, there are elements such as excessive use of chemicals in the industry, expensive facility requirements or operating costs, lack of effective color reduction, and sensitivity to a variable (Farah et al., 2007; Slokar et al., 1997; Gupta et al., 2007). Adsorption processes have always been accomplished to change the color of textile products. However, such applications depend on the cost of the adsorbents. Adsorption is an interface phenomenon and is defined by measuring the concentrations at the interface and

adjacent phases. Today, adsorption is important in many natural physical, chemical, and biological processes. Besides that, the adsorption process is frequently used in the process of removing organic and chemical pollutants from wastewater by keeping them on a suitable solid surface (Ahmad et al., 2014; Asghar, 2012). In this study, grape meal carbon, an agricultural low-cost by-product, was used as an adsorbent. The grape pulp is a complex material that contains lignin and cellulose as the main components. Grape pulp carbon obtained from different methods was used to be used as an adsorbent to remove pollutants such as phenol and heavy metals (Altundogan, 2005; Dursun et al., 2005). However, studies on dye adsorption in grape pulp carbon are not much, there are still not many studies to evaluate the adsorption parameters of the process.

The half-life of the anthraquinone Reactive Blue 19 (RM 19) dye, whose trade name is Remazol Brilliant Blue R, is about 46 years at pH 7 and 25 °C (Altundogan, 2005). It is preferred in the textile industry because it provides bright colors and can be applied effectively to the fabric. The molecular structure of RM 19, whose chemical structure is given in Figure 1, is $C_{22}H_{15}N_2O_{11}S_3$ and its molecular weight is 611.53 g.

The aim of this study is to produce and characterize grape pulp carbon. The effectiveness of the activated carbon obtained as a result of the chemical activation in relief was investigated. In the research, reactive Blue 19 dye, which is highly used in the coloring of materials in the textile industry, was chosen. In adsorption experiments, the effect of initial pH concentration, initial dye adsorbent amount and contact time on dye removal was investigated to find the highest removal value.

Phenol and organic acids commonly found in plum fruits are compounds that show high antioxidant activity by preventing the start of oxidation and peroxidation reactions. This antioxidative effect reduces the risk of many chronic diseases including cancer and cardiovascular diseases (Tang ve Tsao, 2017; Pham et al., 2019). In addition, these compounds are effective against many yeast and bacterial strains that are disease factor. Heritability of phytochemical properties is low and sensitivity to environmental conditions is high. Superior phytochemical properties are possible only cultivation with right variety and suitable ecology. For this reason, researches on the identification and breeding of varieties suitable for ecology have increased recently (Mditshwa et al., 2013; Mezzetti et al., 2016; Blando et al., 2019).

In this study, how the climate change that occurred due to altitude change affects phytochemical and antimicrobial properties in fruits of 'Black Diamond' plum variety was investigated. As a result of the correlation analysis, the antimicrobial potentials of the investigated phytochemical characteristics were determined.

Materials and Methods

Chemicals

Reactive Blue 19 was chosen as adsorbate because of its excessive consumption in the textile industry (Figure 1). It was purchased from Uşak textile factories. The solution was prepared by dissolving 1.0 g of paint in 1 L of pure water. The test solutions were prepared at different concentrations. The concentration range of the prepared dye solutions ranged from 20, 40, 60, 80 and 100 mg /L. The pH of each solution was

concentrated H₂SO₄ and NaOH was adjusted before contact with the adsorbent.

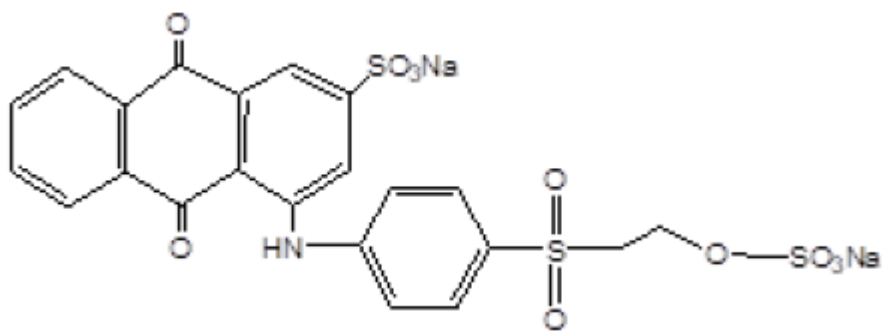


Figure 1. Chemical structure of Reactive Blue 19 dye molecule in aqueous solution

Grape pulp obtained from the grape factories of Manisa was first washed. It was dried in the oven after washing. Grape pulp from the oven was torn from the mill. Sieve analysis

was carried out on the sample passed through the mill. Grape pulp samples of 75 μm size were taken as test samples (Figure 2).



Figure 2. (a) Grape pulp and (b) powders

Preparation of activated carbon

The grape cake was dried in an oven at 70 °C for 22 hours. Dried grape pulp was allowed to be divided into small sizes using mortar. It is divided into micro-grain sizes in the vibrating screen shaker device. Grape pulp, which was brought to a size of 75 μm , was kept in a tightly closed container until the chemical activation process was applied. The grape meal was mixed with ZnCl₂ so that the impregnation ratio was 1:1. It was then activated in a cylindrical bath in a quartz cuvette under a 100 mL/min N₂ atmosphere at a temperature of 20 °C/min for 2 hours at 400 °C. The samples taken out of the oven were washed 3 times with 0.5 M HCl and then with pure water until the chloride ions remained. The AgNO₃ test was performed to determine if the chloride ions remained. After the washing process, the activated carbon was dried at 80 °C for 20 hours, then stored for analysis.

Adsorption equilibrium

It is a derived equation by adding theoretical thinking on some simplifying assumptions. Although it explains gas-solid systems better, it also works well in some simple liquid-solid systems. Langmuir's theory is that the molecule is adsorbed on the surface in one layer limited to situations. As mentioned earlier, single layer adsorption is generally observed in chemical adsorption. Single-layer adsorption; It is distinguished by the fact that the amount of adsorbed reaches a maximum at medium concentrations (the adsorbent surface is completely covered at only one molecule thickness) and remains constant at this value even when the concentration is increased (Langmuir, 1916). The Langmuir model is applicable for single layer adsorption to a surface containing a plurality of identical regions homogeneously distributed over the adsorbent surface. Langmuir model is expressed by the following equation;

$$q_{eq} = \frac{q_{max}K_b C_{eq}}{1+K_b C_{eq}}$$

(1)

Here, q_{eq} is the adsorption equilibrium constant related to the amount of dye adsorbed on carbon in equilibrium, the equilibrium concentration in C_{eq} solution, q_{max} adsorption capacity and K_b , adsorption energy. The Freundlich model forms a basis for the experimental equation in adsorption on a heterogeneous surface in the region of equivalent and non-independent bonds. Freundlich equation (Smith, 1984);

$$q_{eq} = K_f C_{eq}^{1/n}$$

(2)

It is expressed as. Here, K_f shows the adsorption capacity and n the adsorption density.

Adsorption kinetics

It is necessary to know the adsorption rate, operation control and adsorbent evaluation in process design in removing dyes from wastewater. Determination of adsorption kinetics, the substance to be adsorbed effectively has adsorbent contact time, ie retention time. The adsorption kinetics of red 195 in grape pulp carbon is controlled in four stages (Bharathi and Ramesh, 2013; Findon et al., 1993): 1. The substance in the gas or liquid phase diffuses towards the boundary of a film layer covering the adsorbent. This step is often neglected because there is certain mobility (mixing) in the adsorption device, 2. The substance coming to the film layer passes through the stagnant part here, moves towards the pores of the adsorbent, 3. Then it moves towards the surface where the adsorption will occur by moving through the pore spaces of the adsorbent. Finally, the adsorption of the adsorbent to the pore surface occurs.

Pseudo-first-order and pseudo-second-order models

The so-called first and so-called second-order models are suitable for evaluating the results in the adsorption experiments. In general, the first-order reaction velocity model from Lagergren kinetic equation, is widely used (Langergren, 1898).

$$\frac{dq}{dt} = k_1 (q_{eq} - q)$$

(3)

Here, k_1 : the adsorption rate constant (min^{-1}), q_e : the amount of the substance adsorbed on the unit adsorbent (mg/g), q_t : the amount of pollutant adsorbed at time t (q/d) at any given time the amount is. The so-called, the use of the quadratic kinetic model depends on the capacity of the solid phase to absorb dye in the adsorption experiment. Upon this assumption, the sorption process is expressed as involving the chemisorption mechanism (Ho et al., 1999);

$$\frac{dq}{dt} = k_2 (q_{eq} - q)^2$$

(4)

Here, k_2 is the so-called II. The order is the adsorption rate constant (g/mg.min).

Thermodynamic parameters of adsorption

The thermodynamic parameter (ΔG°) of the Gibbs free energy change reverberates the applicability and spontaneous occurrence of the process. The free energy change equation of adsorption is given as follows:

$$\Delta G^\circ = -RT \ln K_b$$

(5)

Here R is the universal gas constant (8.314 J/mol.K) and T is the absolute temperature (K), the K_b equilibrium constant (Langmuir constant). The negative value of the Gibbs free energy indicates the energetic suitability of the adsorption. Balance constant in Van's Hoff equation enthalpy (H°) and

$$\ln K_b = \Delta S^\circ/R - \Delta H^\circ/RT$$

(6)

H° and S° can be obtained from the intersection and slope of the K_b vs. $1/T$ (Smith et al., 1987).

Adsorption studies

In the first stage of the study, 0.15 L reactive blue 19 dye solution was placed on 0.15 g grape pulp in an Erlenmeyer bottle at different concentrations, temperatures, and pH values. The prepared samples were placed in an ultrasonic bath and kept at determined intervals. The mixture was filtered with filter paper to determine the residual color concentration in the medium. 5 mL samples were taken from the samples. Before the analysis, the samples were centrifuged for 5 minutes at 5000 rpm and the remaining color fluid was analyzed. Before the analysis, the samples were centrifuged for 8 minutes at 5000 rpm and the remaining color fluid was analyzed. Mean values were used for the calculations in the experiments.

Analysis

In the adsorption experiments, the concentration of the unadsorbed reactive blue 19 was measured using the Mettler Toledo Spectrophotometer UV Vis instrument. Maximum absorption at the absorbance of the dye was measured at 557 nm. Using a Quanta chrome brand Nova Touch LX4 model, the BET surface area was detected from nitrogen adsorption. To detect the paint adsorption characteristic of activated carbon obtained from grape pulp, the iodine number (IN) of carbon was determined at 0.4°C of each sample, a 100 cm^3 aqueous iodine solution at 25°C . The amount of iodine adsorbed against grams of carbon was taken as the number of iodine. Grape meal carbon infrared spectrum was obtained with the Tetra brand JASCO 6600 model FTIR spectrometer.

Results and Discussion

The capacity of the surface area and the number of iodine to affect the quality and usefulness of the adsorbents are important features. BET surface area of grape cake carbon has been determined as $1542.71 \text{ m}^2/\text{g}$. The iodine number of the activated carbon obtained was determined as 1982,24

mg/12 and the surface area as 1531,89 m²/g. Grape pulp activated carbon adsorption data of reactive blue 19 were examined at distinct initial concentrations, temperatures, and pH values. The results are given as adsorbed units per 19 adsorbed reagent blue. Concentration measurement continued as long as each experimental study did not change significantly in the dye. The adsorbed paint amount is calculated from the time balance, q_t , mass balance, and adsorption capacity (Equation 7) (Alkan et al., 2008).

$$q_t = (C_0 - C_t) \frac{V}{m} \quad (7)$$

Here, C_0 and C_t are the initial and liquid-phase concentrations of the dye solution (mol/L) at any time t ; q_t , dye concentration on the adsorbent at any time t (mol/g); V is the volume of the dye solution (L) and m is the mass (g) of the grape meal carbon sample used (Alkan et al., 2008).

Effect of contact time

Figure 3 shows the adsorption kinetics of reactive blue 19 at a temperature of 25, 35 and 45 °C of time-to-dye capability. Adsorption capacity increased with increasing temperature and contact time, and more paint was removed in the first 100 minutes of contact time. The equilibrium was performed at 150 minutes at the end of fast adsorption for all temperatures studied. Behind an equilibrium time of 180 minutes, it was found that the reactive blue 19 was no longer adsorbed from water.

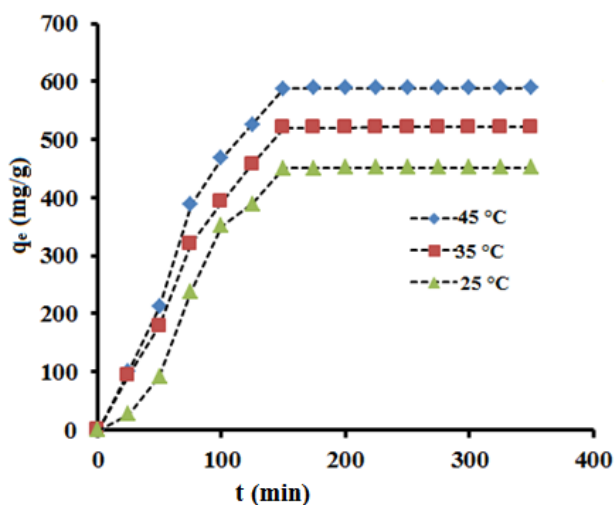


Figure 3. Adsorption curves of reactive blue 19 ($C_0 = 40\text{mg/L}$, $\text{pH} = 3.0$).

Effect of pH

It has been cited in studies published in the literature that pH is an significant effective factor for dye adsorption. To find a pH suitable for the effective adsorption of reactive blue 19, experiments were carried out in the pH range of 1.0-10.0 when the grape pulp was stained with carbon. The change of the initial pH intake equilibrium dye uptake is given in figure 4. The maximum equilibrium uptake value was found to be 488.17 m / g at pH 3.0, and the adsorption of the dye significantly reduced with an rise in pH. All adsorption experiments were done at pH 3.0. According to studies by Coughlin and Ezra (Coughlin et al., 1968), oxidized carbon ones are groups of very small amounts of carbonyl and hydroxyl.

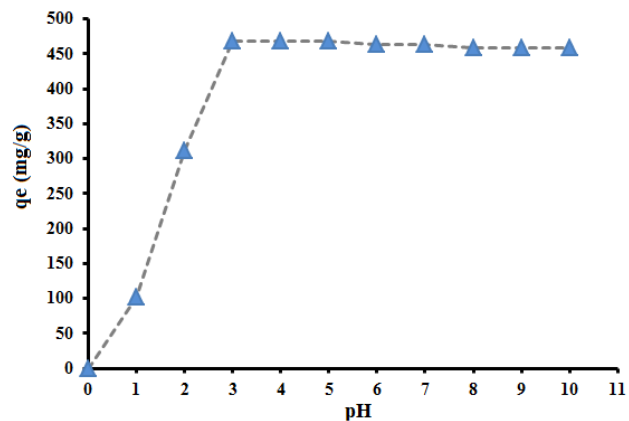


Figure 4. The effect of PH on the adsorption of reactive blue 19 ($C_0 = 40\text{mg/L}$, $T = 45^\circ\text{C}$)

FTIR Analysis

FTIR analysis results of Reactive blue 19 standard dye are given in Figure 5. Reactive Blue 19 dye control showed peaks at 3440, 2947, 1603, 1572, 1541, 1464, 1390, 1360, 1215, 1172, 1120, 1036, 993, 898, 864, 775, 747, 689, 664 and 606 cm^{-1} (Fig. 5). According to the FTIR analysis obtained in Figure 6, the peak indicated by the blue arrow indicates the N-H vibration and the presence of the peak C-H vibration indicated by the green arrow. The FTIR spectrum, which is the result of adsorption of Reactive Blue 19 dye with grape pulp, is compared to the standard dye spectrum, and the peak positions are shown to be significant. In the standard dye samples, the peaks of the wavenumber between 670 and 870 cm^{-1} correspond to aromatic rings. Around 3440 cm^{-1} peak and C-H tension 2947 cm^{-1} , represented by N-H vibration, disappeared after the colorization of Reactive Blue 19 (Ayed et al., 2010). According to the study, the results showed that the mechanism of removal of RB19 dye by activated carbon obtained from grape pulp is related to biodegradation.

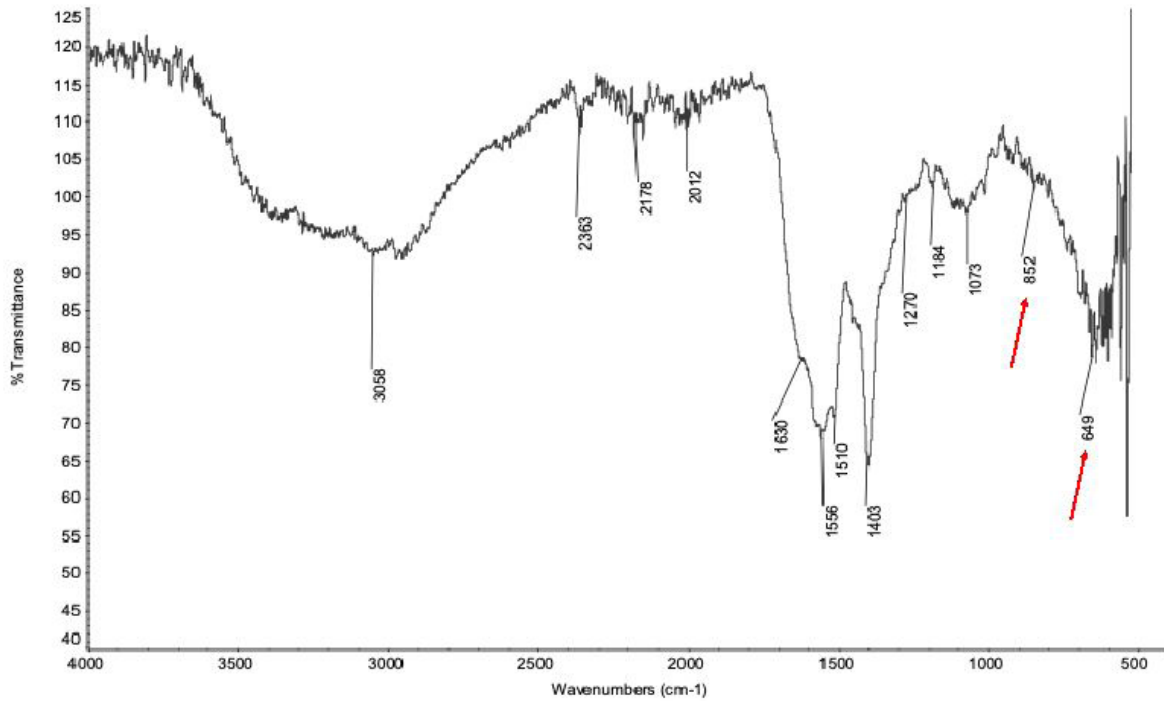


Figure 5. FT-IR spectra of standart reactive blue 19

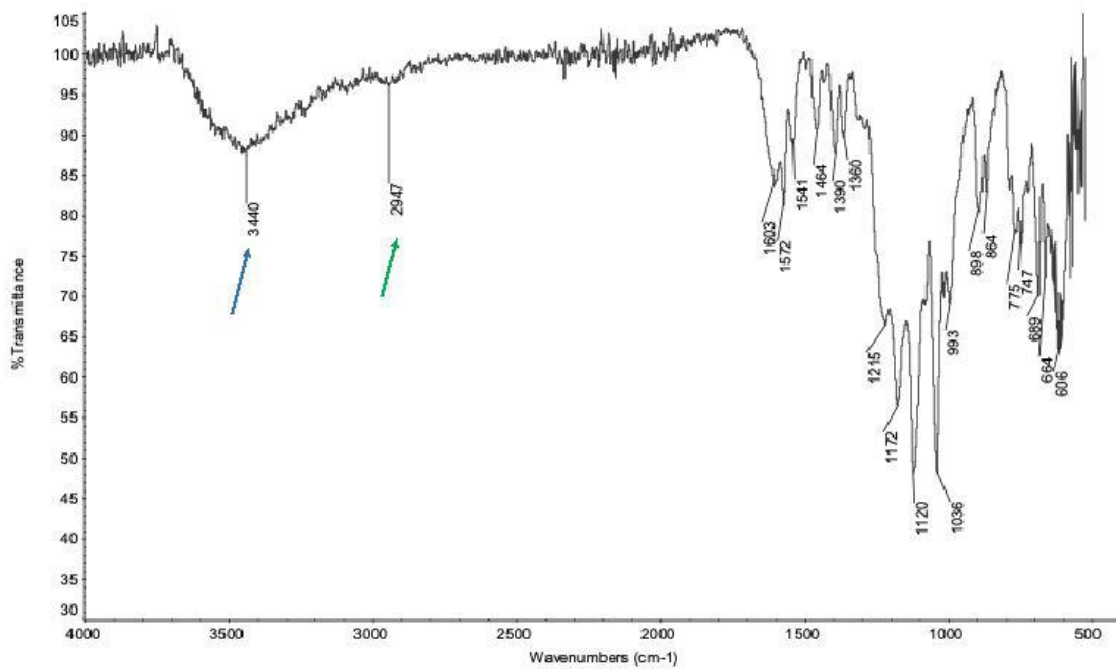


Figure 6. FT-IR spectra of dye with grape pulp

The effect of reactive blue 19 concentration on temperature and adherence to adsorption

The effect of temperature on the adsorption of variable initial dye concentrations of grape pulp carbon of reactive blue 19 in the temperature range of 25, 35 and 45 °C was investigated. Results obtained with initial concentrations of 25, 50, 75 and 100 mg /L are shown in Table 1. It was found that the removal of paint increased with increasing temperature up to 587.7mg/g at 45 °C. It has been determined that with the

increase of adsorption temperature, the diffusion rate of the adsorbate molecules increases along with the outer boundary layer and the inner pores of the adsorbent particle. In addition, if the temperature was changed, a decrease in the viscosity of the solution was observed. This situation has the feature to change the balance capacity of the adsorbent for the test adsorbent. This may also be the result of intraparticle diffusion rate increasing dye molecule and sorbate with an rise in kinetic

energy. Absorption by reactive blue 19 grape meal carbon is not only a physical but also a chemical endothermic process.

Table 1. Equilibrium uptake capacities and adsorption yields at different initial concentrations and temperatures

C0 (mg/g)	25°C		35°C		45°C	
	qe (mg/g)	Adsorption(%)	qe (mg/g)	Adsorption (%)	qe (mg/g)	Adsorption (%)
25	502.5	83.1	534.6	92	587.7	96
50	558.4	74.8	602.7	81.4	633.13	89.7
75	626.3	57.9	713.4	63.4	691.27	68.4
100	687.7	51.2	785.7	59.9	754.11	61.2

In the study of comparing the adsorption capacity of grape meal carbon used for this purpose, 587.7 mg /g 100 mg/L initial reactive blue 19 was 45 °C at the concentration of 195 women, BET surface area was 1542.71m²/g, pore volume was 0.847cc/g and iodine number was 1173 mgI₂/g. Gupta and other researchers (Gupta et al., 2010) worked on the removal of indigo carmine dye from industrial waste with deoiled mustard and charcoal. According to literature studies, adsorption experiments at 30 °C, pH 3.0 for coal and pH 8.0 for deoiled mustard and adsorbant concentration of 2x10⁻⁴ mol /L, adsorbent amounts, 0.40 g/coal for approximately 0.33 x 10⁻⁴ mol/L and 7.5 g /L was 0.25 x 10⁻⁴ mol /L for deoiled mustard. Jain et al. (Jain et al., 2010) removed hazardous paint Naphthol yellow S lady from wastewater using mustard free of active oil as activated carbon. They found that the activated carbon-free mustard's BET surface area of activated carbon was 929.7 ± 2.1 and 326.5 ± 3.4 m²/g, respectively. Mittal et

al. (Mittal et al., 2010) investigated the adsorption of bottom ash and fat-free soy Chrysoidine Y. Paint absorption capacities were found as ash (BET surface area = 870.5 cm²/g) and skimmed soybean (BET surface area = 728.6 cm²/g), 3.61 x 10⁻⁵ mol /g and 1.92 x 10⁻⁵ mol /g. Ferrero (Ferrero, 2007) worked with a nutshell to remove acid blue 25 and found that the maximum dye removal was 60.2 mg/g at pH 4.5

Equilibrium of parameters

Adsorption systems provide the basic requirements of the experimental model by giving information about the interaction of adsorbents with the adsorbent and balance parameters such as the adsorbent capacity. Table 2 shows the surface properties, adsorption mechanisms and values of the adsorption model constants expressing the capacity or affinity of the sorbent.

Table 2. Isotherm constants for reactive blue 19 adsorbed by grape pulp carbon

T (°C)	Langmuir model			Freundlich model		
	qmax	Kb	R2	KF	n	R2
25	457.23	0.1645	0.9923	12.33	3.77	0.9854
35	513.52	0.1872	0.9714	15.21	3.91	0.9880
45	582.6	0.264	0.9687	19.65	4.12	0.9967

KF is one of the Freundlich constants as a relative measure of adsorption capacity. KF values increased with an increase in temperature and the highest KF values were determined as 19.65 at 45 °C. The other Freundlich constant n is an empirical parameter that varies according to the degree of heterogeneity, which indicates the degree of linearity between the adsorbent and the dye uptake capacity and the non-adsorbed dye concentration. Since n values obtained from the isotherms are higher than 1.0, the reactive blue 19 was positively adsorbed by grape pulp carbon at all temperatures. The higher value of K at 45 °C indicates that reactive blue 19 at this temperature was strongly bound to grape pulp carbon. As can be seen from Table 2, although the correlation coefficients of the two equations were obtained quite well, the Freundlich model

showed the most suitable for adsorption data than the other model.

Kinetic parameters of adsorption

The so-called first-order linearized and so-called second-order equations and the values of k₁, k₂, q_{eq} and correlation coefficients are given in Table 3. As can be seen from the table, the first-order model with correlation coefficients closed the correlation coefficients of the second-order kinetic model and all correlation coefficients were increased. Mass transfer so-called 1st and 2nd kinetic models were used in the experiments of the sorption method. Interactions of these models with each other were calculated. Outer mass transfer is characterized by the dissolution start rate for the system being studied.

Table 3. Change of the pseudo-first and second-order reaction rate constants with temperature

T (°C)	qeq (mg/g)	Kinetic model			Kinetic model		
		k1(min-1)	qeq (mg/g)	R2	k2(g/mgmin)	qeq (mg/g)	R2
25	362.66	0.04318	340.18	0.954	0.000467	523.08	0.971
35	500.15	0.06721	473.96	0.982	0.000586	562.85	0.983
45	531.07	0.07136	514.27	0.998	0.000664	591.76	0.997

Conclusions

The purpose of this study, It has been determined that the reactive blue 19 textile dye adsorption kinetics of the activated carbon obtained from the grape pulp is compatible with the so-called second-order kinetic model. It has been observed that the diffusion inside and outside the particle is effective in the adsorption process. Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were determined; It has been concluded that the adsorption of reactive blue 19 is an exothermic, voluntary and stable system that runs without structural changes in the solid/liquid interface. The grape pulp studied was determined by FT-IR analysis to include amine, carboxyl, phosphate and alkane groups as well as C-H and C-N bonds. With this study, it was concluded that grape pulp, which is an inexpensive and environmentally friendly agricultural waste, which is abundant in Manisa, can be used as an effective and efficient adsorbent for the treatment of wastewaters containing acidic dyestuffs by the adsorption method.

It was observed that as the initial dyestuff concentration and temperature increased, the activated carbons obtained from the grape pulp increased the balance sorption capacity. It has been determined that the increase of the ambient pH decreases the capacity of the biosorbent to keep the dyestuff from the aqueous solution and gives the highest values of removal efficiency under acidic ambient conditions. As a result, since the grape pulp is low-priced, natural, abundant and easily available, it has been seen from the results that it can be used as an environmentally friendly activated carbon in the removal of reactive dyes as an alternative to other more expensive methods.

REFERENCES

- Ahmad, M.A., Puad, N.A.A., Bello, O.S. (2014). Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. *Water Resource Industry*, 6, 18–35.
- Akar, T., Celik, S., Akar, S.T. (2010). Biosorption performance of surface modified biomass obtained from *Pyraecanthia coccinea* for the decolorization of dye contaminated solutions. *Chemistry Engineering Journal*, 160, 466–472.
- Ali, I., Gupta, V.K. (2007). Advances in water treatment by adsorption technology. *Nature Protocols*, 1, 2661–2667.
- Alkan, M., Doğan, M., Turhan, Y., Demirbas, O., Turan, P. (2008). Adsorption kinetics and mechanism of maxilon Blue 5G dye on sepiolite from aqueous solutions. *Chemistry Engineering Journal*, 139, 213–223.
- Altundogan, H.S. (2005). Cr(VI) removal from aqueous solution by iron (III) hydroxide loaded sugar beet pulp. *Process Biochemistry*, 40, 1443–1452.
- Asgher, M. (2012). Biosorption of reactive dyes: a review. *Water Air Soil Pollution*, 223, 2417–2435.
- Ayed, L., Chaieb, K., Cheref, A., Bakhrouf, A. (2010). Biodegradation and decolorization of triphenylmethane dyes by *Staphylococcus epidermidis*. *Desalination*, 260, 137–146.
- Baseri, J.R., Palanisamy, P.N., Kumar, P.S. (2012). Adsorption of basic dye from synthetic textile effluent by activated carbon prepared from *Thevetia peruviana*. *Indian Journal Chemistry Technology*, 19, 311–321.
- Bharathi, K.S., Ramesh, S.T. (2013). Removal of dyes using agricultural waste as low cost adsorbents: a review. *Apply Water Science*, 3, 773–790.
- Clarke, E.A., Anliker, R. (1980). *Organic Dyes and Pigments Handbook of Environmental Chemistry. Anthropogenic Compounds*, 3, 181–215.
- Couglin, R.W., Ezra, F.S. (1968). Role of surface acidity in the adsorption of organic pollutants on the surface of carbon. *Environment Science Technology*, 2, 291–297.
- Dursun, G., İcek, H.C., Dursun, A.Y. (2005). Adsorption of phenol from aqueous solution by using carbonized beet pulp. *Journal Hazardous Materials*, 125, 175–182.
- Farah, J.Y., El-Gendy, N.S., Farahat, L.A. (2007). Biosorption of Astrazone Blue basic dye from an aqueous solution using dried biomass of Baker's yeast. *Journal Hazardous Materials*, 148, 402–408.
- Faria, P.C.C., Órfão, J.J.M., Pereira, M.F.R. (2004). Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. *Water Research*, 38, 2043–2052.
- Ferrero, F. (2007). Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust. *Journal Hazardous Material*, 142, 144–152.
- Findon, A., McKay, G., Blair, H.S. (1993). Transport studies for the sorption of copper ions by chitosan. *Journal Environment Science Health A*, 28, 173–185.
- Gupta, V.K., Jain, R., Mittal, A., Mathur, M., Sikarwar, S. (2007). Photochemical degradation of the hazardous dye Safranin-T using TiO₂ catalyst. *Journal Colloid Interface Science*, 309, 464–469.
- Gupta, V.K., Jain, R., Malathi, S., Nayak, A. (2010). Adsorption desorption studies of indigocarmine from industrial effluents by using deoiled mustard and its comparison with charcoal. *Journal Colloid Interface Science*, 348, 628–633.
- Gupta, V.K., Ali, I., Saini, V.K. (2007). Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA13 from aqueous solutions using carbon slurry developed from a waste material. *Journal Colloid Interface Science*, 315, 87–93.
- Hamaaed, B.H., Daud, F.B.M. (2008). Adsorption Studies of Basic Dye on Activated Carbon Derived from Agricultural Waste: *Hevea Brasiliensis* Seed Coat. *Chemical Engineering Journal*, 139, 48–55.
- Ho, Y.S., McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, 34, 451–465.
- Jain, R., Gupta, V.K., Sikarwar, S. (2010). Adsorption and desorption studies on hazardous dye Naphthol Yellow S. *Journal Hazardous Material*, 182, 749–756.
- Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. *Journal of the American Chemical Society*, 38 (11), 2221–2295.
- Lagergren, S. (1898). Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskaps akademien, handlingar*, 24, 1–39.
- Lee, J.W., Choi, S.P., Thiruvengatachari, R., Shim, W.G., Moon, H. (2006). Evaluation of the performance of

- adsorption and coagulation processes for the maximum removal of reactive dyes. *Dyes Pigments*, 69, 196–203.
- Mittal, A., Mittal, J., Malviya, A., Gupta, V.K. (2010). Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. *Journal Colloid Interface Science*, 344, 497–507.
- Robinson, T., McMullan, G., Marchant, R., Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77, 247–255.
- Ramakrishna, K.R., Viraraghavan, T. (1997). Dye removal using low cost adsorbents. *Water Science Technology*, 36, 189–196.
- Slokar, Y.M., LeMarechal, A.M. (1997). Methods of decoloration of textile wastewaters. *Dyes Pigments*, 37, 335–356.
- Smith, J.M. (1981). *Chemical Engineering Kinetics*, 3rd ed., McGraw-Hill. Singapore.
- Smith, J.M., Van Ness, H.C. (1987). *Introduction to Chemical Engineering Thermodynamics*. 4th ed., McGraw-Hill, Singapore.
- Özdüven, M.L., Coşkuntuna, L., Koç, F. (2005). Üzüm posası silajının fermantasyon ve yem değeri özelliklerinin saptanması. *Trakya University Journal Science*, 6(1), 45-50.