Investigation of Dyes Adsorption with Activated Carbon Obtained from *Cordia myxa*

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Abstract: The objectıve of this article is to investigate the adsorption of dye from aqueous solution using Cordia myxa as the target adsorbent. In the adsorption experiments active carbon (*Cordia myxa*) were used in raw form, treated with ZnCl2 and sonic wave. Experimental studies have shown that C.I. Disperse Blue 56 (C.I.D.B 56) dye adsorption of active carbon obtained from (*Cordia myxa*) is maximum at pH 7. The adsorption process was completed in 60 minutes and about 80% were completed in the first 30 minutes. The best adsorption took place at 25°C. All adsorption events are fit in with pseudo 2nd order reaction kinetics and adsorption equilibrium is fit in with Freundlich Isotherm. The using of sonic wave in activated carbon (*Cordia myxa*) preparation increased the surface area 2,5 times. Sonic wave activation created bubbles and new pores when viewed from SEM photographs. In particular, it has been determined that sonic wave is an effective method for preparing activated carbon. When thermodynamic parameters are taken into account, it is determined that no external energy is required for the adsorption to occur and the physical events are more dominant in the adsorption.

Keywords: Adsorption, *Cordia myxa*, Dye, Aqueous solution, Kinetics, Isotherm, Thermodynamics

1. Introduction

Recently waste products to the environment represent one of the important problem in the world that has been highlighted by many research deals with environmentalist field. There are many kinds of waste produced from industries such as colored organic wastes, textiles, rubber, paper, plastic, cosmetics, etc. Discharging of dyes into water resources which can affect the hydrous life and food web. Dyes can also cause different kinds of skin diseases. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms. The possesses of treatment for painter in industrial wastewater have many difficulties since painters are generally difficult degenerate to biologically. Many different techniques have been used for the removal of colored dyes from wastewater such as oxidation, nano filtration, ozonation and coagulation (Yesilada et al., 2002; Ugurlu and Gurses, 2007).

The greatest environmental concern problem deals with dyes absorption and reflection of sunlight that entered to the water which interferes on the growth of bacteria to levels cannot biologically degrade impurities in the water. pigment in effluents can effect as follows:

1. Pigment may have acute and/or chronic effects on exposed organisms dependence on the exposure time and dye concentration.

2. Pigments are inherently highly visible, meaning that concentration as low as 0.005 ppm capture the attention of both the people and the resrechs.

3. Pigments absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosyn article in aquatic plants (Skolar and Marechal, 1998).

The annual production of pigments in the world is about 7×105 t, 5–10% of textile industries. The important of treatment of these pigments are of characteristics origin and toxic in nature with suspected carcinogenic and genotoxic effects (Sudipta et al., 2005). It is clear that 10-25% of textile pigments are lost during the dyeing process, and 2-20% of such dyes are directly released as aqueous effluents in different environmental

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constituents (Baban et al., 2010). Leading to clear water pollution, a great problem in modern era. The World Bank has estimated that almost 20% of dyeing (Kalaiarasi et al., 2012). In general, dyes are low degradable materials or are not effect by environmental conditions (Crini, 2006). The main methods which are used to remove or treat colored effluents are oxidation, coagulation and flocculation, biological treatment, membrane filtration, etc. furthermore, these methods are not enough to remove certain forms of color, particularly those arising from reactive dyes as a result of their high solubility and low biodegradability (Tsai et al., 2001). Adsorption treatment method is an effective alternative method used to remove of paint from waste water. The adsorption treatment has many advantages, such as less sensitivity to daily change, less susceptibility to toxic chemicals, greater flexibility in design and operation, and superiority in the removal of organic pollutants, with less space (half or quaternary as needed in a biological system) (Vijayaraghavan et al., 2009).

The main factors effect on adsorption process are:
1. The main properties of the active carbon (i.e., surface area, pore size, chemical composition, etc.)
2. The main properties of the dyes (molecular size, molecular polarity, chemical composition, etc.).
3. The concentration of the adsorbate in the solution.
4. The characteristics of solution (pH, temperature).
5. The contact time of the system (Amin, 2008).

The adsorption of the activated carbon is highly effective elemant which is used to removing dyes and pigments (Bhatia, 2001), such as clay minerals (Meshko et al., 2001), bottom and fly ash (Forgacs et al., 2004; Kadirvelu et al., 2000), fungi (Wang et al., 2004), waste materials from agriculture representing an essential target for these countries (Wang et al., 2010; Jason et al., 2003).

In addition, a series of recent studies have focused on the adsorption of some dyes (acid, basic, reactive and metal compound) with chips of different woods. In general, there are two processes for preparing activated carbon physical activation and chemical activation process. As compared of physical activation, the chemical activation has two important advantages. The first is that the temperature at which the process is performed is low. The other is that there is not much need for carbonization during chemical

global industrial water pollution comes from the treatment process and different kinds of textiles

activation. Numerous water absorbers or field desiccants include chemical agents commonly used in the preparation of zinc chloride active carbon (Rao et al., 2006). Development of nano porous structure in by chemical activation carbons with Zinc Chloride wıll lead to high adsorption of carbon for dyes and pigments (Ahmadpour and Do, 1997; Mohanty et al., 2005; Kannan and Rengasamy, 2005; Ugurlu et al., 2007). Furthermore, different variables during the activation process are very important in increasing the porosity of carbon sought.

The ultrasonic wave causes the phenomenon known as cavitation in the environment where microscopic bubbles grow in the liquid medium and result in explosion. This Sudden explosive collapse of these bubbles, " hot spots " can enhance various chemical and physical processes. (Mason and Peters, 1999; Suslick et al., 1986). In other words, localized high temperature, high pressure, shock waves and strong cutting force can break chemical bonds. (Kamel et al., 2003; El-Shishtawy et al., 2003). The acoustic flow caused by the sonic wave is the action of liquid, which can be thought of as a kinetic energy conversion of sound. This event increases the mass transfer rate near the surface (Chakma and Moholkar, 2011; Kuppa and Moholkar, 2010). Ultrasonic processing is practically used in wastewater treatment due to the high productivity of chemically hazardous pollutants, biologically degradable biological objects, saprophytes and pathogenic microorganisms, water purification from viruses, microscopic environments. Ultrasonic purification is an effective and ecological method for removing water from organic and microbiological components (Dos Santos Fernandes et al., 2011). The aim of this work is to convert the *Cordia myxa* fruits to active carbon by thermal, chemical and ultrasonic methods to show the potential of adsorbing the C.I. Disperse Blue 56 Disperse dye of the obtained activated carbon.

2. Materials and methods

2.1. Dye solution preparation

C.I. Disperse Blue 56 (C.I.D.B56) is a Disperse dye., (CI= 63,285, chemical formula $C_{14}H_9BrN_2O_4$, CAS 31810-89-6, MW=349,1391 g.mol-1, and λmax=556 nm .dye solutions (1000

mgl-1) were prepared by dissolving 0.005 g of dye 1 L of double distilled water. The dye was filtered 3 time by using a paper filter. Chemical structure of the dye is shown in Figure 1.
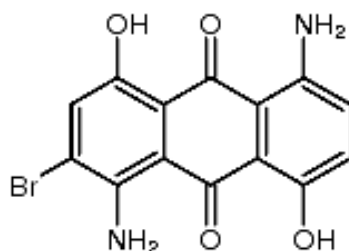

Figure 1. Molecular structure of C.I. Disperse Blue 56.

2.2. Preparation and characterization of activated carbon

2.2.1. Preparation of activated charcoal (raw 400 °C)

C. myxa was collected from local trees in Baghdad (Iraq). The collected material was washed with double distilled water to remove water-soluble impurities and surface-adhered particles. Then, the adsorbent was oven dried at 105 °C to remove the moisture and other volatile impurities.

Two various methods for the prepare the activated carbon: physical activation and chemical activation methods (Ho et al., 2005). Chemical activation provides advantages which the dye removal was applied in batch mode. Adsorption experiments were obtained by suspending charcoal in the effluent and analyzing the supernatant by spectroscopic method. The resulting impregnated solids were placed in the capsule, Nitrogen flow at a rate of 150 cm3 min-1 at the capsule for 3 minutes. And after the capsule was placed in a stainless-steel tubular reactor and heated to a temperature of 400 °C for 2h This process occurs under the nitrogen gas environment. The products were soaked in concentrated 0.5 M HCl in a enough amount to overlay the material completely for 24 hour. The products were washed sequentially with low temperature distilled water to expel residual organic and mineral materials and continuous washing to become. The pH of the wash water is about (6 - 6.5) and then dried at 105°C for 24 h. (Do and Ahmadpour, 1997). The heating rate and nitrogen flow were kept constant in all experiments. Dried *Cordia myxa* grinded with mortar then passed through sieve of 425-micron size. The preparate method of the activated charcoal has been obtained in the following flowchart (Chart 1):
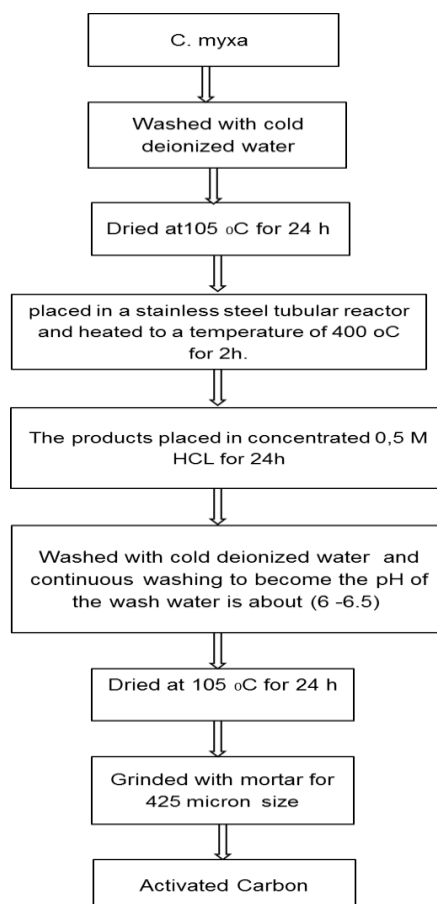

Chart 1. For the preparation of activatedcharcoal from *C. myxa*

2.2.2. Preparation of activated charcoal by use zinc chloride and the sonic wave assisted (400 °C + ZnCl2 + sonic wave)

In this preparation procedure, sonic wave application and chemical activation with $ZnCl_2$ was applied to the activated carbon that was produced by physical activation procedure. The procedure was carried out by diluting 0.5 g activated carbon in 100 mL of $ZnCl_2$ solution and mixing the resulting solution for 12 h on a magnetic stirrer. After mixing completed, the solution filtered and oven dried for 24 h at 105 °C. Then, dried materials were diluted in 100 mL distilled water in a beaker. The solution subjected to sonic wave application by using sonic frequency

of 20 kHz with powers (750 W) for 20 min. Furthermore, after this procedure, the final product was filtered by using a paper filter and dried in oven at 105 °C at 24 h to remove the moisture and other volatile impurities. The procedure of the activated charcoal preparation by using zinc chloride and sonic wave has been presented in the following flowchart:
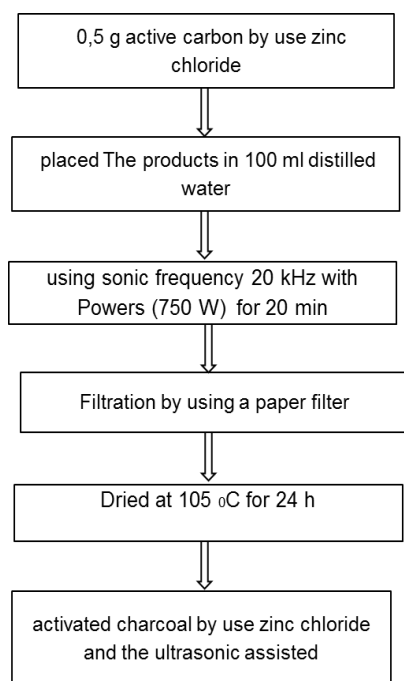

Chart 2. The preparation of activated charcoal by use zinc chloride and the sonic waveassisted from *C. myxa*

2.3. Batch equilibrium studies

The process of dye removal was applied in batch mode for all experiments. These experiments were performed by diluting charcoal in dye solutions. Equilibrium experiments for the adsorption process onto the selected activated carbons were carried out by using 0.1 g of adsorbent per 25 ml of dye solution. The pH value of the solution in each flask was adjusted between 1-9 with HCl and NaOH solutions. The mixtures were agitated on a shaker incubator at a constant speed of 150 rpm for a constant time of 240 min. When the time is over, the solution in each bottle centrifuged at 10.000 rpm for 10 minutes. The influence of pH was also studied by adjusting the reaction mixture to different initial pH values and analyzing the residual color at the equilibrium contact time.

2.4. Analysis

The concentration of C.I. D.B. 56 was determined and it has constant value in the supernatant after and before adsorption with a 1.0 cm light path quartz cells using UV-Visible spectrophotometer (Hach DR 5000). at λ_{max} of 549 nm, Prior to the measurement a calibration curve was calculated by using the standard C.I. D.B. 56 solution with known concentrations.

Then the ratio of dye removal was obtained by using the following relation:

$$\% Ad = (C_0 - C_e) / C_0 * 100 \qquad (1)$$

The amount of dye adsorbed onto the activated carbons, q_e (mgg^{-1}), was obtained according to:

$$q_e = (C_0 - C_e)v/w \qquad (2)$$

Where C_0 and C_e are the initial and the final dye concentrations (mg l^{-1}), respectively, and W is the amount of adsorbent (g), V is the volume of the solution (L) (Ran Zhao et al. 2010).

3. Results and Discussions

3.1. Character of character of *C. myxa*

The BET surface area was obtained from N_2 adsorption isotherms by using the Brunauer–Emmett–Teller (BET) equation (Gregg and Sing, 1982). Physical characterizations of *C.myxa* were given in Table 1. The microstructure of *C.myxa* plays an important role on the adsorption capacity. It is well know from the existing literature that surface area of an activated carbon produced from several agricultural by-products becomes greater than that of its raw form after it is subjected to physical or chemical treatments. In this study, the reason of why surface area of the activated carbons examined did not increase so much can be referred to the low lignin content of the adsorbent material, of which fruits were used as adsorbent.

Table 1. Physical characterization of *C.myxa*

Parameters	Value (raw 400 °C)	Value (400 °C + ZnCl2+ sonic wave)
BET surface area (m²g⁻¹)	1.38	5.95
pore volume (cm³g⁻¹)	0.0023	0.0095
PORTION SIZE (nm)	6.84	6.42

Fig.2 show the Scanning Electron Microscopy (SEM) analysis of activated carbon *(C. myxa)* as raw material (*C.myxa*) and the active carbon from (raw *C.myxa*). SEMs of the (raw *C.myxa*) explain the development of porosity of the prepared activated carbons after activation and carbonization at the optimum operating conditions with x334-1000 magnification. From Figure 2, it appears that the outer surface is filled with voids. Furthermore, SEM showed different preparation conditions with different porosity. In addition, porosity also depends on the starting material (El-Sheikh et al. 2004).
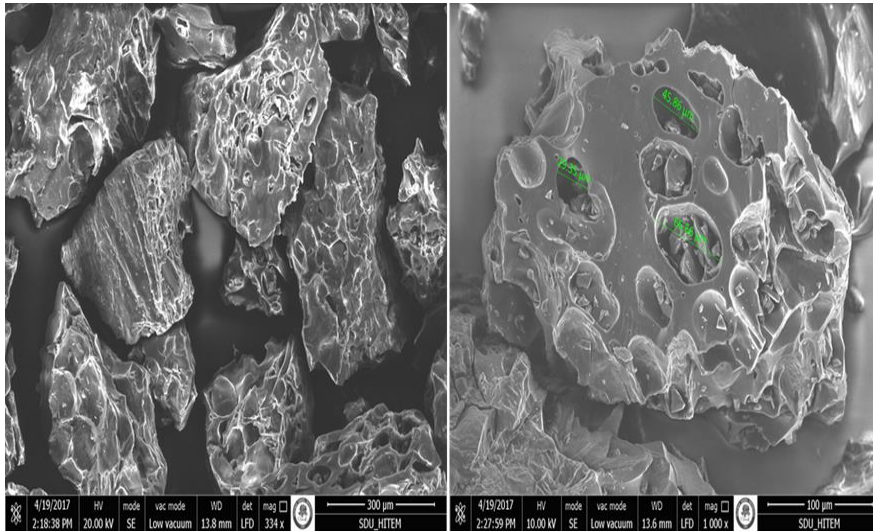

Figure 2. SEM of Produced activated carbon at 400°C raw SEM images of the sample at x334-1000 magnification

Figure 3 shows SEM image of the activated carbon obtained by (physical activation + chemical activation + sonic wave) applications. It is clearly seen that the pores formed in different shapes and sizes. This result imply that this examined activated carbon had more pore openings. It was thought that cracks, which are formed as a result of treatment with $ZnCl_2$, were broken up by the effect of the sonic cavitation, and new pores are formed. In the same way, an increase in the specific amount is observed but the surface area is increased to a small extent.
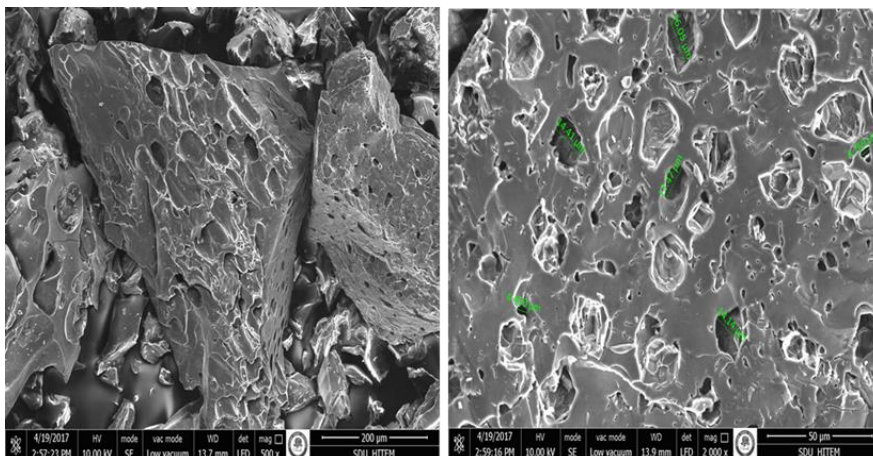

Figure 3. SEM of Produced activated carbon At 400°C+$ZnCl_2$+ sonic wave SEM images of the sample at x500-2000 magnification

3.2. Effect of pH

The results of the experiments carried out to determine the effect of pH change on the adsorption are presented in Figure 4. (a) raw 400 °C. As shown in Figure 4. (a) raw 400 °C, the highest specific capture value was anticipated at pH 1. With higher pH, the specific trapping amount of sorbent dye was reduced to 2,02 mg / g at pH 3. After pH 3, the capture increased to 3.4 mg/g at pH 5. After this value, the pH do not stay constant for capturing, while at pH 7,8 and 9 the trend did not show any appreciable increase and decrease. pH is an important parameter in adsorption since it affects the surface character of the adsorbent, as it affects the behavior of the adsorbate in solution. Therefore, it is absolutely necessary to determine the optimum pH value in each adsorption run. As the pH increased, the negatively charged sites on the sorbent surface increase whereas the positively charged sites decrease. C.I. D.B 56 dye. This means that the positively charged region will allow the electrostatic quartz to enter the circuit. Negatively charged surface areas on the adsorbent do not favor adsorption of dye anions due to electrical repulsion. If the pH value of the solution is high during the adsorption of anionic dyes, the OH- ions enter the dye anions and the adsorbent surface does not prefer to adsorb dye anions (Özcan and Özcan, 2004). For this reason, the raw *Cordia myxa* plant was exposed to 400 °C pyrolysis to obtain activated carbon. By decreasing the pH value, activated carbon surface is protonated and anionic color is retained. The change in adsorption efficiency with pH value is shown in Figure 4.(a) raw 400 °C. Thus, Optimum pH value was taken as 5 despite this value not the maximum. when the pH value taken 1 meaning there is an excess acid in the solution.

The change of adsorption phenomenon by pH value is presented in Figure 4. (b) 400 °C+ZnCl$_2$ + sonic wave. As shown in Figure 4. (b) 400 °C+ZnCl$_2$+ sonic wave, the maximum specific capture value was increased up to 3.22 mgg^{-1} at pH1, while the pH increased, sorbent specific capture amount decreased to this pH was 2.78 mg g^{-1} at pH 3. After pH 3, the capture was increased to 3.11 mg g^{-1} at pH 4. After this value, the pH do not stay constant for capturing. This increase continued until pH 7. The capture amount at pH 7 was approximately 3.47 mgg^{-1}. Therefore, the optimum pH value was taken as pH 7. Subsequent sorption experiments were carried out at pH 7 have indicated that dye solubility pH values play an important role in adsorption capacity and adsorption (Bousher et al., 1997).
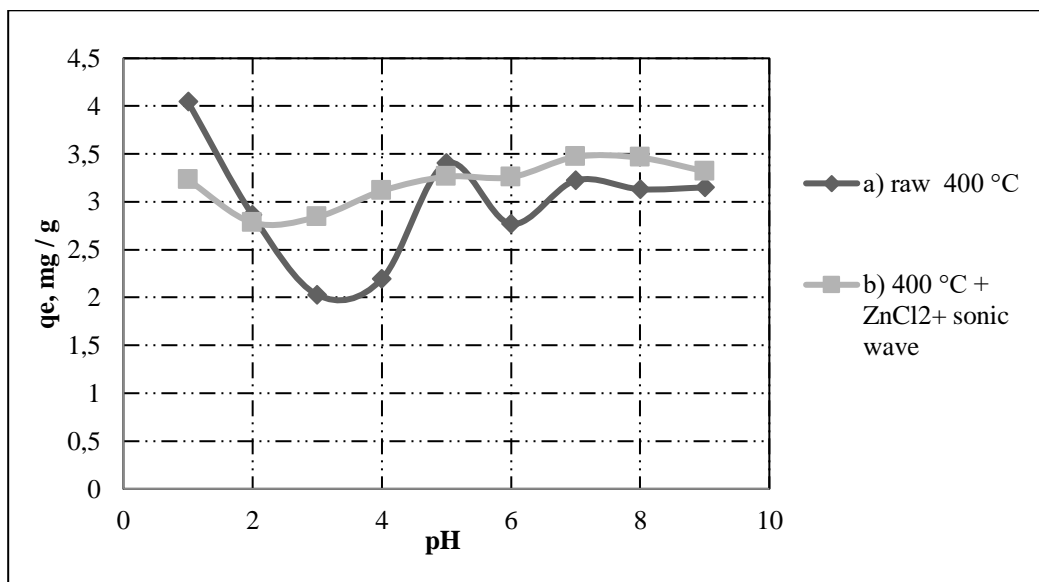

Figure 4. Effect of pH on the removal of dyes (a) raw 400 °C at 25 °C(b) 400°C+ZnCl$_2$+ sonic wave at 25°C

3.3. Effect of adsorbent dosage

Equilibrium data, known as adsorption isotherms, are one of the important parameters that must be known for the design of adsorption systems. Equilibrium data must be obtained experimentally before designing adsorption systems. In this study, it was researched whether the Langmuir and Freundlich isotherms, which have a lot of use in adsorption studies and environmental engineering, fit the experimental data. The coefficients of these isotherms were calculated for a given pH, initial concentration, temperature, and mixing rate. By using these coefficients, it is tried to have knowledge about active carbon dye adsorption. The experimental data obtained during the adsorption of the activated carbon are shown in Figure 5.(a) 400 ° C raw. Figure 5.(a) 400 °C raw shows that capacity decreases as the amount of adsorbent increases. When the amount of adsorbent increases, q_e decreases. Adsorbent adsorbed with increasing dose per gram of adsorbent can be explained by the amount of the dye adsorption q_e reduction unit. As the adsorption dose increases, the amount of adsorbed is actually increased, but when the adsorbent is calculated per unit, the q_e value, ie, the unit adsorption is less. In the adsorption with activated carbon, q_{max} appeared to be 6.80 mgg^{-1} at a dosage of 0.1 g.

The experimental data obtained during the adsorption of C.I.D.B 56 with activated carbon obtained by exposure of the chemically activated carbon to the sonic wave are presented in Figure 5.(b) 400 °C+ZnCl$_2$+ sonic wave. Figure 5.(b) 400 °C+ZnCl$_2$+ sonic wave shows that as the amount of adsorbent increases, q_e decreases. q_e reduction of the amount of adsorbed per gram of adsorbent with increased adsorbent desorption can be explained by unit adsorption. As the adsorption dose increases, the amount of adsorbed is actually increased, but when the adsorbent is calculated per unit, the qe value, ie, the unit adsorption, is less. In the adsorption with activated carbon, q_{max} was found to be 6.93 mg g^{-1} at a dosage of 0.1 g (Karim et al., 2006).
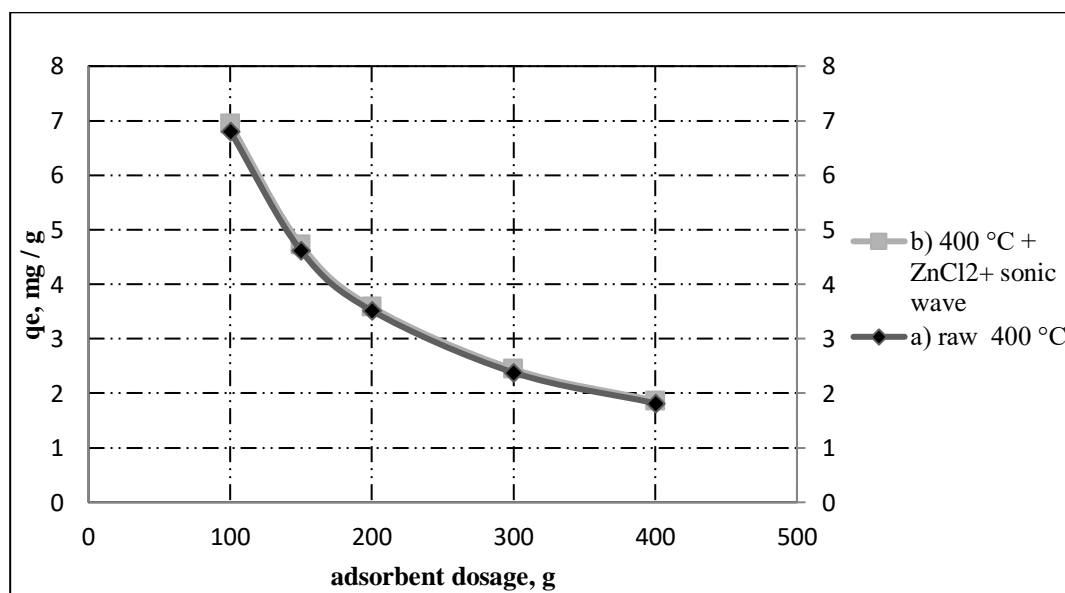

Figure 5. Effect of adsorbent dosage on the removal of dyes (a) raw 400°C (pH 5at 25 °C) (b) 400°C+ZnCl$_2$+ sonic wave (pH 7 at 25 °C)

3.4. Effect of contact time

In order for the adsorption effect to occur, the adsorbent and the adsorbed material must contact for a certain period of time. The determination of the rate of adsorption to reach the equilibrium is important for the application of sorbent. The data obtained during the determination of the contact time also gives information about the speed of the process. In this way kinetic constants are obtained and reactor design data is obtained during application. In order to accurately determine the kinetic data of the adsorption kinetic the dye in the solution it is necessary to carry out test studies

(McKay et al., 1999). The data obtained as a result of kinetic studies are presented in Figure 6. (a) 400 °C. As shown in Figure 6. (a) 400 °C, the effect on the carbon adsorption capacity of the contact time is constantly increasing within the first 30 minutes and at this point approximately 80% of the adsorption phenomenon is patchy. After 240 minutes, the specific capture rate of the sorbent dye is 3.4 mg g^{-1}. After 30 minutes the sorption reaction is completed in approximately 240 minutes, with no significant increase in 60 and 120 minutes. The completion of the majority of the adsorption reactions in the first 30 minutes is an indication that the physical reactions predominate in the adsorption mechanism. By mixing, the water boundary layer around the sorbent particles is broken down. Thus, the layer from which the solubilizing dye molecules will resist the sorbent diffusion is rising. When this layer is raised from the center, the dye molecules can be retained on the surface and pores of the sorbent. The low result may be explained by a discrepancy between the sorbent porous diameter and the size of the dye molecules. The dye molecules are bigger than the pores on the sorbent surface, so the adsorption is not as high as expected. It can be said that chemical reactions are more intense in the trapping process after 30 minutes. The reason for this is that the adsorption phenomenon is slow. performed dye adsorption with activated carbon from sawdust and emphasized that the size of the carbon pore and the size of the dye molecules are important in adsorption at the end of contact time studies. On the other hand, the work carried out was similar to that of this study and most of the adsorption was completed in the first 15 minutes. After 15 minutes the capture slowed down and suggested the idea that the dye was held as a single layer on the sorbent. at the first 15 minutes, the surface of the sorbent with time going inward through the cracks have been found, the voids are filled with the dye molecules in the solution. This is happening slowly (Malik, 2004).

Experiments for the exchange of adsorption phenomenon with contact time are the results obtained. Presented at 6. (b) 400 °C+ZnCl$_2$+ sonic wave. As shown in Figure 6. (b) 400 °C+ZnCl$_2$+ sonic wave, the effect of the contact time on the carbon adsorption capacity is continuously increasing within the first 30 minutes and at this point more than about 90% of the adsorption process is completed. After 240 minutes, the specific capture rate of the sorbent dye is 3.42 mg g^{-1}. After 30 minutes, the sorption reactions is completed in approximately 240 minutes, with no significant increase in 60 and 120 minutes. Data obtained as a result of kinetic studies Presented at Figure 6. (b) 400 °C+ZnCl$_2$+ sonic wave. As shown in Figure 6. (b) 400 °C+ZnCl$_2$+ sonic wave the effect of the contact time on the carbon adsorption capacity is continuously increasing within the first 30 minutes and at this point approximately 92% of the adsorption process is completed. After 240 minutes, the specific capture rate of the sorbent dye is 3.49 mg g^{-1}. After 30 minutes, the sorption reactions is completed in approximately 240 minutes, with no significant increase in 60 and 120 minutes. The completion of the majority of the adsorption reactions in the first 30 minutes, as in the other adsorption runs, is an indication that the physical reactions predominate in the adsorption mechanism. After 30 minutes, the chemical reactions in the capture process may be more intense. The reason for this is that the adsorption phenomenon is slow.
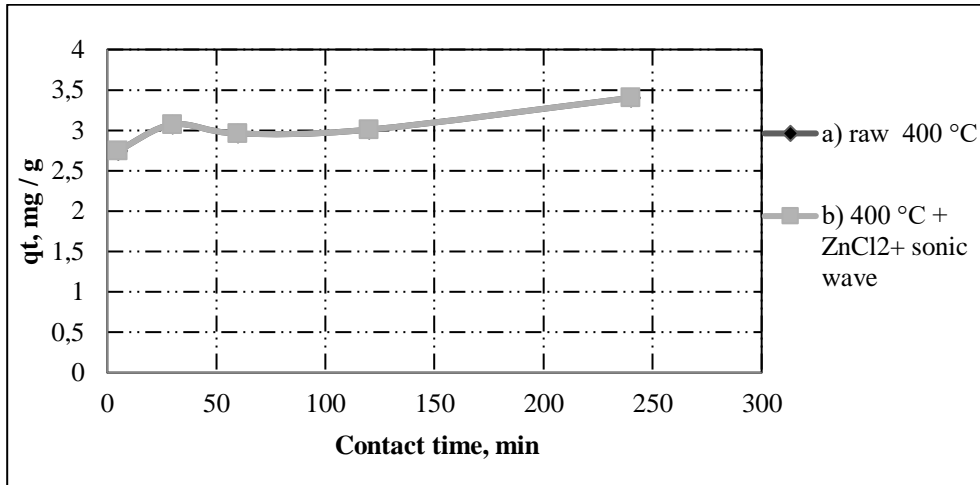
Figure 6. Effect of contact time on the removal of dyes (a) raw400°C (Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 5 at 25°C) (b) 400 °C+ZnCl$_2$+ sonic wave (Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 7 at 25°C).

3.5. Adsorption kinetic study

3.5.1. Pseudo-first-order model

Depending on the absorption capacity of the adsorbent, Lagergren's (McKay et al., 1999) first order velocity expression is shown as follows:

$$dqt/dt=k_1(qe-qt) \tag{3}$$

Where qt is the amount of contaminant adsorbed on the adsorbent at time t, and k1 is the Lagrangian first order adsorption rate constant. After combining and boundary conditions from t = 0 to t = t and qt = 0 to qt = qt, the union of equation 4 becomes:

$$log(qe-qt) = logqe-(k_1/2.303) *t \tag{4}$$

Where qe and qt are the adsorbed amount (mgg^{-1}) at equilibrium and at any time t, and k1 is the velocity constant (min^{-1}). The plot against log (qe-qt) gives a straight line for the adsorption kinetics at first order. The value of the velocity constant from the first order is obtained from the slope of the straight line k$_1$.

3.5.2. Pseudo second order kinetics

The second order equation is based on the absorption capacity of the solid phase. (Martell AE and Smith RM, 1977). Unlike the other model, the concentration predicts behavior over the entire range. This can be called second order kinetic velocity equation and can be written as follow:

$$dqt/dt=k_2(qe-qt)^2 \tag{5}$$

Where K$_2$ is the second order rate constant (min g mg^{-1}), q$_e$ and q$_t$ represent the amount of dye (mg g^{-1}) adsorbed at equilibrium and at any time. The separation of the variables in Eq.6 :

$$dqt/(qe-qt)^2=k_2t \tag{6}$$

Where k$_2$ is the rate constant of the second order adsorption. The combined and linear form of equation 7 for boundary conditions t = 0, t = t and qt = 0, qt = qt is as follows:

$$t/qt=1/(k_2*qe)^2+(1/qe)*t \tag{7}$$

By using the data between the contact time and the adsorption to determine the adsorption kinetics. The data obtained for this purpose were applied to pseudo 1st and 2nd degree kinetic values. The graph drawn for the pseudo first degree kinetic data is shown in Figure 6. (a) 400raw, and the graph drawn for the pseudo second degree kinetic data is shown in Figure 7.(a) raw 400. The constants of the kinetic formulas are given in Table 2. As seen in Table 2, it appears that the kinetics of the adsorption correspond the pseudo second order kinetic equation. Looking at the R^2 values of the plotted graphs, the R^2 value of the pseudo first order kinetic equation is obtained as 0.379, while

the R^2 value of the pseudo second order kinetic equation is obtained as 0.99. When determining the kinetic equations, the first thing to note is that the regression coefficient is high. It is believed that the quinine, which is high in R^2, explains the reactions. Accordingly, the kinetics of the adsorption between the activated carbon obtained by burning at 400 °C and the C.I.D.B 56 dye is explained by the pseudo second order kinetics, because the regression coefficient for the pseudo first order kinetics is 0.379 while the regression coefficient for the second order pseudo is greater than 0.99. On the other hand, when the qe values obtained from the equilibrium are compared, the pseudo second order kinetic equation predicts closer results than the pseudo first order kinetic equation. The qe value estimated by the experimentally obtained q_e=3.40 mg g^{-1}, pseudo first order kinetic equation was q_e=2.51 mg g^{-1} while the q_e value calculated using the pseudo second order kinetic equation was q_e=3.41 mg g^{-1}. Many kinetic models are used to determine the reaction rates of adsorption systems. The commonly used kinetic model is a pseudo-first order reaction equation (Ho and Wang, 2006]. The pseudo first order kinetic equation is a first order equation that evaluates the adsorption ratio according to adsorption capacity (Ho, 2006). The pseudo first-order kinetic equation fits not the whole contact time but the first 20-30 minutes. The k_1 value of the pseudo first order kinetics equation varies depending on the initial adsorbate concentration. Usually, the value of k_1 decreases with increasing adsorbate concentration. The

pseudo second-order velocity equation developed by Ho in 1995 showed that the velocity is independent of the adsorbate concentration, the adsorption capacity in the solid phase and the time dependence. k_2 value often varies depending on operating parameters such as initial concentration of adsorbate, pH, temperature and agitation intensity. Generally, where the k_2 value interprets as a time-scaling factor, the k_2 value decreases as the concentration of adsorbate in the liquid phase increases. The pseudo second degree equality is also interpreted as a special kind of Langmuir kinetics. This interpretation assumes that the adsorbate concentration remains constant over time and depends on the adsorbed concentration of adsorbate (Gupta and Bhattacharyya, 2011).

By using the data between the contact time and the adsorption to determine the adsorption kinetics. The data obtained for this purpose are pseudo. And second-order kinetic values. Figure 6.(b) 400°C+ZnCl$_2$+ sonic wave for pseudo first-order kinetic data, and Figure 7. (b) 400°C+ZnCl$_2$+ sonic wave for pseudo second-order kinetic data. The constants of the kinetic formulas are given in Table 2. By using the data between the contact time and the adsorption, to determine the adsorption kinetics. The data obtained for this purpose are pseudo. First-order kinetic and second-order kinetic values. Figure 6.(b) 400°C+ZnCl$_2$+ sonic wave for pseudo first-order kinetic data, and Figure 7.(b) 400°C+ZnCl$_2$+ sonic wave for pseudo second-order kinetic data. The constants of the kinetic formulas are given in Table 2.

Table 2. Kinetic parameters for the removal of C.I.D.B 56 by *C.myxa*

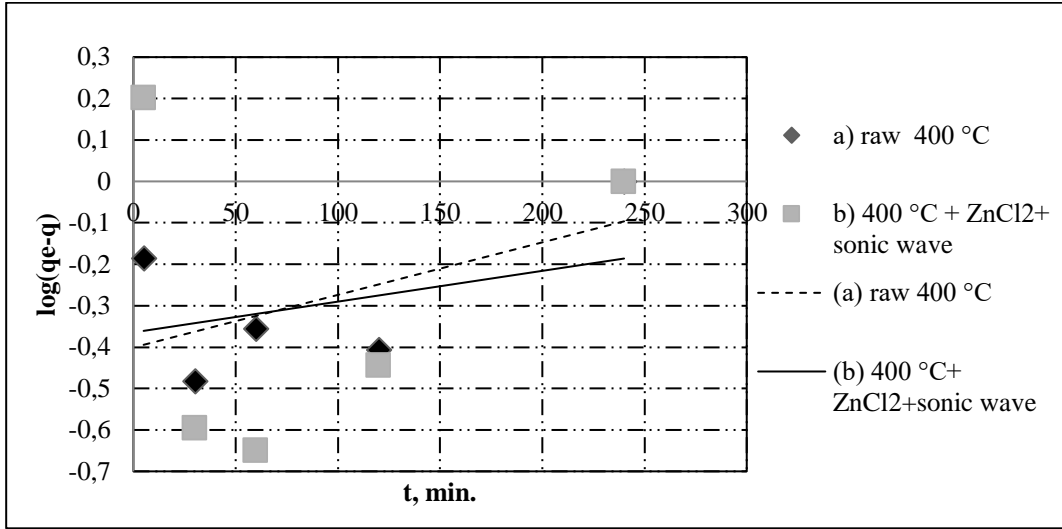| Pseudo-first-order constants	$q_{e(exp)(mg\,g^{-1})}$	K_1	$q_{e(cal)\,(mg\,g^{-1})}$	$R^2_{(liner)}$
raw 400 °C	3,40	-0,0029	2,51	0,37
400°C + ZnCl$_2$+ sonic wave	3,46	-0,0016	2,31	0,33
Pseudo-second-order Constants	$q_{e(exp)(mg\,g^{-1})}$	K_2	$q_{e(cal)\,(mg\,g^{-1})}$	$R^2_{(liner)}$
raw 400 °C	3,40	0,047	3,41	0,99
400 °C + ZnCl$_2$+ sonic wave	3,46	0,051	3,49	0,93

Figure 7. Kinetics of dye removal according to the pseudo-firstorder model (a) raw400°C (Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 5 at 25°C) (b) +ZnCl$_2$+ sonic wave (Carbon content 0.1 g, dye concentration 100 mg l^{-1},pH 7 at 25 °C)
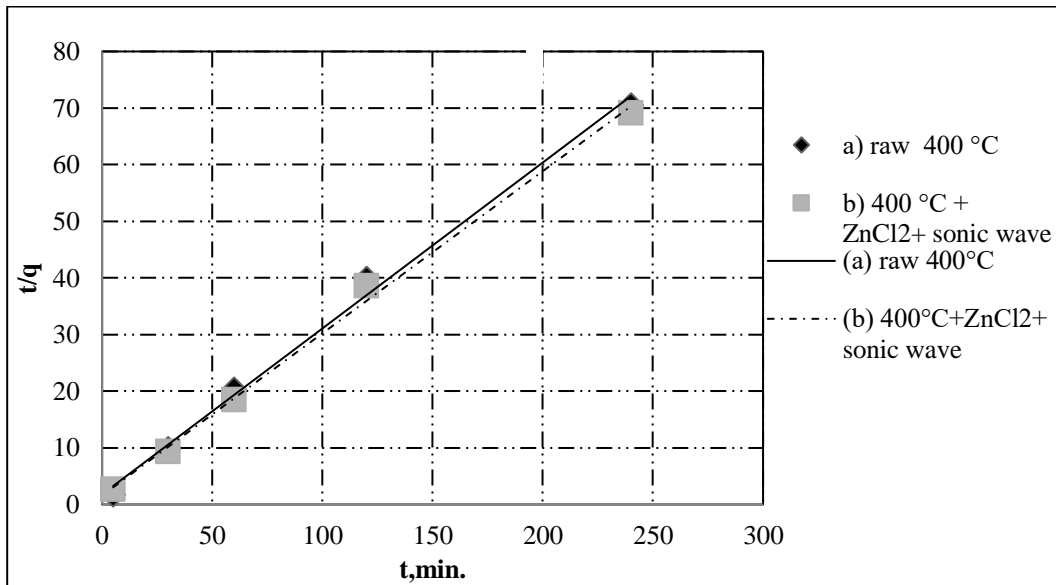

Figure 8. Kinetics of dye removal according to pseudo-second order model (a) raw400°C (Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 5 at 25°C) (b) 400°C+ZnCl$_2$+ sonic wave(Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 7 at 25°C)

3.6. Adsorption isotherm

The adsorption isotherm mentions how the adsorption molecules arrange between the liquid phase and the solid phase when the adsorption process at equilibrium state. The fitting of the isotherm analysis data as different isotherm models

is an important step to obtained the suitable model that can be used for design purposes (El-Guendi, 1991).

The adsorption isotherm is a functional expression for the change of adsorbate against with concentration of substance at temperature with

constant value (Weber, 1972). Upward convection isotherm is suitable because a relatively high solid load can be obtained at low concentration in the liquid. An upwardly concave isotherm is called ineffective because it produces a relatively low solid load and causes a relatively long mass transfer zone in the bed. The linear isotherm passes through and the adsorbed amount is proportional to the concentration in the liquid. From these curves, adsorption will be recorded as a specific property depending on the nature of the adsorbate-adsorbent system (McCabe et al., 1993).

3.6.1. Langmuir isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (T.W. Weber and R.K. Chakravorti., 1974). The Langmuir equation is given in Equation 8 (Langmuir, 1918).

$$qe=(q_{max}*K_L*Ce)/(1+K_L*Ce) \qquad (8)$$

When the equation is rearranged

$$Ce/qe=(1/q_{max}*K_L)+(Ce/q_{max}) \qquad (9)$$

Where qe is the amount of dye adsorbed (mgg^{-1}), q_{max} is qe for a complete monolayer (mgg^{-1}) , K_L is the sorption equilibrium constant (lmg^{-1}) , Ce is the equilibrium concentration (mgg-1) A plot of Ce/qe versus Ce should indicate a straight line of slope (1 / q_{max}) and an intercept of (1/ q_{max} *K_L), (Weber and Chakkravorti, 1974).

The fundamental characteristics of the Langmuir equation can be explained in expression of a dimensionless factor .The basic properties of the Langmuir equation can be expressed in terms of a dimensionless factor R_L given below (Freundlich, 1906), R_L as in the following :

$$R_L=1/(1+K_L*C_0) \qquad (10)$$

The R_L value mentions the kind of the isotherm to be either favorable ($0<R_L<1$), unfavorable ($R_L>1$),

linear ($R_L=1$) or irreversible ($R_L=0$).

3.6.2. Freundlich isotherm

The Freundlich relation is an experimental relation applied to describe heterogeneous systems characterized by the heterogeneity factor 1 / n. Then it can be written as follows: (Freundlich, 1906).

$$qe=K_f*C_e1/n \qquad (11)$$

When the equation is rearranged

$$logq_e=logK_f+(1/n)*logC_e \qquad (12)$$

Where qe is the equilibrium dye concentration on adsorbent (mgg^{-1}), Ce, is the equilibrium dye concentration in solution (mgl^{-1}), K_F is Freundlich constant mg g-1and 1/n is the heterogeneity factor, respectively. A value of 1 / n ranging from 0 to 1 is a measure of the adsorption density or surface heterogeneity and becomes more heterogeneous when the value approaches zero. While the value of 1 / n lower than one value indicates a normal Langmuir isotherm, however, 1/n more than one is indicative of the cooperative adsorption indicator (Tan et al., 2007).

Experimental data in which the effects of adsorbent dose and contact time on the adsorption capacities of carbon samples were determined were analyzed by linear regression analysis and applied to Langmuir and Freundlich isotherm models and isotherm constants were determined. In the equilibrium studies, the initial concentration was selected to be 100 mg l^{-1} by taking advantage of the previous studies. This is to be able to avoid the error due to the lack of ions in the intended environment. In order to determine the maximum adsorption capacity, the concentration of metal in the solution should not be lacking (Lagergren, 1898). The adsorption isotherm allows us to have an idea of the distribution of adsorbed molecules between liquid and solid phase when the adsorption process reaches equilibrium (Veglio and Beolchini, 1997). On the other hand, how much sorbent is important in terms of giving an idea about how much sorbent will be caught. As can be seen from Table 3, that the adsorption of Freundlich isotherm of R^2 is also compatible with Freundlich isotherm. Freundlich provides the condition of 0 <1/ n <1 at 25 °C as seen in Table 3. As the 1/n value approaches zero the surface area of the sorbent becomes more heterogeneous. Therefore, the activated carbon have prepared has a very heterogeneous surface and can be achieved as a result. The adsorption of Freundlich isothermic adsorption suggests that the surface can also have heterogeneous properties and adsorption can physically occur (El-Guendi, 1991).

Appropriate isotherm determination studies have been carried out to demonstrate the equilibrium state of the adsorption phenomenon, and the isotherm constants obtained from the linear analysis of the Freundlich and Langmuir Isotherm Models and the graphs which determine the compatibility of the sorption phenomenon with these models are presented in Figure 8. (b)400°C+ZnCl$_2$+ sonic wave and Figure 9.(b)400°C+ZnCl$_2$+ sonic wave. The isotherm constants and R^2 values obtained from the graph and the calculation result are given in Table 3. As seen from Table 3, R^2 is the correct reverse slope obtained by isotherm graph, although it does not seem to be higher in the Langmuir isotherm. Therefore, the results obtained with the Langmuir isotherm were not considered. For the Freundlich isotherm, the R^2 value of the plotted line is 0.88. The adsorption equilibrium state can therefore be explained by the Freundlich isotherm. Appropriate isotherm determination studies have been carried out to demonstrate the equilibrium state of the adsorption phenomenon, and the isotherm constants obtained from the linear analysis of the Freundlich and Langmuir Isotherm Models and the graphs which determine the compatibility of the sorption phenomenon with these models are presented in Figure 8. (b) 400°C+ZnCl$_2$+ sonic wave and Figure 9. (b) 400°C+ZnCl$_2$+ sonic wave. The isotherm constants and R^2 values obtained from the graph and the calculation result are given in Table 3. As seen from Table 3, R^2 is the correct reverse slope obtained by isotherm graph, although it does not seem to be higher in the Langmuir isotherm. Therefore, the results obtained with the Langmuir isotherm were not considered. For the Freundlich isotherm, the R^2 value of the plotted line is 0.88. The adsorption equilibrium state can therefore be explained by the Freundlich isotherm.

Table 3. Isotherm parameters for the removal of C.I.D.B 56 by *C.myxa*

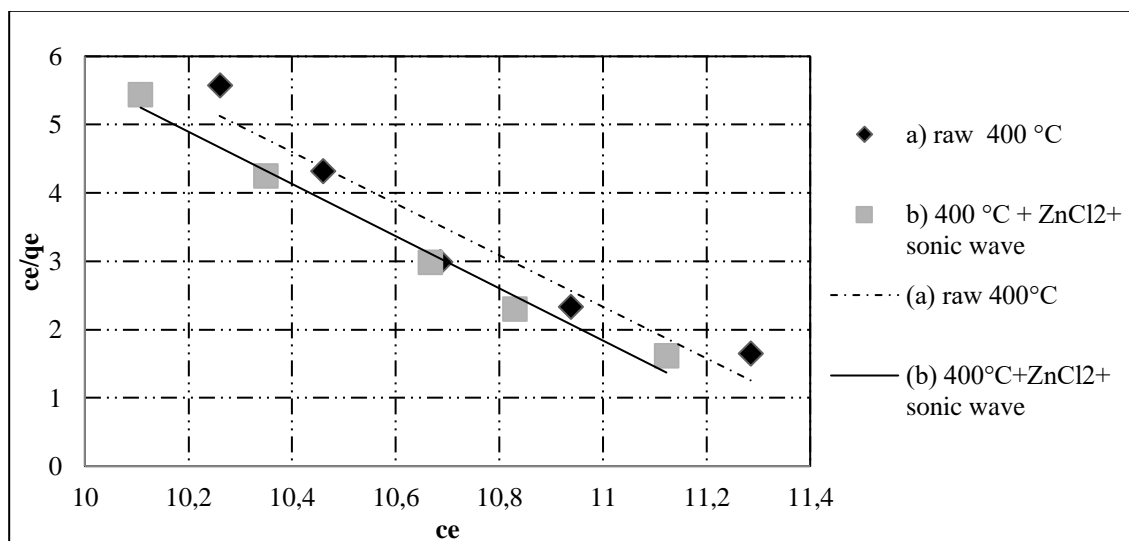| Langmuir constants	$q_{e(exp)(mg\,g^{-1})}$	q_{max}	K_L	R_L	R^2
raw 400°C	6,80	-0,227	0,019	0,038	0,94
400°C + ZnCl$_2$+ sonic wave	6,93	-0,26	0,022	0,038	0,941
Freundlich constants	$q_{e(exp)(mg\,g^{-1})}$	$K_{f\,(mg\,g^{-1})}$	1/n		R^2
raw 400 °C	6,80	3,4E-16	0,064		0,884
400°C + ZnCl$_2$+ sonic wave	6,93	2,2E-14	0,072		0,886

Figure 9. Langmuir isotherm plot for adsorption of dye (a) raw 400°C (Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 5 at 25 °C) (b) 400°C+ZnCl$_2$+ sonic wave (Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 7 at 25 °C)
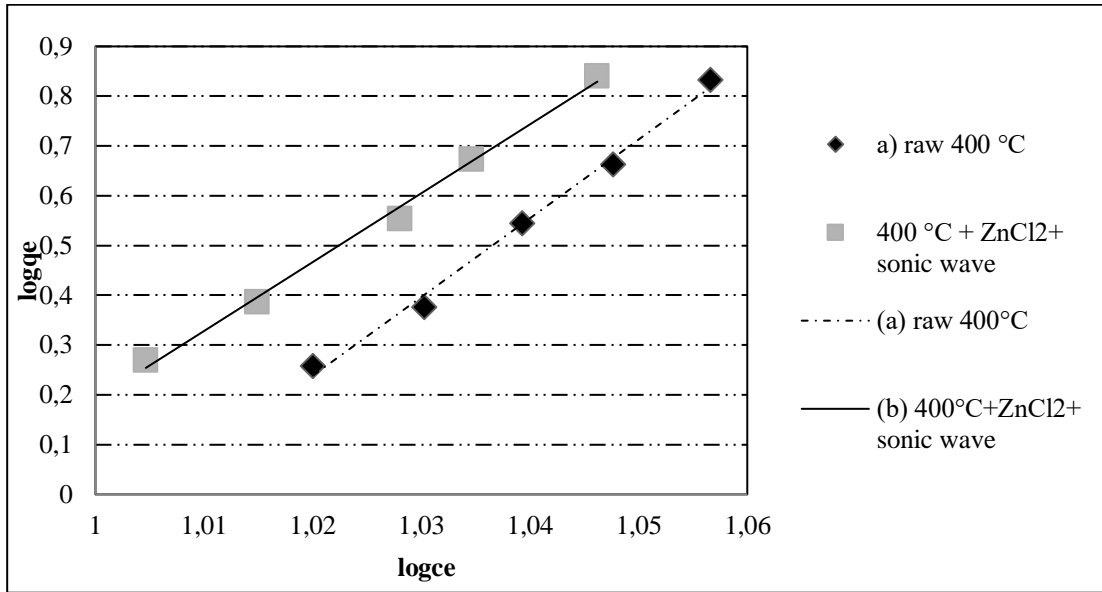
Figure 10. Freundlich isotherm plot for adsorption of dye (a) raw400°C (Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 5 at 25 °C) (b) 400°C+ZnCl$_2$+ sonic wave (Carbon content 0.1 g, dye concentration 100 mg l^{-1}, pH 7 at 25 °C)

3.8. Study of thermodynamic

The thermodynamic parameters were obtained to confirm the adsorption nature of the present search. Gibbs free energy change (ΔG °), enthalpy change (ΔH °) and entropy change (ΔS °) can be calculated to obtained the thermodynamic feasibility and the spontaneous nature of the process. The change in enthalpy (ΔH °) and entropy (ΔS °) was calculated using van't Hoff equation (Murray and Dillard, 1979; Zuhra et al. 2008):

$$\Delta G° = -RT \ln kc \qquad (13)$$

$$\ln kc = \Delta S° /R - \Delta H° /RT \qquad (14)$$

where kc = Fe/(1 - Fe), and Fe = (C$_o$ - C$_e$)/ C$_o$; is the fraction adsorbed at equilibrium, while T is the temperature in degree K and R is the gas constant [8.314 J/mol K]. By plotting a graph of lnkc versus 1/T the values ΔH° and ΔS° Can be estimated from the slope and intercept (ΔG°) was calculated using the following equation:

$$\Delta G° = \Delta H° - T\Delta S° \qquad (15)$$

Where ΔG° = free energy change (kJ mol^{-1}), ΔH° = Enthalpy exchange (kJ mol^{-1}), ΔS° = Entropy change (kJ / mol K), T = Absolute temperature (Kelvin), R = Gas ,constant (8,314 J / mol K), K = Equilibrium constant.

The Gibbs free energy exchange in the sorption system is the driving force and the basic criterion for the spontaneous realization of the sorption. If ΔG° is negative, the event spontaneously occurs (Horsfall and Spiff, 2005). The results obtained from thermodynamic calculations are presented in Table 4. The thermodynamic parameters of the adsorption of the dye on the carbon are calculated according to Equations 13, 14 and 15, and the graph of the plot is given in Figure 10. These results are obtained from the slope of the line obtained by 1/T versus Ln kd and the vertical axis.

Looking at Table 4, it is observed that ΔH° has a positive value. The positive value of ΔH° is a sign of endothermic adsorption of dye and carbon. Positive values of ΔG° indicate us that the process is not self-evident and that a driving force is needed to make adsorption possible. The negative values of ΔS° are evidence of irregularity during adsorption at the solid-solution interface. From Table 4, ΔG° values were obtained positively at all temperatures. Therefore, the adsorption process does not seem possible without a spontaneous process. However, the ΔG° values are quite small. stated that in their study it is difficult to tell us whether the sorption process occurred automatically due to the small ΔG° values (Unlu

and Ersoz, 2006). They stated that it would not be right to state that adsorption did not take place spontaneously. The $\Delta G°$ values are 20.9 kJ/mole, which is the reason for this. Similar results were obtained in this article study. Although $\Delta G°$ is positive, the values are very small. Even under normal conditions it seems that there is a need for an externally driven gust to achieve the adsorption phenomenon due to the positive $\Delta G°$ values, so we can say that the adsorption reactions occurs spontaneously due to the small values. Especially, the explanation of isotherm results with Freundlich isotherm also supports this article. The negative value of $\Delta S°$ indicates that the solution-solution (i.e., adsorbed phase) shows a decrease in the interface adsorbent concentration, while at the same time the adsorbed concentration on the solid phase increases (Goswami and Ghosh, 2005).

A positive $\Delta H °$ value is indicative of an endothermic reaction. This is an indication that the sorption reacation is receiving energy from the outside. We cannot confirm this expression because the value of $\Delta H°$ obtained in the study is small. have achieved the same results in their studies and have concluded that the sorption phenomenon occurs spontaneously because the sorption thermodynamic parameters are very small (Unlu and Ersoz, 2006). On the other hand, it is known that when the $\Delta H °$ changes are less than 84 kJ/mol, the physical reactions dominate the chemical reactions between 84 and 420 kJ/mol (Faust and Aly, 1987). Suggesting that the physical phenomena predominates in the adsorption between the activated carbon obtained from *Cordia myxa* and the C.I.D.B.56 in the light of this information.

Table 4. Thermodynamic parameters for the removal of C.I.D.B 56 by *C.myxa*

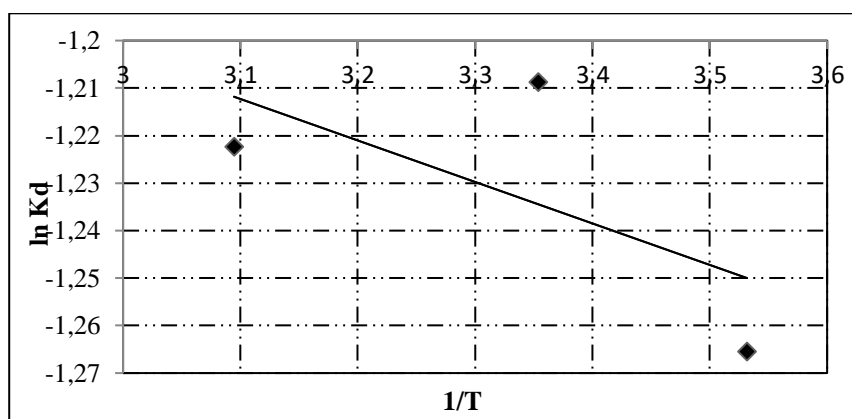| Temperature(K)	Kd	$\Delta G°$ (kJ/mol)	$\Delta S°$ (kJ/mol)	$\Delta H°$ (kJ/mol)
283,15	0,282	2,97		
298,15	0,298	2,99	-7,82	0,72
323,15	0,294	3,28		

Figure 11. Plot of lnKd versus 1/T Change of adsorption equilibrium constant with temperature

4. Conclusion

In this article study, the activated carbon obtained from the fruit of *Cordia myxa* plant was investigated for absorbable capacity of disperse blue 56 (C.I.D.B.56) in aqueous solution. In this context, the optimum environmental conditions for the adsorption process, the methods of preparing activated carbon from *Cordia myxa* to be used in adsorption, the mechanism of adsorption process, the kinetic and isotherm studies explaining the

adsorption process have been done in laboratory scale.

In this context, activated carbon was prepared by 2 methods from *Cordia myxa* fruit. It was determined how the adsorption capacity was changed by pH, time and dose changes for the adsorption of activated carbon obtained. While there is no significant change in the adsorption capacity of the different activated carbons generally obtained, the highest capture capacity is

obtained with activated carbon (q_e = 6.93 mg l^{-1}) prepared by the combined use of chemical treatment and sonic wave application. The main reason why there is no increase in specific capture is that the dye used is disperse dye. Disperse dye cannot penetrate into the sorbent and cannot be caught. For this reason, the sorbent is considered to have a high hardness.

The surface area of the obtained activated carbon was measured and it was determined that the highest surface area was the activated carbon obtained by chemical treatment and sonic wave. Given the results of the surface area, it was determined by SEM images that the cavitation bubbles formed by the sonic wave guide formed small pores on the surface of the activated carbon. The surface area of the activated carbon obtained by burning at 400 °C and the sonic wave has been increased from 1.38 m^2 g^{-1} to 5.95 m^2 g^{-1} this increase is approximately 2,5 times. On the other hand, the surface area of activated carbon obtained

by chemical treatment and sonic wave has increased.

The optimum sorption pH at work was variable, with the highest sorption at pH 4. Nearly every group completed the study in the first 30 minutes, nearly 80% of the adsorption. Isotherm Freundlich, which best describes adsorption stability. The rapid realization of adsorption and the disclosure of the equilibrium with the Freundlich isotherm indicate that physical reactions predominate in the sorption. Given the thermodynamic parameters obtained as a result of the exchange studies of temperature and sorption processes, it has been observed that adsorption does not require any external energy, it can form spontaneously. From the thermodynamic parameters Gibbs Free Energy Change ($\Delta G°$) values are positive, but very small, indicating that the adsorption phenomenon can occur spontaneously, and that the sorption phenomenon is not too much affected by heat, which is very small at its enthalpy value.

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