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THE USE OF CONSUMED BLACK TEA WASTE AS NATURAL ADSORBENT IN REMOVING THE METHYLENE BLUE DYE

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Abstract

The current study research aimed to investigate the effect of three environmental factors including the dye concentration at a range (20, 30, 40 and 50 ppm), contact time (30, 45, 60 and 75 minutes). In addition to an adsorbent dose at a range (0.5, 1, 1.5 and 2g) on the adsorption efficiency of the powder obtained from the black tea used after drying it in the adsorption of the Methylene blue dye without using any kinetic system (constant system). The results showed that the adsorption process efficiency using the used cooked black tea powder and after converting it into a powder, and the results also showed that the optimal dose has reached (1 g) and the percentage of dye removal (97%). The optimal time was (45 minutes), with a dye removal percentage (96.74%), and the optimal concentration of the Methylene blue dye solution was (20 ppm), with a removal percentage (93.2%). When studying the adsorption isotherms, they were proven from the experimental adsorption scheme consistent with the Langmuir equation, and the correlation coefficient value was ($R^2 = 0.986$), when using dose (1 g), time (30 minutes), acidity function (PH = 7), temperature (30°C) within a range of the dye solution concentrations (20, 30, 40 and 50 ppm).

Key words: Black tea waste as an adsorbent, optimal conditions, Methylene blue dye solution for adsorption

Introduction

The chemical or physical change for any food and water is not desirable, which were considered as pollution of these materials and they are not suitable for human consumption (Crompton, 1997). Furthermore, the great pollution that has occurred recently due to the great development in the fields of industry and oil exploration and population complexes considered as the dangers facing both the environment and the human being. As well as, it represents one of the main factors that contribute to occurred large environmental pollution, especially water resources. as a result that these factors are directly or indirectly close to rivers and water bodies (Thirumalaisami and Subbayan, 2012), by throwing it in the sewage channels as industrial waste or fouling that is thrown into the wastewater or as herbicides. In addition, organic and inorganic pesticides, where all of these factors lead to major pollution events, whether they are in the form of ions of toxic dyes and with different concentrations. These factor have a role in threatening marine life in all its forms, whether it is vegetation or living creatures or directly on humans, represented by drinking water or indirectly such as its use in various food industries, in addition to what it contains the carcinogens that threaten humans (Sarioglu and Atay, 2006; Ehrampoush *et al.,* 2011). One of these pollutants that are studied is the dyes, where there are many dyes, including organic and inorganic. As the dyes of organic origin their concentration increase in wastewater, and about 30% of the dyes that cause a pollution and formed as a by-product of the dyes used in industrial processes, including the dyes industry, rubber or paper, textile industries, cosmetics, leather industries and other industries as well as pharmaceuticals (O·zer and Dursun, 2007). This problem urged many scientists to search for natural materials that have the ability to remove pollutants with high efficiency and low costs. Since the processes of removing pollutants for the environment, whether the traditional chemical or physical methods, such as the use of ion exchange processes, chemical deposition, membranous separation, evaporation and many other methods require time and effort in addition to the high costs in their use (Fu and Wang, 2011). Among these materials, which are highly efficient in getting rid of pollutants, are tea waste despite the presence of other

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materials, including activated carbon, eggshells waste, sunflower waste, etc. It's considered as one of the drinks that come after water in consumption, where the production of tea of various types reached annually (30,000,000) tons (Wan *et al.,* 2008). Moreover, the tea cultivation is mainly concentrated in the countries of Asia, because of its great economic returns in its production, as India's production of tea reached about 857,000 tons per year, with an average of 27.4% of the total world production. (Wasewar *et al.,* 2008) pointed out, that the amount of dry tea that is wasted at a rate of 4 kg per 100 kg of produced tea, in addition to the quantities of tea that are disposed of as waste after direct consumption. Altogether gives an indication of the huge amounts of waste that are not suitable for consumption and must be disposed of by throwing it as waste (Cay and Ozasik, 2004). In addition to possession of tea leaves on materials of a high nature in the adsorption of many dyes, because of these leaves possess cellulosic and tannin materials and many phenolic compounds that are the basis of carboxyl, Aromatic carboxyl, phenolic hydroxyl, and these oxyl groups. These are all functional groups that have an effective role in the high adsorption of many dyes that pollute the environment such as Methylene blue dye. Methylene blue dye is one of the organic dyes, which has a negative charge and is characterized by its toxicity in case of being thrown into the water, which causes many medical conditions when inhaled or taken orally.

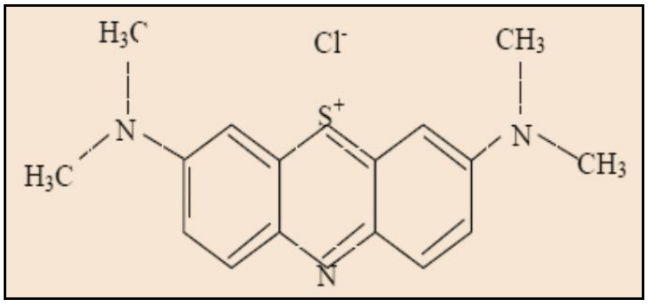

Fig. 1: Structural formula for Methylene blue dye.

Therefore, it is necessary to get rid of and remove it from contaminated water, and this dye is a heterocyclic with a specific weight of 241.9 g/mol in a chemical formula $3H_2O$ $C_{16}H_{18}CIN_3S$ and a wavelength of 668 nm (Hameed and Ahmad, 2009) as shown in Fig. 1. Therefore, the aim of the research was to obtain materials with low costs, available in large quantities, easy to obtain, and with a high ability to remove the pollution.

Materials and Methods

Samples Collecting:

The sample formed from the black tea waste was prepared from a group of cafes, and after collecting, it was cleaned from dirt and washed well with tap water, then it was soaked with distilled water. Subsequently, it was heated until boiling and then the water was removed and the process was repeated several times until obtained clear water without any dye. Furthermore, it was dried with an oven at a temperature of 105°C for 3 hours; where the process is repeated until fully dry tea leaves are obtained. Finally, it was crushed by a mill several times to obtain a smooth sample, and the sieving was done to it with a 700-micron laboratory sieve, then it was soaked in distilled water and conducting the heating process until boiling several times for the purpose of obtaining a sample free of any dye that might affect the results. After completing the proper preparation of the required sample, it was kept in a sealed plastic container until used in the process of removing the dye.

Preparation of adsorption bags:

Groups of bags used for tea were collected, including Lepton tea bags, and after being emptying it from the suitable tea for consumption. Then it was confirmed from not affecting the dye concentration by soaking the bags in the dye solution at a concentration of (20ppm) for a period of 24 hours and measuring the residual concentration with the spectrophotometer. After that, the tea waste (the sample used for adsorption) that was previously prepared and with different weights was placed inside these bags in the form of longitudinal straps and kept in a sealed box until use.

Study the factors affecting on adsorption process:

Study the effect of dye concentration on adsorption:

The concentrations represent by (20, 30, 40 and 50) ppm whose effect is studied on the adsorption process with a constant volume of (50) ml, constant dose (1) g, acidity function (pH =7). As well as, a constant temperature (30)°C, constant time (30) minutes and the particle size (700) microns, and then the residual concentration of the dye was measured by the spectrophotometer after filtering with filter paper and centrifuging the filtrate.

Effect of time on adsorption:

For the purpose of studying the effect of the best time for the adsorption process, four different contact times were chosen (30, 45, 60 and 75) minutes in a volume of (50) ml of the dye solution with a constant concentration of the dye (20ppm). Ten it was placed inside the glass cylinders with a capacity of (100 ml), at a constant acidity function (PH = 7). Moreover, the constant dose of the adsorbent used as black tea waste (1) grams at a constant temperature (30)°C, and the particle size of the sample (700) microns without using any kinematic

mechanism. After completing, the process by the specified time, the bags that contain the adsorption were pulled and the filtering process was carried out with filter papers to get rid of the residue of the adsorbent if, exist. Then the centrifugal process of the filtrate was performed and then the residual concentration of the filtrate from the dye was estimated with the spectrophotometer with a wavelength of (668) nm.

3- Effect of adsorbent dose on adsorption:

The effect of a number of doses on adsorption process was studied by selecting four doses (0.5, 1, 1.5 and 2) g in a constant volume (50) ml of the dye solution and with a constant concentration of (20) ppm and acidity function (pH =7) at a constant temperature (30) °C. In addition to the particle size of (700) microns at a constant time (45) minutes, and measure the residual concentration of the dye by spectrophotometer after the filtering and centrifugation of the filtrate.

4- Measurement of adsorption capacity and percentage of removal

The adsorption capacity and the removal percentage were calculated by measuring adsorbent concentrations after the adsorption process (through equilibrium) Ce for all solutions in which the effect of variables on the adsorption process was studied, which includes (studying the effect of change in contact time, dye concentration, and contact time) (Shisuo *et al.,* 2016) as follows:

$$Qe \quad \frac{(Co \quad Ce)Vsol}{W}, \qquad Qe \quad \frac{(Co \quad Ce)}{W} \quad 100$$

Where:

Qe = Adsorbent capacity (g/mg)

Co = Initial concentration of the adsorbent solution (ppm)

Ce = Concentration of the adsorbent solution after equilibrium

V = Total volume of the adsorbent solution (liters)

W = Absorbent material weight (g)

R = Removal percentage

5- Study of adsorption isotherms:

Through preparing the different concentrations of the Methylene blue dye (20, 30, 40 and 50) ppm with a constant size of (50)ml, constant temperature (30)°C. In addition, constant time (30) minutes and constant acidity function (pH = 7) and the particle size of (700) microns, a constant dose (1)g. Furthermore, the absorbance was measured by the spectrophotometer to calculate the concentrations values at equilibrium (Ce) and then extract the adsorption capacity (Qe) in units (mg/g) from the following equation (Wang *et al.,* 2009):

$$\frac{Ce}{Qe} \quad \frac{1}{a} \quad \frac{b}{a} Ce$$

Ce= Solute concentration at equilibrium (ppm)

Qe = Adsorbent amount (mg/g)

b, a are the constants of Langmuir and represent

b = Adsorption intensity (L/g), but (a) = adsorption capacity (mg/g).

Results and Discussion

The effect of dye concentration on adsorption process:

The study of the change effect in the dye solution concentration within the range (20, 30, 40 and 50 ppm) with constant temperature (30°C), contact time (30 minutes), acidity function (PH = 7). In addition, a dose (1g), and the particle size of (700) microns in four constant volumes (50ml) there was an inverse relationship between the dyes concentration and the adsorption speed. The results of Table 1 and Fig. 2 showed that the removal percentage increases at the concentration (20ppm) and by (93.2%) and begins to decrease gradually when the concentration of the dye solution increases. As (Azlined *et al.,* 2007) mentioned that the reason for this, the dye molecules have occupied all the active sites located on the adsorbent surface. Therefore, any increase in the dye concentration remains constant, which leads to an increase in the dye concentration residual in the solution, because the dye molecules do not have sites on the adsorbent surface for binding with it and thus remain to bind with the solution particles. Thus, increase the residual dye concentration as it reaches at a concentration (50 ppm) to (4.21 ppm), where the removal percentage was (92.1%).

The effect of contact time on the adsorption process:

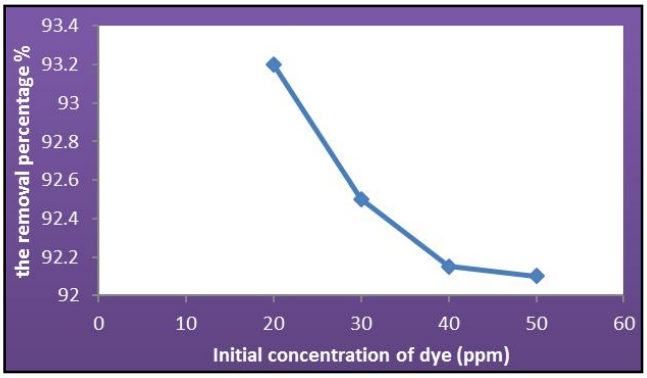

Fig. 2: Effect of dye initial concentration on adsorption process.

The results of Table 2 showed the effect of contact time on the dye adsorption process where the rest of the variables remained constant (the acidity function (PH = 7), temperature (30°C) and the solution volume (50mL), dose (1g) and the particle size of the adsorbent powder (700) microns. As it was observed that the adsorption capacity increased at the time (30 and 45 minutes) and the residual dye concentration increased at the time (60 and 75 minutes), because of the dye solution increase its attraction speed to the adsorbent surface at (45 minutes). Then the percentage of attraction between the dye solution and the adsorbent surface decreases due to the fact that the effective sites on the surface of the adsorbent are empty at the beginning of the adsorption process, and when a complete the full adsorption of the dye on the surface of the adsorbent.

There are no effective sites to complete the adsorption of the rest of dye, which leads to the stability of the adsorption process because the dye particles are directed to the adsorbent surface quickly for the purpose of adsorption on its surface when sufficient time is available to complete the process (Mall *et al.,* 2005). When saturation the surface containing the active sites, any increase in time has no effect of increased adsorption due to saturation of the adsorbent surface (Prasad and Santhi, 2012). Additionally, it was observed that the removal percentage is by (96.74%) at (45 minutes), while the percentage for adsorption at the time (60 and 75 minutes) decreases at a rate of (75.65-81.52%), respectively, as shown in Fig. 3.

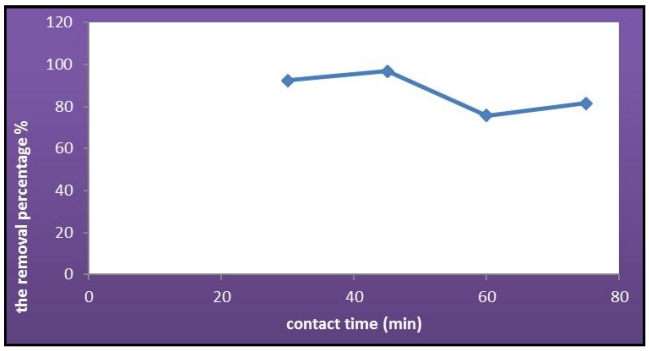

Fig. 3: The effect of contact time on the adsorption process.

Effect of adsorbent dose:

Through studying the removal effect of Methylene blue dye by black tea waste powder using a concentration of (20) ppm, a constant time (45) minutes, a constant temperature (30°C), a constant acidity function (PH = 7), and a constant particle size of (700) microns in doses (0.5, 1, 1.5 and 2) g as shown in Table 3 and Fig. 4. As it was observed that the relationship between the adsorbent dose and the adsorption speed is direct relationship, and was observed that increase the adsorbent dose has an effective role in increasing the adsorption speed of the dye (dye Removal), and the removal percentage increases at the doses of (0.5 and 1)g (93% and 97%), respectively. The residual dye concentration after adsorption at both doses was (1.4 and 0.6) ppm respectively, where an inverse relationship observed between the material dose and the adsorption speed.

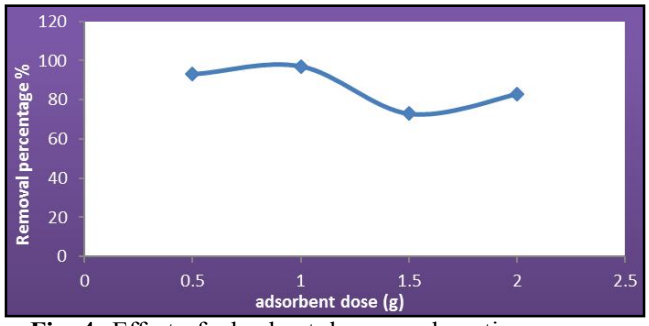

Fig. 4: Effect of adsorbent dose on adsorption process.

Table 1: Effect of dye initial concentration on adsorption process and Ce / Qe values.

Amount of absorbent (gm)	The initial concentration of dye (ppm)	Concentration of equilibrium Ce (mg / L)	Adsorption capacity Qe (mg / g)	Ce / Qe values	Removal percentage %
(gm)1	20	1.36	0.093	14.62	93.2
	30	2.253	0.139	16.21	92.5
	40	3.14	0.184	17.07	92.15
	50	4.21	0.229	18.4	92.1

Table 2: the effect of contact time on the adsorption process.

Initial concentration of dye (ppm)	Time (min)	Concentration of equilibrium Ce (mg / L)	Adsorption capacity Qe (mg / g)	Removal percentage %
20 (ppm)	15	1.522	0.9239	92.39
	30	0.652	0.9674	96.74
	45	4.130	0.7935	75.65
	60	3.695	0.8152	81.52

However, the reason for this is that the increase in the adsorbent dose increases the adsorbent surface area, which in turn increases the number of active sites on the surface that allowing for increase bond speed between the adsorbent molecules and the dye (Hadi, 2010). Then the process was reversed and the relationship becomes inverse between the adsorbent dose and the adsorption speed when the dose exceeds (1g). As the residual dye concentration increases and the adsorption percentage decreases, the reason for this is due to the agglomeration of the adsorbent particles, which causes a decrease in the number of effective sites on the adsorbent surface and in turn decreases adsorption speed (Khalid and Ahmed 2010).

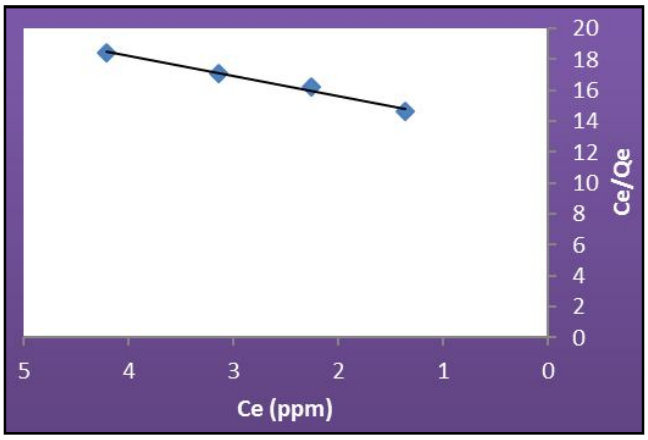

Fig. 5: Langmuir isotherms for Methylene blue dye.

Table 3: Effect of adsorbent dose on adsorption process.

Initial concentration of dye (ppm)	Adsorbent dose (g)	Concentration of equilibrium Ce (mg / L)	Adsorption capacity Qe (mg / g)	Removal percentage %
20 (ppm)	0.5	1.4	1.86	93
	1	0.6	0.97	97
	1.5	5.4	0.487	73
	2	3.4	0.415	83

Table 4: The correlation coefficient value and experimental Langmuir constants.

Adsorbent	Correlation coefficient R^2	Adsorption intensity b (L/g)	Adsorption capacity a (mg/g)
Black tea used	0.986	0.0594	0.0766

Study of adsorption isotherms:

By choosing four concentrations of the solution for the blue methyl dye solution (20, 30, 40 and 50 ppm) with constant temperature (30°C). In addition, constant acidic function (PH = 7), constant dose (1g), time (30 minutes) and the particles size (700) microns, for the purpose of completing the study of adsorption isotherms for the dye, as shown in Table 4 and Fig. 5. The study results from the conformity of the dye adsorption process to the Langmuir equation by drawing the linear relationship of the equation and the correlation coefficient value (R^2 = 0.986), this indicates a linear relationship between the adsorption capacity (Qe) and the resulting ratio from the equilibrium concentration to equilibrium capacity (Ce/Qe).

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