Plant Archives Volume 20 No. 1, 2020 pp. 3029-3038 **e-ISSN:2581-6063 (online), ISSN:0972-5210**

HIGHLY EFFICIENT REMOVAL OF TEXTILE DYE "DIRECT YELLOW (DY12) DYES" FROM AQUEOUS SYSTEMS USING COCONUT SHELL AS A WASTE PLANTS

Aseel M. Aljeboree[1*], Abass Noor Alshirifi[2] and Ayad F. Alkaim [3]

[1,3] Department of Chemistry, College of Sciences for women, University of Babylon, Hilla, Iraq.
[2]Department of Chemistry, College of Science, University of Babylon, Hilla, Iraq.

Abstract

The adsorption characteristics of Direct Yellow (DY12) dye from aqueous solution were evaluated. The effect of various parameters such as initial concentration of DY12, solution pH, temperature, adsorbent dose, and shaking contact time have been investigated. Adsorption capacity was found to increase with an increase in the initial concentration of DY12 and agitation time. The adsorption capacity and percentage of color removed increase with increasing contact time, and surface area, and decreasing with increasing of temperature and pH of the dye solution and the adsorption capacity decreasing with increasing of adsorbent dosage. Optimum contact time for equilibrium to be achieved is found to be 1 hours (60 min). It is basically due to saturation of the active site which do not allow further adsorption to take place.

DY12 dye adsorbent surfaces maximum adsorption found to be at pH = 3. In fact adsorption found to decrease with increase in pH of the solution. The applicability of adsorption isotherms to study the adsorption behavior has also been analyzed by Langmuir, Freundlich and Tempkin isotherm models were used to illustrate the experimental isotherms and isotherm's constants, It was found Freundlich isotherm model give good fittings when compare with Langmuir and Tempkin model for dye. The extent of adsorption was found decrease with the temperature increased. The thermodynamic parameters (ΔG, ΔH, and ΔS) were calculated, (ΔG) was calculated from equilibrium constant, and were explained in the mean of the chemical structure of the adsorbate.

Key words : Adsorption, Coconut Shell, Textile Dyes, Langmuir, Freundlich and Tempkin.

Introduction

Dyes are an organic chemicals which on binding with materials, it will give a colour to the materials. The colour of a dye is provided by the presence of a chromophore group. A chromophore is a configuration consisting of conjugated double bonds containing delocalised electrons. Other common chromophoric configurations include azo (-N=N-), carbonyl (-C=O); carbon (-C=C-); carbon-nitrogen (>C=NH or -CH=N-); nitroso (-NO or N-OH); nitro(-NO_2 or =NO-OH); and sulphur (C=S). The chromogen, which is the aromatic structure normally containing benzene, naphthalene or anthracene rings, is part of a chromogen-chromophore structure along within an auxo-chrome(A. E. Siegrist 1999; K. Hunger 2003).

Activated carbon, a widely used adsorbent in industrial processes, is composed of a microporous, homogenous structure with high surface area and shows radiation stability (Enas M Alrobayi 2017). The process for producing high-efficiency activated carbon is not completely investigated in developing countries. Furthermore, there are many problems with the regeneration of used activated carbon. Nowadays, there is a great interest in finding inexpensive and effective alternatives to the existing commercial activated carbon (Alkaim 2017; Aseel M Aljeboree 2018; Aljeboree, Alshirifi *et al.*, 2019). Exploring effective and low-cost activated carbon may contribute to environmental sustainability and offer benefits for future commercial applications. The costs of activated carbon prepared from biomaterials are very low compared to the cost of

---

***Author for correspondence :** E-mail: annenayad@gmail.com

commercial activated carbon. Waste materials that have been successfully used to manufacture activated carbon in the recent past include waste wood coir pith, orange peel, coffee husk, pine cone, coconut tree, sunflower seed hull, pine-fruit shell, hazelnut husks, rice hulls, oil palm shell, and Coconut husk (Aljeboree and Alshirifi 2018; Aljeboree and Alshirifi 2018; Aljeboree and Alkaim 2019 ; Aljeboree, Hussein *et al.*, 2019)

Materials and Methods

Adsorbents

preparation of activated coconut shell surface

Coconut shell was collected from Hilla market and the source of coconut under study is India, it was prepared by taking the shells and crushed very well, and put in the furnace for 2 hr at 300^{0}C, after this cooling at room temperature then sink in Hydrochloric acid (5% HCl), for 24 hr. The samples were washed by deionized water several times and dried in an oven at 105°C overnight and was ground into fine powder form before being used.

Adsorbant

The textile dye direct yellow (DY 12) was obtained from textile factory in Hilla, Iraq (Swidish company). Solutions of the test reagents were made by dissolving these dyes in deionized water. The adjusted pH of the dye (6.02). The chemical formula along with their structures and other properties of the DY 12 dye are given as follows:

Direct yellow (DY12)

The direct yellow (DY12) is a direct dye. The solution is yellow in colour. Chemical formula: $C_{30}H_{26}N_4Na_2O_8S_2$, and the chemical structure is shown in Fig. 1. λmax = 403nm. The calibration curve under different pH values is shown in Fig. 2. Direct Yellow 12 (DY), a diazo dye widely used as a cotton dye and also in the leather and paper industries, due to its stability towards both acidic and alkali solutions being an ethylated product. Studies in the treatment of the wastewater containing this dye are very limited.

Effect of different parameters on the adsorption process

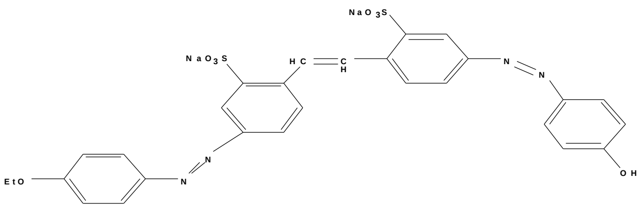

Fig. 1: Chemical structure of Direct yellow DY 12.

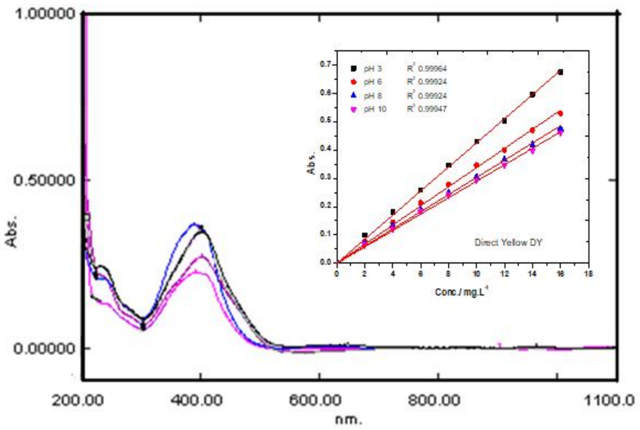

Fig. 2: Calibration curve of DY dye in the presence of different pH.

Effect of contact time

100ml of dye solution with dye concentration (10mg.L^{-1}) is to be prepared in Erlenmeyer flasks adsorbent concentration (0.05g/100ml) of coconut shell and kept inside the shaker water bath. Dye concentration to be estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λmax, using a spectrophotometer (Apel PD-303 uv (Japan)). The samples with interval time separated by using centerfugation process. The absorbance of the solution is then measured, the dye concentration is to be measured after (5, 10, 20, 30,60, 90 and 120) mins until equilibrium will be reaches. A graph is to be plotted with qe vs time. The qe is expressed as (M. Dogan 2006):

$$qe = \frac{((C)_0 - C_e) * V_L}{m_{gm}} \qquad \text{....(1)}$$

Where: qe = Amount of dye adsorbed per unit mass of adsorbent (mg/g). C^o= Initial dye concentration (mg/ L).C_e= Equilibrium dye concentration (mg/L).m = Dose of adsorbent (g).VL= is the volume of solution (L). The percentage removal of the dye was calculated on the basis of reduction in absorbance at max value of the dye as follows:

$$\text{Dry Removal \%} = \frac{C_0 - C_e}{C_0} * 100 \qquad \text{....(2)}$$

Where: C^0 and C_e are initial and equilibrium dye concentrations, respectively

Effect of dye solution pH

The effect of dye solution pH on the dye removal was examined by varying the initial pH of the dye solutions (3, 6, 8, and 10) using Erlenmeyer flasks (250 mL) simultaneously at the same concentration. The pH was adjusted using (0.1M) HCl and/or (0.1M) sodium hydroxide (NaOH) and was measured using pH meter. Then amount of adsorbent surface coconut shell (0.05 gm). The flasks were put inside the incubator shaker (220 rpm fixed throughout the study) maintained at 20°C and the final concentration of dye was measured using UV-visible spectrophotometer and the calibration plot of the dye after 1 hour.

Effect of Temperature

The adsorption experiments were performed at different temperatures (10, 20, 30 and 40°C) in a thermostat attached with a shaker. The effect of temperature was investigated with (0.05gm) dose of adsorbent coconut shell of (75µ) average particle size mixing with (100 ml) aqueous solution of dye concentration (2-16) mg.L^{-1} and the sample was shaking at a period for (1 hour) at pH 6.

Effect of adsorbent dose

The study was carried out with different dose (0.005, 0.01, 0.05, and 0.25) gm for coconut shell of (75µ) average particle size The concentrations of the samples were (2-16) mg.L^{-1}. The solutions were kept inside shaker water bath at (220 rpm) about (1 hour) in fix temperature (20^{0}C) at pH 6.

Effect of acidic treatment

The study was carried out with different acids such as (H_2SO_4, HCl, and HNO_3), the same process has been done in section 2.1 but with different acids. After this all samples prepared using as adsorbent for two dyes under study (0.05gm) dose adsorbent coconut shell of (75µ) average particle size mixing with (100 ml) aqueous solution of dye concentration (2-16) mg.L^{-1} and the sample were shaking a period for (1 hour) at fix temperature (20^{0}C) at pH 6.

Effect of particle size

The study was carried out with different particle size (100,200, and 300) mesh (0.05gm) dose of adsorbent coconut shell mixing with (100 ml) of (2-16) mg.L^{-1} aqueous solution of dye concentration, and the sample was shaking a period for (1 hour) at a fix temperature (20 ^{0}C) at pH 6

Results and Discussion

FT-IR characterization for adsorbent/adsorbate

FTIR technique was used to examine the surface groups responsible for dye adsorption. Adsorbent surfaces (coconut shell) and dyes-loaded adsorbent sample after adsorption were placed in oven at 80ºC for 5 h. Samples were made as pellet and then the infrared spectra of dyeon adsorbent before and after the adsorption process were recorded in the range 4000–400 cm^{-1} on a Bio Rad FTS 175C spectrophotometer (Fig. 3).

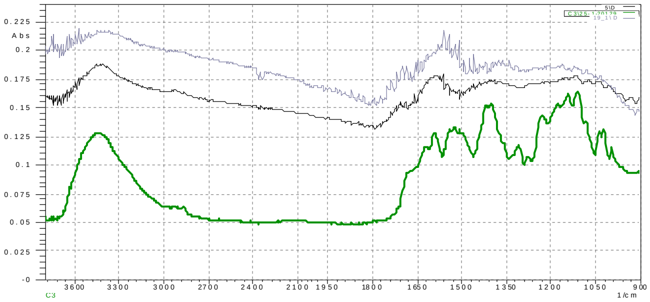

Fig. 3: FT-IR spectra for adsorption of DY 12 on the surface of coconut shell.

The adsorption band at 1637.8 cm^{-1} were assigned to SO_3 and –N=N– groups on the samples. The strong bands at 993.3, 1120.9 and 1149.4 cm-1 regions are attributed to S=O stretching and the bands at 1626–1637.8 cm^{-1} attributed to –N=N– stretching of DY12.

The stretching adsorption band of O–H in the crystal structure of the adsorbent is observed at 3445 cm^{-1} assigned to free hydroxyl and diminished after adsorption with the adsorbent dyes. All these findings suggest the attachment of dyes on the coconut shell. (D. L. Guerra 2011)

SEM characterization for adsorbent/adsorbate

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. SEM of adsorbent material were taken before and after dye adsorption on coconut shell surfaces (Figs. 4 and 5).

From Figs. 4,5 it is clear, there is a good possibility for dye to be trapped and adsorbed into these pores. The SEM pictures of adsorbed samples show very distinguished dark spots which can be taken as a sign for effective adsorption of dye molecules in the cavities and pores of this adsorbent. The micrographs presented in Figs. 4 and 5 show clearly the dye-loaded adsorbent coated by dye molecules over the whole surface at natural pH conditions. The dye molecules seem to have formed a void-free film masking the release of particles and porosity of the aggregates. (V.K. Gupta 2011; Y. Kismir 2011) On the contrary, the adsorbent before adsorption exhibit well distinguishable particles and a porous structure (Fig. 4).

Effect of contact time

Contact time is one of the important parameters for the assessment of practical application of adsorption

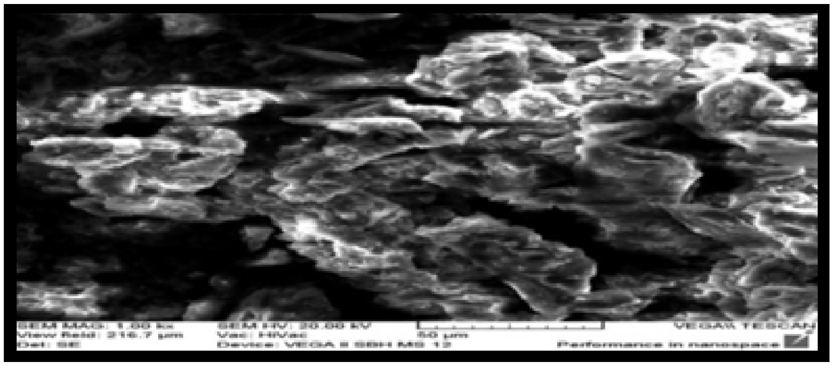

Fig. 4: SEM image for Coconut shell surface before adsorption.

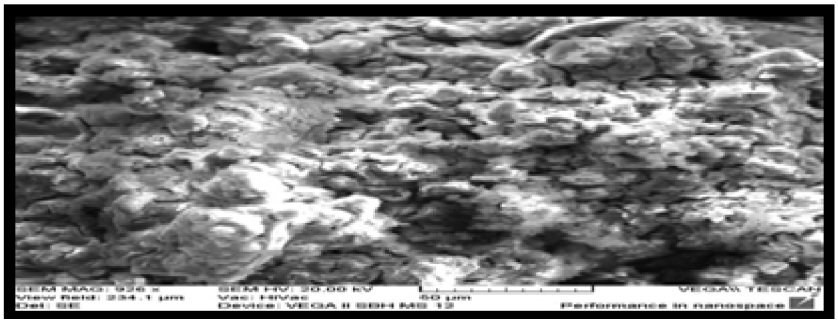

Fig. 5: SEM image for Coconut shell surface after adsorption by DY 12 dye.

process. The experimental results of adsorption of direct yellow (DY) on the surfaces of the coconut shell with contact time are illustrated in Fig. 6. The equilibrium data are shown in Figs. 6, reveal that the adsorption capacity increases with the increase in contact time to reach the equilibrium, because with time of adsorption increased the active sites of absorbent surfaces will saturate, indicating reaching an apparent equilibrium, (M. Zhu 2007; Aljeboree and Alshirifi 2019) so the adsorption efficiency will decrease. The equilibrium is established within 60 min for all kinds.

Results for contact time suggest that, adsorption takes place rapidly at the initial stage on the external surface of the adsorbent followed by a slower internal diffusion process, which may be the rate determining step. In addition, the fast adsorption at the initial stage also may be due to the fact that a large number of surface sites are available for adsorption but after a lapse of time, the remaining surface sites are difficult to be occupied. This is because of the repulsion between the solute molecules of the solid and bulk phases, thus, make it take a long time to reach equilibrium (M. Hema 2007).

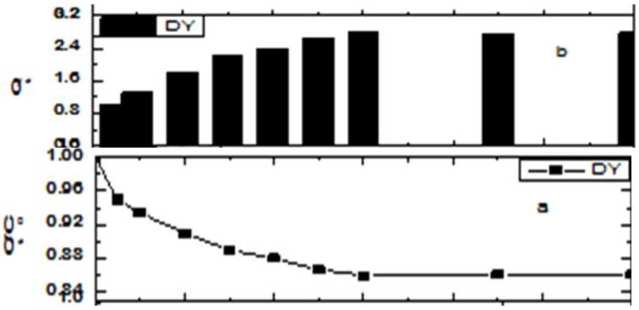

Fig. 6: Effect of contact time on a) initial concentration, and b) adsorption capacity for removal of DY dyes by coconut shell surface at pH 6, dye conc. 10 mg.L^{-1}, Temp. 293.15 K and mass catalyst 0.05 gm.

Effect of pH

The pH of an initial dye solution exerts profound influence on the adsorptive uptake of adsorbate molecules, presumably due to its influence on the surface properties of the adsorbent and ionization/dissociation of the adsorbate molecule, the changes in the structural and color stabilities as well as the degree of ionization for such adsorbate is also dependent on the pH of the solution (A. Saeed 2010). Therefore one of the most important factors in adsorption studies is the effect of acidity on the medium of adsorption (B. Royer 2010).

The effect of pH on the adsorption of direct yellow DY12 dyes onto coconut surface was studied at a pH range of (3, 6, 8, and 10) in the presence of different initial dye concentrations (2-16 mg.L^{-1}). Results are given in shown in Fig. 7.

As shown in Fig. 7 the dye uptake was found to decrease with an increase in pH. At lower pH, the surface charge may be positively charged which enhance the

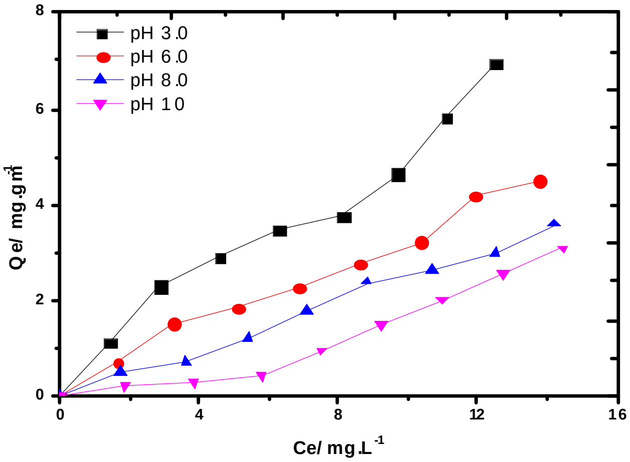

Fig. 7: Effect of pH on the adsorption of DY dye on the surface of Coconut shell (T 293.15 K, mass catalyst 0.05 gm/ 100 ml, particle size 200 mesh).

adsorption process, and at higher pH the surface of on coconut shell may be negatively charged which enhance the negatively charged on DY dye through electrostatic force at repulsion. (E. Demirbas 2008) Lower adsorption of DY, at alkaline pH is provable due to the presence of excess of OH^- ions competing with the dye anions for the adsorption sites. At the acidic pH, the number of positively charged sites increase, which favors the adsorption of the anions due to electrostatic attraction. Moreover, the decrease in the adsorption of DY, with an increase of pH value is also due to the competition between anionic dye and excess OH^- ions in the solution, which may be due to the fact that the high concentration and high mobility OH^- ions are preferentially adsorbed compared to dye anions (A. Khaled 2009).

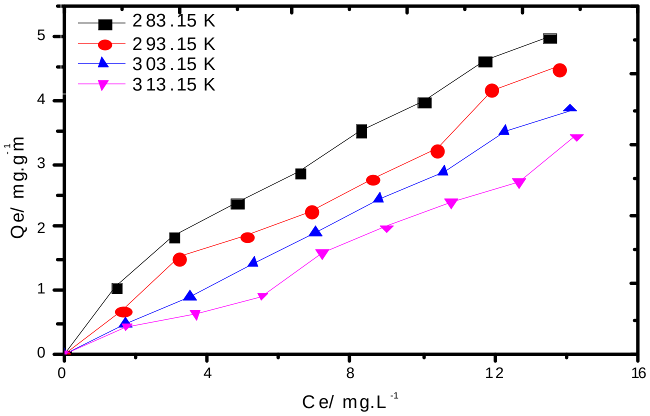

Fig. 8: Effect of temperature on the adsorption of DY 12 dye on the surface of Coconut shell. (pH 6, mass adsorbent 0.05 gm/ 100 ml, particle size 200 mesh.)

Effect of temperature

To determine whether the ongoing adsorption process was endothermic or exothermic in nature. The adsorption isotherms were determined for various dye-adsorbent systems. The removal of direct yellow DY12 has been studied at a temperature of (283.15, 293.15, 303.15, and 313.15 K) at various initial dye concentrations (2-16 $mg.L^{-1}$) results are presented in Fig. 8.

The result shows that the equilibrium adsorption capacity of DY 12 dyes was decreased while increasing the solution temperature for all initial dye concentrations.

As generally observed from Fig. 8, the uptake capacity of coconut shell decreases with increasing temperature, due to the enhanced magnitude of the reverse (desorption) step in the mechanism. This is possibly due to the exothermic effect of the surroundings during the adsorption process. However, the adsorption phenomenon is usually affected by many parameters, particularly temperature (Aljeboree 2019). In fact, the temperature affects two major aspects of adsorption: the equilibrium position in relation with the exothermicity of the process and the swelling capacity of the adsorbent.

Increasing temperature may decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing adsorption capacity. The removal of dyes with temperatures would increase the mobility of the ions of dyes and produces a swelling effect within the internal structure of adsorbent, thus enabling the large molecules of dyes to penetrate further., or it could be explained that desorption rate increased in adsorption–desorption balance at higher temperature.(K. Xie 2011)

The study of the temperature effect on adsorption will also help in calculation the basic thermodynamic functions such as Gibbs free energy) ΔG), change enthalpy (ΔH) and change entropy (ΔS) of the adsorption process. The equilibrium constant (Ke) of the adsorption process at each temperature, was calculated from the equations (3) (A.F. AlKaim 2007):

$$K_e \frac{(Q_{\max}) * \mathrm{Wt}(0.05\,\mathrm{gm})}{(C_e) * V(0.1\mathrm{L})} * 1000 \qquad ....(3)$$

Where Qmax is the amount adsorbed in ($mg.gm^{-1}$), C_e is the equilibrium concentration of the adsorbent expressed in ($mg.L^{-1}$), 0.05g represents the weight of the coconut shell adsorbent and 0.1L represents the volume of the DY 12 solution used in the adsorption process.

The change in the free energy could be determined from the equation (4) :

$$\Delta G = -RT \ln \mathrm{Ke} \qquad ....(4)$$

Where R, is the gas constant (8.314 $J.K^{-1}.mole^{-1}$), T is the absolute temperature in Kelvin.

The enthalpy of adsorption may be obtained from the following equation (5) (I. Mobasherpour 2011):

$$\mathrm{LnXm} = -\Delta H/RT + \mathrm{constant} \qquad ....(5)$$

When Xm: is the maximum value of adsorption at a certain value of equilibrium concentration (C_e). Table 1 give Xm values at different temperatures for DY 12.

The quantitative thermodynamic data of DY 12 on the adsorbent surfaces coconut shell are presented in table 1 shows the ΔH values of DY 12 is negative indicating that the adsorption process is exothermic reaction. All process of adsorption considered spontaneous from the negative value of ΔG. While, ΔS have positive value for each DY 12 that refer the interaction of molecules caused random of the total system.

Table 1: Maximum adsorption quantity Xm values of DY 12 on the coconut shell surfaces at different temperature.

T/K	Coconut Shell	
	DY 12	
	C_e/mg.L^{-1}	X_m/mg.g^{-1}
283.15	13.7	4.99
293.15	13.7	4.48
303.15	13.7	3.76
313.15	13.7	3.10

Table 2: Thermodynamic functions ΔG, ΔS and, ΔH of DY 12 adsorbed on the coconut shell surfaces.

Coconut shell adsorbent/ DY 12 adsorbate				
Thermodynamics parameters / T/K	K_e	$-\Delta G^o$/ kJ.mol^{-1}	$-\Delta H^o$/kJ.mol^{-1}	ΔS^o/J.K^{-1}.mol^{-1}
283.15	182.1168	12.2523	11.769	1.706903
293.15	163.5036	12.4223		2.228406
303.15	137.2263	12.4044		2.096077
313.15	113.1387	12.3111		1.731072

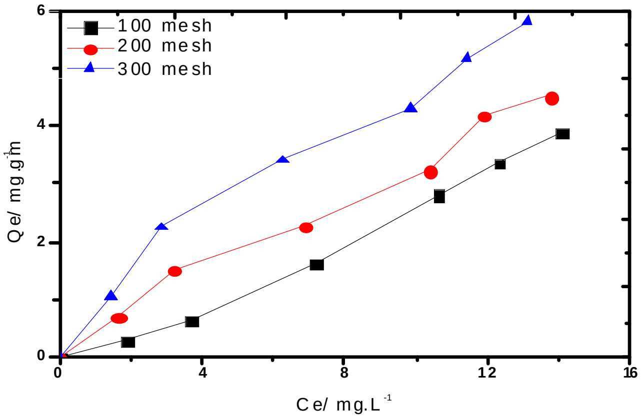

Fig. 9: Effect of particle size on the adsorption of DY 12 dye on the surface of coconut shell (pH 6, T 293.15 K, and mass adsorbent 0.05 gm/ 100 ml).

From results in table 2, the enthalpy change ΔH and entropy change ΔS for adsorption are assumed to be temperature independent. The enthalpy of the adsorption ΔH is a measure of the energy barrier that must be overcome by reacting molecules. (E.I. Unuabonah 2009; Aljeboree and Alshirifi 2019)

Effect of Particle Size

The particle size has an important role to play in the amount of the dye adsorbed. In the present investigation particle sizes (100, 200, and 300 mesh) were used for the adsorption of DY 12 over coconut shell shown in Fig. (9).

It was obvious from Fig. (9) on increase in the mesh size, the amount of the dye adsorbed increase of coconut shell. The pore structure of the adsorbents affects the adsorption of the dyes in two ways: (1) the size exclusion limits the adsorption of the adsorbates of a given size and shape (sieve effect), and (2) the adsorption capacity may increase with the increase in the specific pore volume. The increase in the adsorption capacity is more significant for the increase in the surface area, through decreasing in the particle size. This is mainly due to the increase in the surface area and accessibility of the adsorbent pores for the dye with the increase in mesh size. (A. Mittal 2010)

An increase in capacity with decreasing particle size mainly suggests that the dye molecules do not completely penetrate the particle or partly that the dye molecules preferentially adsorb near the outer surface of the particle. Considering the characteristics of porous materials that it would come into being a boundary layer to resist the adsorbate enter the interior of adsorbent in the process

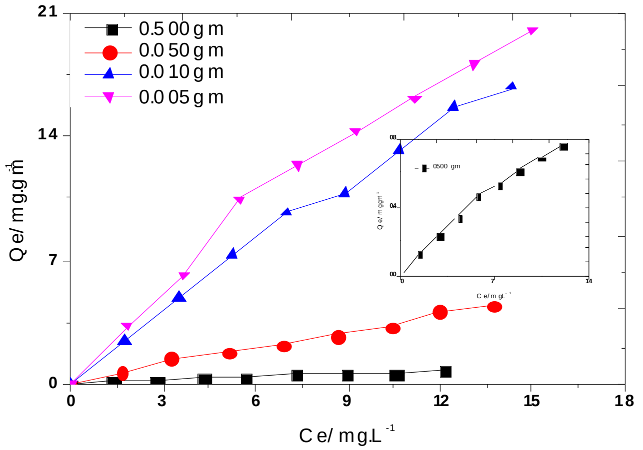

Fig. 10: Effect of mass adsorbent on the adsorption of DY 12 dye on the surface of coconut shell (pH 6, T 293.15 K, and particle size 200 mesh.)

of adsorption. As known the adsorption is limited to the external surface area of the adsorbent, therefore, the decreased particle size reduces the external mass transfer resistance and helps adsorbate to enter into the interior of adsorbent for contacting more active sites during the adsorption process. (V. Vimonses 2009)

Effect of Adsorbent Dose

The effect of the amount of the adsorbents was necessary in order to observe the minimum possible amount, which shows the maximum adsorption stoichiometric. The amounts of the adsorbent were varied from 0.005 to 0.500 g/100 ml of coconut shell. The results are illustrated in Fig. 10.

An increase in the percentage of the dye removal with adsorbent mass was related to increases in the adsorbent surface areas, enhancing the number of adsorption sites available for adsorption as reported already in other cases. (Z. Hua 2010) The increase in removal of dye with adsorbent dose due to the introduction of more binding sites for adsorption. The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction whereas the number of sites available for adsorption site increases by increasing the adsorbent dose. (R. Malik 2007).

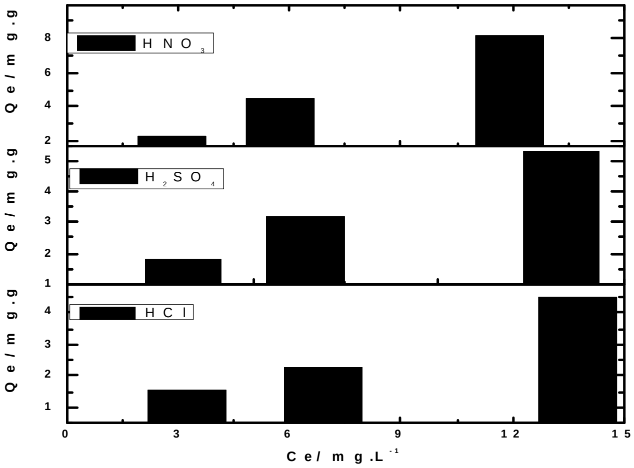

Fig. 11: Effect of different acid treatment on the activity of coconut shell surface for the adsorption of DY dye (pH 6, T 293.15 K, particle size 200 mesh., and mass catalyst 0.05 gm).

Effect of acid treatment on the adsorbent surfaces

The study of the effect of acid treatment was necessary to show the maximum adsorption. The adsorbent were treated by different acids such as (HNO_3, H_2SO_4, and HCl). The results are illustrated in Fig. 11.

It was obvious from the results shown in Fig. 11, the best adsorption capacity when the catalyst treated by HNO_3, this is may be due to the increased in acid acidity caused to re-activated the active sites for adsorbent surface.

Adsorption Isotherms

Freundlich Isotherm

The empirically derived Freundlich isotherm is defined as follows equation 6 (M. Özacar 2003)

$$q_1 e = K_1 f\, C_1 e^1 (1/n) \qquad ....(6)$$

where q_e : Amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), (mol/g), C_e : Equilibrium concentration of adsorbate in solution after adsorption (mg/L), (mol/L), K_f : Empirical Freundlich constant or capacity factor ($L.g^{-1}$), 1/n : Freundlich exponent, K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto adsorbent for unit equilibrium concentration. 1/n is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; if the value is above unity adsorption is a favorable physical process. (P. Senthil Kumar 2010)

The applicability of the Freundlich equation to a particular case is tested by plotting log q_e against log C_e from the logarithmic form of Equation 7.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad ....(7)$$

Such a plot should yield a straight line with intercept equal to log K_f and slope equal to 1/n. the Freundlich constants are illustrated in table 3.

Langmuir Isotherm

The Langmuir isotherm is most widely used for the adsorption of pollutants from liquid solutions. An alternative equation was derived by Langmuir on the basis of a definite case of the nature of the process of adsorption from solution. The Langmuir adsorption isotherm is defined in equation 8 (I. Langmuir 1918)

$$q_\downarrow e = (q_\downarrow 0 K_\downarrow L C_\downarrow e)/(1 + K_\downarrow L C_\downarrow e) \qquad ....(8)$$

Where q_e : amount adsorbed per unit weight of adsorbent at equilibrium (mg/g).C_e : equilibrium concentration of adsorbent in solution after adsorption (mg/L). q_0: Empiricial Langmuir constant which represents maximum adsorption capacity (mg/g).K_L: empiricial Langmuir constant (L/mg) The q_0 represents

Table 3: Coeffecient isotherm parameters of Freundlich equation by adsorption of DY12 on the coconut shell surface.

Adsorbent/Adsorbate	**Variable parameters**	**Freundlich Parameters**			**Langmuir Parameters**			**Tempkin Parameters**		
		K_f*1000	**1/n**	**R^2**	**Q_0**	**K_L**	**R^2**	**B**	**K_T**	**R^2**
Coconut Shell /DY 12 Dye	pH(6)	192.93	0.19	0.97752	146.84	0.03	0.19250	619.20	0.72	0.87458
	T/K(293.15)									
	Catalyst[0.0 5 g/100ml]									
	Particle Size[200 Mesh]									

the total number of surface sites per mass of adsorbent. In the ideal case, q0 would be equal for all adsorbates. However, q_0 may vary somewhat between different compounds because of differences in adsorbate sizes. Therefore, it usually represents the maximum achievable surface concentration of a given compound. The constant K_L which is commonly referred to as the Langmuir constant is defined as the equilibrium constant of the adsorption reaction. The K_L also implies a constant adsorbate affinity for all surface sites (I. Langmuir 1918)). Assuming the above equation (9) as :

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \qquad ....(9)$$

And plotting of $\frac{C_e}{q_e}$ vs C_e give a straight line with slope $\frac{1}{q_0}$ and intercept $\frac{1}{q_0 K_L}$, the Langmuir isotherm is limited in its application to adsorption in monolayer. Results are shown in Figs. (3.58-3.72), and the Langmuir constants are illustrated in (Table 3).

Temkin Isotherm

Temkin adsorption isotherm was developed assuming that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbent interactions adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Temkin isotherm is represented by the following equation 10 (M. Özacar 2005)

$$q_e = \frac{RT}{b} \log(K_T C_e) \qquad ....(10)$$

Equation 11 can be expressed in its linear form as:

$$q_e = B_T \log K_T + B_T \log C_e \qquad ....(11)$$

where BT: (RT/b) Tempkin constant related to the heat of adsorption(kJ/mol) R : Gas constant (8.314 J/mol.K) T : Temperature (K) K_T : Empirical Temkin constant related to the equilibrium binding constant related to the maximum binding energy (L/mg), (L/mol) The adsorption data can be analyzed according to the Equation (11). A plot of the qe versus log C_e enables the determination of the isotherm constants K_T and B_T. Results are shown in Fig. (3.74-3.89), and the Tempkin constants are illustrated in table 3.

The Tempkin isotherm takes into account the effects of the interaction of the adsorbate and the adsorbing species. By ignoring the extremely low and large concentration values, the model assumes that the heat of adsorption (a function of temperature) of all of the molecules in the layer would decrease linearly rather than logarithmically with coverage due to adsorbate-adsorbent interactions

The equilibrium binding constant corresponding to the maximum binding energy, kT, decreased as the experimental temperature increased from 283.15 to 313.15 K, which implies that the adsorption process is exothermic and favored at higher temperatures. This result was also confirmed by the increase in the RT/b values. (L.Wang 2012)

Conclusions

1. The adsorption capacity and percentage of color removed increase with increasing contact time, and surface area, and decreasing with increasing of temperature and pH of the dye solution and the adsorption capacity decreasing with increasing of adsorbent dosage
2. DY12 dyes on adsorbent surfaces maximum adsorption found to be at pH = 3. In fact adsorption found to decrease with increase in pH of the solution.
3. The negative value of ΔG confirms the spontaneous nature adsorption process. The positive value of ΔS showed the increased randomness at the solid–solution interface during adsorption and the negative value of ΔH indicated the adsorption process was exothermic.
4. All effective parameters give good fitting of Freundlich model better than Tempkin and Langmuir models because suggests that adsorption is heterogeneous in nature.

References

AlKaim, A. F., A. N. AlShirifi and A. H. AlDujaili (2007). "Kinetic study of adsorption of phenol on the novel polymer prepared AUFP from aqueous solution." *National Journal of Chemistry*, **27**: 428-455.

Aljeboree, A.M. (2019). "Removal of Vitamin B6 (Pyridoxine) Antibiotics Pharmaceuticals From Aqueous Systems By ZnO." *International Journal of Drug Delivery Technology*, **9(2)**: 125-129.

Aljeboree, A.M. and A.F. Alkaim (2019). "Role of plant wastes as an ecofriendly for pollutants (crystal violet dye) removal from aqueous solutions." *Plant Archives*, **19(2)**: 902-905.

Aljeboree, A.M. and A. Alshirifi (2018). "Spectrophotometric Determination of phenylephrine hydrochloride drug in the existence of 4-Aminoan tipyrine: Statistical Study." *International Journal of Pharmaceutical Research*, **10(4)**.

Aljeboree, A.M. and A.N. Alshirifi (2018). "Colorimetric Determination of phenylephrine hydrochloride drug Using 4-Aminoantipyrine: Stability and higher sensitivity." *Journal of Pharmaceutical Sciences and Research*, **10(7)**: 1774-1779.

Aljeboree, A.M. and A.N. Alshirifi (2019). "Colorimetric determination of Amoxicillin using 4-Aminoantipyrine and the effects of different parameters12." *Journal of Physics: Conference Series*, **12(5)**: 052067.

Aljeboree, A.M. and A.N. Alshirifi (2019). "Oxidative coupling of Amoxicillin using 4-Aminoantipyrine: Stability and higher sensitivity." *Journal of Physics: Conference Series*, **1294(5)**: 052001.

Aljeboree, A.M. and A.N. Alshirifi, *et al.,* (2019). "Activated carbon (as a waste plant sources)–clay micro/ nanocomposite as effective adsorbent: process optimization for ultrasound-assisted adsorption removal of amoxicillin drug." *Plant Archives*, **19(2)**: 915-919.

Aljeboree, A.M. and F.H. Hussein, *et al.,* (2019). "Removal of textile dye (methylene blue MB) from aqueous solution by activated carbon as a model (corn-cob source waste of plant): as a model of environmental enhancement." *Plant Archives*, **19(2)**: 906-909.

Alkaim, A.F., Alrobayi, M. Enas, Algubili, M. Abrar, Aljeboree and M. Aseel (2017). "Synthesis, characterization, and photocatalytic activity of sonochemical/hydration–dehydration prepared ZnO rod-like architecture nano/ microstructures assisted by a biotemplate." *Environmental technology*, **38(17)**: 2119-2129.

Aseel, M. and A.N.A. Aljeboree (2018). "Adsorption of Pharmaceuticals as emerging contaminants from aqueous solutions on to friendly surfaces such as activated carbon: A review." *Journal of Pharmaceutical Sciences and Research*, **10(9)**: 2252-2257.

Demirbas, E., M. Kobya and M.T. Sulak (2008). "Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon." *Bioresour. Technol.*, **99**: 5368-5373.

Dogan, M., M. Alkan, O. Demirbas, Y. Ozdemir and C. Ozmetin (2006). "Adsorption kinetics of maxilon blue GRL onto sepiolite from aqueous solutions." *Chem. Eng. J.*, **124**: 89-101.

Enas, M., A.M.A. Alrobayi, A.M. Aljeboree, A.F. Alkaim and F.H. Hussein (2017). "Investigation of photocatalytic removal and photonic efficiency of maxilon blue dye GRL in the presence of TiO2 nanoparticles." *Particulate Science and Technology*, **35(1)**: 14-20.

Guerra, D.L., W.L. Silv, Helen, C.P. Oliveira, R.R. Viana and C. Airoldi (2011). "Organofunctionalized Amazon smectite for dye removal from aqueous medium-Kinetic and thermodynamic adsorption investigations." *Journal of Hazardous Materials*, **186**: 675-682.

Gupta, V.K., B. Gupta, A. Rastogi, S. Agarwal and A. Nayak (2011). "A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye-Acid Blue 113." *Journal of Hazardous Materials*, **186**: 891-901.

Hema, M. and S. Arivoli (2007). "Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon." *International Journal of Physical Sciences*, **2(1)**: 010-017.

Hunger, K. (2003). "Industrial Dyes: Chemistry, Properties, Applications." Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Hua, Z., H. Chen, F. Ji and S. Yuan (2010). "Removal of Congo Red from aqueous solution by cattail root." *J. Hazard. Mater.*, **173**: 292-297.

Khaled, A., A. El Nemr, A. El-Sikaily and O. Abdelwahab (2009). "Treatment of artificial textile dye effluent containing Direct Yellow 12 by orange peel carbon." *Desalination*, **238**: 210-232.

Kismir, Y. and A.Z. Aroguz (2011). "Adsorption characteristics of the hazardous dye Brilliant Green on Saklýkent mud." *Chemical Engineering Journal*, **172**: 199- 206.

Langmuir, I. (1918). "The adsoption of gases on plane surfaces of glass, Mica and platinum." *J. Am. Chem. Soc.*, **40(9)**: 1361–1403.

Malik, R., D.S. Ramteke and S.R. Wate (2007). "Adsorption of malachite green on groundnut shell waste based powdered activated carbon." *Waste Manage.*, **27**: 1129-1138.

Mittal, A., J.Mittal, A. Malviya, D. Kaur and V.K. Gupta (2010). "Adsorption of hazardous dye crystal violet from wastewater by waste materials." *J. Colloid Interface Sci.*, **343(2)**: 463-473.

Mobasherpour, I., E. Salahi and M.Pazouki (2011). "Removal of nickel (II) from aqueous solutions by using nano-crystalline calcium hydroxyapatite." *Journal of Saudi Chemical Society*, **15(2)**: 105-112.

Özacar, M. and Ý.A. Þengil (2003). "Adsorption of reactive dyes on calcined alunite from aqueous solutions." *J. Hazard. Mater.*, **B98**: 211–224.

Özacar, M. and Ý.A. Þengil (2005). "Adsorption of metal complex dyes from aqueous solutions by pine sawdust." *Bioresour. Technol*., **96**: 791–795.

Royer, B., N.F. Cardoso, E.C. Lima, T.R. Macedo and C. Airoldi (2010). "Sodic and acidic crystalline lamellar magadiite adsorbents for removal of methylene blue from aqueous solutions. Kinetic and equilibrium studies." *Sep. Sci. Technol*., **45**: 129-141.

Saeed, A., M. Sharif and M. Iqbal (2010). "Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption." *J. Hazard. Mater*., **179**: 564-572.

Senthil Kumar, P., S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi and S. Sivanesan (2010). "Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions." *Desalination*, **261**: 52-60.

Siegrist, A. E., C. Eckhardt, J. Kaschig and E. Schmidt (1999). "Optical Brighteners. in Ullmann's Encyclopedia of Industrial Chemistry." VCH, Weinheim, **A18**: 153-176.

Unuabonah, E.I., G.U. Adie, L.O. Onah and O.G. Adeyemi (2009). "Multistage optimization of the adsorption of methylene blue dye onto defatted *Carica papaya* seeds." *Chemical Engineering Journal*, **155**: 567-579.

Vimonses, V., S. Lei, B. Jin, C.W.K. Chow and C. Saint (2009). "Kinetic Study and Equilibrium Isotherm Analysis of Congo Red Adsorption by Clay Materials." *Chem. Eng. J*., **148**: 354-364.

Wang, L. (2012). "Application of activated carbon derived from 'waste' bamboo culms for the adsorption of azo disperse dye: Kinetic, equilibrium and thermodynamic studies." *Journal of Environmental Management*, **102**: 79-87.

Xie, K., W. Zhao and X. He (2011). "Adsorption properties of nano-cellulose hybrid containing polyhedral oligomeric silsesquioxane and removal of reactive dyes from aqueous solution." *Carbohydr. Polym*., **83**: 1516-1520.

Zhu, M., L. Lee, H. Wang and Z. Wang (2007). "Removal of an anionic dye by adsorption/precipitation processes using alkaline white mud." *Journal of Hazardous Materials*, **149**: 735-741.