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REMOVAL OF TEXTILE DYES FORM AQUEOUS SOLUTIONS BY USING COCONUT AS A SOURCE OF ACTIVATED CARBON: AS A MODEL OF EQUILIBRIUM AND THERMODYNAMIC STUDIES

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Abstract

The adsorption characteristics of Maxilon blue (GRL) dyes dye from aqueous solution were evaluated. The effect of several parameters for example primary concentration of GRL, solution pH, temperature, adsorbent mass, and shaking contact time have been investigated. Adsorption capacity was found to increase with an increase in the primary concentration of GRL dye and agitation time. The percentage removal of color increase with increasing contact time, and surface area, and decreasing with increasing of temperature and pH of the dye solution. Optimum contact time for equilibrium to be achieved is found to be 1 hours (60 min). It was found Freundlich isotherm model give good fittings when compare with Langmuir and Temkin model for two dyes. 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, Activated Carbone, Coconut Shell, Textile Dyes, Maxilon blue(GRL) , isotherm model.

Introduction

Generally, the dyes used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulfur dyes (A. Demirbas 2009), where azo derivatives dyes are the major class of dyes that are used in the industry today (E. Forgacs 2004). Adsorption is a rapid phenomenon of passive sequestration separation of adsorbate from an aqueous/gaseous phase onto a solid phase (S. Ardizzone 1993; Aljeboree and Alshirifi 2018). Adsorption occurs between two phases in transporting pollutants from one phase to another. It is considered to be a complex phenomenon and depends mostly on the surface chemistry or the nature of the adsorbent, adsorbate and the system conditions in between the two phases. Adsorption processes offer the most economical and effective treatment method for removal of dyes from waste water. The process is often carried out in a batch mode (Y.S. Ho 1998), The term adsorption is used also to describe two kinds of forces of interaction between the adsorbate and the adsorbent. These interaction forces are broadly described as physisorption (physical adsorption) and chemisorption (chemical adsorption) (Aseel M Aljeboree 2018). Physical adsorption (physisorption) is relatively non-specific and is due to the operation of weak forces between molecules. In this process, the adsorbed molecule is not affixed to a particular site on the solid surface; it is free to move over the surface (N.C. Sawyer 1994; Aljeboree and Alshirifi 2018). Chemical adsorption, (chemisorption) occures a chemical bonding is also based on electrostatic forces, but much stronger forces act a major role in this process (N.C. Sawyer 1994). In chemisorption, the attraction between adsorbent and adsorbate is a covalent or electrostatic chemical bond between atoms, with the occurrence of shorter bond length and higher bond energy (J.M.Montgomery 1985).

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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 basic maxilon blue (GRL) 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 (6.13). The chemical formula along with their structures and other properties of the GRL dye are given as follows:

Maxilon blue dye

The Maxilon Blue GRL dye is a basic cationic dye. Chemical formula: $C_20H_26N_4O6S_2$, and the chemical structure are shown in Fig. 1. λmax =599 nm. The calibration curve under different pH values is shown in Fig. 2.

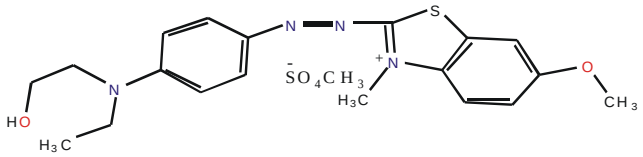

Fig. 1: Chemical structure of Maxilon Blue GRL dye (M. Doðan 2006; Enas M Alrobayi 2017).

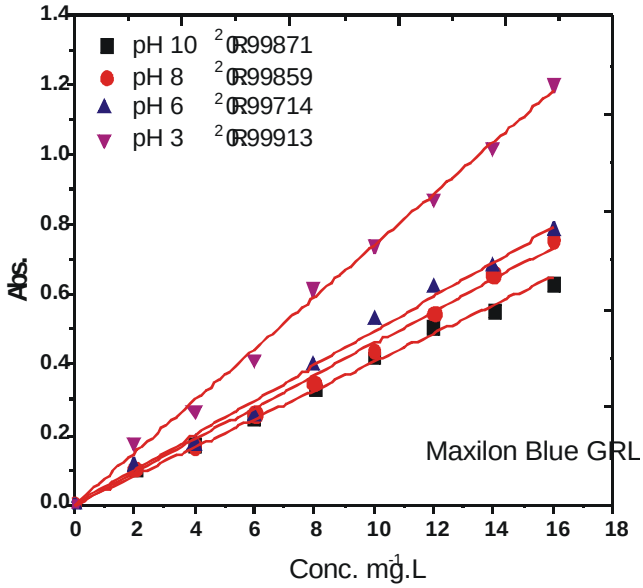

Fig. 2: Calibration curve of Maxilon Blue GRL dye in the presence of different pH.

Effect of different parameters on the adsorption process

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. Doðan 2006):

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

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: (R. Ahmad 2009)

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

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

Effect of pH solution

The effect of pH solution was studied by agitating 0.05 g of coconut shell (particle size 75 lm) and 100 mL of GRL dye concentration using water-bath shaker at 20°C. The experiment was conducted at different pH from 3, 6,8, 10. Agitation was provided for 1 h contact time at a constant agitation speed. The pH was adjusted by adding a few drops of diluted 0.1 N KOH, or 0.1 N HCl and measured by using a pH meter (220 rpm fixed throughout the study).

Effect of Temperature

The adsorption experiments were performed at several temperatures (10, 20, 30 and 40°C) in a thermostat attached with a shaker. The effect of temperature was investigated with (0.05gm) mass 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 the mass of coconut shell

The effect of mass of coconut shell was studied by agitating of different masses (0.005, 0.01, 0.05, and 0.25) gm, in 100 mL of GRL dye concentration (2-16 ppm). The experiment was conducted at pH 6. Agitation was provided for 1h contact time at a constant agitation speed and using water-bath shaker at 20 °C, 220 rpm, (particle size 75µ).

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 (20^0C) at pH 6.

Effect of particle size

The effect of particle size to the adsorption capacity of coconut shell was carried out in (100,200, and 300) mesh, at 20^0C, pH 6, 220 rpm, 0.05 g of coconut shell and 100 mL of dye concentration (2-16)ppm .

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 80°C for 5 h. Samples were made as pellet and then the infrared spectra of two dyes on 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).

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 GRL dye.

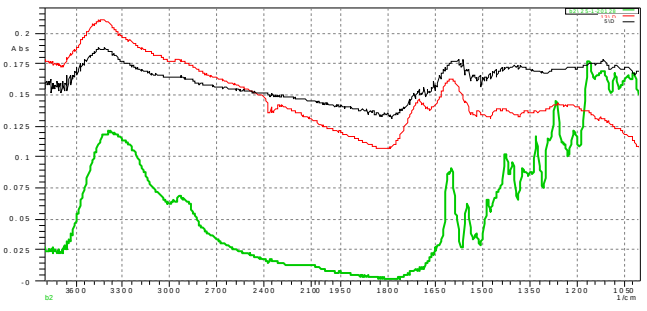

Fig. 3: FT-IR spectra for adsorption of GRL on the surface of coconut shell.

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 dye on the coconut shell. (D. L. Guerra 2011; Alkaim 2017)

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 process. (C.F. Iscen 2007) The experimental results of adsorption of Maxilon blue (GRL), on the surfaces of the coconut shell with contact time. The equilibrium data are shown in Figures 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) 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

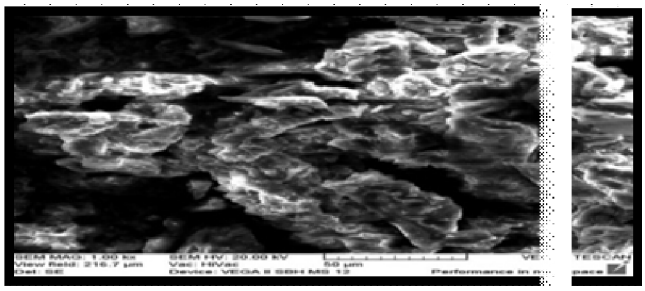

Fig. 4: SEM image for Coconut shell surface before adsorption.

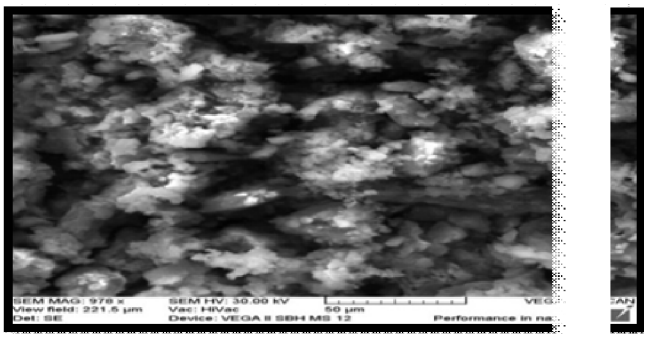

Fig. 5: SEM image for Coconut shell surface after adsorption by GRL dye.

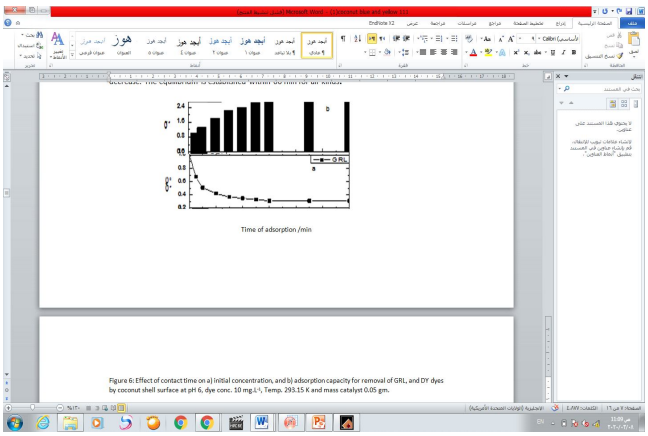

Fig. 6: Effect of contact time on a) initial concentration, and b) adsorption capacity for removal of GRL, by coconut shell surface at pH 6, dye conc. 10 mg.L^{-1}, Temp. 293.15 K and mass catalyst 0.05 gm.

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 (S. Senthikumar 2005; M. Hema 2007; Aljeboree and Alshirifi 2018).

Effect of pH

The effect of pH on the adsorption of Maxilon blue GRL dye 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.

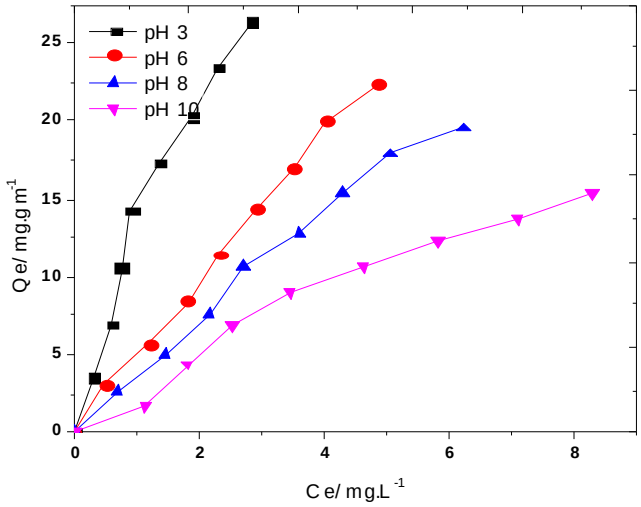

Fig. 7: Effect of pH on the adsorption of GRL dye on the surface of Coconut shell (T 293.15 K, mass catalyst 0.05 gm/ 100 ml, particle size 200 mesh.)

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 adsorption process (Mosaa, Bader *et al*. 2019), and at higher pH the surface of on coconut shell may be negatively charged which enhance the negatively charged on GRL dye through electrostatic force at repulsion. (E. Demirbas 2008; Aljeboree and Alshirifi 2019; Bader, Zaied-A-mosaa *et al*. 2019) Lower adsorption of GRL, 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 GRL 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).

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 Maxilon blue GRL 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 GRL, dye 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

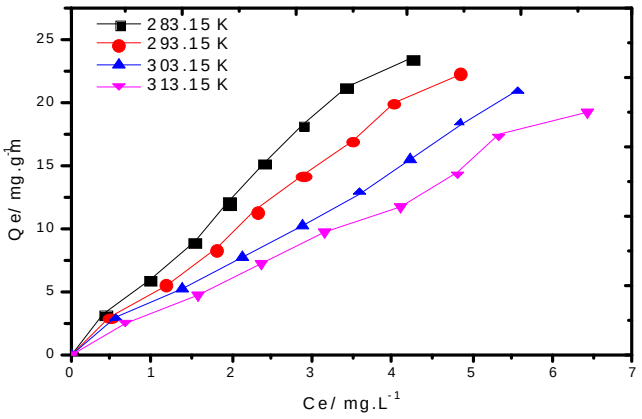

Fig. 8: Effect of temperature on the adsorption of GRL dye on the surface of Coconut shell. (pH 6, mass catalyst 0.05 gm/ 100 ml, particle size 200 mesh.)

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. (G.O. El-Sayed 2011) 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.

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 GRL or 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 GRL.

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

T/K	Coconut Shell GRL C_e/mg.L^{-1} / X_m/mg.g^{-1}	
283.15	4.3	23.00
293.15	4.3	20.50
303.15	4.3	15.70
313.15	4.3	12.40

The quantitative thermodynamic data of GRL on the adsorbent surfaces white marble and coconut shell are presented in (Table 1) shows the ΔH values of GRL are 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 and GRL that refer the interaction of molecules caused random of the total system.

From results in table 2, the enthalpy change ΔH and entropy change ΔS for adsorption are assumed to be temperature independent. (Z. Wu 2005; Aljeboree 2019) The enthalpy of the adsorption "H is a measure of the energy barrier that must be overcome by reacting molecules.(E. I. Unuabonah 2009)

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 GRL, over coconut shell shown in Fig. (9).

It was apparent from Fig. (9) on increase in the particle 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 chemical structure of the dye molecule (its ionic charge) and its chemistry (its ability to form hydrolyzed species), and (2)

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

Coconut shell adsorbent/ GRL 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	2674.419	18.5774	15.558	10.66368
293.15	2383.721	18.9531		11.58133
303.15	1825.581	18.9272		11.11413
313.15	1441.86	18.9373		10.79119

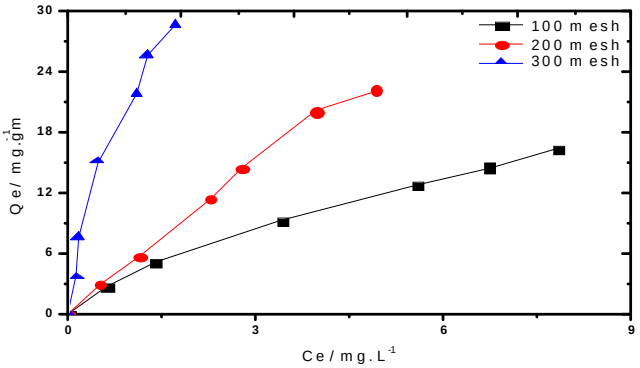

Fig. 9: Effect of particle size on the adsorption of GRL dye on the surface of coconut shell (pH 6, T 293.15 K, and mass adsorbent 0.05 gm/ 100 ml).

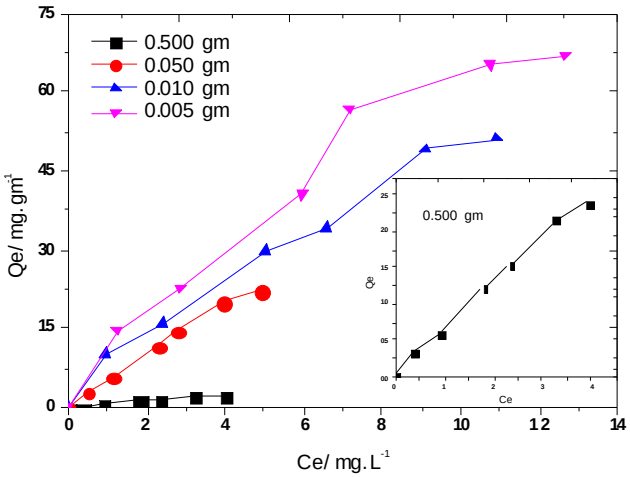

Fig. 10: Effect of mass adsorbent on the adsorption of GRL dye on the surface of coconut shell (pH 6, T 293.15 K, and particle size 200 mesh.)

the adsorption capacity may increase with the increase in the specific pore volume. Fig. 9 shows the effect of particle size on dye adsorption. Results shows minimum particle size showed greater adsorption than larger size, increase in adsorption capacity with decreasing particle size suggests that the drug preferentially adsorbed on the outer surface and did not fully penetrate the particle due to steric hindrance of large drug molecules (Gouamid M. 2013).

Effect of Adsorbent Dose

From an economic point of view, the study of adsorbent mass is useful for selecting the appropriate amount of adsorbent for industrial applications. The effect of adsorbent dose on the GRL dye removal was studied by varying dosage from 0.005 to 0.500 g/100 ml of coconut shell at dye initial concentration of 1-16 ppm mg L^{-1}. The results are shown 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.(C. Xia 2011). 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. (Aljeboree 2016; Ruwaida A Raheem 2016).

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

In order to analyze the characteristics of the adsorption isotherms, several models including Freundlich, Langmuir and Temkin have been used to analyze the equilibrium adsorption data. The non-linearized form of Langmuir isotherm model can be described as the following equation (Langmuir 1918).

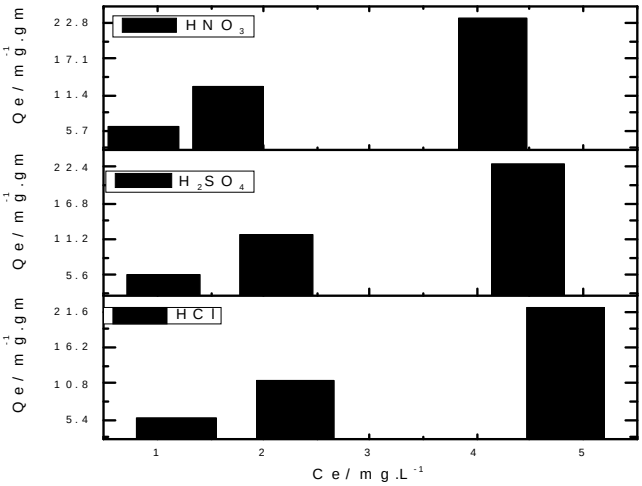

Fig. 11: Effect of different acid treatment on the activity of coconut shell surface for the adsorption of GRL dye (pH 6, T 293.15 K, particle size 200 mesh., and mass catalyst 0.05 gm).

$$qe = qm\ K_L Ce / 1 + KLCe \quad ....(6)$$

where qm is the maximum adsorption capacity of the adsorbent, KL is Langmuir constant represents the adsorption affinity (L/mg) and corresponds to the monolayer surface coverage (mg/g), and qe the equilibrium adsorption capacity (mg/g) The non-linearized form of Freundlich isotherm model is given as the following equation (Freundlich H 1939):

$$qe = Kf\ Ce\ 1/n \quad ....(7)$$

Kf can be defined as the adsorption or distribution coefficient and represents the quantity of drug adsorbed onto adsorbent for unit equilibrium concentration. 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 is below to unity, this implies that adsorption process is chemical, if the value is above unity adsorption is a favorable physical process ,if the value of n is equal to unity, the adsorption is linear. The values of the model parameters obtained from the plot of qe against Ce shown in Fig. 6 are presented in table 1.

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 8 :

$$q_e = \frac{Rt}{b}\log(K_t C_e) \quad ....(8)$$

Equation 9 can be expressed in its linear form as:

$$q_e = B_T \log K_T + B_T \log C_e \quad ....(9)$$

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 (9). A plot of the qe versus log C_e enables the determination of the isotherm constants K_T and B_T. The Tempkin constants are illustrated in (Table 3).

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)

Conclusion

Coconut Shell consider new efficient, low-cost, economical, and environmentally safe adsorbent with potential for practical application in the treatment of dye-contaminated wastewater. The percentage removal of color and adsorption capacity decreasing with increasing of temperature and pH of the dye solution and the adsorption capacity decreasing with increasing of adsorbent dosage and increase with increasing contact time, and surface area, GRL dye on adsorbent surfaces

Table 3: Coefficient isotherm parameters of Freundlich, Langmuir and Tempkin equation by adsorption of GRL, 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 /GRL	pH(6)	47398.00	0.90	0.98939	63.178	0.312	0.8223	123.94	2.22	0.86962
	T/K(293.15)									
	Catalyst[0.0 5 g/100ml]									
	Particle Size[200 Mesh]									

maximum adsorption found to be at pH = 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.

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