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Adsorptive Removal of Aqueous Phase Crystal Violet Dye by Low-Cost Activated Carbon Obtained from Date Palm (L.) Dead Leaflets

Adsorpcyjne usuwanie wodnej fazy fioletu krystalicznego z wody za pomocą taniego aktywowanego węgla uzyskanego z martwych liści palmy daktylowej (L)

Up to now, water pollution is still one of the important issues and challenges worldwide, due to its environmental, economic and human life impacts. It is also remains a challenge to environment scientists and technologists. Nowadays, the textile dyeing industry is considered one of the largest water consuming industries and produces large volumes of colored wastewater in its dyeing and finishing process. In this study, date palm tree leaflets (DPL) has been selected as a natural renewable source for the production of a new activated carbon (AC) utilized for the removal of crystal violet (CV) from water-dye system using a batch mode technique. The experiments studies were carried out at different initial dye concentration, contact time, adsorbent dose, and pH. The sorption exhibited high efficiency for CV adsorption and the equilibrium state could be achieved in 30 minutes for the different CV initial concentrations. CV removal was proved to increase with the increase in ACDL dose, pH, and contact time. Agitation rate and total volume of the reaction mixture were kept at 200 rpm and 20 mL respectively. The applicability of Langmuir and Freundlich isotherm equations was investigated and it was found that experimental data fitted very well to both Freundlich and Langmuir models. The maximum adsorption capacity (q_m) was found to be 36.63 mg/g.

Keywords: **adsorption, batch mode, crystal violet, date palm leaflets, isotherm**

Introduction

Today one of the major problems in worldwide is water pollution. According to the United World Water Development Report, 2,000,000 tons of wastes are discharged to the receptor water bodies every day, including industrial wastes, dyes and chemicals and etc. [1]. More than 600 organic and inorganic pollutants have been reported in receptor water [1]; about 10,000 of various commercial dyes and pigments exist and over 700,000 tons are produced annually, worldwide [2]. Dyes usually have synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade [3]. Dyes and their degradation products may be carcinogens and toxics if these effluents are treated inefficiently before discharging to the streams; they could bring problems to human health and animals [4] and are not limited to themselves but also may be passed onto future generations by the way of genetic mutations, birth defects, inherited diseases [5]. It is estimated that 2.0% of dyes produced annually are discharged in effluent from manufacturing operations while 10% is discharged from textile and associated industries [6]. Water pollution accounts for the deaths of more than 14,000 people, every day [1].

CV is widely used in textile manufactories for dying of cotton and silk and also in manufacturing of paints and printing inks [7]. CV causes eye burns of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, and mental confusion [8]. The dyes absorb and reflect sunlight entering water and so can interfere with growth of bacteria and hinder photosynthesis in aquatic plants [6]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters. Hence, it is environmentally very important to remove the synthetic dyestuff from the waste water before discharging it into any natural receptor waters with a high removal efficiency [9].

In general, several difficulties are encountered in removal of dyes from waste waters. By design, dyes are highly stable molecules, made to resist degradation by light, chemicals, biologicals and other exposures. Dyes vary widely in chemical composition. Basic dyes are considered as one of the more problematic classes of dye which are consider as toxic colorants. As a result, improved or cost effective technologies are required to remove them from textile effluents [10]. A number of treatment processes for the removal of dyes from wastewater are in practice. They comprise the followings: microbial degradation [11], electrochemical degradation [12], an advanced oxidation processes [13], cation exchange membranes [14]. However, each of these processes aforementioned has its merits and limitations in application.

Among these processes, adsorption currently appears to be the best in order to remove colours from wastewater. Adsorption process has gained interest as a more promising method for the long term as it is seen to be more effective and economic approach for dye removal [15].

Adsorption using activated carbon obtained from agricultural by-products/wastes such as cherry stones [16], palm ash [17] and pommel peels [18] are inexpensive adsorbents, easily available and handled, and simply operated [19]. Other materials, most available and abundant particularly in public gardens and woods which are plant and tree leaves have been proposed and reported as economic, suitable, and simple agro-adsorbents for the study of dyes removal [20-25]. Carbonization of these high-in-carbon content plant and tree leaves can also be used in production of AC [26, 27]. One main advantage of utilizing the agricultural by-products/waste is the ability to synthesize and produce cheap and eco-friendly AC as an alternative substitution for commercial AC. These agricultural by-products/waste materials usually have no economic value. They, as alternatives, may present a disposal problem leading to environmental pollution. Therefore, considerable economic value would be attained from the conversion of these waste materials into AC. Carbon-containing materials such as agricultural by-products/waste are converted to AC through a process called activation which is essentially composed of a two phase process. Phase one requires a pyrolysis of an agricultural by-products/wastes such as wood, coal, peat, fruit stones, leaves, and shells. It is burn off of amorphous decomposition products (tars) which work on freeing the pore openings, and increasing the number of pores. While in phase two, enlargement of pores in the carbonized material is achieved [28]. They are considered one of the feasible alternatives both in terms of environmental and economical point of view. In additional, activated carbons derived from agricultural by-products/wastes present comparable adsorption capacities and in some cases even better than of commercially made AC [29, 30].

Date palm trees need a climate with plentiful sun, minimal rain, yet good access to water, which to a large extent is only provided by oases. They are very cold tolerant, salt tolerant; they can also take extreme heat, dry and wet conditions [31]. Maximum temperatures of around 50°C as they occur do not harm the palm [32]. In Arab countries, the date palm tree is considered one of the main fruit crops. Arab countries possess 70% of the 120 million world's date palms and are responsible for 67% of the global date production [33]. The global production of dates was recorded 7,429,811 tons in 2009 [34, 35], while 198,000 tons of date leaf are produced each year in Tunisia [35, 36], the main components of the date palm leaves are cellulose 38.10%, hemicelluose 22.74%, lignin 11.95%, ash 7.71% [37].

Libya is considered one of the major countries engaged in taking care and cultivating date trees that the number of these trees cultivated and distributed in many regions of the country at many regions particularly at the oases were estimated to be around 5.0 million trees [38]. Therefore, a great advantage can be taken from the huge number and abundance of this type of trees for the production. Modern technological developments have made it possible to look at the palm as a raw material and renewable source for industrial purposes. Practically all parts of the date palm, except perhaps the roots, are used for a purpose best suited to them [33].

1. Related works

Gouamid et al. [37] have investigated the ability of Date palm Leaves powder (DPLP) to remove Methylene Blue (MB) from aqueous solutions using batch mode adsorption study. The experiments studies were carried out at different initial dye concentration, contact time, solution pH, adsorbent dosage, particle size of (DPLP), and temperature. The results showed that equilibrium was reached within 160 min. The used sorbent gave the highest adsorption capacity at pH 6.5. The maximum adsorption capacity has been improved from 43.103 to 58.14 mg/g as the temperature increased from 30 to 60°C. The enthalpy ΔH° and entropy ΔS° values for the process were estimated at $8.098\ \mathrm{kJ\ mol^{-1}}$ and $12.97\ \mathrm{J\ K^{-1}\ mol^{-1}}$ respectively. Yasamin Majedi et al. [39] have investigated the adsorption efficiency of three different dyes (malachite green, methylene blue, and methylsulfonazo-III) by activated carbon prepared from date palm leaf wastes. Adsorption studies was conducted by batch mode and fixed-bed column system using activated carbon prepared from date palm leaf wastes with chemical activation using H_2SO_4 [39].

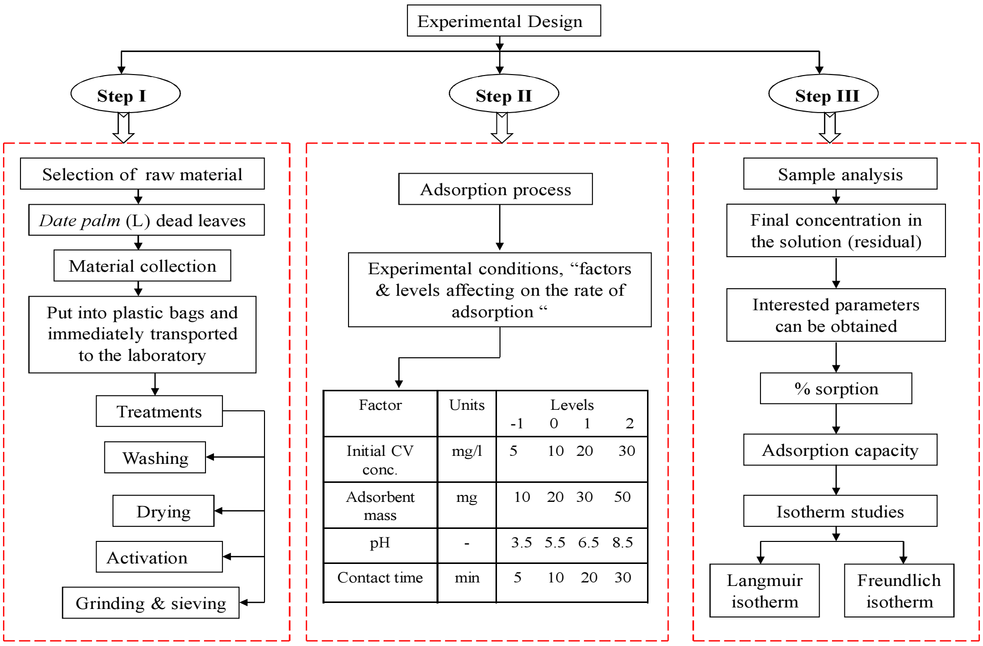
The adsorption of crystal violet (CV) onto date palm fibers (DPFs) from aqueous solution was conducted by Mashael et al. [40]. In this study the percentage removal of CV dye by adsorption onto DPF at different pH and temperatures showed that these factors play a role in the adsorption process, and greater adsorption occurred at low temperature and pH. The study was also concluded that the thermodynamic calculations indicated that the process was spontaneous and exothermic. The kinetics analysis revealed that the pseudo-second-order model was a better fit of the experimental data than the first-order kinetic expressions. In a related study Hussein et al. [41] have produced three types of the activated carbon (AC) from three different positions from date palm. These three positions are the palm fronds (AC1), the date palm seeds (AC2), and the palm fiber (AC3) using physiochemical activation method with H_3PO_4. This study proved that AC1 showed higher efficiency for removal of the Bismarck brown (BBG) in comparison with AC2 and AC3 [41].

In the current study, activated carbon obtained from date tree fronds was studied to evaluated its efficiency in adsorption of CV from water-dye system. Batch mode experiments were conducted to determine the factors affecting the CV adsorption process.

2. Materials and method

2.1. Preparation process of AC

In Summer season 2013, Dry date palm L. Dead leaf were collected from few local planted date trees in city of Tripoli in Libya. Then the dry leaves were put into plastic bags and immediately transported to the laboratory. The leaves were washed with warm water to remove dirt particles, impurities and undesirable materials, subsequently was washed many times with distilled water, and dried once at sunlight for 7 days and the other in an oven at 100°C for 24 hours. After drying, leaves were crushed to small pieces at the size range of (1.0÷2.5 cm), after that activated by soaking them with phosphoric acid solution (65% by weight). Next, the impregnated leaves of 100 g were packed in 15x15 $\mathrm{cm^2}$ aluminium foil which was then placed inside a thermal furnace. The temperature was raised at heating rate of 10°C/min from room temperature to 420°C where it was kept at that temperature for 1 hr. after cooling, the sample was washed thoroughly using hot distilled water until pH reached 7. And finally, the carbonized leaves were grinded manually and passed through the 0.2 mm sieve plate to produce carbon of uniform size inform of powder for use in batch mode experiment. The step by step of experimental design work in this study, as well as; the raw and AC from date palm leaflets are shown in Figures 1 and 2 respectively.



Factor	Units	Levels -1	 0	 1	 2
Initial CV conc.	mg/l	5	10	20	30
Adsorbent mass	mg	10	20	30	50
pH	-	3.5	5.5	6.5	8.5
Contact time	min	5	10	20	30

Fig. 1. Experimental design involved in this study

Fig. 2. Rawpalm leaflets (a), and activated carbon from DL storage into colsed glass container (b)

2.2. Characteristics and Preparation of CV Adsorbate

CV dye is a triphenylmethyl cation ($C_{22}H_{30}N_3Cl$; molecular weight 408 g; λ_{max} 584 nm), was obtained commercially from B.D.H. Chemicals Ltd., England. It is used in this study as a model molecule for organic pollutants in general and basic dyes in particular, and thus no further purifications were needed. The molecular structure of CV dye is illustrated in Figure 3. CV dye stock solution (1000 mg/L) was prepared by dissolving accurately the weighed quantity of the dye in double distilled water. The working solutions of different concentrations were prepared by diluting the stock solution to give the appropriate concentrations. All chemicals used throughout this study were of analytical-grade reagents. From an analytical point of view, each experiment was performed three times under the same conditions and the average results were taken.

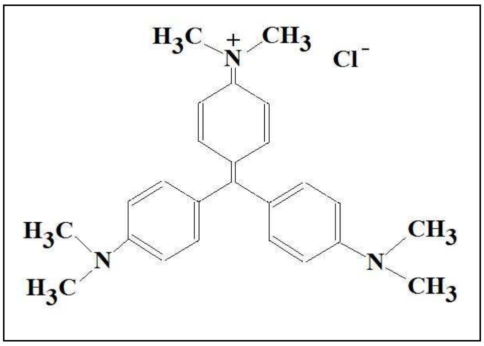


Fig. 3. Molecular structure of crystal violet

3. Instrumentations

A number of equipments were used in this study: (i) UV/visible spectrophotometer (Specord 205, UV-Analytikjena, Germany) at λ = 586 nm for the determination of the CV concentrations; (ii) 740 Inolab WTW model pH meter using a SenTix 20 pH model double electrode calibrated with standard buffer solutions was used for measurements of pH of the solutions; (iii) digital shaker (GFL 3005 model, Germany) was used for Batch mode adsorption experiments. A Tensor 27 Bruker, USA Fourier Transform Infrared Spectroscopy (FT-IR) for the characterization of the ACDL functional groups at the range of 500÷4000 cm^{-1} before and after batch mode adsorption process for CV dye.

Brunauer-Emmett-Teller (BET) nitrogen adsorption technique is conducted to evaluate the surface area and pore volume of the non-activated carbon DL which involved the application of physical adsorption of nitrogen at 77 K in a Micromeritics ASAP 2020 apparatus, USA. The content of C, H, N, and O atoms with the non activated DL was determined by FLASH 2000 CHNS/O Analyzer (Thermo Scientific model, USA). Thermo-gravimetric experiments were recorded on a TA instrument SDT Q 500 operating under nitrogen with a flow rate of 100 mL/min through a furnace. Samples weight about 10 mg, varying heating rates of 10°C/min, temperature range of (30÷800°C). At last, scanning electron microscope (Quanta FEG, USA) was used to study surface of the DLAC at very high magnifications.

4. Batch mode experiment

In general, batch adsorption system are easy for researchers to use in the laboratory studies, but they definitely less convenient for pilot scale work (i.e. industrial applications) [42]. Most of the reported studies on the adsorption of dyes by AC were conducted in batch mode technique [43, 44]. The effluent contains V (L) of water and an initial pollutants concentration C_o, which is to be reduced to C_1 in the adsorption process. In the treatment stage W (g) adsorbent (pollutant-free) is added to solution and pollutant concentration on the solid changes from $q_o = 0$ (initially) to q_1 [44].

In this study, batch mode sorption experiments were performed in a shaker at a constant agitation rate of 200 rpm and room temperature of 27 ± 1°C for different periods of contact time 5÷30 min and a pH of 3.5÷8.5 using 100 mL Erlenmeyer flasks. All sorption experiments were conducted by mixing different quantities 10, 20, 30, and 50 mg of ACDL with CV solutions containing different initial concentrations of 5, 10, 20, 30 mg/L.

After termination of the adsorption experiments, the remaining concentration of CV in each three samples were determined by UV spectroscopy after filtering the adsorbent with Whatman filter paper to make it carbon free. The amount of adsorption at equilibrium q_e (mg/g) was calculated as follows:

$$q_e = (C_0 - C_e) \cdot (V/M) \tag{1}$$

where C_0 and C_e are the liquid-phase concentration of dye at initial and final, mg/L, respectively. V (L) is the volume of the solution and M (g) is the mass of dry sorbent used.

The percentage removal (%) was calculated using the following equation:

$$\%\ \text{removal} = \{(C_0 - C_e)/C_0\} \cdot 100 \tag{2}$$

5. Isotherm studies

The study of adsorption isotherms is to understand the nature or behaviour of the adsorption. It is a very important tool of study that it demonstrates the relationship between the amount of a substance adsorbed per unit mass of adsorbents at a certain temperature and its concentration in the equilibrium solution. Langmuir and Freundlich isotherms are the most frequently used equations to study the nature of isotherm [46, 47].

Langmuir isotherm model represents the simplest in all known isotherm models for monolayer adsorption [48]. Langmuir isotherm model is developed by assuming that the force of interaction between the adsorbed molecules are negligible, fixed number of accessible sites are available on the adsorbent surface in which these sites are energetically equivalent and once an adsorbate molecule occupies a site, no further adsorption takes place [47-49]. In other wards, the Langmuir presumes a specific homogenous type of the adsorption, i.e., once a molecule of CV takes an active site, no other one can take same site. The linear form of the Langmuir model is used as in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \tag{3}$$

where q_e is the solid phase adsorbate (ACDL) concentration at equilibrium, mg/g, C_e is the equilibrium (CV) concentration, mg/L, q_{max} is the maximum adsorption capacity corresponding to complete monolayer adsorption, mg/g, and finally b is the Langmuir isotherm constant. The slope and the intercept of linear plots of C_e/q_e vs. C_e are used to calculate the constant parameters of q_{max}, mg/g, and b. However, Freundlich isotherm model is an empirical model and widely used for many years. It assumes that adsorption takes place on a heterogeneous surface, and can be used for non-ideal adsorption [23, 50-52]. The linear form of Freundlich is expressed as follows:

$$\log q_e = 1/n \log C_e + \log K_f \tag{4}$$

where K_f and n are Freundlich constants with "n" giving an indication of the facility with which adsorption process takes place, K_f is the adsorption capacity of the adsorbent mg/g(L/mg)$^{1/n}$.

6. Results and Discussion

6.1. Adsorbent characteristics

6.1.1. Physical-chemical analysis of the adsorbent

The characteristics of activated carbon product from date palm leaflets are shown in Table 1. While, the provides surface areas of some other inactivated carbon obtained from different agricultural by-products/waste reported in literatures can be comparable to the results obtained in this research study are shown in Table 2 respectively.

Table 1. **Characteristics of activated carbon product from date palm leaflets**

Parameter	Value
Elemental analysis, %	
C	48.40
H	5.75
N	3.27
O	37.52
Porous characteristics (without activation)	
BET surface area, m^2/g	14.0
Total pore volume V_m, cm^3/g	0.13
BJH adsorption average pore diameters, nm	5.40
BJH desorption average pore diameters, nm	7.30
Micropore volume $V\mu$, cm^3/g	0.09
Characteristics of AC by (65% H_3PO_4)	
Surface area, m^2/g	
BET Surface area	161.86
Langmuir surface area	214.88
t-Plot micropore area	129.30
t-Plot external surface area	32.56
BJH adsorption cumulative surface area	27.99
Pore volume, cm^3/g	
Total pore volume, cm^3/g	0.098
t-Plot micropore volume, cm^3/g	0.06
BHJ adsorption cumulative volume, cm^3/g	0.041
Pore size	
Adsorption average pore width (4V/A by PET), nm	24.29
BHJ adsorption average pore diameter (4V/A), nm	59.06
Alpha-S	
Slope, cm^3/g STP	18.78 ± 1.59
Y - intercept, cm^3/g STP	33.34 ± 1.17

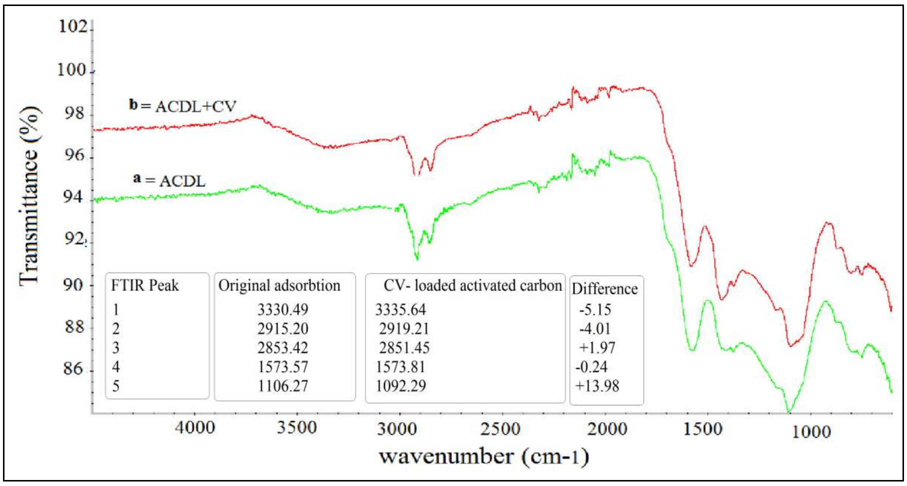
Table 2. **Compression of surface area of some activated carbons**

Activated carbon type	S_{BET}, m^2/g	Reference
AC-Hazelnut shell	5.0	[54]
AC-Hazelnut shell	10.1	
AC-Hazelnut husk	4.31	
AC - *Posidonia oceanic* (L.), 0% activation	38.9	
AC - from oak leaves, 0% activation	4.0	
AC - from date palm leaflets, 0% activation	14.0	Present study

6.1.2. FTIR analysis

The functional groups, on the surface of activated carbon analyzed by FTIR demonstrated the existence of carboxyl, hydroxyl, and amine groups which were mostly negatively charged. The FTIR transmission spectra in the range of 400÷4000 cm^{-1} for the original activated carbon, the activated carbon laden with

CV is shown in Figure 4a, and 4b. The functional groups involved in the adsorption were as follows: broad bands at 3330.49 cm^{-1} representing bonded –OH groups; 2915.20÷2853.42 cm^{-1} the aliphatic C–H group [54]; 1430 cm^{-1} represent the CH_2. While, the band around 1106 cm^{-1} is ascribable to either C–OH stretching in phenols or C–O stretching in cyclic ethers [55]. Between 450 and 900 cm^{-1}, there is a number of broad overlapping bands which are superimposed. They cannot, therefore, be described in terms of simple motion of specific functional groups or chemical bonds. It must be noted that characteristic bands below 900 cm^{-1} are C–H out-of- plane bending absorption in aromatic ring and C–C stretching [54]. While, the ACDL spectrum in Figure 4 (line b) demonstrating the AC after batch mode sorption shows the presence of new peak at 1429.61 cm^{-1}, and also a little shift to almost all aforementioned peaks. Comparing the two spectrum, one can conclude that some of these peaks were shifted or disappeared and new peaks were detected. These findings of changes observed in the spectra, indicated the possible involvement of those functional groups on the surface of the ACDL in sorption process.



FTIR Peak	Original adsorbtion	CV- loaded activated carbon	Difference
1	3330.49	3335.64	-5.15
2	2915.20	2919.21	-4.01
3	2853.42	2851.45	+1.97
4	1573.57	1573.81	-0.24
5	1106.27	1092.29	+13.98

Fig. 4. FTIR spectrum of ACDL adsorbent before (a) and after the batch mode sorption process (b)

6.1.3. Thermogravimetric analysis (TGA)

According to the results and data obtained from TGA analysis, the percentage weight loss during TGA for Date palm leaflets. Two major weights lost that took place in this graph. The first range of decomposition happened at approximately 50 to 110°C, which represents almost 8.0% weight lost. This is most possibly due to the moisture released by the sample during heating. The largest weight loss occurred at temperature range of about 450 to 650°C. This is due to decomposition of chemical bonded water, cellulose, hemicellulose and lignin to carbons [56-58]. These types of decompositions probably explain the reason behind the absence of any intensive peaks at the region between 400 cm^{-1} to at least 1700 cm^{-1} on FTIR spectrum at carbonization temperature of 650°C (figure not shown). Further heating above 650°C reveal a lowering trend of weight loss indicating formation of volatile materials like CO, CO_2 and etc. (figure not shown) [59]. A similar phenomenon was obtained for oak leaves activated carbon by TGA analysis at carbonization temperature of 650°C [53].

6.1.4. SEM analysis

SEM was used in order to obtain information about the surface area morphology of the activated carbon. The surface texture of the sorbent is shown in Figure 5. It can be seen from the figure that particles are almost irregular in shape with a very good porous.

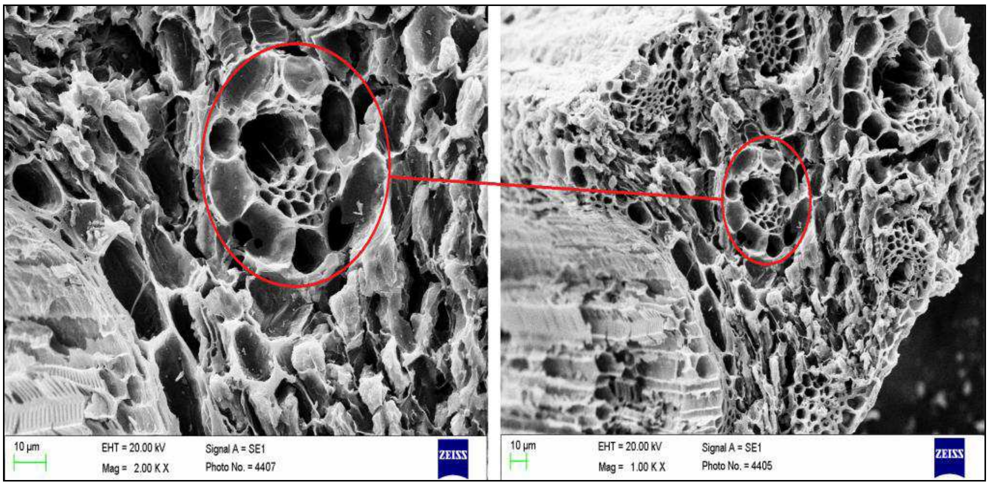


Fig. 5. SEM image of the adsorbent (AC) from date palm leaflets

6.2. Effect of adsorbent mass on the rate of adsorption

The effect of adsorbent ACDL doses (10, 20, 30, 50 mg) on CV dye adsorption capacity (the amount of CV dye sorbed per unit mass of ACDL sorbent, is shown in Figure 6; these data have been obtained from starting constant pH of 6.5, constant agitation rate of 200 rpm, contact time of 30 min at room temperature. The results showed that as the adsorbent ACDF dose is increased from 10 to 50 mg, the CV dye concentration, remained in the solution (residual), decreased from 30.0 to 1.61 mg/L. The reason for this is attributed to the increase in the number of active sites available for adsorption of CV molecules with increase in quantity (weight) of ACDL causing higher CV percentage removal [50, 60-62]. Equation (1) was used to calculate the adsorption capacity which could be seen that it has been gone down from 42.60 mg/g using 10 mg of ACDL to 11.36 mg/g using 50 mg of the same AC. The active sites may not be available during the CV adsorption process due to the overlapping between these active sites themselves at high doses, which reduce the total surface area and thus the amount of the Adsorbates (i.e. CV molecules) adsorbed by the adsorbents (i.e. ACDL) is decreased; it has been reported in a number of articles [50, 51, 62].

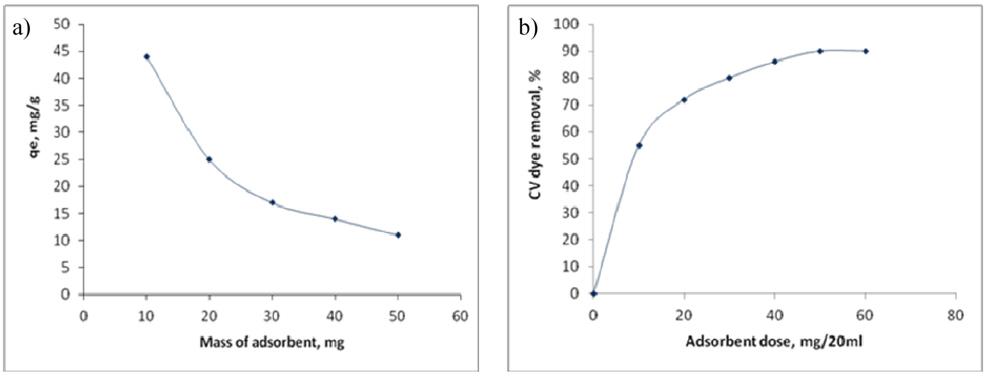


Fig. 6. Variation of CV adsorption as a function of ACDL amounts (20 mL of 30 mg/L of CV, temp. 27 ± 1°C and pH 6.5) (a), the effect of ACDL dose on the CV adsorption (percentage removal) (b)

6.3. Effect of pH

The initial pH of CV dye solutions 30 mg/L were adjusted to 3.5, 5.0, 6.5, and 8.5 while the CV batch mode adsorption was carried out at room temperature of 27°C, agitation rate at 200 rpm, contact time of 30 min (Fig. 7). The pH is a very effective factor in removing the CV dye molecules under the conditions employed, through the protonation of the amino groups located at the aromatic rings (Fig. 3). The three amino groups of the CV molecule become protonated at low pH and the number of them decrease from three to one with the increase of pH.

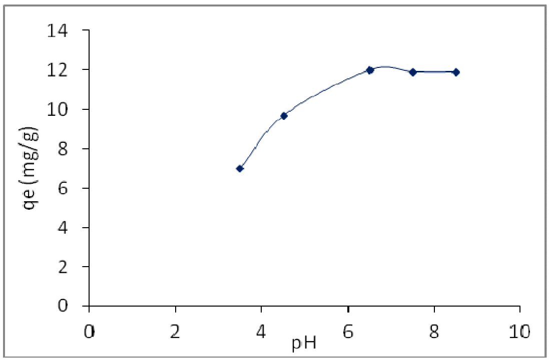


Fig. 7. The effect of the pH on the removal of CV basic dye by the ACDL (20 mL of 30 mg/L of CV, temp. 27 ± 1°C, agitation rate of 200 rpm, and contact time 30 min)

It was observed that the CV solution had different colours as pH was changed from 3.5 to 9.0 which agreed with reported findings [61]. Figure 7 demonstrates that the adsorption capacities of CV increased with the increase of pH; for pH < 6.5 the residual CV dye decreased with increase in pH from 3.5 to ≤ 6.5, and above this pH value the CV residual became nearly steady. This was attributed to the fact that, at low pH (3.5 and 5.0), the protonation of the negatively binding active sites was enhanced and thus the number of these active sites became lower for the adsorption of CV molecules in contrast, when the pH was higher (≥ 6.5) the ACDL possibly and gradually become deprotonated (i.e negatively charged) and the electrostatic process of attraction of the cationic CV dye molecules became enhanced [61-67].

6.4. Effect of contact time

Batch process was conducted at different contact time ranging from 5÷30 min. The effect of contact time on CV dye adsorption capacity at CV initial concentration of 30 mg/L is presented in Figure 8. From the figure, it can be observed that the adsorption capacity rapidly increased with the increase of contact time at first ten minutes. It seemed thereafter the adsorption process continued slowly until gradually reached saturation and the adsorption capacity was said to reach equilibrium which was attained after 30 minutes at the employed conditions. The rate of adsorption capacity was higher in the beginning due to the larger surface area and the availability of the binding active sites of the adsorbent ACDL at the start [50] and the driving force provided by the initial concentration at the beginning which overcomes all mass transferred resistance of the CV between the aqueous and solid phases [18, 66]. It is worth mentioning that data on adsorption kinetics of dyes by a number of adsorbents have demonstrated a range of adsorption rates. For example, Rammel et al. have reported a contact time of 15 min, as sufficient for attainment of equilibrium for the adsorption of CV onto *Chaetophora elegans* algae [61]. Alaa reported that equilibrium in the solution of CV dye was attained within 30 minutes when ACDS was applied as an adsorbent [67]. However, in 2006, Mall et al., reported that a contact time of 4 hr was accepted for reaching a quasi-equilibrium situation for the adsorption of Orange-G and CV by bagaase fly ash [68]. In a similar, Gouamid M. et al. studied the ability of raw date palm leaves powder (DPLP) to remove methylene blue (MB) from aqueous solutions by the biosorption process. Their results showed that the equilibrium was reached within 160 min [37].

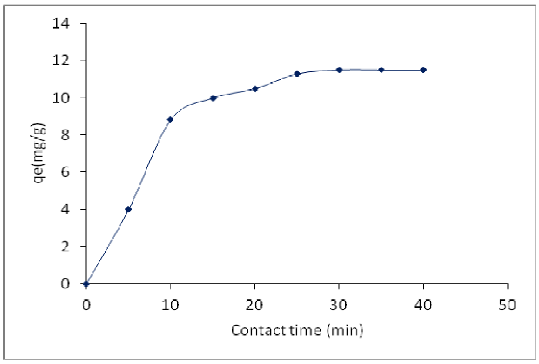


Fig. 8. The effect of contact time on the removal of CV by ACDL at the same conditions

6.5. Effect of initial CV concentrations

The effluents of different industries may have different dye concentrations. The initial dye concentration is one of the important factors that effect adsorption kinetics [51]. The initial dye concentration of 5, 10, 20, and 30 mg/L were used in our study at room temperature, an adsorption pH of 6.5, constant contact time of 30 min and agitation rate of 200 rpm and in conjunction with ACF adsorbent dose of 50 mg/L, and their effects on the CV dye removal were thereafter shown in Figure 9a, while the adsorption capacities of CV was in Figure 9b.

From the figure, it can be observed that the CV dye adsorption percentage decreased from 96.0 to 86.0% with the increase of initial CV concentration from 5.0 to 30.0 mg/L. However, further examination of the data by using Equation (1) revealed that the amount of CV absorbed per unit mass of adsorbent (q_e) increased from 4.78 to 25.8 mg/g (Fig. 9b), with the increase in initial concentration from 5.0 to 30.0 mg/L. This may be attributed to the fact that the initial concentrations provides an important driving force to overcome all mass transfer resistance of the CV between the aqueous and the solid phases, as referred to in a number of literatures [18, 23, 62].

In a similar mode technique, the effect of the initial mthylene blue (MB) concentration on the adsorption rate by coconut bunch waste (CBW) at adsorbent dosage of 0.20 g and mixing speed of 100 rpm has been investigated by Hameed et al. [45]. During their study, they discovered that the adsorption at different concentrations was rapid in the initial stages and gradually decreases with the progress of adsorption until equilibrium was reached. The amount of MB adsorbed at equilibrium (q_e) increased from 30.42 to 65.55 mg/g as the concentration was increased from 50 to 500 mg/L. But, the MB percentage removal decreased from 57 to 13% [18].

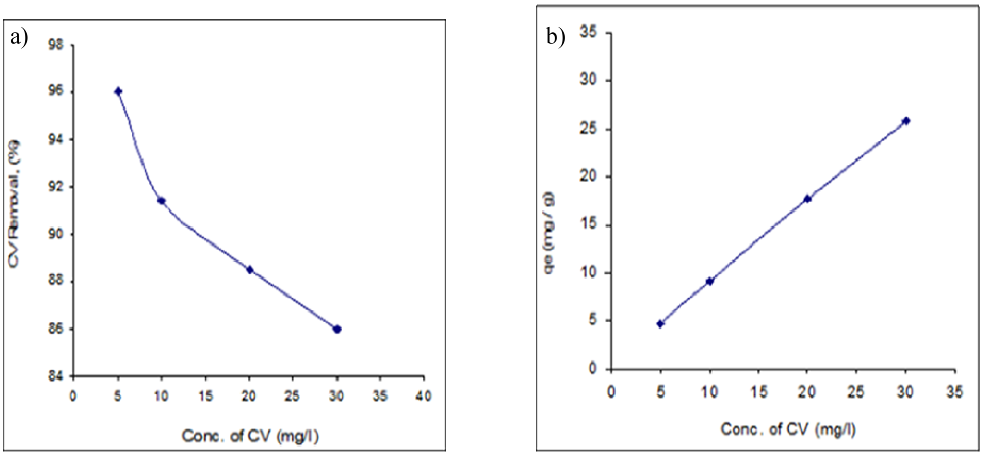


Fig. 9. CV adsorption as a function of CV Conc. (a) and CV removal as a function of CV Conc. (b)

6.6. Isotherm analysis

Figures 10 and 11 show linear plot obtained between C_e/q_e and C_e and $\log q_e$ and $\log C_e$ with linear regression of 0.9178 and 0.9929 respectively. The slopes and the intercepts of linear plots were used to calculate the constant parameters in both equations of Langmuir and Freundlich isotherms. The obtained data are shown in Table 3.

Table 3. **Langmuir and Freundlich constant parameters**

Langmuir model			Freundlich model		
q_{max} mg/g	b L/mg	R^2	K_f L/g	n	R^2
36.63	0.485	0.9178	2.82	1.74	0.9929

The calculated constants for Langmuir and Freundlich isotherm based on the data collected are shown in Table 3. The Langmuir constants q_{max} (mg/g) and b (L/mg) were determined from the plot of C_e/q_e versus C_e. The q_{max} which represents the total maximum capacity of ACDL adsorption for CV dye is found to be 36.63 mg/g while b is 0.485 (L/mg). However, for Freundlich isotherm, the constants are K_f (L/g) and n value which are used to represent adsorption capacity and adsorption intensity, respectively. It is well known that the closer the n value to zero, the more heterogeneous the system becomes [69]. From Table 3 the calculated n value which was 1.74 indicates that the system is heterogeneous making it more suitable for Freundlich isotherm.

Table 4 reported maximum adsorption capacities q_m in the literature.

Table 4. **Maximum adsorption capacities q_m presented in the literature**

Adsorbent	Adsorbate	Temperature °C	q_{max} mg/g	Ref.
Citrulus lanatus rind	Crystal violet	50	11.99	[51]
Acacia *nilotica leaves*	Crystal violet	27	33.0	[23]
Arundo donax root carbon	Malachite green	40	8.69	[70]
Waste tea activated carbon	Acid blue 25 dye	50	203.34	[71]
AC - from *Oak leaves*	Crystal violet	25	41.15	[53]
Rice husk	Methylene blue	32	40.58	[72]
Tomato paste waste	Crystal violet	50	68.97	[73]
Date palm leaves powder	Methylene blue	60	58.14	[37]
Used black tea leaves	Basic Violet 10	30	71.40	[74]
Orange peel	Methylene blue	30	18.60	[75]
AC - from date stones	Methylene blue	30	340.0	[76]
AC - from date palm leaflets	Crystal violet	27	36.63	This study

Considering the values of the linear regression coefficients for both isotherms, it can be observed that regression value obtained for Langmuir model was low as compared to that obtained for Freundlich model. Therefore in this present study, It can be inferred that a CV uptake is best interpreted in terms of Freundlich isotherm model. This indicates that the CV uptake on the surfaces of ACDL occurs heterogeneously.

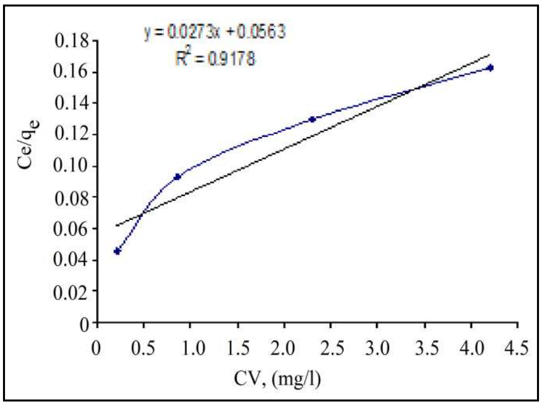


Fig. 10. **Langmuir plot for CV adsorption on AC**

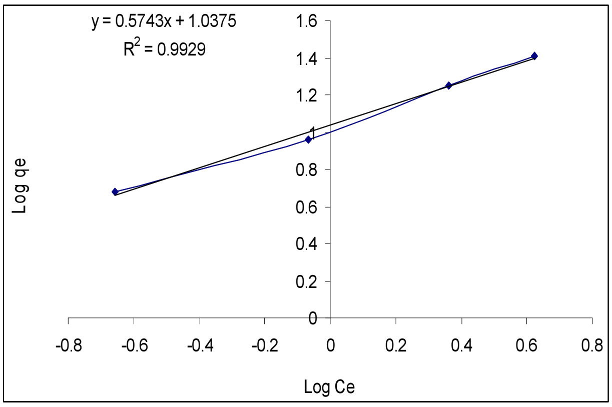


Fig. 11. **Freundlich plot for CV adsorption on AC**

Conclusions

The major conclusions of this study are drawn as follows:

1. The results of the study show that local adsorbent prepared from date fronds materials, can be successfully used as an adsorbent for the removal of CV from aqueous solution.
2. The batch mode system used in this study have a good effect on the rate of adsorption.

3. The adsorption process was influenced by a number of factors such as ACDL adsorbent dose concentration, pH, contact time, and the initial CV concentration.
4. The adsorption rate increased with increase in the amount of the adsorbent (ACDL) and contact time, while agitation rate and total volume of the reaction mixture were kept at 200 rpm and 20 ml respectively.
5. The highest CV removal was obtained at pH 6÷6.5.
6. The adsorption parameters for the Langmuir and Freundlich isotherms were determined and the equilibrium data were in good agreement with both Langmuir and Freundlich isotherms model.
7. The ACDL used in this work are abundantly available, requires almost no cost, and more important very effective in removing CV from aqueous solution. Therefore, the eco-friendly adsorbent is expected to be economically feasible for the removal of CV dye from wastewater treatment i.e. textile industries, tanning industries.
8. As a result and from environmental point of view, the use of date palm leaflets as a raw material source for production such AC.
9. Another main advantage of recycling date palm leaflets as a raw material source for production such AC is also environmental solution by reducing the large accumulate quantities of DPL, and hence broad areas of lands are preserved from solid waste pollutions.

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Streszczenie

Poziom zanieczyszczenia wody jest jednym z najważniejszych problemów do rozwiązania i wyzwań dla technologii remediacyjnych. Także przemysł farbiarski ma wpływ na zanieczyszczenie wód powierzchniowych ze względu na wytwarzanie dużych ilości ścieków powstałych w procesie barwienia i wykańczania materiałów. Liście palmy daktylowej zostały wybrane jako naturalne, odnawialne źródło materiału organicznego do wytwarzania węgla aktywnego, który może być wykorzystany w procesie usuwania fioletu krystalicznego. W trakcie badań zbadano wpływ stężenia barwnika, czasu kontaktu, masy złoża węgla aktywnego oraz pH wody na efektywność procesu usuwania barwnika. Na podstawie uzyskanych wyników można stwierdzić, że izotermy Freundlicha i Langmuira dobrze opisują przebieg procesu adsorpcji fioletu krystalicznego na złożu węgla aktywnego uzyskanego z martwych liści palmy daktylowej.

Słowa kluczowe: **zanieczyszczenie wody, fiolet krystaliczny, usuwanie, węgiel aktywny, adsorpcja, izotermy adsorpcji**