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Research Article

# Green Environmental Approach for Adsorption of Hazardous Dye from Water Using Tree and Sea Plant Leaves (Dead L.)

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## Abstract

Currently, management of waste and quality of water are the two important tasks of human life. However, this work is based on the use of biomass residues including dead leaves of oak trees and sea plant (*Posidonia oceanica* L.) for the adsorptive elimination of hazardous dye such as crystal violet (CV) and methylene blue (MB) from aqueous solution. To meet the approaches of green chemistry and sustainable environment. The biomass adsorbents were applied without previous chemical or physical treatment. Also the natural value of pH (pH 7) has been used during the whole process. The important factors which directly effect on dye removal were investigated in batch process. The optimum values of parameters were established as contact time of 60 min, 50 mg/l as the initial dye concentration, and 0.1 g as the adsorbent mass, while the value of temperature was fixed at 25°C. The characterization study of biomass was performed using Fourier Transform Infrared (FTIR) and Scanning Electron Microscope (SEM) techniques. The maximum adsorption capacity for CV and MB onto oak L. was found to be 31.65 and 33.5mg/g, and as 22.93 and 27.78 mg/g for CV and MB, respectively onto *Posidonia oceanica*.

**Keywords:** Adsorption; Agricultural; Batch Process; Biomass; Oak; Sea Plant

## Introduction

Globally, water is a commonly used component that is playing an important role in our lives, which is followed by an increase in the generating of waste effluents. In recent years water consumption has been growing all over the world because the global population, as well as industrialization, has been rapidly increasing. The world population is estimated to reach 7.9 billion by the end of 2020 [1]. This increase is generating a huge volume of wastewater every day, containing pollutants such as heavy metals, dyes, chemicals, and oils, etc. Unfortunately, such waste is still discharged into the natural water streams in many countries, particularly when the treatment technology is absent [1-3]. Several industrial processes involve dyes as important components for dying applications. Paint and textile manufacture are the main sources of dyes in industrial wastewater, which consume substantial volumes of water in their manufacturing process. For instance, dyes are widely used in textiles to color the products, and at the same time they generate thousands of tons of wastewater every year [2-5]. Dyes are known to be particularly hazardous organic pollutants for the environment, surface and ground waters, and they are also harmful to human beings [4-7]. However, such wastewater must be treated before discharge to the environment [2,3]. Various technologies for the treatment of dyeing wastewater have been advanced by researchers in their works. They include chemical precipitation, flotation, membrane separation, and adsorption by activated carbon. Commercially activated carbon (CAC) is almost the highest adsorbent material with a wide range of applications in wastewater treatment due to its excellent adsorption efficiency for the organic and inorganic substances. Coal, asphalt, and petroleum coke are the major sources for the production of CAC which is very expensive. Furthermore, these sources are non-renewable and contribute to the high cost in the preparation of activated carbon [3,7,8]. For this reason, as well as in case of utilization of new adsorbent, it is very beneficial to use by-products resulting from the processing of various renewable potential raw materials. Therefore, researchers and scientists all over the world are interesting for the production of different alternative adsorbents to replace the expensive activated carbon [9]. Agricultural products and by-products/wastes, as well as forestry residues are inexpensive materials in comparison to the commercial AC. They have proved very efficient for dye removal from dyeing-waste water because the main components of these materials are cellulose, hemicelluloses, and lignin which contain various functional groups like hydroxyl (OH) and carboxyl groups (COOH). These functional groups can act as binding sites, which offer advantages of these wastes. They can also be easily modified by one step chemical activation for improving the adsorption capacities [9-12]. From the comparison stand of view, they are better than other adsorbents because the biomass residues including agricultural by-products/wastes are usually used with or without a little bit of modifications and thus reduce production costs by using abundant and cheap resources [10,13]. However, adsorption technology using such residues as bio-adsorbents have been shown to be an excellent way currently used for the elimination of hazardous substances like dyes and heavy metals from wastewater and are

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considered to be relatively superior to other technologies due to many advantages such as lower cost of adsorbent, easiness to operate, simplicity of design, availability and eco-friendly technique, higher output with high-quality treated effluent, and the fact that adsorbents can be reformed by the suitable desorption process for dye recovery, and mobile treatment unit can be designed for the same purpose, which can be used at the site job [3,7,14,15]. Utilization of biomass including agricultural solid waste for liquid-phase adsorption of pollutants (e.g. synthetic dye) is called a bio-adsorption system. Due to use lignocellulosic materials made from agricultural solid wastes contain a number of functional groups which is responsible for the system of adsorption. Unlike, the use other adsorbent (e.g. zeolites and clay) that can only be called "adsorption" system because the responsible "cellulose " for the liquid-phase adsorption is absent

The environment equally faces the problem of the huge amounts of the withered leaves and sea plants that fall from the trees and sea plants every autumn. The leaves that fall from oak trees create piles in public gardens and national woods, while dust can cause panic in the environment due to its impact on health [6]. Fallen leaves often block the cesspits constructed specially for the discharge of rainwater in cities. Also, the accumulated dead leaves are a potential fire hazard that could damage hundreds of hectares of woods and release gases along with large amounts of black smoke and other contaminants into the atmosphere [6]. Dead plant leaves of *Posidonia oceanica L*. is also readily available in large amounts and have no economic value in many countries, particularly in Mediterranean countries like Libya, Tunisia, Algeria, and Turkey. It was reported that the total primary production of sea plant *P. oceanic* (L.) in the Mediterranean basin alone is in the range of 5 to 50 million tons per year [3]. In Libya, about 125000 cubic meters of *Posidonia oceanica* is accumulated around Libyan beaches, which is more than 1900 kilometers long. Reports in Turkey indicate that the dried biomasses of this species that are accumulated around the beach are gathered and burned to eliminate them at some touristic beaches. Unfortunately, these methods of disposal lead to resource loss and environmental problems as reports show that *P. oceanica* is an adsorbent [16]. Moreover, both wastes presented remain unused materials and lack technical applications as far as we know. Therefore, this study is meant to investigate their effectiveness as a green solution for sustainable development through the use of these materials as adsorbents for treatment of colored wastewater. This would subsequently raise the confidence to scale down landfill disposal of these wastes and thus afford a valuable solution to this global problem. Another benefit of the study is that no chemical consumption was performed before the adsorption system, and since the removal dyes were basic in their classes the natural pH works well for removing dyes from the colored effluent. But using oak leaves without chemical treatment is a new approach since no previous works have applied it. All these benefits can also be added to the social impacts on local communities, like the creation of new jobs and tourism friendliness. Figure 1-a shows the collection of oak leaves from the campus garden at Gdansk University of Technology, while figure 1-b shows the accumulated biomass of *Posidonia oceanica* leaves (dead L.) on the Tripoli Beach (Libya).

**Figure 1:** Biomass of *Posidonia oceanica* and leaves of oak tree (dead L.)

## Experimental procedure

### Collection, processing, and characterization of adsorbents

In present study, two biomass waste materials, including sea plant (*Posidonia oceanica* L.) and oak leaves (OL) were used as an alternative zero-cost adsorbent for elimination of hazardous CV, and MB dyes from water. The raw material of the dead leaves of *Posidonia oceanica* L. were obtained from Tripoli Beach in Libya, while oak leaves were obtained from the campus gardens of Gdansk University of Technology in Poland. The raw material was soaked three times into fresh water for 10 minutes for removing salt, then cut into small pieces and washed completely with warm water and soap using mixing system at a mixing speed of 200 rpm for 120 min. This washing without soap was repeated three times to remove impurities and other undesirable materials. Then, about 50 g of each adsorbent was kept with warm water at 84 ± 2oC for 24 hr. After that, they were washed several times with distilled water and dried at 100$^{o}$C for 24 hr. Finally, the dried material was crushed using an eclectic grinder (DeLonghi, EAC, China) to obtain powder material of uniform size less than 0.20 mm and stored in a plastic container for further use. There is no chemical or physical treatment performed prior to adsorption studies. For elemental analysis, the powdered adsorbents were analyzed by FLASH 2000 CHNS/O Analyzer, USA. To measure bulk density, a glass cylinder 25 ml was filled to a specified volume with each material and dried in an oven at 80oC for 7 hr. The cylinder was tapped for few minutes to compact the material and the bulk density estimated and presented as g/ml. The procedure was similar to that used in the literature [17-19]. Two dyes, namely crystal violet (CV) and methylene (MB), are used in the current study for adsorption experiments which are provided from B.D.H. Chemicals, Ltd., England. CV has the chemical formula $C_{22}H_{30}N_3Cl$ (Mol. wt. 408g/mol) while MB has chemical formula $C_{16}H_{18}N_3SCl$, which were used without purification. Both dye solutions were prepared as follows: stock solution (SS) of each dye was prepared by dissolving 1.0 g of dye in distilled water using 1.0 liter volumetric flask and made to a concentration of 1000 mg/l. The working dye solutions were obtained by diluting the stock solution to give the appropriate concentrations (10-70 mg/L). Since the adsorptive removal of both dyes was cationic in nature, the pH solution was kept at the natural value "7" during the whole process. All chemicals used throughout this study were of analytical-grade reagents.

### Batch equilibrium studies

Batch adsorption experiments were carried out under laboratory conditions using 250 ml flasks,. The working solution, temperature of reaction and pH were kept constant at 50 ml, room temperature and 7, respectively. The flasks were shaken at 250 rpm for 60 min until equilibrium was reached using a digital shaker (GFL 3005). Variations affecting factors on the rate of adsorption system for both dyes were investigated. The final concentration of CV and MB in each sample was estimated at $\lambda_{max}$ = 584 nm for CV and 665 nm for MB using UV-Vis spectroscopy. The percentage removal and amount of dye adsorbed per gram of adsorbent were calculated using Equations 2 and 3, respectively [2]. Standard deviation (SD), which is the square root of the variance, is the measure of dispersion of individual results around the mean. It is described by Equation 4. Bulk density and the yield of adsorbent obtained were calculated by formulas 5 and 6, respectively.

where Xm = Mean, n = The number of results for the series.

% adsorption = $( C_o - C_e/C_o ) \times 100$ ............(2)

$q_e = (C_o - C_e) \times (V/M)$ .....................(3)

Where $C_o$ and $C_e$ are the initial and equilibrium dye concentrations, respectively (mg/l), V is the dye solution volume (L), and M is the amount of sorbent (g), $q_e$ is the adsorption capacity at equilibrium (mg/g).

Bulk density = weight of dried biomass (g)/final volume (ml) ....(5)

Yield = $(W_2) / (W_1) \times 100$ ...........(6)

Where: $W_2$ and $W_1$ are the dried and initial weight of the leaves.

### Operating parameters

It is well know that at any experimental work there are various conditions of reaction which are affected by a number of physical and chemical parameters, in case of liquid- adsorption system, there are different parameters such as, initial concentration of pollutants, temperature of reaction, agitation rate, pH, and adsorbent mass [2,3]. In this study three major parameters have been studied which are initial dye concentrations, adsorbent mass, and time of reaction, respectively. While the other parameters were kept constant during the whole adsorption process as presented in the next section.

### Effect of initial concentrations of dyes

The influence of the initial concentration of both dyes, CV and MB, was studied as a first step. Since, the initial dye concentration is an important parameter for adsorption system that affects adsorption kinetics [2]. To study the effect of the initial dye concentration, 50 ml of each dye solution at various concentrations ranging from 10 to 70 mg/l were shaken with 0.1 gram of each adsorbent (included oak tree leaves and the sea plant, *Posidonia oceanica* L) at a constant agitation speed of 250 rpm, pH solution of 7 until the equilibrium time was reached. After that, filtered samples were analyzed using UV/visible spectroscopy. Data will be expressed as mean ± standard deviation.

### Effect of adsorbent content

The amount of adsorbent also plays an important parameter role in the liquid-adsorption system and greatly affects the removal of dyes from water because it estimates the capacity of adsorbents [10,20]. A range of *P. oceanica* powder (varying from 0.03 to 0.5g) were respectively added into fixed initial concentration of 50 mg/L of CV dye solution and MB dye solution. The mixtures were shaken at 25°C, 250 rpm, and pH of 7 until the equilibrium time was attended. Then, all samples were filtered and analyzed using UV/visible spectroscopy and the optimum level adsorbent mass was selected for use in the next step. The same procedure was applied in case of oak leaves adsorbent.

### Effect of contact time

Adsorption time is also a very interesting factor for studying the economical design of wastewater treatment in case of application [3]. The effect of contact time was studied by the following steps: a weight of 0.1g of oak leaves powder was weighted and added to six different conical flasks containing 50 ml of each dye solution with the best initial concentration of dyes which were selected from the first step, pH of 7, using working solution of 250 ml; the flasks were agitated at 250 rpm for an adsorption time of 5–90 min at room temperature. The content of each sample was then filtered and the filtrates were analyzed by UV/visible spectroscopy, The same procedure was used with *Posidonia oceanica* L. for CV and MB, respectively. Finally, the optimum conditions of the adsorption process were reported.

### Adsorption isotherm

The analysis and study of the equilibrium data are very important with a view to developing a model equation which can accurately represent the results and could be used for the design purposes [19,21,22]. The Langmuir (1918) [23] and Freundlich (1906) [24] models were applied to test the equilibrium adsorption data of the adsorbents. The equilibrium isotherms for the adsorption of dyes onto oak and leaves (dead dried L.) were employed for experiments using the best doses of each adsorbent, contact time, and pH at different initial concentrations from 10 to 70 mg/l of each dye.

### Langmuir isotherm model

Langmuir isotherm model represents the simplest of all known isotherm models for monolayer adsorption. Langmuir isotherm model is developed by assuming that the force of interaction between the adsorbed molecules is negligible and a 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 [19,22,25,26]. The Langmuir isotherm Equation is presented by the formula (7):

$q_e = (q_{max} K_L C_e) \div (1+K_L C_e)$ ............(7)

This can be derived into linear is given as:

$C_e / q_e = (1/q_{max} K_L) + (C_e/q_{max})$ ..............(8)

Where $q_e$ is the adsorption capacity in the equilibrium state (mg/g), $C_e$ is the equilibrium concentration of dye (mg/l), $q_{max}$ is the maximum adsorption capacity corresponding to complete monolayer adsorption (mg/g), and finally KL is the Langmuir isotherm constant (equilibrium constant l/mg). 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 is the Langmuir constant.

### Freundlich isotherm model

The Freundlich isotherm model has been widely used for many years and is mainly applied to describe characteristics of the heterogeneous surface. The model assumes that adsorption takes place on a heterogeneous surface and can be used for non-ideal adsorption [19,25,26]. The Freundlich Equation is given as:

$q_e = K_f C^{1/n}$ ..............(9)

The linear form of Freundlich model is given by:

$\ln q_e = 1/n \ln C_e + \ln K_f$ .............(10)

Where $K_f$, = Freundlich adsorption constant (l/mg) related to the adsorption capacity of the adsorbent; n = heterogeneity factor of adsorption sites, which can be used to explain the extent of adsorption and the adsorption intensity between the solute concentration and adsorbent, respectively [10].

## Results and Discussion

### Characterization of the adsorbents

### Elemental analysis and bulk density

The chemical character based on elemental analysis of dried adsorbents including C, H, N, and O was analyzed and is presented in Table 1. Bulk densities (K) of both adsorbents were also calculated regarding Equation 5 and are also shown in Table 1. From the table it can be seen that both leaves have a high proportion of nitrogen. Unlike most other agricultural solid wastes that have a low content of nitrogen element such as coconut shell (0.4 wt%), almond shell (0.2 wt%), raw rice husk (0.86), raw bagasse (0.03 wt% ), etc., as clarified and reported in an extensive review paper [3]. This could be plying one key benefit for the liquid-adsorption system. Similar phenomenon was observed for orange peel which is containing a level of nitrogen element about 2.6 wt% [19].

| **Property** | **Values** | |
|---|---|---|
| | **Tree leaves** | **Sea plant L.** |
| C (%) | 47.55 | 53.83 |
| H (%) | 5.23 | 4.31 |
| N (%) | 3.79 | 5.68 |
| O (%) | 38.43 | 30.14 |
| Y(%) | 0.13 | 0.15 |
| K (g/ml) | 0.68 | 0.65 |
| K is the bulk density; Y is the yield of adsorbent | | |

**Table 1:** Most elements found as constituents of dried leaves and their bulk density, and the yield.

### Spectral analysis: (FT-IR)

Tensor 27 Bruker model of Fourier Transform Infrared Spectrophotometer, FTIR, was used to obtain the IR spectra of dried leaves. Samples were analyzed in a spectral range of 500–4000 cm-1. Original raw materials of dried *Posidonia oceanica* L., as well as the adsorbent laden with CV and MB, are shown in figure 2-a, 2-b, and 2-c, respectively, while Original raw materials of dried oak L. powder, as well as the adsorbent laden with CV and MB, are shown in figure 3-a, 3-b, and 3-c, respectively. The presence of strong and broad intensity band around (3271.12 $cm^{-1}$) was assigned to phenolic OH stretching [2,19,27]. The peak at 2920.75 $cm^{-1}$ corresponds to –CH stretching that might be due to H-bond formation at a higher concentration [27]. The peak at 1734 infers the presence of C=O groups of carboxylic acids [28,29]; 1430 $cm^{-1}$ represents 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 as reported in the literature [15]. 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 the 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, which are also reported in this work [15]. On the other hand, both adsorbent spectra in figure 2-b and 2-c, as well as 3-b and 3-c demonstrating the adsorbent after batch mode sorption, shows the presence of a little shift to almost all aforementioned peaks for both dyes. Comparing the three spectra in both cases, one can conclude that some of these peaks were shifted or disappeared. These findings of changes observed in the spectra indicated the possible involvement of those functional groups on the surface of solid sorbents in the sorption process. The FTIR study showed that the following functional groups—O-H, C=O, C-H and N-H—were involved in binding CV and MB dye to the adsorbent. From the figures, it can be concluded that they are similar in results for both adsorbents.

**Figure 2:** FTIR spectra of dried *Posidonia oceanic* L. (a), CV loaded dried *Posidonia oceanica* L, (b), and MB loaded dried *Posidonia oceanica* L. (c).

### Surface morphology of adsorbents (SEM)

The surface area of adsorbents was studied by Scanning electron microscopy (SEM), a Zeiss EVO 40 (Germany), and it is shown in figure 4. Researchers, Titi and Bello (2015) [9] report in a review work that the modified biomass was clearly different in the surface morphology of adsorbent and high adsorption capacity when

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**Figure 3:** FTIR spectra of dried OL (a), CV loaded OL (b), and MB loaded OL (c).

compared to unmodified adsorbents. For example, Kalavathy and Miranda (2010) [27] have focused on the adsorption of a copper ion from its aqueous solution by raw saw dust (RSD). Phosphoric acid and sodium hydroxide were used for the modification. They found that surface modification of saw dust made significant contributions to the development of microspores. The surface was also more homogeneous for sawdust modified with NaOH compared to saw dust modified with phosphoric acid and unmodified saw dust which shows more heterogeneity on its surface. Moosa., *et al.* [15] used modified and unmodified bioadsorbents to remove Zn (II) from aqueous solution. According to their results, the surface area of activation Aloe Vera powder went up from 13.8 $m^2$/g to 24.6 $m^2$/g using chemical activation with [$2HNO_3$:$1H_2SO_4$]. However, no difference occurred in the maximum adsorption capacity which was reported as 5.0839 and 5.4113 mg/g onto Aloe Vera powder and activation Aloe Vera. Viewed from the environmental and economic angles, the use of natural adsorbent materials from renewable sources like *Posidonia oceanica* L. and oak leaves without chemical treatment has gained increasing attention due to recent developments in science and technology, particularly in the area of green and sustainable chemistry, since adsorbents are modified with chemical treatment with the aid of alkali, acid, or salt media. It was reported that zinc chloride and alkali hydroxide might be skipped because of their corrosive nature and the harmful effects associated with their disposal [30], especially where they are used without pollution control. In this study, there is a semi-clear pore surface and regular morphology, particularly with oak L (Figure 4). The removal of significant organic by-products and minerals presented in the solid sorbents by soaking them in warm water for a long period could be the cause of the regular morphology. Kalavathy and Miranda reported a similar morphology [27].

## Optimization study

### Optimization of initial concentration of dye

The influence of initial CV and MB dye concentrations on the rate of removal efficiency were investigated. Adsorption experiments were studied at different initial concentrations of both CV and MB ranging from 10 to 70 mg/l, respectively, at adsorption conditions using dried *Posidonia oceanica* L. and oak leaves as adsorbents. Table 2 showed the results. From the table, the percentage removal decreased with an increase in the concentration of initial dye. For example, there were decreases from 99.4% to 81.09% for MB and from 98.05% to 75.31% for CV, respectively, when the initial concentration of both dyes went up from 10mg/l to 70mg/l using oak L. With the use of *Posidonia oceanica* L as adsorbent, the present removal went down from 96% to 65.25% for CV and from 98.2% to 71.3% for MB, respectively, when the initial concentration of both dyes went up from 10 mg/l to 70 mg/l. This outcome is due to the limited available number of adsorption sites and the surface area of adsorbent by increasing the initial concentration of liquid phase at constant dosages of adsorbents. In addition, it is due to the saturation of most adsorption sites on the adsorbents. This agrees with the literature [2,10,31]. On the other hand, in the case of oak leaves adsorbent, the adsorption capacity was increased from 4.21 to 27.25 mg/g for CV and from 4.95 to 28.65 mg/g for MB, when the initial dye concentration increased from 10 to 70mg/l, while was increased from 4.8 to 22.75 mg/g for CV and from 4.92 to 24.85 mg/g for MB in the case of *Posidonia oceanica* L. at the same level of initial dye concentration. Table 2 also shows that the adsorptive removal of MB onto both adsorbents was a little higher than that of CV, which may be because of the difference in the molecular weight. 50 mg/l for both dyes, CV and MB, has been deemed the best concentration level for the next step. Conversely, oak L. showed the best adsorbent for both dyes in comparison to *Posidonia oceanica* L. This observation may be traceable to some impurities such as salt remaining on the surface of the adsorbent. And also, due to high (% O) which were 38.43% for oak L., and 30.14% for *P. oceanic*.

**Figure 4:** SEM of the raw material of dried *Posidonia oceanica* L (a), and oak L. (b).

### Optimization of agitation time

Results obtained from the influence of adsorption time are shown in Table 3. From the Table, it can be observed that the adsorptive removal was rapidly increased with the increase of adsorption time in the first 30 min for both CV and MB. Then the adsorption process continued slowly until it reached saturation and the adsorptive removal was said to reach an equilibrium, which was attained at 60 min at the used conditions of 0.1g of oak L., 50 mg/l of dye solutions, pH 7, agitation rate of 250 rpm, and room temperature 25oC with percentage removal of 95% and 99% for CV and MB, respectively, by using oak L., while the adsorption capacity was found to be 23.75 mg/g and 24.5 mg/g for CV and MB, respectively. Therefore, 60 min was found to be the optimum con-

| Initial conc., mg/l | Untreated oak leaves | | | |
|---|---|---|---|---|
| | Removal efficiency, % | | Adsorption capacity, mg/g | |
| | CV | MB | CV | MB |
| 10 | 98.05 | 99.40 | 4.21 | 4.95 |
| 30 | 96.71 | 98.14 | 12.11 | 14.75 |
| 40 | 95.02 | 94.72 | 18.75 | 19.10 |
| 50 | 90.10 | 92.25 | 22.51 | 23.21 |
| 70 | 75.31 | 81.09 | 27.25 | 28.65 |
| ± standard deviation | 0.063-0.131 | 0.085-0.172 | 0.027-0.118 | 0.089-0.271 |
| Initial conc., mg/l | Untreated *posidonia oceanica* L. | | | |
| | Removal efficiency, % | | Adsorption capacity, mg/g | |
| | CV | MB | CV | MB |
| 10 | 96.02 | 98.2 | 4.8 0 | 4.92 |
| 30 | 93.13 | 95.9 | 13.90 | 14.31 |
| 40 | 90.01 | 92.7 | 18.06 | 18.54 |
| 50 | 87.41 | 88.1 | 21.75 | 22.21 |
| 70 | 65.25 | 71.3 | 22.75 | 24.85 |
| ± standard deviation | 0.047-0.135 | 0.019-0.162 | 0.045-0.230 | 0.085-0.152 |

**Table 2:** Effect of initial dye concentration on the percentage removal of dyes and adsorption capacities onto adsorbents under adsorption conditions (50 ml, 60 min, 0.1 g, 250 rpm, and pH 7).

tact time by using oak leaves as an adsorbent. A further increase in adsorption times shows no significant effect on the adsorption efficiency of dye due to reach the equilibrium state between the solid phase (adsorbents) and the liquid phase (dye solution) as shown in Table 3. This is in agreement with the study done by Seidmohammadi., *et al.* [32]. The initial rate of adsorption capacity was rapid in the first stage due to the larger surface area and the availability of the binding active sites of the adsorbent [2,33] and the driving force provided by the initial concentration at the first stage which overcomes all mass transferred resistance of dyes between the aqueous and solid phases [34,35]. In a similar trend, Etim., *et al.* [10] observed that more than 80% of MB dye was removed in the first minute of adsorption and increased slowly until equilibrium was reached at about 20 min. Similar results were also observed in the case of *Posidonia oceanica* for the adsorption of CV and MB. According to the data obtained, removal efficiency was a little lower in comparison to oak leaves. It is reported as 93.0% and 95.17% for CV and MB, respectively, while the maximum adsorption capacity for MB and CV was found to be 23.3 and 23.8 mg/g, respectively, at pH 7, room temperature and agitation rate of 250 rpm and equilibrium time of adsorption was achieved in 60 minutes as also presented in Table 3. It is well known that the initial concentration of dyes has a great effect on the equilibrium time. According to data obtained in this part, the equilibrium time was only 15 and 20 min for 10 mg/l CV and MB onto oak L. and *Posidonia oceanica* L., respectively, while increased to 60 min for 50 mg/l. Ho and Ofamaja (2006) found a similar phenomenon for cupper adsorption onto chemical-treated palm kernel fiber [36], and work [19] for adsorption of basic dye by treated-orange peel powder using chemical treatment with NaOH.

| Contact time, min | Untreated oak leaves | | | |
|---|---|---|---|---|
| | Removal efficiency, % | | Adsorption capacity, mg/g | |
| | CV | MB | CV | MB |
| 5 | 55 | 65.0 | 13.75 | 16.25 |
| 10 | 72 | 77.5 | 17.51 | 19.37 |
| 20 | 85 | 95.0 | 21.25 | 13.75 |
| 30 | 90 | 98.0 | 22.50 | 32.40 |
| 60 | 95 | 99.1 | 23.75 | 24.50 |
| 90 | 97 | 99.4 | 24.25 | 24.72 |
| ± standard deviation | 0.027-0.178 | 0.057-0.126 | 0.128-0.397 | 0.126-0.300 |
| Contact time, min | Untreated *Posidonia oceanica* L. | | | |
| | Removal efficiency, % | | Adsorption capacity, mg/g | |
| | CV | MB | CV | MB |
| 5 | 49.13 | 57.26 | 12.25 | 14.32 |
| 10 | 67.52 | 70.91 | 16.75 | 17.73 |
| 20 | 77.40 | 81.35 | 19.35 | 20.34 |
| 30 | 89.47 | 94.61 | 22.45 | 23.41 |
| 60 | 93.0 | 95.17 | 23.31 | 23.79 |
| 90 | 94.71 | 95.95 | 23.75 | 23.99 |
| ± standard deviation | 0.027-0.153 | 0.057-0.126 | 0.128-0.397 | 0.126-0.301 |

**Table 3:** Effect of adsorption time on the percentage removal of dye and adsorption capacity onto adsorbents at 50 ml, 50mg/l, 0.1 g, 250 rpm, pH 7 and 25°C.

## Optimization of adsorbent dosage

According to data obtained from the effect of adsorbent dosages on the amount of dye adsorbed and percentage removal using oak leaves, it can be concluded that the percentage of dye removal increased rapidly with an increase in the mass of adsorbent. For instance, an increase from 67.0% to 97.0% for CV and from 75.3% to 99.0% for MB was observed with SD ranging from ± 0.014 to ± 0.019 when the adsorbent mass increased from 0.03 to 0.1 g. With a further increase in the concentration of oak leaves beyond 0.1 g, the adsorption of dyes cannot increase; this indicates that adsorption was almost finished with 0.1g of the adsorbent and may be due to the saturation of vacant spaces or the aggregation/agglomeration of adsorbent particles with each other [20]. The increase in adsorption with an adsorbent mass of oak leaves is due to greater availability of adsorbent surface [10,37,38], while adsorption capacity was decreased with the increasing amount of the adsorbent mass. This behavior has been explained as a result of overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorption surface area available to the day and an increase in the diffusion path length. In a related study, Al-Azabi., *et al*. (2018) have investigated the efficiency of raw orange peel powder modified with NaOH for the removal of methylene blue (MB) and crystal violet (CV) from aqueous solution. They found that the percentage of dye removal increased from 57% to 97.5% for CV dye and from

61.4% to 99.2 for MB dye respectively, when the dosage increased from 0.05 to 0.3g and the equilibrium was reached with 0.3g of the peel powder [19]. In the present study, the same behavior of results was observed in the case of *Posidonia oceanica*. For instance, the percentage removal has been increased from 50.1 to 94% for CV and from 53.7% to 96.2% for MB when the adsorbent mass increased from 0.03 to 0.3 g, and then the percent removal values were very close, indicating that adsorption was almost finished with 0.3g of the adsorbent and the equilibrium was reached with 0.3g of the adsorbent. In the current study, therefore, 0.1g and 0.3 g of oak leaf and *Posidonia oceanica* L., respectively, were optimized (table not shown).

## Adsorption isotherms

### Langmuir isotherm

The experimental data were fitted into Equation 8 for linearization by plotting Ce with Ce/qe (Figure 6). Langmuir isotherms of CV and MB obtained using oak L and *Posidonia oceanica* L. as adsorbents are presented in Table 4. The slopes and the intercepts of these linear plots have been used to determine the constant of Langmuir isotherm parameters [19,26]. Langmuir parameters were obtained from the slope and intercept of the straight line for CV and MB dye removal using oak leaves (OL), as well as *Posidonia oceanica* leaves, which are presented in Figure 5 and Table 4. Both leaves adsorption data fit well to the Langmuir model, indicating that the active sites of adsorbents surface are homogenous for CV and MB binding. Besides, the high value of correlation coefficient (R2) was found to be 0.993 and 0.991 for CV and MB, respectively, using oak L., and 0.9816 and 0.97085 for CV and MB by *Posidonia oceanica* L. indicate a good agreement between the Langmuir constants and confirm the monolayer adsorption of both dyes by the adsorbent surface [39]. The Langmuir constant $q_{max}$ representing the maximum adsorption capacity of OL was found to be 31.65 mg/g and 33.50 mg/g for CV and MB, respectively, while it was 22.93 and 27.78 mg/g for CV and MB onto *Posidonia oceanica* L. Although there is no chemical treatment was performed prior to adsorption process. But, according to the Langmuir isotherm studies, both adsorbents showed a good maximum adsorption capacity. Similar trend has been observed by Etim., *et al.* (2016) when they investigated the removal of MB onto untreated coconut coir dust [10]. From comparative point of view, researchers who have used activated and non-activated date pits for adsorption of Cu(II) and Zn(II) as reported in a review work done by Ahmed and his coworkers (2012). The authors found that the raw date pits have higher Cu(II) and Zn (II) uptake than activated date pits carbon [40]. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor for the equilibrium parameter, RL, which is used to predict whether an adsorption system is favorable or unfavorable. The separation factor is defined by the following Equation [37,41-45].

$R_L = 1/(1+bC_o)$ ........(11)

Where $R_L$ is a dimensionless separation factor, $C_o$ is the initial dye concentration (mg/l), and b is Langmuir isotherm constant (l/mg). The value of $R_L$ indicates the type of the isotherm to be either unfavorable ($R_L > 1$ ), linear ($R_L = 1$), and irreversible $R_L = 0$. The estimated values of $R_L$ for the adsorption of CV and MB onto both adsorbents are shown in figure 6. The $R_L$ values were found to be from 0.0314 to 0.185, and from 0.015 to 0.097 for CV and MB onto oak leaves, respectively. In case of *Posidonia oceanica* $R_L$ value was found to be from 0.0179 to 0.114 for and from 0.0145 to 0.094 for CV and MB dye onto *Posidonia oceanica*, respectively at initial dye concentration from 10 to 70 mg/l. Such results confirmed favorable adsorption of both dyes onto each adsorbent. Similar findings has been reported in previous studies [19,37,41-44].

### Freundlich isotherm

The experimental data were fitted into Equation 10 for linearization by plotting lnCe with lnqe (Figure 7). The Freundlich parameters were obtained from the straight line for CV and MB dye removal using oak leaves, as well as *Posidonia oceanica* L., which are the slopes and the intercepts of the linear plots as shown in Figure 7 and Table 4. The Freundlich constant $K_f$ and n are used to represent the adsorption capacity and the adsorption intensity, respectively. Figure 8 shows the research methodology of the study.

**Figure 5:** Langmuir isotherm plot fot the adsorption of CV on oak L. (a), MB onto oak L. (b), and CV onto *Posidonia oceanica* L.(c), and MB onto *Posidonia oceanica* L. (d).

**Figure 6:** Separation factor as function of initial dye concentration.

**Figure 7:** Freundlich isotherm plot fot the adsorption of CV on oak L. (a), MB onto oak L. (b), and CV onto *Posidonia oceanica* L.(c), and MB onto *Posidonia oceanica* L. (d).

| **Adsorbents** | **Langmuir** | | | | | |
|---|---|---|---|---|---|---|
| | **CV** | | | **MB** | | |
| | **$q_{max}$, (mg/g)** | **$K_L$, (l/mg)** | **$R^2$** | **$q_{max}$, (mg/g)** | **$K_L$, (l/mg)** | **$R^2$** |
| Oak leaves | 31.65 | 0.44 | 0.9932 | 33.5 | 0.93 | 0.9905 |
| *Posidonia oceanica* L | 22.93 | 0.78 | 0.9816 | 27.78 | 0.96 | 0.9708 |
| Adsorbents | Freundlich | | | | | |
| | CV | | | MB | | |
| | $\ln k_f$ | 1/n | $R^2$ | $\ln k_f$ | 1/n | $R^2$ |
| Oak leaves | 2.0981 | 0.5298 | 0.8858 | 2.5382 | 0.3767 | 0.9717 |
| *Posidonia oceanica* L | 2.1443 | 0.3941 | 0.8735 | 2.3941 | 0.3432 | 0.9237 |

**Table 4:** Langmuir and Freundlich isotherm for CV and MB adsorption onto leave adsorbents.

**Figure 8:** Scheme of research methodology involved in this work.

## Conclusion and Final Remarks

Results from this research work indicated that the dead leaves of biomass, including oak tree leaves and sea plant leaves "*Posidonia oceanicas*," can successfully be employed in elimination of CV and MB dyes from liquid madia. Its key property is the presence of OH and COOH groups on the adsorbent surface that can bind functional groups of MB and CV dyes during the adsorption process. The adsorption capacity of dyes was found dependent on contact time, adsorbent dose and initial concentration of dyes. The maximum adsorption capacity for CV and MB onto oak L. was found to be 31.7 and 33.5 mg/g, respectively, while 22.9 and 27.8 mg/g was recorded in the case of *Posidonia oceanica* L. Adsorption parameters obtained from Langmuir and Freundlich isotherms are useful for the explanation of the mechanisms of the adsorption technique as indicated by the high correlation coefficient value ranging from 0.8735 to 0.9932. Figure below shows the adsorption mode technique and MB dye solution treated by different amounts of biowaste based adsorbent. Future work will focus on the studies of adsorption thermodynamic and kinetic as a second part of the present study.

**Figure 9:** Batch adsorption experiment (A), and MB dye solution treated by different mass of oak leaves-based bio-adsorbent (1-6) compared to the stock solution (SS).

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