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New Approach for In-House Treatment of Colored Wastewater Using Olive-Waste Cake as an Alternative Adsorbent

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Abstract: *Nowadays, one of the major problems in the world is water pollution. 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 processes. The effluents of such industries, wastes from households and other manufacturing activities pose a serious environmental problem as they cause harm to the biota of receptor water (i.e. sea water, rivers, etc). This research is intended to conduct an experimental study of laboratory colored wastewater at universities, colleges, and research centers using three methods of sorption process and the dynamic system including packed bed column and batch experiments. Another method used in this study is static adsorption system. Olive mill waste, namely olive cake (OC), was selected at low cost; good properties and biodegradable materials were also used for the removal of crystal violet (CV) and methylene blue (MB) from the dye-water system. A number of factors affecting the rate of adsorption by both dynamic and static were investigated. The adsorbent mass used in this study was fixed at 0.3 g for the batch process, while room temperature was used in both systems of adsorption. The results obtained from the experiment showed that the rate of adsorption was affected by conditions in the adsorption process such as the initial influent concentration of dye, contact time and pH for the batch process, and flow rate and bed height for the continuous process. The following results were obtained: i) the contact time of 120 min, initial concentration of both dye of 30 mg/l, and solution pH 6.5, were selected as the optimum conditions by the batch process; ii) the equilibrium of both dyes sorption was reached within 4 days and the maximum adsorption capacity and removal percentage of CV and MB was found to be 89% and 86.86%, and 9.2 mg/g and 8.9 mg/g respectively by static sorption system, iii) the maximum breakthrough time of 200 min and 190 min for CV and MB respectively was achieved at the operating condition of 7 ml/min influent flow rate, and initial dye concentration of 30 mg/l by packed bed column; and iv) the adsorption capacity of the adsorbent was found to be 16.7 mg/g and 16.1mg/g for CV for MB respectively. This study indicates that olive-waste cake presents great potential as an inexpensive, easily available alternative and biodegradable adsorbent for the removal of basic day in wastewater treatment. A design set up of a sorption column system is proposed for construction for on-the-spot utilization where these University laboratories are considered locations of SD involvement in research and scientific studies, yet in small scales.*

Keywords: *Adsorption**,** crystal violet, dyes, methylene blue, olive cake, packed bed column, static system.*

I. Introduction

As a result of development and expansions of industries and the activities of humans, the environment has continued to face serious threats of pollutants [1]. Synthetic dyes (SD) are considered as one of the most dangerous pollutants in the world and its effect is of a great concern worldwide, due to their toxicity to many life forms. 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 [2]. More than 600 organic and inorganic pollutants have been reported in receptor water[2]; around 40,000 dyes and pigments are listed which consist of more than 7000 different chemical structures[3], and over 700,000 tons are produced annually, worldwide[4]. Water pollution is a major global problem which requires a continuous evaluation and the revision of water resources policy at all levels. Water pollution accounts for the death of more than 14,000 people, every day [2]. Pollution resulting from Dyes can be produced as wastewater streams from many industries like paper mills, leather, textile, paint manufacture, paper and plastic, food, and others [5]. Therefore, it is environmentally very important for the concerned industries to remove synthetic dyestuff from the wastewater before discharging it into any natural receptor waters [6].

In the last few years, the utilization of synthetic dyes (SD), such as Methylene blue (MB), Crystal violet (CV), Basic Violet-10 (BV-10), and Malachite Green (MG), in the field of scientific research has increasingly become the main axis of researches. This practice is common especially at Universities and Research Centers where students and researchers at organic, analytical, microorganisms, medical, and pharmaceutical laboratories customarily intend to engage a number of them [6]. This was demonstrated when sheets of the questionnaire were handed out to researchers, technicians, and students by the author to evaluate how intense the situation concerning the use of SD is.

Conducting laboratory studies and researches is considered an essential part of academic and post-graduate studies where SD is usually engaged. However, huge volumes of colored liquids mostly derived from SD solutions are generated in form of wastes. These wastewaters mostly find their ways to the sinks and then to the main sewage network. In many countries, particularly in developing countries, the final reservoir is usually a body of superficial waters represented by the sea water and rivers [6].

Due to the low biodegradation of dyes, a conventional biological treatment process is not very effective in treating dye wastewater [7]. Research work done by Pearce and his coworkers (2003) had reviewed a method of using bacteria cell for dye removal in textile industries [8]. Since the biological method is not very efficient in dye removal, the only other option becomes either the physical or chemical process. Currently, there are different technologies applied in the removal of dyes from wastewater [1] such as ion exchange, chemical precipitation, and etc. However, these processes are either too costly and cannot efficiently be used to treat a wide range of dye wastewater[7]. The cost of water purification by these technologies, ranges from 10 to 450 $/m3 of treated water, while the cost of water treatment using adsorption technique ranges 5 to 200 $/m3 [2]. The adsorption process has gained interest as a more promising method for the long term as it is seen to be a more effective and economic approach to pollutants removal (i.e. heavy metals and dyes) from polluted water sources. Adsorption is a fundamental process today due to its low space requirements for batch and continuous operation unit, simplicity and flexibility of design and ease of operation, it does not pollute water, it has no odor emissions and low cost of adsorbent. Another main advantage of the adsorption technique in removing or minimizing the pollutants such as heavy metals and dyes event at low concentration is that it enhances the application of adsorption as one practical treatment [2, 5].

In recent years, special attention has been on the utilization of an available-in-nature, abundant and eco-friendly sorbents to replace the conventional and expensive sorbents based on economic and environmental considerations [9, 10]; Environment-friendly utilization of agricultural by-products/waste materials represent such an example.

II. Sources, Quantities And Environmental Impacts Of Some Agricultural By-Product/Wastes

Expanding fruit production has naturally resulted in increased amounts of waste, every year [11]. Several million tons of agricultural wastes are disposed every year, around the world. In India alone, more than 400 million tons of agricultural residues are generated annually [12]. It is estimated that 0.5 million tons of Coir pith are produced in India every year and eventually disposed of as wastes. The accumulation of these around coir-processing centers is creating a menace to inhabitants [13]. According to the records of the United Nations Food and Agriculture Organization (FAO), Tomato is the most widely grown product in fresh vegetables around the world with a production of 145.6 million tons [14]. A new nonporous carbon from tomato waste as low-cost adsorbent was prepared by Fuat *et al.* (2014) [14]. In India, the national walnut production oscillates between 40,000 to 45,000 tons per year, and the process involved in obtaining unshelled walnut generates more than 25000 tons of shell. This also generates approximately 11000 tons of almond shell waste every year [15]. The amount of agricultural by-product in Egypt ranges from 30 to 35 million tons annually of which only 7milion tons are used as animal feed and 4million tons as organic manure [16].

In the United States, about 30 million tons of oak leaves are collected and burned annually. A new activated carbon from Oak L. dead leaves as low-cost adsorbent for dye removal was prepared by Sulyman *et al.* (2014) [17]. While 68 million tons of global orange are production annually, according to FAO, the generation of these solid wastes is estimated to be in the range of 15 to 25 million tons; a big volume of which is still being dumped every year, which causes both economic and environmental problems such as high transportation cost, insufficient dumping sites, and the accumulation of high organic content material [18].

Olive oil is nearly totally produced in the Mediterranean region. As the demand for olive oil rapidly increases worldwide, environmental pollution posed by olive mill wastes (OMW) such as olive cake becomes a growing problem, especially in the Mediterranean region. The olive mill generates a big quantity of waste accumulated around the olive mill. It was reported that the 1000 kg of olive fruit can produce about 350 kg of olive cake. Most of the farmers were not able to specify the quantities of olive cake generated from the extraction process, as olive cake is not stored but dumped near the olive mill facility. 93.1% of the olive cake produced is granted to farmers, who use it for heating after drying, as well as for animal feeding. The remaining quantities are then dumped in open lands [19]; the exhausted olive cake which had high lignin, cellulose, and hemicelluloses, as well as, a low ash, were found to be 14.18%, 24.14%, 11.0%, and 2.36%, respectively [20]. Due to its high cellulose, hemicelluloses, and lignin content, a proper method of disposal and recycling of olive cake has to be developed.

The current study focuses on two major types of environmental pollution: the first type is the waste and exhaust liquids represented by SD engaged by research and study processes at universities and colleges, as well as research centers, while the second type of pollutants is the olive-waste cake produced by the olive mill process. Therefore, to approach environmental, economic and social sustainability, and be a part of the green chemistry science, few main goals of the project must be performed. The goal is to conduct a sorption process which would be able to eliminate these pollutants and hazardous chemicals from the wastewater source at the laboratories of universities. And thus, in this way, there will be no risks of utilizing the end treated water as an additional resource of water for other tasks (i.e. washing laboratory glass wear, or even irrigating the green areas at the university). In addition to this goal, there would be a possibility of reducing the large quantity of the OMW, as part of the Olive mill process, by utilizing it as low cost and biosorbent materials.

After the termination of waste-water treatment at the University, these quantities of sorption material usually become exhausted, and only then may be collected for another final task. This can be done by utilizing the collected final exhausted sorbent as a source for energy recovery.

III. Materials And Methods

3.1 Preparation of adsorbent

In this study, olive-waste cake (OWC) was selected as a low cost and biosorbent material for the removal of crystal violet (CV) and methylene blue (MB) from their aqueous solution. The raw olive-waste cake was obtained from oil mill process at Tripoli, Libya. Raw materials were collected and put into plastic bags and immediately transported to the laboratory. Then, the material was washed completely with boiling water and soap using mixing at speed of 180 rpm for 2 hr. This washing was repeated three times to remove oil, impurities and other undesirable materials. After that, the olive-waste cake was activated chemically by being soaked in KOH solution for 24 hr. It was subsequently washed several times with distilled water and dried once at room temperature for 5 days. The other was dried in the oven at 100 ^{o}C until constant weight was recorded. Finally, the dried material was crushed and blended using a mechanical mill, and passed through the 0.2 mm and 0.8 mm sieve plate to produce powder adsorbent material of uniform size and stored in plastic bags for further use. The figure below shows olive cake (a) and olive cake powder (b).

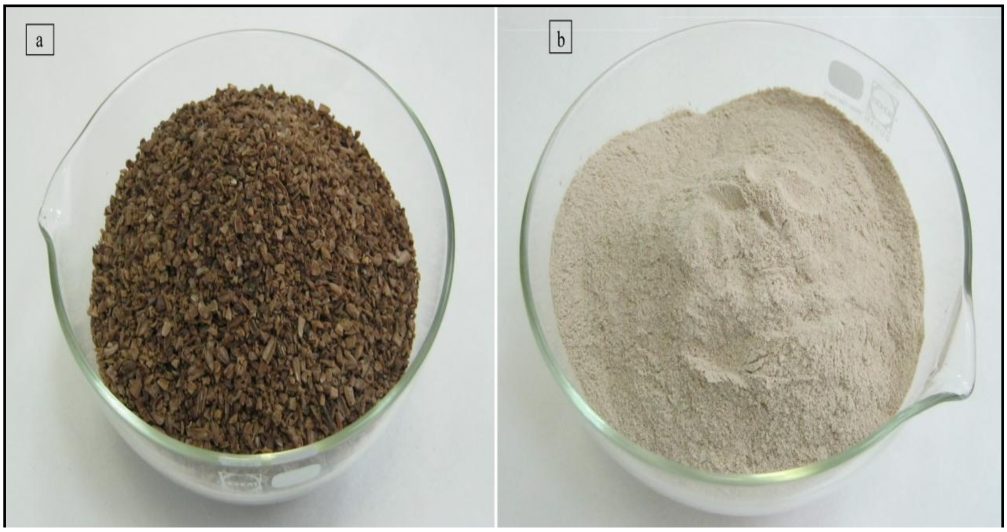

Fig 1: olive cake in form of granular (a), and olive cake in form of olive cake powder (b).

3.2. Instrumentations

All glassware used (conical flasks, measuring cylinder, pipettes, beakers, test tubes, etc.) were washed with nitric acid and deionized water before use. The list of instruments is listed in Table 1.

Table.1: The list of instruments used in this study

Instrument	**Manufacture/ type**
Electronic weight balance	Sartorius, 1000±0.0001g
pH meter	740 Inolab WTW with a SenTix 20 pH model double electrode
Digital shaker	GFL 3005 model, Germany
Infrared Spectroscopy (FT-IR)	Tensor 27 Bruker, USA- at the range of 450 - 4000 cm^{-1}
UV/ visible spectrophotometer	Specord 205, UV-analytikjena Germany
Elemental analyzer	FLASH 2000 CHNS/O Analyzer, USA.
Scanning electron microscope	Quanta FEG, USA
Themogravimetric (TGA)	TA instrument (SDT Q500)
Mechanical mill	Two places. Each one has three stainless steel ball, Germany
Sieve plats	Ranging 0.125 – 1.0 mm
Glass column	ID- 2cm, height-30cm, controlling value at the bottom
Glass wool	Normal

3.3. Preparation of CV and MB Dye Solutions

Crystal violet (CV) is the triphenylmethyl cation ($C_{22}H_{30}N_3Cl$; molecular weight 408; λ_{max} 584 nm). 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 shown in Figure 2, while, Methylene blue (MB) is a 3, 7-bis (dimethylamino) phenolthiazin-5-ium chloride cation. The dye has some commonality in that it represents a reasonably large organic cation, sharing an iminium quinoa unit. Both dyes were obtained commercially from B.D.H. Chemicals, Ltd., England. It has the molecular formula C16H18N3SCl and the molecular weight of 319.85 g.mol/1. The molecular structure of MB dye is illustrated in Figure 3. CV and MB dyes and the stock solution 1000 mg/l were prepared by accurately dissolving the weighed quantity of the dye in distilled water. The working solutions of different concentrations were prepared thereafter by diluting the stock solution to give the appropriate concentrations. All chemicals used throughout this study were of analytical-grade reagents.

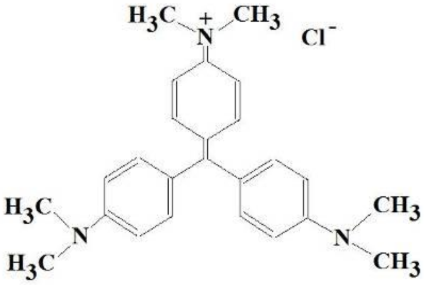

Fig. 2: Molecular Structure of CV [21].

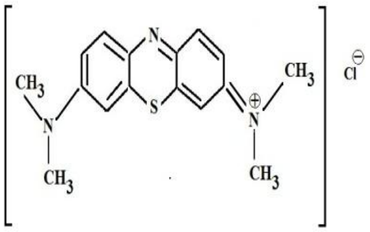

Fig. 3: Molecular Structure of MB [22].

3.4. Adsorption experiment

Sorption experiments were carried out at room temperature using the dynamic and static system. The dynamic system was carried out using two processes, which are the batch and continuous processes. Details of three experiments system were performed as follows: **First**, batch experiment was carried out by shaking a mixture of 0.3 g of olive cake with particle size of 0.2mm and 100 ml of both dye solution using 250 ml Erlenmeyer flasks, at agitation rate of 180 rpm, initial concentration of 10 mg/l for 120 min until equilibrium was reached. Each experiment was performed three times under the same conditions and the average results were taken. **Second**, the continuous process was carried out by using packed bed column which consisted of a 300 mm long column with 12 mm internal diameter (ID). The calculated amount of olive cake sorbent was packed into the column with two layers of glass wool at the top and the bottom. Influent dye solution of specific concentrations was selected as the best concentration level from the batch process charged from the top of the column in a down flow method (spontaneously) at a fixed inflow rate using a controlling container filled with dye solution on top of it. Prior to each experiment, distilled water was passed through the column to get rid of the column impurities and air bubbles. pH and adsorption temperature were fixed. Three different flow rates of 5ml/min, 7 ml/min, and 12 ml/min, as well as three different bed heights of adsorbent 3cm, 5cm and 7cm were evaluated and the optimum levels were selected. **Third**, the static system was performed by using the dye solution with initial concentration and pH, which were selected as optimum levels of the batch process (first method) and then poured into 100 ml using 250 ml Erlenmeyer flasks and shaken manually for 0.5 min. All samples were then placed in a dark place at room temperature without stirring for 7days. After the termination of the adsorption experiments, the remaining concentration of CV in each sample was determined by UV spectroscopy after filtering the adsorbent with Whatman filter paper to make it solid phase free. The amount of adsorption at equilibrium, q_e (mg/g) was calculated as follows (1):

$$q_e = (C_0 - C_e) \times (V/M) \quad (1)$$

Where C_0 and C_e (mg/l) are the liquid-phase concentration of dye at the initial and final stages respectively. V (l) is the volume of the solution and M (g) is the mass of dry sorbent used.
The percentage sorption (%) was calculated using the following equation:

$$\%\ sorption = \{(C_0 - C_e)/C_0\} \times 100 \quad (2)$$

In this study, variations in different contact time, initial dye concentrations, and pH and the investigations of their effects were all aimed at, while temperature, agitation speed, and adsorbent dose were kept at room temperature 200 rpm and 0.3g respectively. On the other hand, at the continuous process, flow rate and bed height were evaluated using optimum conditions such as initial influent concentration, and solution pH, which were selected from the batch process. The reaction temperature was fixed at room temperature for both processes.

3.4.1. The Effect of pH

The pH value of the aqueous solution is an important controlling parameter in the adsorption process of SD. In general, the adsorption of most dyes on adsorbent materials increased with the increase of pH [23]. The effect of pH on both dyes adsorption was studied by agitating 0.3 g of olive cake powder and a series of 100 ml dyes solution with concentration of 10 mg/l at different pH value, ranging from 2-10. The samples were agitated for 120min to reach equilibrium, and agitation rate was maintained at 200 rpm. Solution pH was adjusted by hydrochloric acid (HCl) and sodium hydroxide (NaOH) of various molarities. Finally, the optimum pH was selected.

3.4.2. *Effect of initial the concentrations of dyes*

The effluents of different industries may have different dye concentrations. The initial dye concentration is one of the important factors that affect adsorption kinetics [24]. The effect of initial concentration was investigated by agitating 0.3 g of olive cake in 100 ml of 10 mg/l of CV and MB solution at pH 7 for 120 min at a constant agitation speed of 200 rpm. The step was then repeated using 20 mg/l and 30 mg/l and 50 mg/l of dyes solution respectively. Finally, the optimum initial concentration was selected.

3.4.3. *The effect of contact time*

Equilibrium time is a very important element to study when considering economical wastewater treatment application [25]. The effect of contact time was investigated by agitating 0.3g of sorbent in 100 ml and initial concentration of 10 mg/l, pH 7 over time periods ranging from 15 to 180 min at a constant agitation speed of 200 rpm and room temperature. The optimum contact time was used in this study.

3.4.4. The effect of sorbent bed height

The effect of bed height was investigated by using initial influent concentration of 30 mg/l, pH 6.5 at different bed heights of adsorbent at room temperature. The optimum bed height at break point for treated volume was selected.

3.4.5. The effect of flow rate

At the continuous process, the effect of flow rate was investigated by using initial influent concentration of 30 mg/l, pH 6.5 at different flow rates of influence using controlling valve at the top of the column, at room temperature. The optimum flow rate for treated volume was selected. The removal percentage and adsorbent capacity at break point were recorded.

IV. Results And Discussion

4.1. Elemental analysis of olive cake

The chemical character based on elemental analysis of raw olive cake adsorbent was analyzed and the following Table (2) represents most constituent C,H,N,O found within the olive cake along the quantity of each in percentage.

Table 2. Most elements found as constituents of raw olive cake adsorbent

Element	C	H	N	O
Content, (%)	49.99	5.37	0.70	30.77

4.2. FTIR analysis

Figure 4 below represents the FTIR spectra of OC raw material with indications of a mini broad band around 3356.83 cm^{-1} ascribed to isolated –OH groups [26, 27]. There are other weak peaks at 2920.19 cm^{-1} and 2860.61 cm^{-1} suggesting the -CH stretching mode, assigning that alkyl functions or an alkyl backbone is present in OC raw material [26]. Beyond that wave numbers, the infrared of the olive cake sample shows a complex pattern, pointing to a complexity of functionalities on the surface of and potentially within the OC raw material. The absorbance peaks of OC at 1713.27 cm^{-1} is due to the presence of C=O stretching of carbonyl or most likely, a carboxylic group [23]. Furthermore, the figure indicates that the presence of a small peak at 1594.30 cm^{-1} is due to the presence of C=O stretching of the amide group (I); the presence of nitrogen moiety is confirmed by Elemental Analysis (N = 0.7%). Furthermore, the figure indicates the presence of a small peak at 1504.91 cm^{-1} due to the presence of N-H bending types of bonds of amide (II) [28]. The bands appeared at 1033 cm^{-1} and 1156 cm^{-1} probably assigned to C-O stretching in alcohols. Finally, Peaks at 898.16 cm^{-1} and down to 565.79 cm^{-1} may indicate that aromatic units are still present within the material. Thus, the IR spectral study revealed that the adsorbent OC contain mainly –OH, C=O, and –NH functional groups which are mainly responsible for the adsorption of adsorbates (i.e. MB) through chemical bondings [29].

4.3. Thermal analysis- TGA

Thermo-gravimetric analysis of the raw olive-waste cake was performed by heating the sample up to 600 °C under nitrogen flow rate of 100 ml min^{-1} through a furnace of a temperature range of 30–800 °C. It can be observed from Figure 5 that there had been a very little drop in OC weight of approximately a total of 3.0% between initial temperature and 200 °C in relation to the elimination of hygroscopic water, and some volatile matters from the sample, which were determined gravimetrically in a separate part. Beyond this point, increasing temperature has led to a semi-sharp drop in weight to almost 65%, representing the degradation of the main components by dehydration, decarboxylation and decarbonizations [30]. Therefore, at the oven drying temperature; that was 100 °C, there would be neither chemical nor structural modifications to occur by heating. Degradation of lignin and cellulose responsible probably for the adsorption of CV and MB would be avoided. In particular, in addition to the aforementioned peak, the derivative weight curve displays two main endothermic peaks; one sharp peak at about 300 °C attributed to the degradation of cellulose, another peak as a shoulder at 450 °C attributed to degradation of lignin as indicated elsewhere [31].

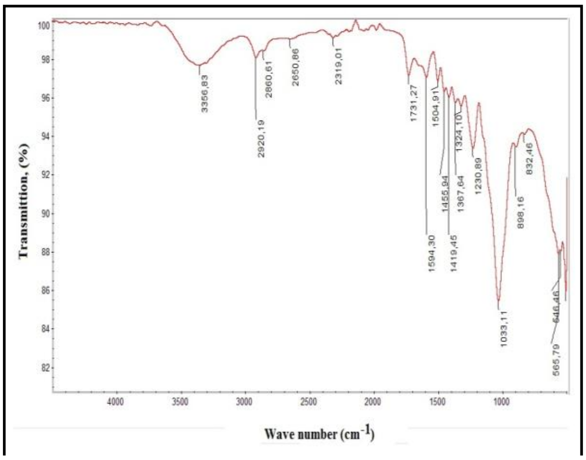

Fig. 4: FTIR analysis of olive cake

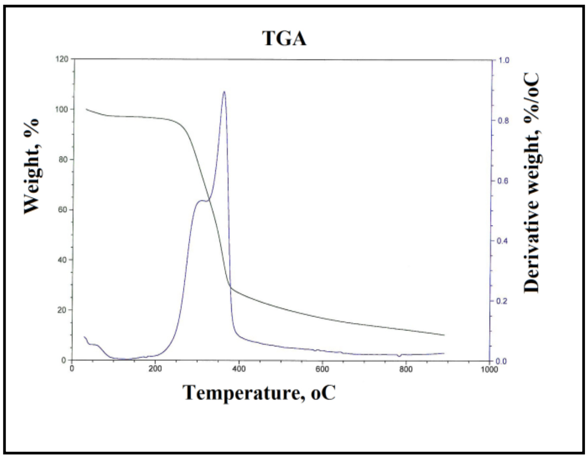

Fig.5 : TGA experiment of olive cake

4.4. Affecting factors on the rate of adsorption

4.4.1. Using batch process

4.4.1.1. Effect of pH

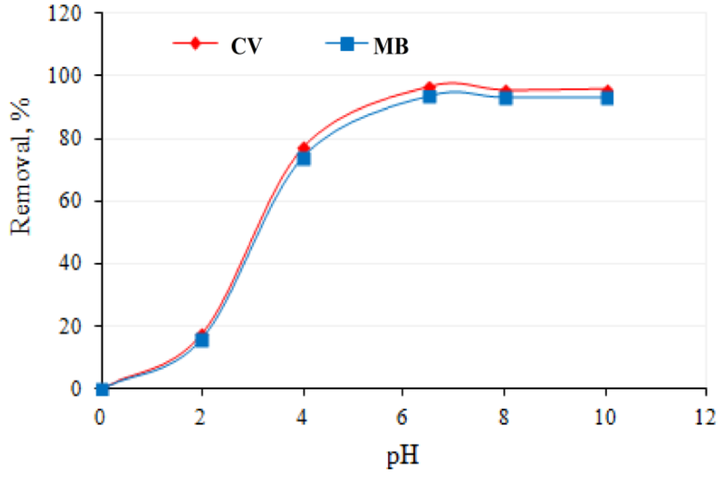

Fig. 6: The effect of pH on dye removal (10mg/l, 0.3g, 200 rpm, and room temperature)

The pH is very effective in protonation of the three amino groups of CV and MB dye molecule and the number of the positive charges of these three amino groups decreases to none with the increase of pH towards alkalinity. A number of CV and MB dye solutions with an initial concentration of 10 mg/l were adjusted to 2, 4, 6, 8 and 10. Each solution has been characterized with different colors as a result of different charged state. Figure 6 represents the effect of pH on the adsorption capacity and removal efficiency. According to this figure, with the increase of pH from 2 to 10, CV and MB removal will be increased from 17.41% and 15.85% to 96.3% and 93.4% for CV and MB respectively. Both dye removal percentage in pH 6.5 and pH 10 were almost near to gather 91.9%, 90.7% and 96.3% , 93.4% for CV and MB respectively, therefore pH 6.5 was found to be the optimum pH value. Seidmohammadi *et al. (*2015) [32] showed that maximum MB removal from aqueous solution on Quercus branti activated carbon was found to be 92.3% and pH 6 selected as optimum pH value. At low pH from 2.0 to < 6.0, the protonation of the negatively binding active sites was enhanced by the high increase in proton (H$^+$) and thus the number of free active sites became lower for the CV and MB molecules uptake. In contrast, when the pH was higher ($\geq$ 6.5) the free active sites of adsorbent gradually become deprotonated (i.e negatively charged) and the electrostatic process of attraction of the cationic CV and MB dye molecules became enhanced [26, 33, 34, 35]

4.4.1.2. The effect of initial dye concentrations

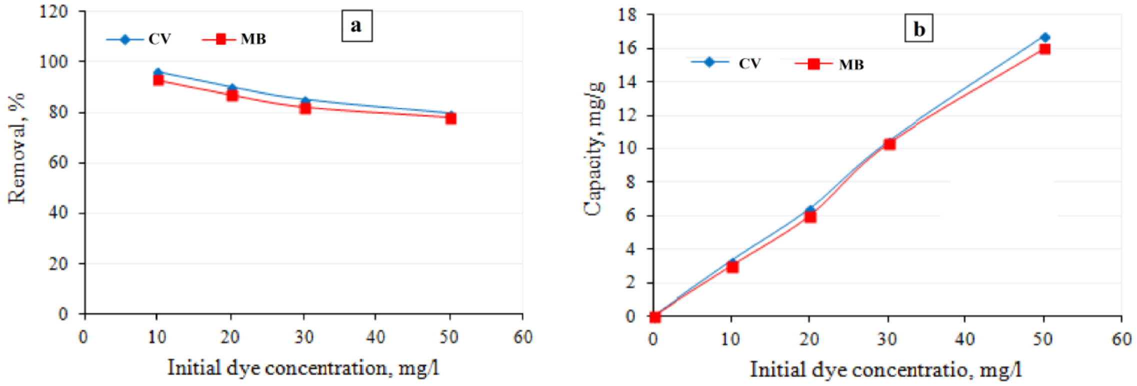

Fig. 7: Initial dye concentrations as a function of removal % (a), and adsorbent capacity (b)

From the Figure 7a, it can be observed that the CV and MB dye adsorption percentage decreased from 96.0% to 79.48% and 93.0% to 77.75%, respectively with the increase of initial concentration from 10 mg/l to 50 mg/l. However, further examination of the data by using Equation 2 revealed that the amount of CV and MB absorbed per unit mass of adsorbent (q_e) increased from 3.3 mg/g to 16.7 mg/g for CV and from 3.0 mg/g and 16.1mg/g for MB Figure 7b with the increase in initial concentration from 10 mg/l to 50 mg/l. This may be attributed to the fact that the initial concentrations provide an important driving force to overcome all mass transfer resistance dyes between the aqueous and the solid phases, as referred to in some of the literature [6, 23, 28]. In a related study, *Citrullus lanatus rind* was used as bio-sorption of a basic dye CV using batch mode system. The obtained results showed that the percentage removal increased from 87% to 91% as the initial concentration increased from 10mg/l to 30 mg/l. The maximum removal was found to be 89%, 95%, and 97% at a dosage of 1.4g/l, 1.8g/l, and 1.8g/l for a temperature of 30 °C, 40 °C, and 50°C respectively [24].

In a similar mode technique, the effect of the initial methylene blue (MB) concentration on the adsorption rate by coconut bunch waste (CBW) at an adsorbent dosage of 0.20g and mixing speed of 100rpm was investigated by Hameed *et al.*, 2008. 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 (qe) 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%) [36].

4.4.1.3. Effect of contact time

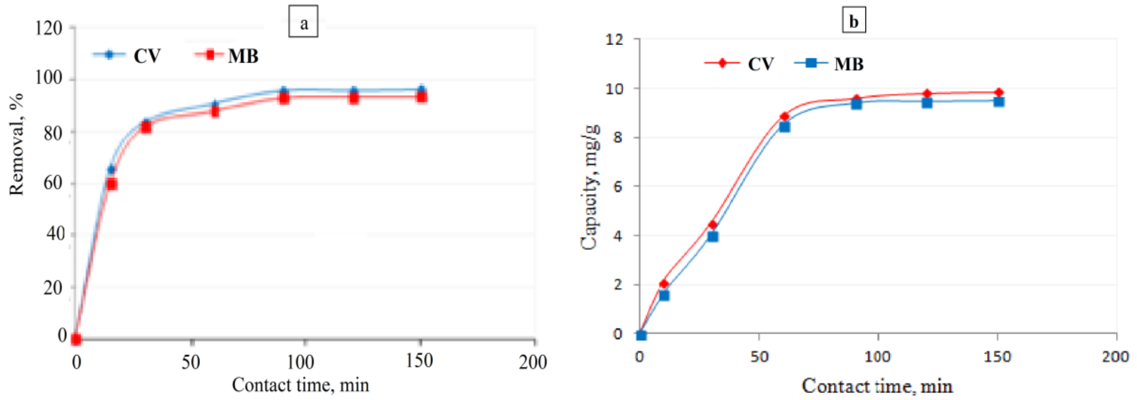

Fig. 8 : The effect of contact time on dye removal (a) and adsorption capacity (b) at room temperature, 100ml of 30 mg/l of dye solution, 0.3 g of adsorbent, and pH 6.5

From the figure, it can be observed that the adsorption removal increased rapidly with the increase of contact time at first 90 min for both CV and MB. It seemed thereafter that the adsorption process continued slowly until it reached saturation and the adsorption removal was said to reach an equilibrium, which was attained after 90 min at the employed conditions with removal percentage of 96% and 94% for CV and MB, respectively. Both dye removal percentage in pH 6.5 and pH 10 were almost near to gathering 91.9% and 90.7% as well as 96.3% and 93.4% for CV and MB, respectively. Therefore, 90 min was found to be the optimum contact time in this study while the adsorption capacity was found to be 9.6 mg/g and 9.4 mg/g for CV and MB, respectively at the optimum contact time. It was cleared that increasing time over 120 min had no significant effect on adsorption capacity. It can be stated that in this time with regard to dynamic equilibrium, similar results were reported by Seidmohammadi *et al.* (2015) [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 at the start [37] 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 [38, 39]. 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, Sharma *et al. (*2009), reported that Methylene Blue (MB) basic dye was adsorbed into an activated carbon and equilibrium was reached within 60 minutes when the initial concentration of MB was 150 mg/l [40].

Rammel *et al. (*2011) have reported a contact time of 15 min, as sufficient for the attainment of equilibrium for the adsorption of CV onto *Chaetophora elegans* algae [41]. Saeedeh *et al. (*2013) reported that equilibrium of MB with 72% removal onto STL was attained at 60 minutes [42]. Alaa reported that equilibrium in the solution of CV dye was attained within 30 minutes when ACDS was applied as an adsorbent [43]. 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 [44]. In a similar vein, Sharma and Janveja (2008) [45] conducted a study on the removal of Congo red dye from the effluent of a textile industry using rice husk carbon (RHAC) activated by steam. The study reported that a small amount (0.08 g/l) of rice husk carbon could remove 10 to 99 % of the dye from an aqueous solution of 25 mg/l with the contact time increasing from 20 min to 200 min. Another related work conducted by Bharathi and Ramesh, 2012 [24], reported that the biosorbent studied exhibits high efficiency for crystal violet adsorption onto *Citrullus lanatus rind* and the equilibrium states could be achieved in 180 min for the different initial concentrations.

4.4.2. Using continues process

4.4.2.1. The Effect of bed height of sorbent

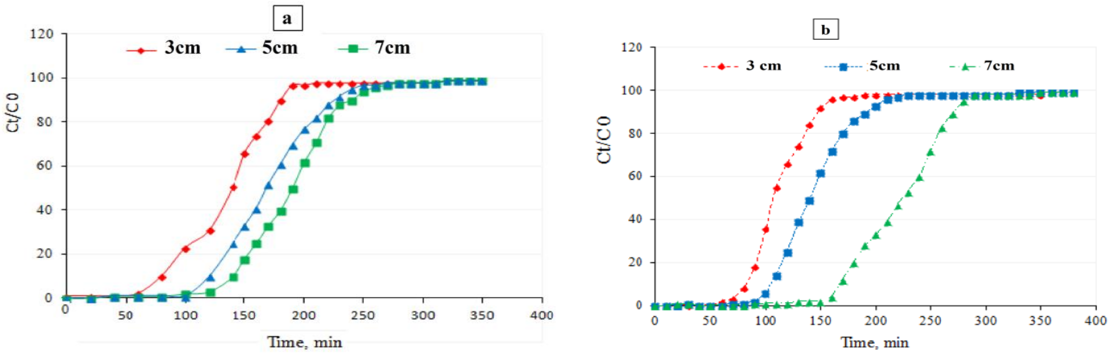

Fig. 9: Breakpoint curve for CV (a) and MB (b) adsorption by olive-waste cake at different bed heights at an initial concentration of 30 mg/l, flow rate of 5ml/min, pH 6 and room temperature.

In order to estimate the effect of bed height on the breakpoint time curve, an initial CV and MB influent concentration of 30 mg/ml (proved in previous section as the best of three) and a flow rate of 5 ml/min were kept constant, while three different bed heights of 3cm, 5cm and 7cm were evaluated. From Figure 9, it can be observed that the breakpoint time increased from about 70 min to 125 min, and the exhaustion time increased from 155 min to 250 min with the increase of bed height from 3 cm to 7 cm. As the bed height increases, the adsorbate material, (i.e CV molecules, Figure a) would have more time to contact with the adsorbents (i.e. OC) which, in turn, would result in a higher CV removal efficiency in the column as shown in Figure 9a. The increase in bed height from 3 to 7 cm leads to a decrease in adsorbate material concentration (i.e. CV concentration) in the effluent at the same time [46]. The slope of the breakpoint curve was slightly decreased with increasing bed height, which resulted in a broadened mass transfer zone. A similar phenomenon was recorded with MB and the results shown in Figure 9b. Hamdaoui (2006) [47] and Vijayaraghavan *et al. (*2004) [48] have both stated that with the increase in bed height, the mass of the adsorbents increase and so does the surface.

4.4.2.2. The effect of flow rate

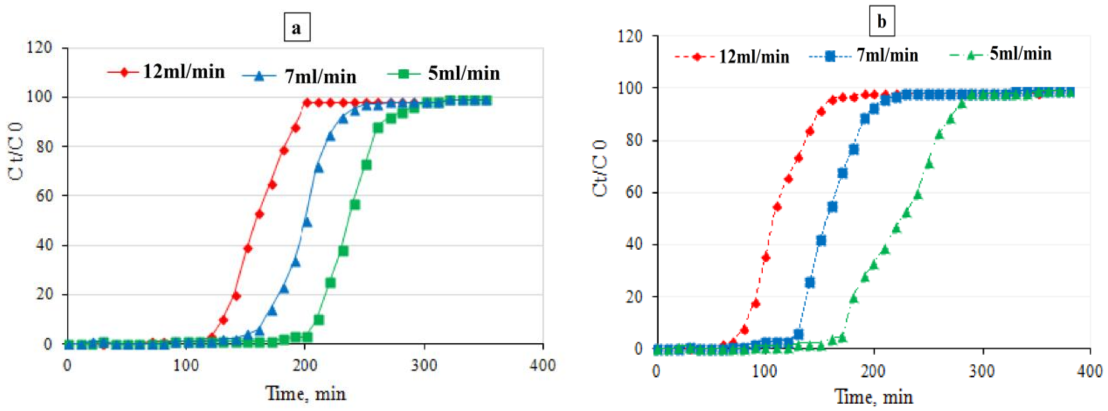

Fig. **10**: Breakpoint curve for CV (a) and MB (b) adsorption by olive-waste cake at different flow rates at (initial concentration of 30 mg/l, bed height of 7 cm, pH 6 and room temperature)

When dealing with optimizing the operating conditions of the continuous treatment of wastewater on an industrial scale, the flow rate of such influent wastewater is an essential parameter to evaluate [26]. In general, the effect of flow rate on sorption of adsorbate material (i.e. dye molecules) onto adsorbents by varying the flow rates, while all other parameters keeping constant at optimum values. The breakpoint time, as well as the sorption efficiency of adsorbate, was lower at higher flow rate [49, 50]. It is clear that rapid uptake is noticed in the initial stages of flow rate and the rate of uptake starts to decreases thereafter and finally reaches saturation. As increasing the flow rate of the pollutant influent solution, the breakpoint curves becomes steeper and reaches the breakpoint time faster to lower. This is attributed to the fact that as the flow rate becomes higher, the contact time between the adsorbate solutes and the adsorbent is minimized in time, hence, the adsorbate molecules do not have enough time to uptake the binding sites on the adsorbent surface or diffuse into the pores of the adsorbents, causing the adsorbate solutes to leave the column before equilibrium to occur and breakpoint time to be reached earlier. These results were corroborated by a number of reported findings [51, 52].

In this study, the effect of the flow rate on the adsorption of CV and MB by OC was investigated by varying the flow rate of the CV and MB inlet solution of 5, 7, and 12 ml/min with a bed height of 7 cm, while the influent CV and MB's initial concentration and pH were used according to the optimum levels selected at first part by using batch process, which are 30 mg/l and 6.5, respectively. From Figure 10a, it is clear that rapid uptake is noticed in the initial stages of flow rate, and the rate of uptake starts to decrease thereafter, and finally reaches saturation. As the flow rate of CV influent solution increases from 5 to 12 ml/min, the breakthrough curves becomes steeper and reaches the breakthrough time faster, from almost 200 min to 130 min or less, while the exhaustion time decreased from about 300 min to 160 min when the flow rate increased from 5 ml/min to 10 ml/min. Similarly, as the flow rate of MB influent solution increases from 5 to 12 ml/min, the breakthrough becomes steeper and reaches the breakthrough time faster from almost 180 min to 80 min, while the exhaustion time decreased from about 300 min to 190 min when the flow rate increased from 5 ml/min to 12 ml/min as shown in Figure 10b. The highest dye removal, which was 87.4%, was recorded when the flow rate value was 7 ml/min. The column having an ID of 2cm, with bed height 7cm, influent initial concentration 30mg/l, and flow rate 7 ml/min could treat 1050 ml and 950 ml of CV and MB respectively at breakthrough. From the economic point of view, the operating design conditions of 7cm bed height, 7ml/min flow rate, and 30mg/l initial influent concentration were selected as the best conditions of adsorption rate for both dyes using packed bed column. It was also established through the result that about 6.0 g of olive cake was required per liter of dye treatment. Results obtained from experimental studies conducted by Hairlu *et al.* [30], Goel *et al.* [31], Abass *et al.* [53] and Han *et al.* [54] exhibited similar trends as was observed in the present study.

4.4.3. Using static system

In general, at research centers and universities, the batch process is usually a more reliable and applicable technique, for reasons mentioned before. Therefore, the team of study has planned preliminarily, the use of this process. However, in order to save energy, no agitation or activation was made in the adsorption process using static sorption system. This will naturally slow down the process, but time was compared to cost [1].

In this part of the study, where no shaker device was used but the conical flasks filled with 100 ml dye solution at the optimum levels were selected by first part of the study, which are 30 mg/l, and pH 6.5 using 250 ml Erlenmeyer flasks, 0.3 g of olive cake powder with particle size of 0.2 mm was added to the solutions. After that, all samples were placed in a dark place, at room temperature for 7 days to reach equilibrium. The mass of sorbent and working volume of dye solution were both kept constant during the whole process. Each experiment of both CV and MB dye was performed three times under the same conditions and the average results were taken.

The equilibrium of both dyes sorption was reached within 4 days and the maximum removal percentage of CV and MB was found to be 89.0% and 86.86% respectively as shown in Figure 11, while the adsorption capacity was found to be 9.2 mg/g and 8.9 mg/g for CV and MB respectively. In a related study, activated carbon was prepared from oak leaves and used for the removal of CV from aqueous solution. The static sorption system took 2 days of soaking at room temperature [23]. Another study conducted by Khudhair et al.,2015 showed that the best removal of cresol red dye by recycled waste tire rubber reached more than 81% at adsorbent weight 12 g, particle diameter 2mm and duration of 21 days using static system without agitation and activation made during the adsorption process[1].

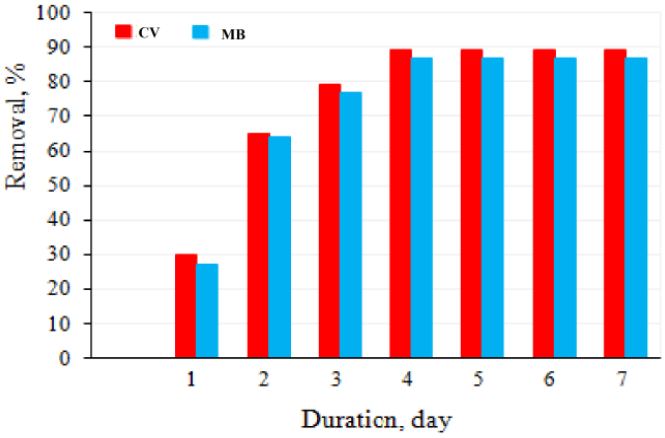

Fig. 11 : Effect of duration on CV and MB adsorption by the static system at room temperature and 100 ml of 30 mg/l of dye using 0.3g of olive cake, and pH 6.5.

V. Conclusion

The major conclusions of this study are drawn as follows:

1- The results of the study show that local adsorbent prepared from olive mill wastes, namely olive cake, can be successfully used as an adsorbent for the removal of CV and MB from aqueous solution.

2- The dynamic and static systems used in this study have a good effect on the rate of adsorption.

3- pH, contact time, and initial dye concentration were the main parameters used to evaluate the rate of adsorption in a batch experiment.

4- 30mg/l of initial dye concentration, pH 6.5, and contact time of 90min were the optimum conditions of the adsorption process using the batch system.

5- The adsorption rate increased with increase in contact time, while agitation rate, working volume of the reaction mixture, and reaction temperature were kept at 200rpm, 100ml and room temperature respectively, and the adsorption removal was found to be 96% and 94% for CV and MB respectively.

6- The column having an ID of 2cm, with bed height 7cm, influent initial concentration 30mg/l, and flow rate 7 ml/min could treat 1050 ml and 950 ml of CV and MB respectively at breakpoint.

7- Static adsorption system showed that the equilibrium of both dyes sorption was reached within 4 days and maximum removal percentage of CV and MB was found to be 89.0% and 86.86% respectively

8- From the economic point of view, the operating design conditions of 7cm bed height, 7ml/min flow rate, and 30mg/l initial influent concentration were selected as the best conditions of adsorption rate for both dyes using packed bed column. This result also showed that about 6.0 g of olive cake was required per liter of dye treatment.

9- As a result and from an environmental and economic point of view, the use of olive-waste cake instead of conventional adsorbents is a possible and preferable recycling method for these wastes, resulting in cost savings, lower energy consumption and lower environmental pollution.

VI. Recommendation

1- Results and data obtained from this current study by the utilization of inexpensive agricultural by-product/waste materials should be used as a database and source for development of more specific studies in the regions where pollutants are used extensively, yet, treated briefly.

2- Encouragement and support should be provided to those dealing with the production of adsorbents from locally available agricultural by-product/waste materials for treatments of receptor waters contaminated with other classes of dyes, heavy metals, some other organic toxins.

3- Attention must be paid to receptor waters so that they can be clean and free from any pollutants.
4- Universities and other similar places must announce the use of chemicals in their laboratories and the lack of any system for wastewater treatment
5- A sampling of receptor waters close to Universities and other similar places should be periodically analyzed for chemical levels, and the authorities should be forewarned against elevated pollutants.
6- There should be a proposal for an in-house wastewater treatment re-changeable fixed-bed column model.

Through this study, the authors recommend the use of the following framework of a proposed design for wastewater treatment at Universities Figure 12. The design is intended to install at the laboratory and exactly to connect the old waste-water discharge system with two receiving tanks. One of these tanks will further be connected to fixed bed column filled with a low-cost adsorbent obtained from olive mill waste namely olive cake (OC). However, the other tank will be bedded with layers made of OC adsorbents (in a way similar to batch mode technique). Simply, the first tank could be used for dynamic adsorption system by fixed bed column technique and the other for static adsorption system as shown by figure 12. An adsorbent such as OC is known to effectively adsorb basic dyes such as CV and MB. It is economic and non-harmful to the environment. Finally, it is biodegradable. Furthermore, the design is often easy to develop.

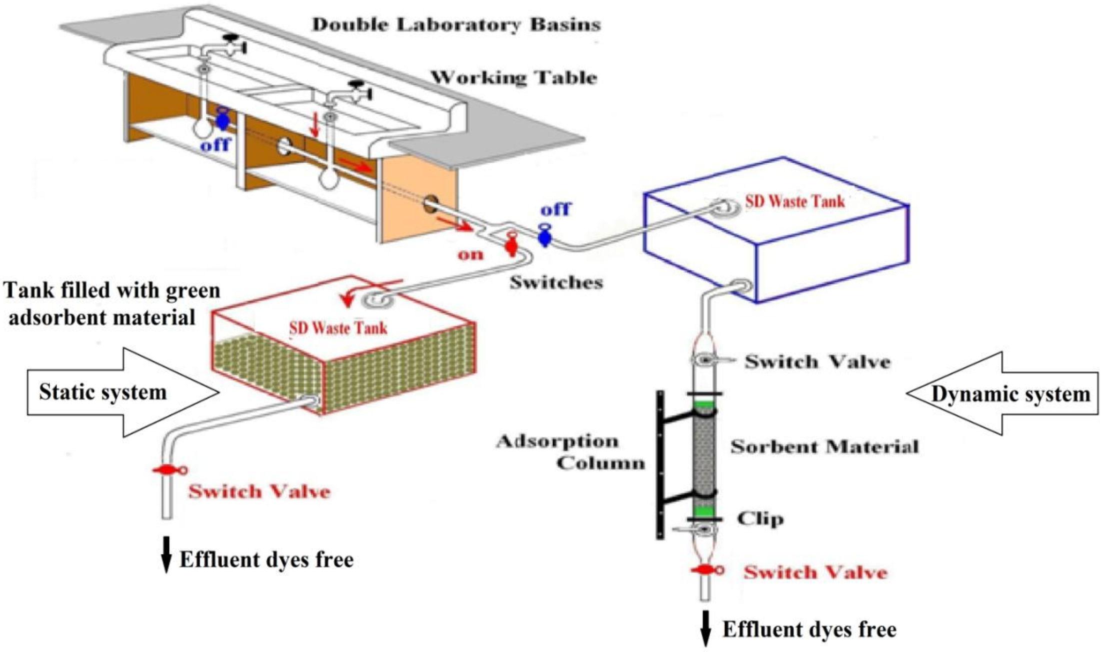

Fig. **12**: The proposed design of the OC bed adsorption system for In-Lab wastewater treatment.

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