The Thermal Pre-Processing Technique of the Bio-Waste for Contaminated Water Treatment: Histological and Experimental Study

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ABSTRACT: *The current study suggested a thermal treatment as a necessary proactive step in improving the adsorption capacity of bio-waste for contaminants removal in wastewater. This approach was based on the experimental and histological investigation of biowaste pod shells. This investigation showed that these shells composed of parenchyma cells that store secondary metabolites compounds produced from cells were exhibited in the present study. The results also reported that these compounds are extracted directly from the cells as soon as they are exposed to an aqueous solution, hampering their use as an adsorbent material. The increase in the weight of bio-waste adsorbent at unit liquid volume increases the production of secondary metabolites compounds under normal conditions. While thermal conditions accelerate the exit of these compounds from their storage places. After suggested thermal processing, the bio-waste was examined for azo dye removal under different operational conditions (adsorbent weight (1, 0.1 g), contact time (24 and 48 h), and temperature (30, 40, 50, and 60 °C). In general, the experimental data showed a good improvement in adsorption potential. The results presented clearly that the increase in temperature has a positive effect on the performance of pollutant removal. The maximum adsorption capacity was 0.035833 mol/g at a temperature of 40°C, and 0.036417 mol/g at a temperature of 50°C. This behavior may be counterproductive with high temperatures as a result of the release of more secondary metabolite compounds. For other operating conditions, increasing the concentration of the pollutant also improves the efficiency of the process, while this efficiency decreases with the increasing weight of the adsorbent material. For example, the removal capacity was (0.000275, 0.00675 mol/g) with 1 and 0.1 g of the adsorbent weight, respectively. Finally, the present study concluded that the adoption of thermal pre-treatment technology for bio-mass waste is a necessary step in improving the adsorption processes.*

KEYWORDS: *Bio-adsorbent; Azo dye; Biowastes; Thermal pre-treatment.*

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INTRODUCTION

Wastewater effluents without serious treatment are contributors to a variety of water pollution problems. The importance is related to risking human health and other organisms; such as aquatic organisms, animals, and plants, especially with the increasing diversity of industrial development [1-4]. The traditional methods still fall short of achieving their desired goals. In addition, some of them may require expensive materials, advanced control systems, and hard operating conditions [5]. However, the type and complexity of the pollutant find the suitable treatment method [6]. This complication may come from the nature of the pollutant and its chemical stability, as happens in the aqueous wastes that contain industrial dyes. These dyes are toxic compounds and, In addition to their environmental challenges, they have a risk of bioaccumulation via entering the food chain for both humans and animals [4, 7]. Moreover, the dyes are strongly resistant to biological and chemical degradation due to their synthetic origin and complex chemical structure such as azo dyes, which are one of the widely used dyes [8-10]. 2-[4-(dimethyl-amino) phenylazo] benzoic acid, as an example, belongs to azo dye [11]. It uses in many industries such as paper and textiles. The inappropriate treatment methods may exacerbate the current environmental problems by contributing to an increase in the toxic and carcinogenic compounds proportion [12-14]. In fact, the removal of azo dyes from wastewater is difficult, since they are stable in heat, light, oxidizing agents, poorly biodegradable, thus, it is not easily to remove [4, 7].

Generally, there are three main methods to remove the organic dyes and pigments from wastewater: (i) biological methods including aerobic and anaerobic degradation, (ii) chemical methods such as reduction, ion exchange, solvent extraction, coagulation, oxidation, and electrochemical, (iii) physical methods include adsorption, nanofiltration, and flotation [9, 15-20]. However, there has been increased interest to use biowaste as an alternative approach to chemicals used in water treatment processes, due to their abundance and lower collection cost [21, 22]. The thermal treatment of bio-waste is a necessary step to enable these materials to be promising adsorbents for removing industrial dyes, as hypothesized in the current study. In addition, the suggested pod shells from the Albizia tree, species lebbeck, as a bio-waste are effective, eco-friendly, biomaterial, inexpensive, and are widespread in Asia. It is noteworthy that this type of biowaste accumulates in large quantities annually. Consequently, these wastes entail expensive costs for removal and burning outside the city. Therefore, the current article addresses this problem by utilizing this type of biomass for wastewater treatment as a principle of mutually beneficial.

EXPERIMENTAL SECTION

Preparation of the Bio-waste

The shells of pods as a suggested adsorbent material were collected and washed many times with water to remove dirt and impurities. After that, the samples were dried for 24 hours at 60 °C by using the oven (Memmert UNB300) to remove the moisture. The grinding process of the samples was performed after the drying process to get the two sections; < 300 μm and 600-1000 μm. Fig. 1 presents a general layout of the preparation of the biomass material in the preliminary preparation stages.

Preliminary experiments

Preliminary experiments aimed to verify the quantity and nature of secondary metabolites compounds produced from the pods. In typical experiments, (0.1, 0.5, 1, 1.5, and 2.0) g of ground biowaste (less than 300 and 600-1000 μm) were added to distilled water at a temperature of 37 ^{o}C. The pH was monitored during those experiments, while the concentration of the compound was measured according to a standard curve of azo dye using a spectrophotometer (UV1800, Shimadzu).

Preparation of biowaste adsorbent

Preparation of biowaste aqueous extract was carried out through the weight of a sample (0.1 and 1) g of pods shell powder by adding (25 mL) of hot distilled water. Then, the sample was placed in the incubator for 24 hours at 37 ^{o}C. Removal of the extract solution from solid particles (adsorbent) was accomplished after completion of the incubation period to be ready for subsequent operations as shown in Fig. 2, which is a general layout of the thermal treatment as preparation stages of the suggested adsorbent materials.

Parametric study

Performance of the removal process using the pre-treated biowaste was evaluated by three main variables that include temperature (30, 40, 50, and 60) ^{o}C, adsorbent

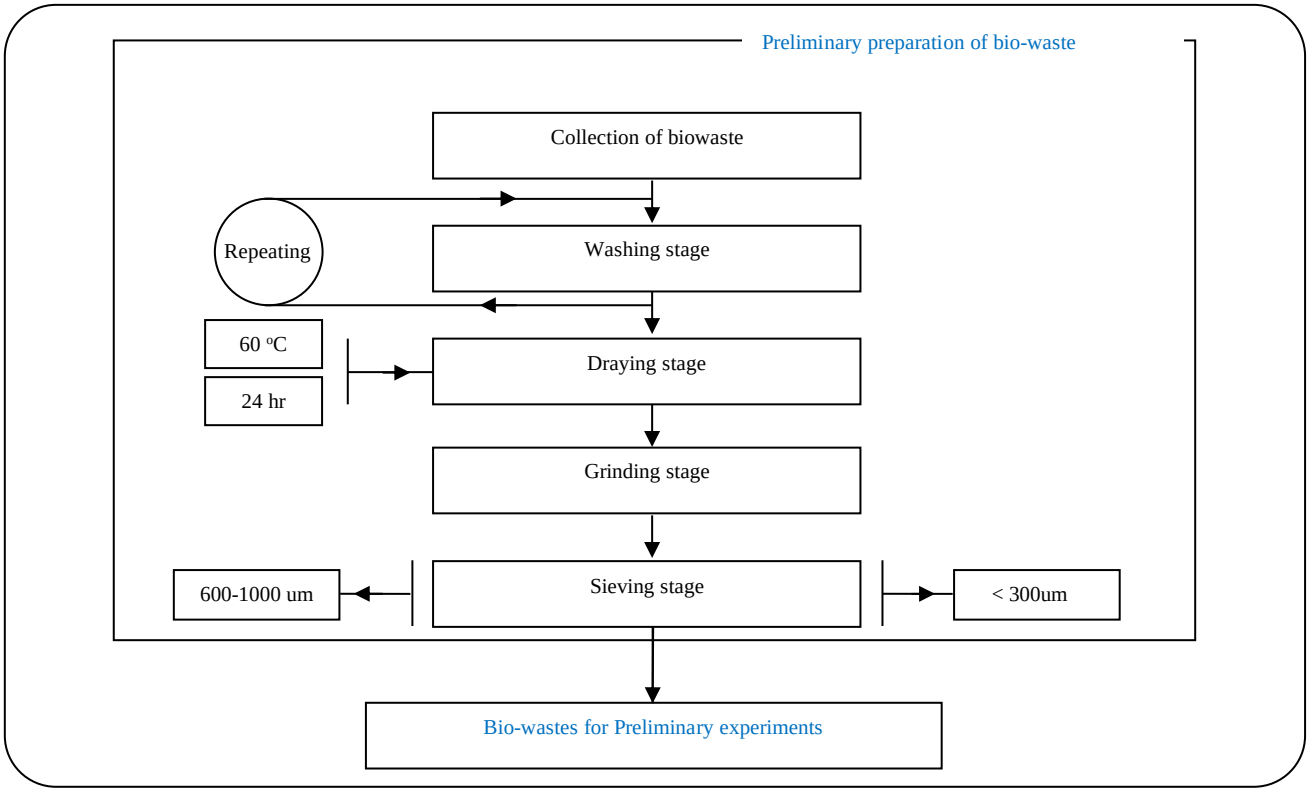

Fig. 1: A general layout of the preparation of the suggested adsorbents materials as preliminary preparation stages.

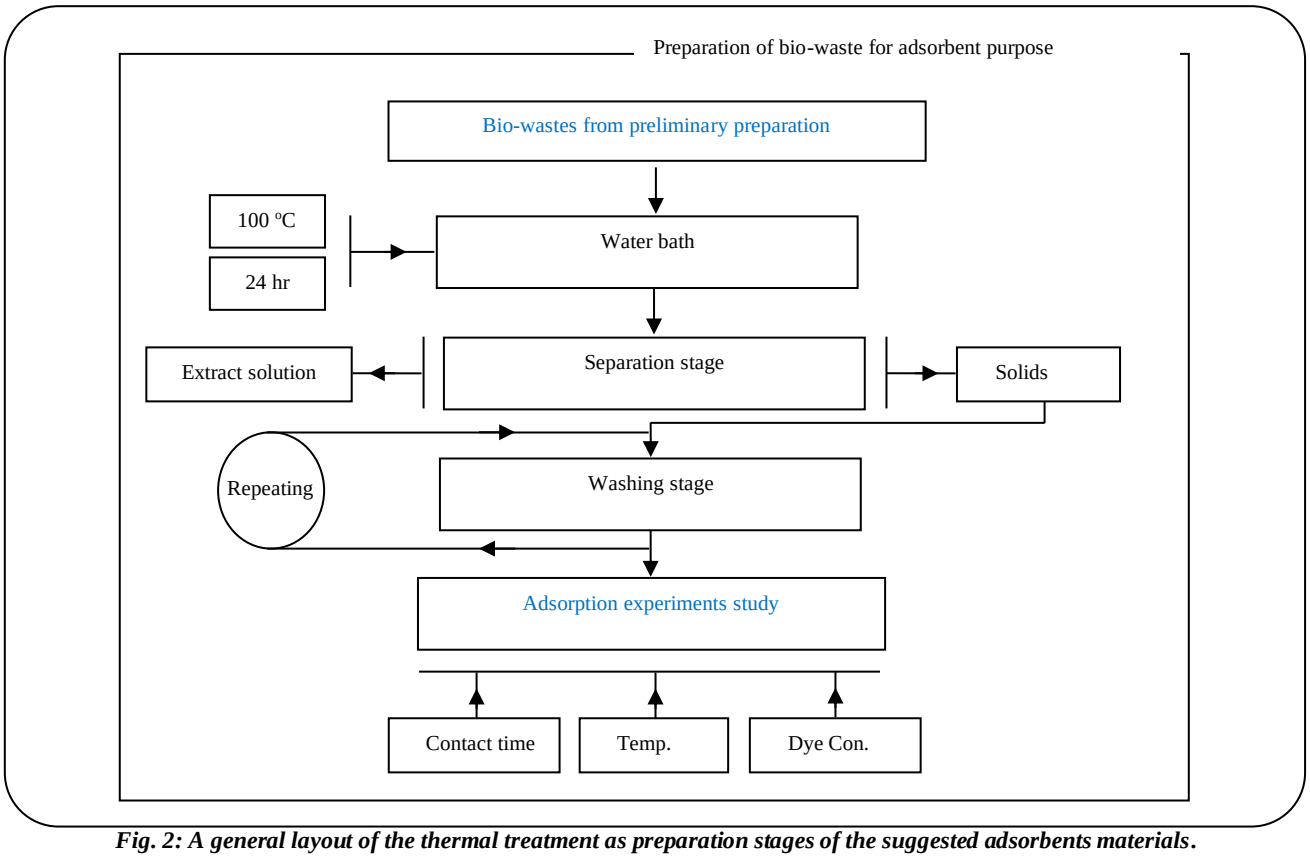

Fig. 2: A general layout of the thermal treatment as preparation stages of the suggested adsorbents materials.

materials weight (0.1 and 1g) g, and azo dye concentration ($1 \times 10^{-4}, 5 \times 10^{-4}, 10 \times 10^{-4}, 20 \times 10^{-4}$ mol/L). While the adsorption capacity was determined according to the following equation:

$$Qc = \frac{(C1 - C2)\, V}{W} \quad (1)$$

Where *Qc* is adsorption capacity (mol /g), *C1* is the blank concentration of dye (mol/L); *C2* is final concentration of dye (mol / L), *V* is volume of stock solution (L), and *W* is the weight of biowaste (g).

Preparation of the* biowaste *cross-section

The green biowaste (pods shell) was washed with distilled water several times to remove the dust and impurities to be put, then, in a solution of formaldehyde alcohol acetic acid (FAA). This solution is prepared from 50 mL of ethyl alcohol, 10 mL of formaldehyde (30 – 40) %, and glacial acetic acid and completed into 100 mL of distilled water. The sample was left in this solution for a period of (20 - 24) hours at room temperature. Then it was transferred to a 70% ethyl alcohol solution and preserved in it for making cross-sections [23, 24].

Phytochemical tests of* biowaste *aqueous extract

Glycosides compounds detection

The detection of glycosides compounds in aqueous extract of shells was carried out according to the Keller-Killiani-Phytochemistry method by creating two layers. The bluish-green color in the bottom layer indicates glycosides content in the aqueous extract [25].

Alkaloids compounds detection

The detection of the alkaloids in the plant extract was carried out by adding a few drops of Mayer reagent to 5 mL of biowaste extract. The appearance of white deposits, and indicates the presence of alkaloids [26-28].

Saponins compounds

Detection of the saponins in the shell extract was achieved by stabilizing a 1 cm layer of foam for 15 min after shaking the diluted plant extract with distilled water [29].

Phenolic compounds

The presence of phenols has been verified through the appearance of blue-green color in shell extract after adding a few drops of 1% $FeCl_3$ [30].

Tannins compounds

The acetate solution (1%) and the $FeCl_3$ solution (1%) were adopted in the process of detecting the tannins by checking the appearance of white-gelatin-precipitants to the plant extract after adding a few drops from these reagents [31].

Resins compounds

The resins were also examined in the biowaste extract by monitoring the formation of turbidity in the solution after adding 5 mL of ethyl alcohol (95% purity) to the pod extract. Then, the samples in the water bath were boiled for 2 min before adding the HCL to the extract [32].

Flavonoids compounds

The process of detection of these compounds was done by mixing one milliliter from the plant extract with 4 mL of ethanol (95%) and placing it in a water bath for half an hour. The appearance of a dark yellow color after adding sodium hydroxide to the extract is a clear indication of the presence of these compounds [32].

RESULTS AND DISCUSSION

Extraction of secondary metabolites

The primary study of bio-waste was aimed to investigate the effect of the secondary metabolites compounds on the performance of the removal process. The absorption spectrum of the secondary metabolites produced from the material (biowaste) was measured. Two different mesh sizes (< 300 and 600-1000) μm, (0.1, 0.5, 1, 1.5 and 2) g and contact time (24 and 48) hr in 25 mL of distilled water were adopted in the present study. All the experiments in this stage were done simultaneously under three replications for the purpose of the error bar based on standard deviation, while a long monitored pH. Fig. 3 explains the concentration of secondary metabolites extracted from the biowaste in the distilled water. It can be noticed that an increase in the weight of biowaste materials with a constant volume of distilled water, increases the concentration of secondary metabolites compounds (Fig. 3A and 3B). For example, at the section size of the adsorbent material less than 300 μm, half a gram of pods produced 0.182 mol/L of secondary metabolites compared to those that produced 0.65 mol/L at a weight of 2 gm of the same pods. The same response was observed at the section size of the adsorbent materials 600-1000 μm,

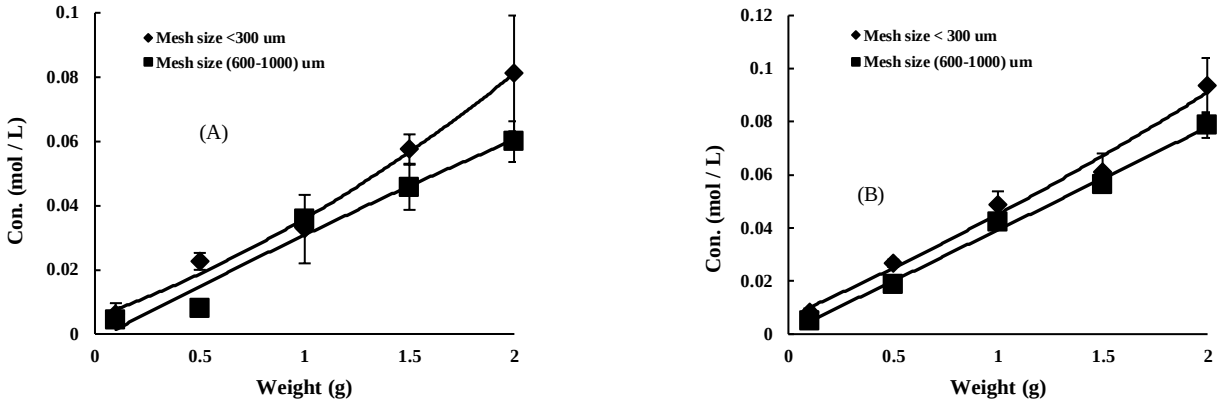

Fig. 3: Concentration of secondary metabolites compounds extracts that produced from bio-waste at mesh sizes (< 300 and 600-1000) µm, weight of bio-weste (0.1, 0.5, 1, 1.5 and 2) g in 25 ml D.W. A: Contact time 24 hr, B: Contact time 48 hr.

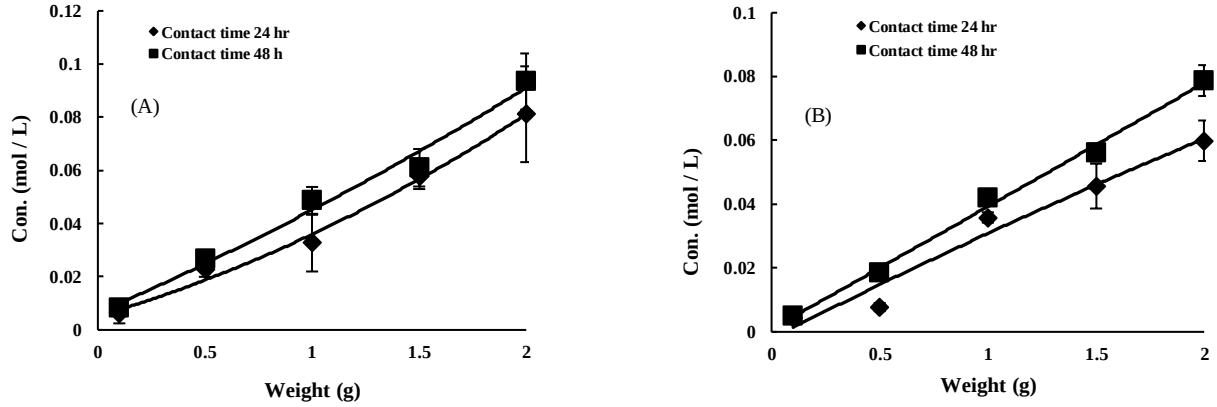

Fig. 4: Concentration of secondary metabolites compounds extracts that produced from bio-waste at mesh sizes weight of bio-weste (0.1, 0.5, 1, 1.5 and 2) g and contact time (24 and 48) hr in 25 mL distilled water A: mesh sizes (< 300) µm , B: mesh sizes (600-1000) µm.

but with lower concentrations. It is due to more vacuoles in cells being broken at the small section size (i.e < 300 µm) compared to the larger section size (i.e 600-1000 µm).

The contact time between the biomass solids and the distilled water has an effect on the amount of excreted substances (Fig. 4A and 4B). It shows that the doubling contact time causes an increase of about 20-30% of compound concentration, concluding that most of the compounds of secondary metabolites are excreted in less than 24 hours.

In addition, the higher concentration of secondary metabolites compounds was obtained at sections less than 300 µm, compared to that obtained from sections 600-1000 µm. The results explain that increasing the grinding process is enough to increase the cracking of the storage vacuoles of the metabolites. In the presence of water (as a solvent), these compounds dissolve, causing a significant increase in their concentration. Therefore, through the results, the increase in the concentration of compounds at the section size of < 300 µm was about 25% of what was obtained under the same operating conditions at the section size of 600-1000µm. Thus, the small section size needs to be processed with more steps than it is with the larger section size, and this is what was observed in the stage of preparing the selected plant material for the adsorption process. Fig. 5 also presents a picture of samples of secondary metabolites compounds that are produced from bio-waste cells at different conditions. For all samples and under different operating conditions, pH was monitored. The results presented in Fig. 6 show that the change extent of the pH was within the moderate range, confirming that the pH did not have a role in the occurrence of these metabolic secretions.

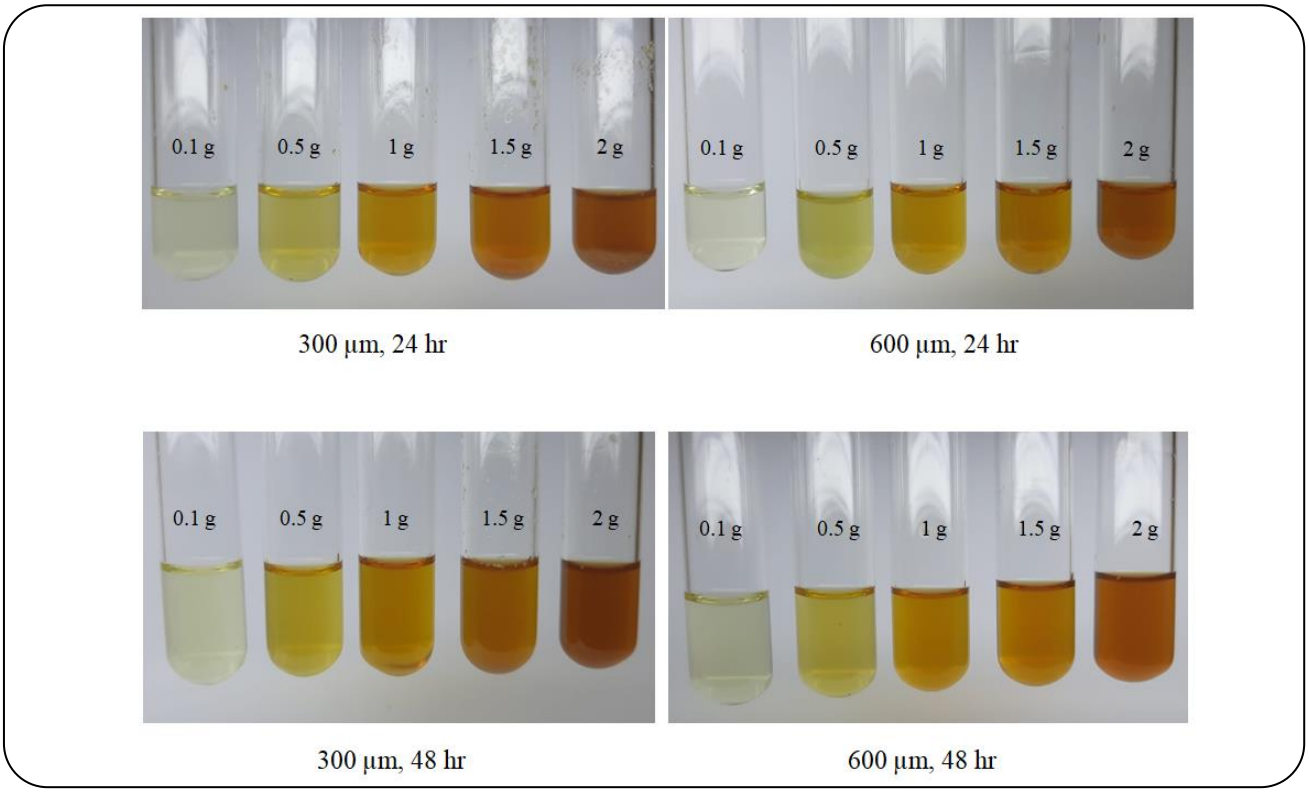

Fig. 5: Samples of secondary metabolites compounds extracts produced from bio-waste of* biowaste *at mesh sizes (< 300 and 600-1000) µm, weight of bio-waste (0.1, 0.5, 1, 1.5 and 2) g and contact time (24 and 48) hr in 25 mL D.W.

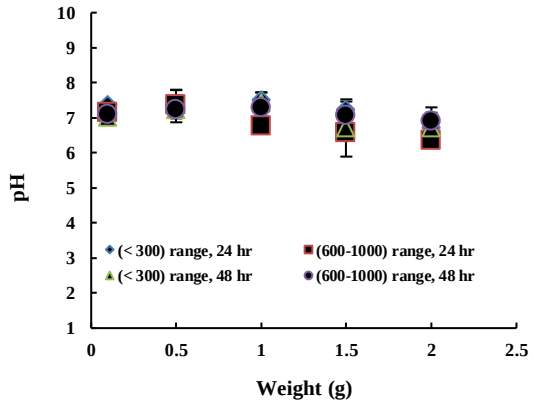

Fig. 6: pH values of samples of secondary metabolites compounds extracts produced from bio-waste at mesh sizes (< 300 and 600-1000) µm, weight of bio-waste (0.1, 0.5, 1, 1.5 and 2) g and contact time (24 and 48) hr in 25 mL D.W.

Histological study of the biowaste

Excessive amounts of secondary metabolites produced from cell vacuoles are an important obstacle to the use of this type of biological waste in adsorption processes. The results show that the secretions of these compounds start from the first hours of their presence in the solvent (i.e distilled water in the current study) as shown in Fig. 7. Thus, its use in the case is not feasible in removing contaminants. Therefore, the study of tissues has become important in diagnosing the reasons for the production of these quantities of metabolic compounds, and opening a door towards finding the appropriate treatment for this plant before going to use it as an adsorbent.

The longitudinal section of the biowaste green pods was studied in the present work. The findings indicate that it is composed of parenchyma cells, which represent most components of the pods' walls as shown in Fig. 8. These cells are considered temporary storage cells for starch, sugars, and nitrogen materials. Because of their closeness to the seeds, they are stored and later distribute to these compounds then transport to the seeds [23, 24]. The differentiated cells have central vacuoles that may reach 90% of the cell. The vacuole is a multi-purposed functional compartment; such as the storage of compounds such as proteins, dyes, and different secondary metabolites [33, 34]. The parenchyma cells in plant pods have large vacuoles as illustrated in this figure. They store secondary metabolites that are produced from pods' cell walls such as

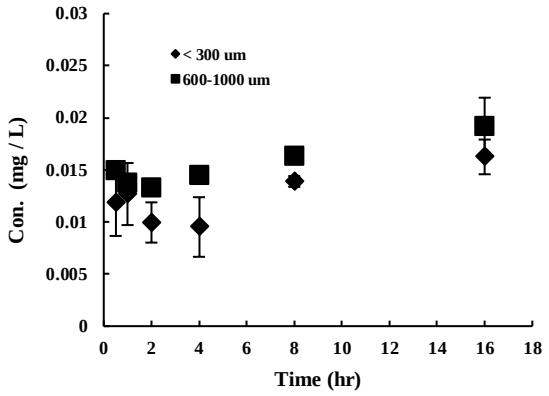

Fig. 7: Absorption spectrum at 521 nm of secondary metabolites compounds extracts that produced from bio-waste at mesh sizes (< 300 and 600-1000) µm, and contact time (0.5,1,2,4,8,and 16) hr in 25 mL D.W.

saponins, phenols, flavonoids, tannins, and glucosides that are displayed in Table 1 and these results are similar to the results of *Kokila* and *Kaur* [35, 36]. The pre-treatment process used in this research removed some of the secondary metabolites compounds in pod cells (adsorbent material) by soaking and shaking the adsorbent material in distilled water for 24 hours. However, other amounts of these compounds are still stored inside the pods' cells for two reasons; firstly, the pod cells contain a large amount of secondary metabolites compounds such as saponins and phenols which have to be extracted by using alcohols rather than distilled water [37, 38].

Secondly, the adsorbent material particle size was relatively large (1mm), consequently, the process of grinding the adsorbent material was not high enough to break all the pod cells. Accordingly, some of the secondary metabolites were subtracted from the water during the first pre-treatment process, while the other amounts were subtracted during the second treatment process for azo dye via chemical reactions that occur between them leading to disintegrate the dye and remove it by converting the water from red color to colorless.

The appropriate environmental and operational conditions are enough to make the secondary metabolites compounds release to the medium, causing the color change in the solution, subsequence the adsorption process reduces. It is worth mentioning that these referred environmental conditions are often within the Iraqi environment in three seasons. Therefore these conditions were adopted in the main experiments of the current study. Because of this problem, the pre-processing of this adsorbent was necessary to reduce the effect of the secondary metabolites compounds from the pods on the removal efficiency of dye. Pre-treatment of the samples was carried out by adding twenty-five millilitres of distilled water on the adsorbent for 24 hours at 40 ^{o}C temperature. The samples were then emptied from the aqueous extract to then wash with distilled water several times to remove the extract residue produced from the extraction process. The biomass adsorbents were then ready for subsequent experiments. In fact, the dye reaction with secondary metabolism compounds was also a possible hypothesis in the present study. However, the results indicated that there was no decrease in the dye concentration when mixing the biowaste aqueous extract with the aqueous wastewater at 40 ^{o}C and for 24 hours. While the decrease in dye concentration was clear when using the solid (after removing the secondary metabolites) as an adsorbent. Thus, these results confirm that the adsorption process occurs on the surface of the adsorbent material as a result of the presence of functional groups.

Effect of weight of adsorbent on removal efficiency

Two different weights of pre-treated biowaste were taken for adsorption purposes. This step targeted to know the effect of increasing the amount of the adsorbent on the azo dye removal. In the processes that used conventional adsorbents, the increase in weight of adsorbents increases the removal efficiency of pollutants, followed by a steady-state. But if the removal capacity calculations are adopted, the reversed response will be obtained [39]. In the current study, the results illustrated that 1 g of adsorbent material reduced the removal capacity of azo dye to be (0.0002 mol/g) compared with that obtained (0.006 mol/g) of removal capacity if the weight of 0.1 g is adopted as shown in Table 2. The main reason is the presence of residues of materials stored in shell cells. This case was also confirmed by several observations, in which the amount of secondary metabolisms compounds discharged from 1 g of biowaste was more than what was observed if 0.1 g of the same bio-waste is used as can be seen in Fig 5. Explanatory, the quantity of secondary compounds excreted from that weight gain is not proportional to the amount of dye adsorbed from the same adsorbent substance. In addition, increasing the adsorbent material increases the number of unsaturated active sites present on the adsorbent surface [39, 40]. Therefore,

Table 1: Chemical Analyzes of aqueous extract.

Chemical tests	Indication of the test
Saponins	+++
Resins	-
Flavonoids	+
Tannins (Viber)	+
Alkaloids (Viber)	-
Glycosides	+
Phenols	++

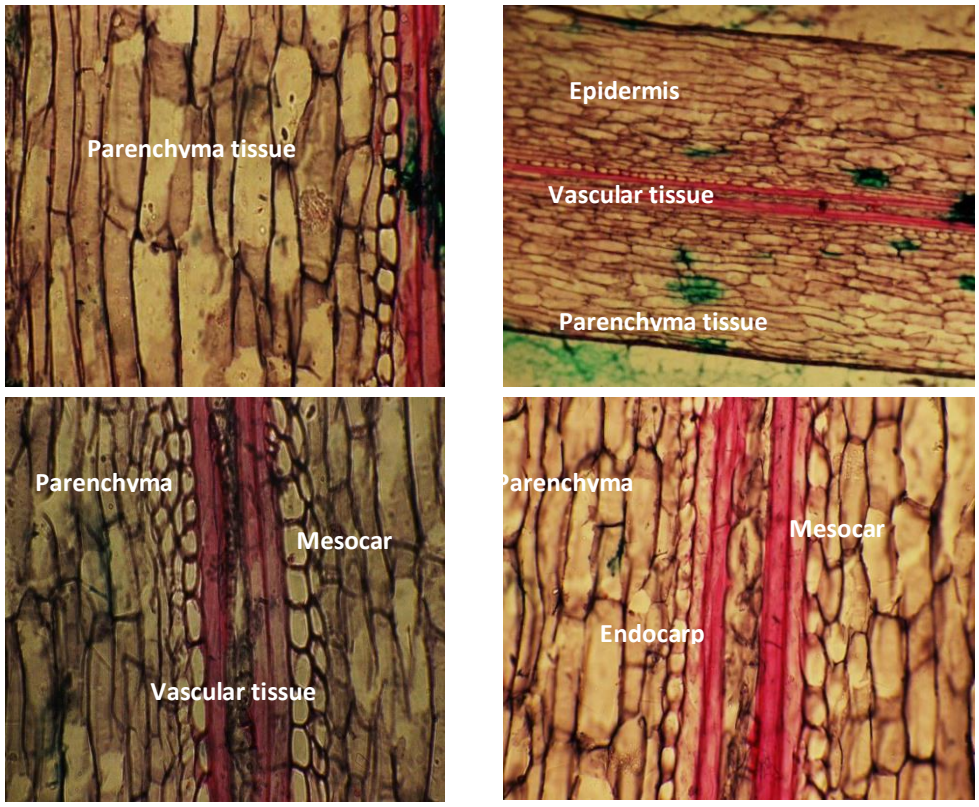

Fig. 8: Light micrographs and normal photo of* biowaste *(A) ; cross section of the green pods (·184); (B)(C)(D) cellular structure of the pods wall (·460). Endo, Endocarp; Ep, Epidermis; Meso, mesocarp; Pa, parenchyma; Pt, Parenchyma tissue; Pt, Parenchyma tissue; Vt, Vascular tissue.

0.1g of pre-treated adsorbents in 25 mL of the stock solution was adopted in the investigation of the effect of adsorption times on removal efficiency.

Effect of initial dye concentration

The current research also dealt with the role of the initial concentration of the dye pollutant on the efficiency of adsorption. Fig. 9 shows the study of the effect of four concentrations (1×10^{-4}, 5×10^{-4},10×10^{-4},20×10^{-4} mol/L) with constant temperature (40 °C) and weight of the adsorbent material (100 mg), but at two contact times (24 and 48 hours). The results of the experiments show a significant increase in the removal efficiency with the increase of the primitive dye concentration. This increase is due to the concentration of pollutant ions around the active sites on the surface of the adsorbent materials, providing opportunities to form bonds between the pollutants and these sites and overcoming

Table 2: Effect of Pre-treated* biowaste *on the removal capacity.

Bio-waste weight (mg)	Contact time (hr)	Temperature (°C)	Initial dye concentration (mol / L)	Removal capacity (mol/g)
100 mg	24	40	1×10^{-4}	0.00675
1000 mg	24	40	1×10^{-4}	0.000275

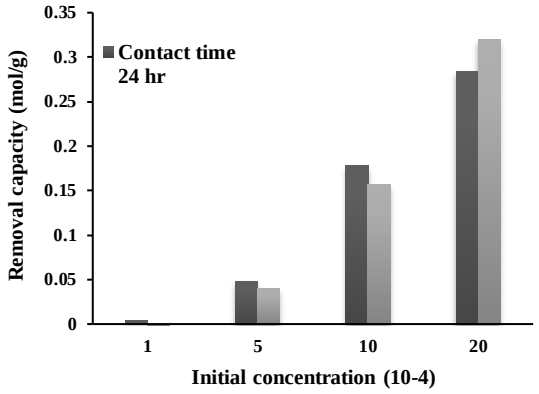

Fig. 9: Concentration of dye on the removal capacity when the contact time is 24 and 48 hr.

the resistance of mass transfer. Regardless of the type of pollutant and adsorbent, the same response was obtained by previous studies [39, 41]. They justified the increase in the number of collisions between dye ions and functional groups on the surface of the adsorbent material. Therefore, the time to reach an equilibrium state will increase until the chances of pollutant ions binding to the active sites are reduced. From another standpoint, the increase in the contact time between the pollutants and the active sites increases the complete saturation of those sites with the pollutant ions. However, the potential excretion of secondary metabolite compounds that are still stored in the microcompartments is possible, and it has been proven by the lower removal efficiency within 48 hours compared with those obtained after 24 hours.

In fact, the experiments were accomplished even during the first hours; however, the adsorbent did not have enough time to remove the dye from the solution. Therefore, increasing the time adsorption up to 48 hr was adopted in the current study. The results, however, indicate that the increase in an adsorption time of more than 48 hours had no great effect on the efficiency of the removal process. According to these results and in terms of economic and application aspects, 24-hour processing time has the advantage over 48 hours to save time and effort. The temperature effect on removal capacity was also investigated as shown in Table 3. It can be seen, that the maximum adsorption capacity was obtained at 50 °C followed by 40 °C. Nevertheless, the increase of adsorption rate between 40 °C and 50 °C did not exceed 1.5%. Thus, from an economic point of view, this small ratio of the adsorption capacity against a difference of ten degrees Celsius is unreasonable, which makes 40 °C an advantage over the other temperature. On the other hand, the ratio of dye removal is inversely proportional to temperature change. One of the most important reasons is that the rate of the secondary metabolites compounds that release from plant cells in aqueous extract, increases by increasing the temperature. This is what happens when the extracting process for the plant occurs at high temperatures. In addition, Baghdad city is one of the hottest areas during most months of the year, however, the water temperature does not exceed 40 °C often based on several experiments in this regard. Therefore 40 °C was adopted as an appropriate natural environmental condition for wastewater treatment.

Finally, and through the above results, it can be deduced that the current study introduces another alternative adsorbent material that could be promising, available, less expensive, and environmentally friendly as well as without any additives. Comprehensively, this article also emphasized the economic importance resulting from the use of biowaste in the contaminated water treatment unit, especially that the disposal of these plant wastes outside the cities has become a costly and worrying factor for local governments in recent times.

CONCLUSIONS

Adoption of the thermal method in preparing the biowaste to be an active adsorbent material was proposed in this study. The experiential and the histological study concluded that one of the main reasons for the reduction in the performance factor of the adsorption process is that this bio-waste contains parenchyma cells that consider as temporary storage cells for secondary metabolism compounds. These compounds may be released into

Table 3: Effect of temperature on efficiency removal.

Bio-waste weight (mg)	Contact time (hr)	Temperature (°C)	Initial dye concentration (mol / L)	Removal capacity (mol / g)
100	24	30	1×10^{-4}	0.033167
		40		0.035833
		50		0.036417
		60		0.022833

polluted water when the appropriate operational and environmental conditions are present, which affects the adsorption process. According to the parametric study, the experimental data concluded that an increase in the amount of adsorbent material, even if it was previously treated, does not necessarily increase the amount of dye removed.

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REFERENCES

[1] Watiniasih N.L., Purnama I.G.H., Padmanabha G., Merdana I.M., Antara I.N.G., Managing Laundry Wastewater, *IOP Conf. Ser.: Earth Environ. Sci.*, **248**: 012084, (2019).

[2] Zhang X., Liu Y., Circular Economy-Driven Ammonium Recovery from Municipal Wastewater: State of the Art, Challenges and Solutions Forward, *Bioresour. Technol.*, **334**: 125231, (2021).

[3] Yet Z.R., Rahim M.Z.A., Removal of Methyl Red from Aqueous Solution by Adsorption on Treated Banana Pseudostem Fibers Using Response Surface Method (RSM), *MJAS*, **18 (3)**: 592 - 603, (2014).

[4] DIM P.E., Adsorption of Methyl Red and Methyl Orange Using Different Tree Bark Powder, *Acad. Res. Intern.*, **4 (1)**: 330-338, (2013).

[12] Bentahar S., Dbik A., Khomri M.E., Messaoudi N.E., Lacherai A., Adsorption of Methylene Blue, Crystal Violet and Congo Red from Binary and Ternary Systems with Natural Clay: Kinetic, Isotherm, and Thermodynamic, *J. Environ. Chem. Eng.*, **5(6)**: 5921-5932 (2017).

[5] Al-mashhadani M.K., Wilkinson S.J., Zimmerman W.B., Laboratory Preparation of Simulated Sludge for Anaerobic Digestion Experimentation, *JE*, **21(6)**: 131-145, (2015).

[6] Azimi S.C., Shirini F., Pendashteh A., Advanced Oxidation Process as a Green Technology for Dyes Removal from Wastewater: A Review, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **40(5)**: 1467-1489 (2021).

[7] Haris M.R.H.M., Sathasivam K., The Removal of Methyl Red from Aqueous Solutions Using Banana Pseudostem Fibers. *Am. J. Appl. Sci.*, **6(9)**: 1690-1700 (2009).

[8] Al-Hemiri A.A., Abed K.M., Al-Shahwany, A. W., Extraction of Pelletierine from Punica granatum L.by Liquid Membrane Technique and Modelling, *IJCPE*. **13 (1)**: 1- 9 (2012).

[9] Enenebeaku C.K., Okorocha N.J., Uchechi E.E., Ukaga I.C., Adsorption and Equilibrium Studies on the Removal of Methyl Red from Aqueous Solution Using White Potato Peel Powder, *Int. Lett. Chem. Phys. Astron.*, **72**: 52-64 (2017).

[10] Patil N.P., Bholay A.D., Kapadnis B.P., Gaikwad V.B., Biodegradation of Model Azo Dye Methyl Red and other Textile Dyes by Isolate Bacillus Circulans *NPP1*, *J. Pure Appl. Microbiol.*, **10(4)**: 2793-2800 (2016).

[11] Khouri S.i.J., Abdel-Rahim I.A., Alshamaileh E.M., Altwaiq A.M., Equilibrium and Structural Study of m-Methyl Red in Aqueous Solutions: Distribution Diagram Construction, *J. Solution Chem.*, **42(9)**: 1844-1853 (2013).

[13] Yaoqiang H., Chaoming Q., Min G., Xiushen Y., Zhijian W., Preparation of Fe3O4-octadecyltrichlorosilane for Removal of Methyl Orange and Methylene Blue: Influence of pH and Ionic Strength on Competitive Adsorption, *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, **32(6)**: 1413-1419 (2017).

[14] Katheresan V., Kansedo J., Lau S.Y., Efficiency of Various Recent Wastewater Dye Removal Methods: A Review, *J. Environ. Chem. Eng.*, **6(4)**: 4676-4697 (2018).

[15] Shariati-Rad M., Irandoust M., Amri S., Feyzi M., Ja'fari F., Removal, Preconcentration and Determination of Methyl Red in Water Samples Using Silica Coated Magnetic Nanoparticles, *J. Appl. Res. Water and Wastewater*, **1**: 6-12 (2014).

[16] Khosravi A., Karimi M., Ebrahimi H., Fallah N., Sequencing Batch Reactor/Nanofiltration Hybrid Method for Water Recovery From Textile Wastewater Contained Phthalocyanine Dye and Anionic Surfactant, *J. Environ. Chem. Eng.*, **8 (2)**: 103701 (2020).

[17] Singh A., Pal D.B., Mohammad A., Alhazmi A., Haque S., Yoon T., Srivastava N., Gupta V.K., Biological Remediation Technologies for Dyes and Heavy Metals in Wastewater Treatment: New Insight, *Bioresour. Technol.*, **343**: 126154 (2022).

[18] Shaikh A.R., Chawla M., Hassan A.A., Abdulazeez I., Salawu O.A., Siddiqui M.N., Pervez S., Cavallo L., Adsorption of Industrial Dyes On Functionalized and Nonfunctionalized Asphaltene: A Combined Molecular Dynamics and Quantum Mechanics Study, *J. Mol. Liq.*, **337**:116433(2021).

[19] Li D., Ning X.-a., Yuan Y., Hong Y., Zhang J., Ion-Exchange Polymers Modified Bacterial Cellulose Electrodes for the Selective Removal of Nitrite Ions from Tail Water of Dyeing Wastewater, *J. Environ. Sci.*, **91**: 62-72 (2020).

[20] Thasneema K.K., Dipin T., Thayyil M.S., Sahu P.K., Messali M., Rosalin T., Elyas K.K., Saharuba P.M., Anjitha T., Hadda T.B., Removal of Toxic Heavy Metals, Phenolic Compounds and Textile Dyes from Industrial Waste Water Using Phosphonium Based Ionic Liquids, *J. Mol. Liq.*, **323**:114645 (2021).

[21] Danlami U., Elisha E.P., A Comparative Study on the Phytochemicals and Antimicrobial Activities of the Ethanol and Petroleum Ether Extracts of the Leaves of Albizia Lebbeck and Its Mistletoe, *Int. J. Pharm. Chem.*, **3 (2)**:13-18 (2017).

[22] Hadi S.M., Al-Mashhadani M.K.H., Eisa M.Y., Optimization of Dye Adsorption Process for Albizia Lebbeck Pods as a Biomass Using Central Composite Rotatable Design Model, *Chem. Ind. Chem. Eng. Q.*, **25(1)**: 39-46 (2019).

[23] Thorne J., Assimilate Redistribution from Soybean Pod Walls During Seed Development, *Agron. J.*, **71**: 812-816 (1979).

[24] Wang H.L., Grusak M.A., Structure and Development of Medicago truncatula Pod Wall and Seed Coat, *Annals of Botany*, **95 (5)**: 737-747 (2005).

[25] Matulja D., Grbčić P., Bojanić K., Topić-Popović N., Čož-Rakovac R., Laclef S., Šmuc T., Jović O., Marković D., Pavelić S.K., Chemical Evaluation, Antioxidant, Antiproliferative, Anti-Inflammatory and Antibacterial Activities of Organic Extract and Semi-Purified Fractions of the Adriatic Sea Fan, Eunicella cavolini. *Molecules*, **26 (19)**: 5751(2021).

[26] Smolenski S.J, Silinis H., Farnsworth N.R., Alkaloid Screening, *VI. Lloydia.*, **38(3)**: 225-255 (1975).

[27] Abed K.M., Kinetic of Alkaloids Extraction from Plant by Batch Pertraction in Rotating Discs Contactor, *IJCPE*, **15(2)**: 75-84 (2014).

[28] Abed K.M., Al-Hemiri A.A., Separation of Alkaloids from Plants by Bulk Liquid Membrane Technique Using Rotating Discs Contactor, *Diyala Journal of Engineering Sciences*, **8(4)**: 785-793 (2015).

[29] Bhandary S.K., Kumari N. S., Bhat V.S., K.P. Sh., Bekal M.P., Preliminary Phytochemical Screening of Various Extracts of Punica Granatum Peel, Whole Fruit and Seeds. *N.U.J.H.S.*, **2(4)**: 34-38 (2012).

[30] Atiyah, K.H.; Kadhum, E.J., Isolation and Identification of Phenolic Compounds from Dianthus orientalis Wildly Grown in Iraq, *Iraqi. J. Pharm. Sci*, **30(2)**:122:134 (2021).

[31] Rao U.S.M.; Abdurrazak M., Mohd K.S., Phytochemical Screening, Total Flavonoid and Phenolic Content Assays of Various Solvent Extracts of Tepal of Musa Paradisiaca, *Malaysian J. of Anal. Sci.*, **20 (5)**: 1181-1190 (2016)

[32] Rehman N.U., Al-Riyami S.A., Hussain H., Ali A., Khan A.L., Al-Harrasi A., Secondary Metabolites from the Resins of and Mitigate Lipid Peroxidation, *Acta. Pharm*., **69(3)**:433-441 (2019)

[33] Vági P.,"Structure of Plants and Fungi", Kristóf, Z., Ed. IT Study Hungary Ltd (2013).

[34] Martinková M., Čermák M., Gebauer R., Špinlerová Z., Plant Botany an Introduction to Plant Anatomy, Morphology and Physiology, *Mendel University in Brno Faculty of Forestry and Wood Technology* (2014).

[35] Kokila K., Priyadharshini S.D., Sujatha V., Phytopharmacological Properties of Albizia Species: A Review, *Int. J. Pharm. Pharm. Sci.*, **5(3)**: 70-73 (2013).

[36] Kaur H., Harisha C., Galib R., Prajapati P., Pharmacognostical and Preliminary Phytochemical Profiles of Pod of Shirisha (Albizia lebbeck Benth.). *Annals of Ayurvedic Medicine*, **5 (3-4)**: 78-87 (2016).

[37] Majinda R.R.T., Extraction and Isolation of Saponins, *Methods Mol Biol*., **864**: 415-26 (2012).

[38] Deore S.L., Baviskar B.A.; Rangari A.S., Rapid and high yield Extraction method for Saponins from Safed Musli, *Pharmacogn. J.*, **7(4)**: 210-214 (2015).

[39] Aljeboree A.M., Alkaim A.F., Role of Plant Wastes as an Ecofriendly for Pollutants (crystal Violet Dye) Removal from Aqueous Solution, *Plant Arch.*, **19(2)**: 902-905 (2019).

[40] Gecgel U., Kolancilar H., Adsorption of Remazol Brilliant Blue R on Activated Carbon Prepared from a Pine Cone, *Nat. Prod. Res.*, **26 (7)**: 659-664 (2012).

[41] Moghaddam S.S., Moghaddam M.R.A., Arami M., Decolorization of an Acidic Dye from Synthetic Wastewater by Sludge of Water Treatment Plant, *Iran. J. Environ. Health. Sci. Eng.*, **7(5)**: 437-442(2010).