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Efficiency of adding DD3+(Li/Mg) composite to plants and their fibers during the process of filtering solutions of toxic organic dyes

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ABSTRACT

A comparison was made between two types of plants, cauliflower and Anisosciadium, to find out which one is better and to address the main catalyst and the factors that achieve the white color of the solution in the filtering process. Where this process takes place under the sun's rays. We worked on two methods, the first is to use a portion of cauliflower leaves and peas stalks, and the second is to extract the fibers that make up the two aforementioned materials and work on them. To improve the process of filtration and photocatalysis together, we used a new method that gives excellent efficacy in just minutes, by depositing (Li/Mg) materials on one side, and on the other hand depositing (Li/Mg)+kaolinite type DD3 on these plants without heat treatment.

This process preserves the shape of the fibers, leaves or leg, according to the types used, without being damaged. The results showed effectiveness in filtering both polluting solutions without discrimination, but the fastest degradation time was by using the fibers of both plants with precipitants (Li/Mg + DD3) in the case of solutions with organic dye MB, where we obtained a percentage of 100 within 60 mn. Compared with the OII, where is the estimated time to get the full liquidation 120 mn. The samples were studied before and after the filtration process by infrared to confirm the presence of impurities belonging to the two highly toxic organic solutions, and also the obtained solution was analyzed after the operation and it was found that it matches the spectrum of distilled water.

1. Introduction

Water is a vital resource for humans and although it seems inexhaustible, water is distributed unevenly on the planet and all countries, in the short or long term, have to face the problem of its scarcity. The search for adequate means to purify and reuse treated wastewater has become an attractive and essential alternative option in order to mobilize larger volumes of water and thus meet the growing demand, especially in arid and semi-arid countries [1].

Furthermore, components of wastewater and factory pigments (pathogens, salts, minerals, toxic organic compounds, etc.) pose risks to the environment and can harm public health [2]. Treating these secretions is essential to combat their harmful effects. Various treatment techniques are used, whether biological (natural or aerobic lakes, activated sludge or bacterial beds), physicochemical (coagulation - flocculation, sedimentation or oxidation) or membrane (reverse osmosis, nanofiltration or electrowashing) [3].

Dyes such as methylene blue and orange II are among the most dangerous pollutants for living organisms in general and humans in particular. The organic dye, methylene blue, is a heterogeneous cyclic chemical compound with the formula $C_{16}H_{18}ClN_3S$, and it is in the form of a dark green powder [4,5]. It is one of the dyes used in the field of chemistry and biology and is also used as a drug and pharmaceutical preparation. It is considered as a low toxic agent, but it can cause various harmful effects [6]. It is also used in doses or concentrations less than 7 mg/kg, and in excess of this value may cause harm to humans such as nausea, abdominal pain and confusion [7]. While the organic dye Orange II is a powder with chemical formula $C_{16}H_{11}N_2NaO_4S$ that is highly toxic, dangerous to human health and can cause cancer [8,9].

The world's need for new technologies and materials that have characteristics that allow people to benefit from them and get rid of these dyes, prompted many researchers to prepare materials that have a

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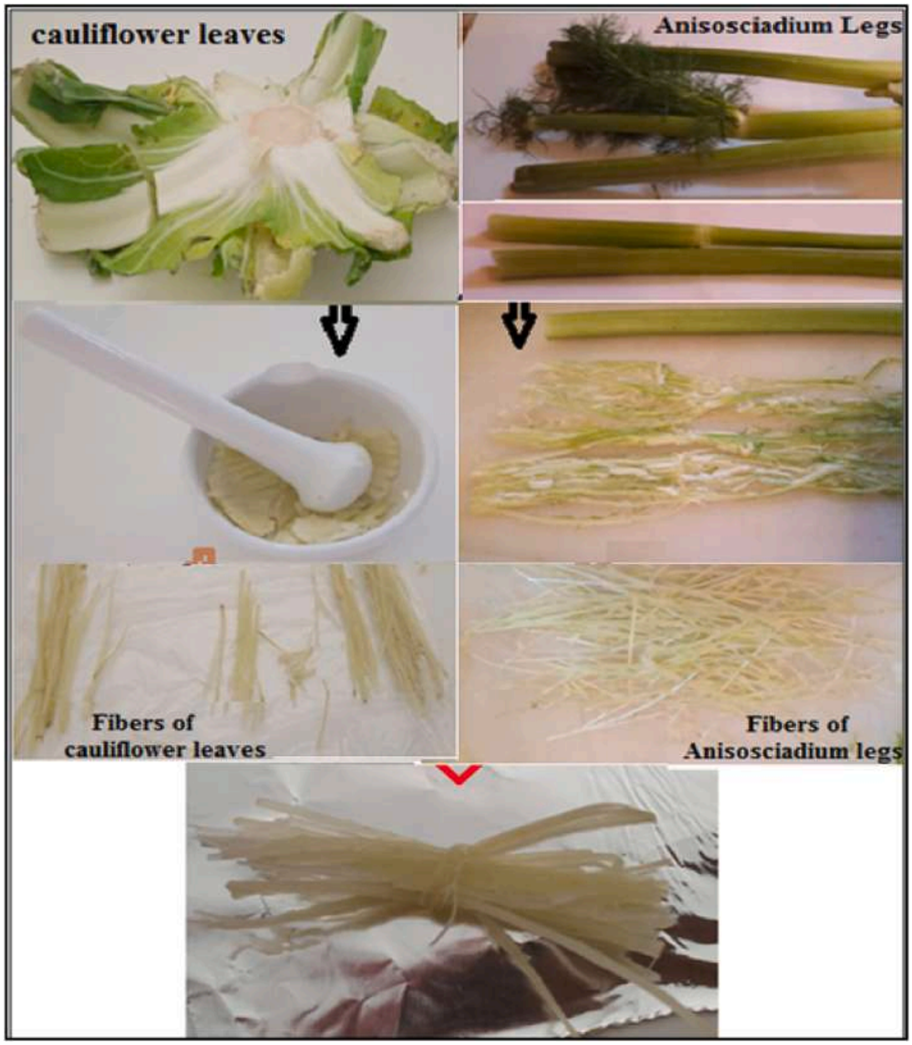

Fig. 1. A portion of a cauliflower leaf and an anisosciadium leg and a method showing how to extract the fibers from the two plants.

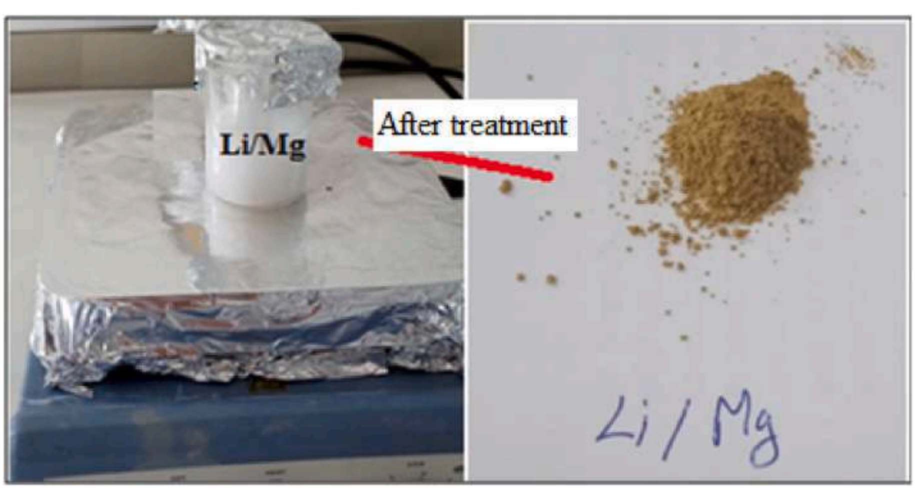

Fig. 2. Powder (Li/Mg) obtained after heat treatment at 500 °C within 2 h.

positive effect while using them for various research purposes and special applications whose source is a cheap resource and easy production methods. It does not come from natural sources. Therefore, each researcher had a study on different elements to know their importance and effectiveness in this process; among them the methods used by C. Zheng to treat some organic dyes are coagulation and filtration [10], while using S.P. Nandi activated carbon and raw carbon since 1971 as an adsorbent for removing some acidic and basic dyes from aqueous solutions [11]. S. D. Lambert was also interested in studying the adsorption of some active dyes on inorganic adsorbents and some natural materials

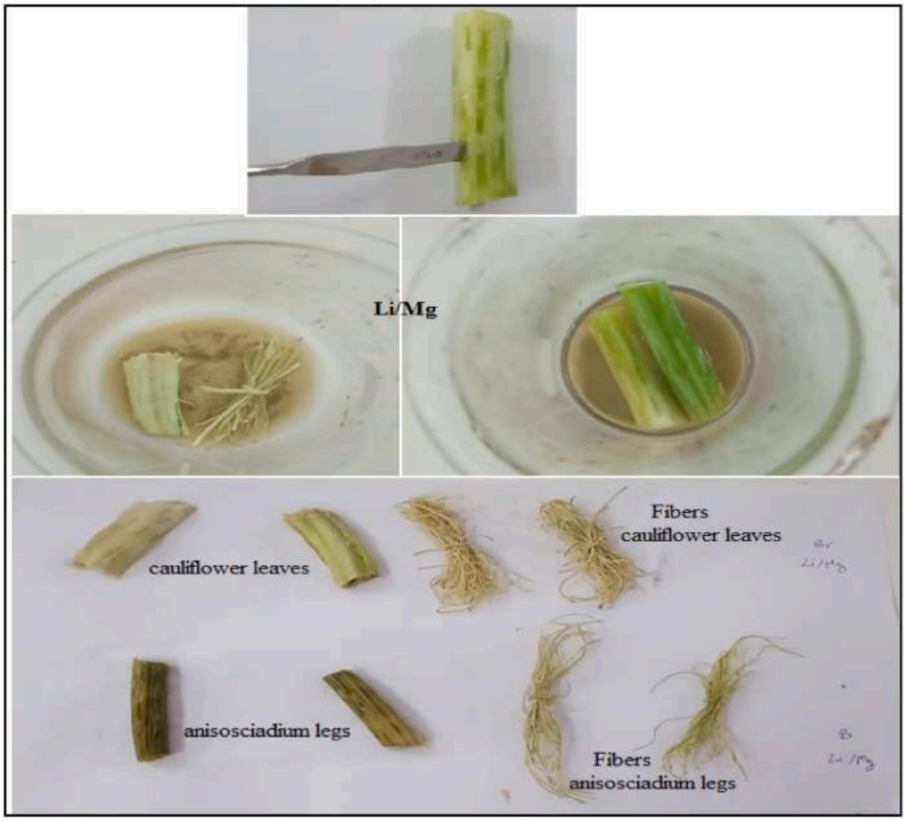

Fig. 3. The new shape of the samples after deposition of Li/Mg using cauliflower leaves, anisosciadium legs and their fibers.

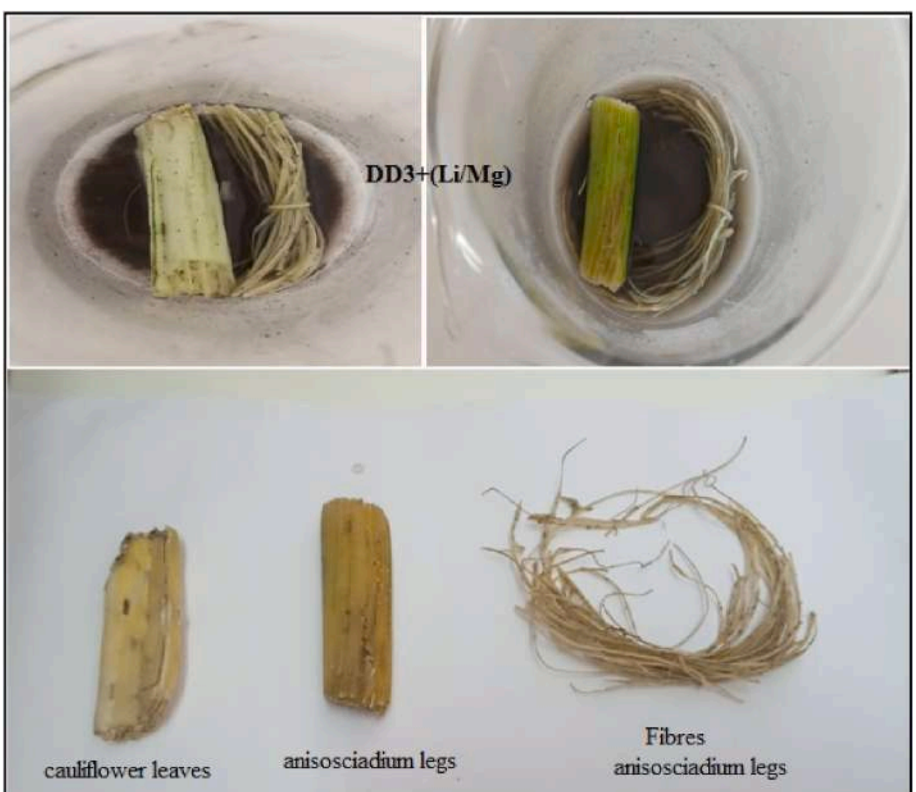

Fig. 4. The new shape of the samples after deposition of (Li/Mg)+DD3 using cauliflower leaves and anisosciadium legs and their fibers.

Fig. 5. The filtration process of the two organic dye solutions.

such as palm waste [12], and as worked before on ceramic materials of the type DD3 kaolinite in the field of photocatalysis and adding other elements to it to increase the catalytic process and obtain greater efficiency [13,14].

In this work, these dyes were treated using abundantly available plants, not consumed by humans, and natural sources of energy such as sunlight, and other stimulating sources such as the abundant earthen clay. Cauliflower and anisosciadium are high in vitamins, and their antioxidant content helps fight any health problems and diseases. It is also naturally rich in dietary fiber that the body greatly needs, which reduces the chances of human disease. Among the elements, magnesium and lithium were chosen as catalysts, in addition to that they are non-toxic, the shape of their nano-crystalline particles gives them a high-quality surface as a catalyst for the reaction, causes structural defects on their surface and is suitable for the catalytic fractionation of water and hydrogen generation [15,16]. Among its applications are groundwater treatment, sewage treatment, drinking water treatment, air emissions treatment, toxic waste treatment and it has great potential as an antibacterial agent [17]. Whereas, the local kaolinite type DD3 was chosen from among the three types of kaolin, which is rich in impurities of MnO, CaO, K_2O and Fe_2O_3. This material is characterized by its gray color and a volumetric mass of 2.53 g/cm^3. This material was picked from Jebel Dabbagh, west of the city of Galma, located in the east of Algeria. As its main component is alumine (Al_2O_3) and silica (SiO_2) [18].

From this point of view came the importance of the photocatalytic process, as it is a reaction in which sunlight is used as a stimulant for the types of plants used for the first time, such as cauliflower and anisosciadium, with additives for the DD3 clay type, which contributed significantly to increasing the rate of the chemical reaction. This technique has shown a high efficiency in removing the pollutants of the two organic dyes used in record time while maintaining its coherent shape.

2. Experimental study

2.1. Materials

The types of plants used are: cauliflower and anisosciadium. As an additive we use the kaolinite type DD3. To prepare solutions: absolute ethanol (C_2H_5OH), lithium carbonate (Li_2CO_3), magnesium nitrate (Mg (NO_3).$2H_2O$) and MEA (C_2H_7NO). Two types of organic dyes were used: Methylene blue ($C_{16}H_{18}ClN_3S$), Orange II (C_{16} $H_{11}N_2NaO_4S$).

2.2. Cauliflower and anisosciadium plants

4 g of cauliflower leaves and anisosciadium stalks were cut and weighed for the study, and to know the main component responsible for the stimulation, it was compared with the fibers extracted from each plant.

2.3. Fiber's extraction

The fibers are extracted by hand only without the use of any chemical ingredients and without processing, to preserve all its rich elements. Then they were tied together to form bundles with the same fiber (Fig. 1).

2.4. Preparation of powder (Li/Mg) by Sol-Gel method

We prepare the solution from 30 ml of absolute ethanol (C_2H_5OH) plus each of lithium carbonate (Li_2CO_3) and magnesium nitrate (Mg), the mixture is placed over a magnetic stirrer for a period (T = 2h, CT = 80°) with the addition of 0.5 ml of MEA catalyst (C_2H_7NO).

Then it was placed in a heat treatment furnace at 500 °C for 2 h, to obtain an amount of 0.3 g of Li/Mg powder (Fig. 2).

2.5. Method of adding the prepared powder to the used plants

In Becher we put the prepared powder Li/Mg in a solution with a rapid evaporation (I chose acetone), then put part of the anisosciadium

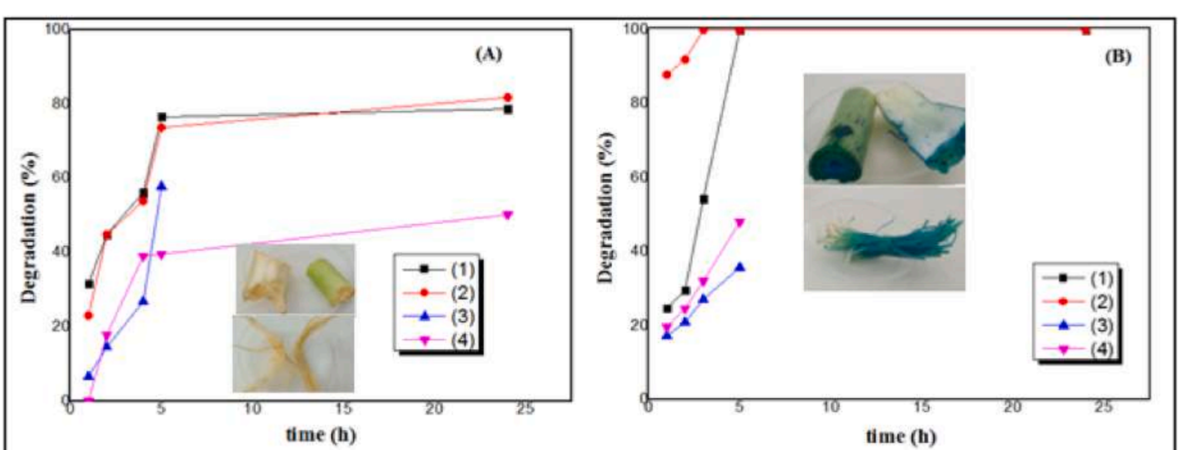

Fig. 6. Degradation of the solution during the filtration process for (1) cauliflower leaves fibres, (2) anisosciadium leg fibres, (3) cauliflower leaves and (4) anisosciadium stalk. (A) For OII solution, (B) for solution MB.

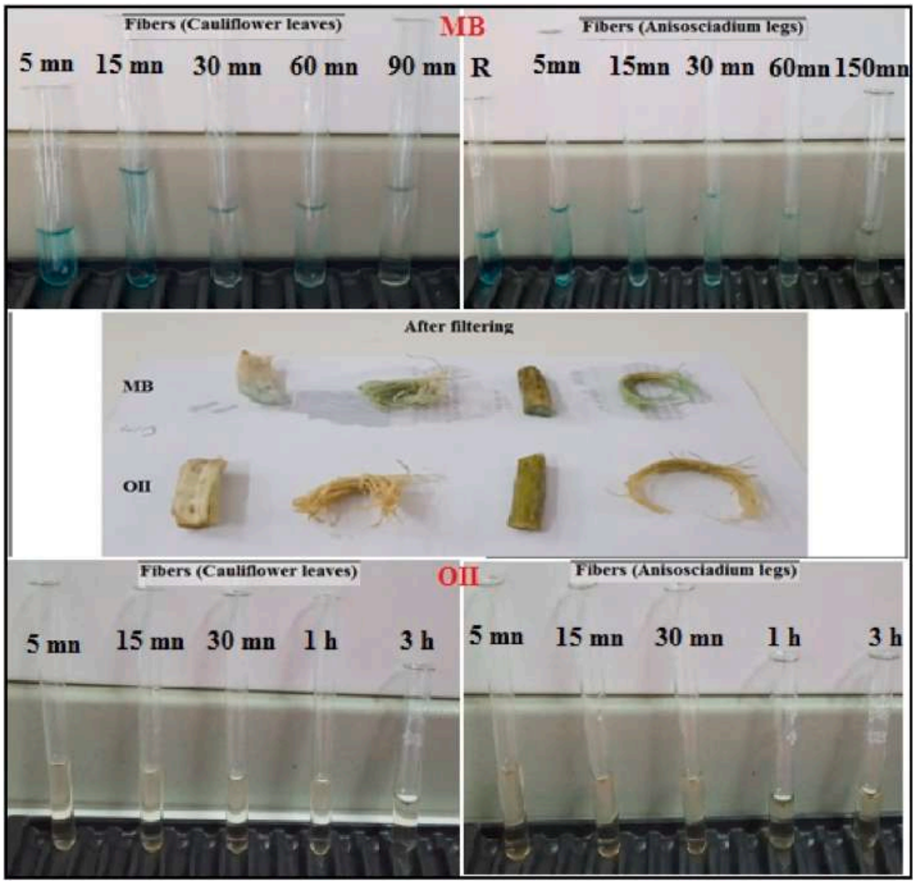

Fig. 7. Visibility of the effect of organic dye deposits on the samples used with the addition of powder (Li/Mg).

leg and cauliflower leaves, while creating holes on the rest of the surface, and the same method is followed for their fibers inside this solution. We leave it for 3 h, stirring from time to time (which is enough time for the substance to absorb the powder). At the end of the predetermined period, we pull the fibers and leaves and leave them to dry for a whole night, then we perform the filtering process, and the pictures in Fig. 3 show that.

2.6. *Deposition of the powder (Li/Mg + DD3) on the plants*

For better results, we added 0.3 g of untreated kaolinite type DD3 (clay) to the prepared powder to further speed up the catalytic process. We used the automatic breaker to mix the powders perfectly, thus we got the new powder DD3+(Li/Mg)). We follow the same previous steps to deposit the powder on the used plant species (Fig. 4).

2.7. *Measurement of photocatalytic activity*

To find out the gradient of the solution, after placing the four samples (with a weight of 4 g) in four beachers of 25 ml capacity filled with MB (4 mg/l) and OII (8.25 mg/l) solution and then closing them well (Fig. 5), during every 15 min 2 ml of the solution is withdrawn and the ratio is calibrated absorbance using UV–visible device. The positive thing about the process is that, before measuring the absorbance of the solutions, it is not necessary to comment it on the centrifuge, due to the coherent shape of the samples.

The degradation ratio of the contaminated solution was calculated (the maxima of absorbance spectra: λ_{max} (OII) = 484 nm, λ_{max} (MB) = 664 nm) from the following relationship [18]:

$$D\ (\%) = \frac{C_o - C}{C_o} \times 100\ \% \qquad (1)$$

C_o and C represent the initial concentration before and after filtering.

3. Results and discussion

3.1. *Photocatalytic performance*

3.1.1. *Plants without addition*

In the case of the MB solution, the gradient during a time of 5 h reached 82.51%, 96.71%, 67.24% and 79.83% for each of the materials, cauliflower leaves fiber, anisosciadium leg fiber, cauliflower leaves and anisosciadium leg, respectively. After a period of 24 h, we obtained a purification of 88.89%, 100%, 65.55% and 82.88% for the same samples and in the same order mentioned above (Fig. 6 b).

In the case of the second solution OII, we reached a 100% non-polluting solution by using the anisosciadium leg fibers within 3 h only, and the cauliflower leaves fibers within 5 h. While it did not reach half of the percentage of cauliflower leaves 35.8% and anisosciadium leg 48.15% (Fig. 6 a). This is also due to the color of the plant itself, as it releases its green color into the solution, which made us filter the solutions after completing each filtering process.

3.1.2. *Addition of Li/Mg to the raw materials*

For the methylene blue (MB) solution, it was found that the fibers were better than the stem and paper of the two materials in the filtering process (Fig. 7). Where the degradation rate of cauliflower fibers reached 76.35% within 1 h (60 min), and it reached 70.29% for anisosciadium fibers within 150 min (Fig. 8 b and d). While the anisosciadium leg was better than cauliflower leaves, the percentage of filtering was

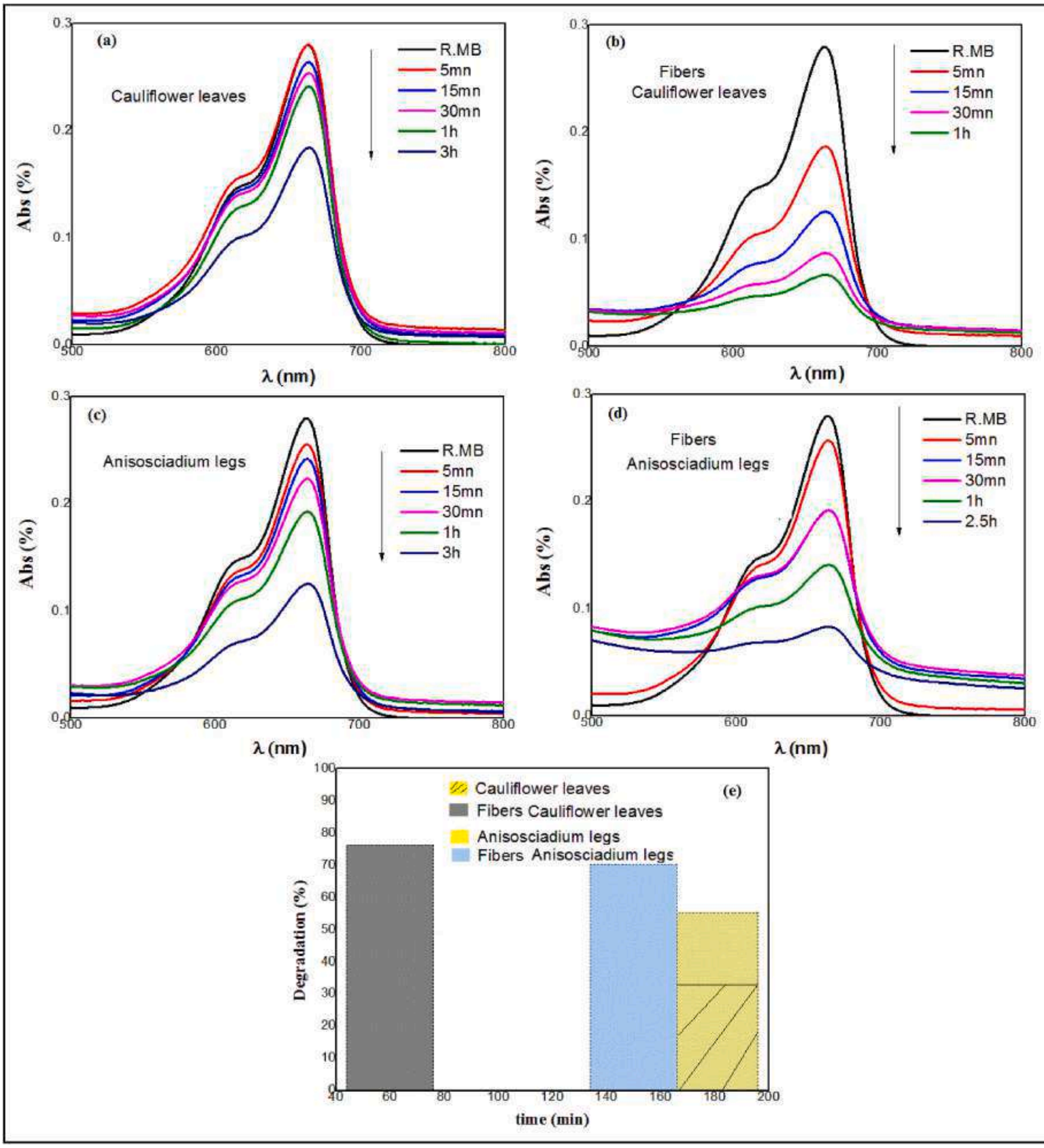

Fig. 8. Degradation of the MB solution during the filtering process for (b) cauliflower leaf fibers, (d) anisosciadium leg fibers, (a) cauliflower leaf and (c) anisosciadium leg, after powder addition (Li/Mg).

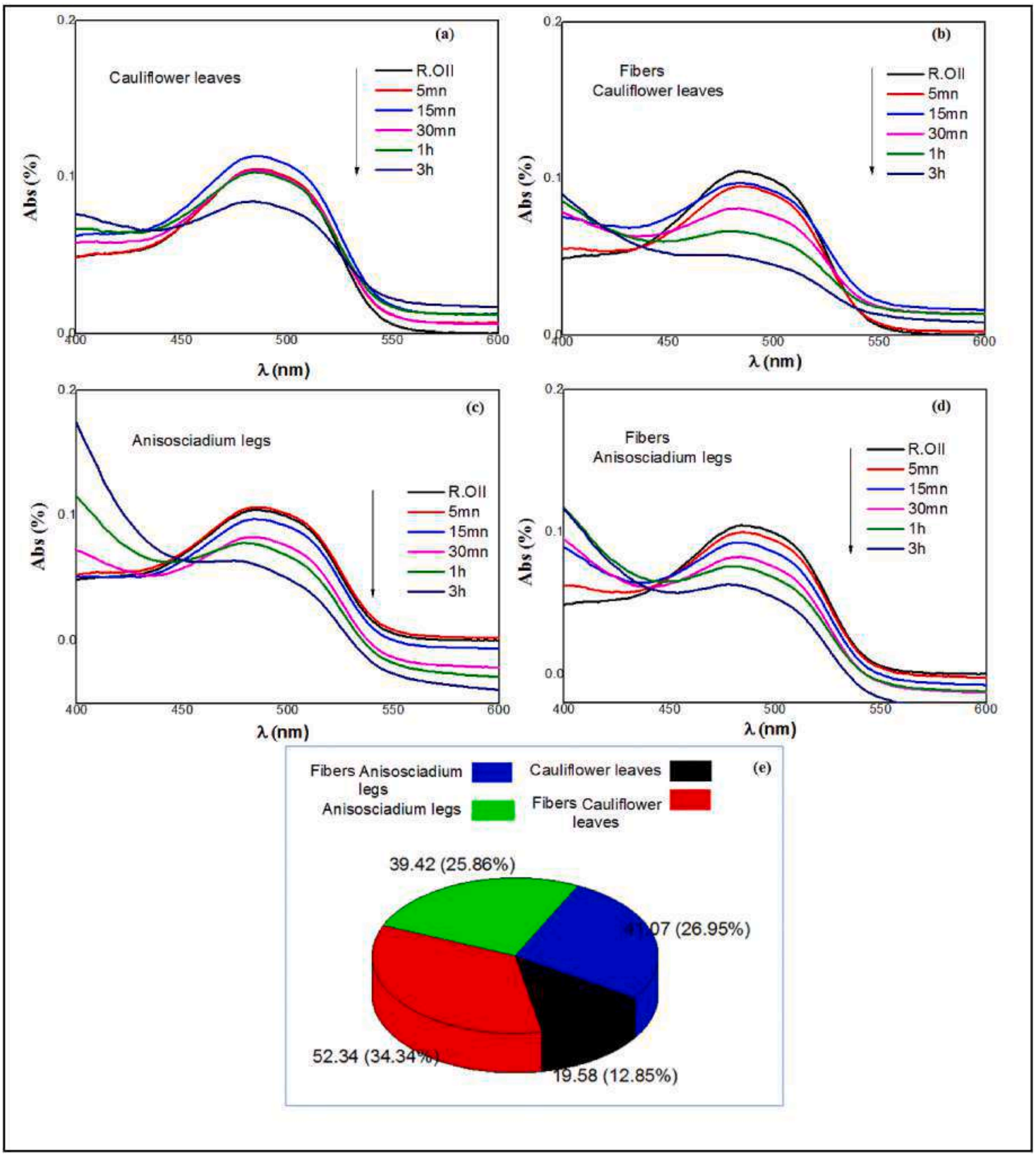

Fig. 9. Gradient ratio of OII solution during the filtering process for (b) cauliflower leaves fibers, (d) anisosciadium leg fibers, (a) cauliflower leaves and (c) anisosciadium leg, after powder addition (Li/Mg).

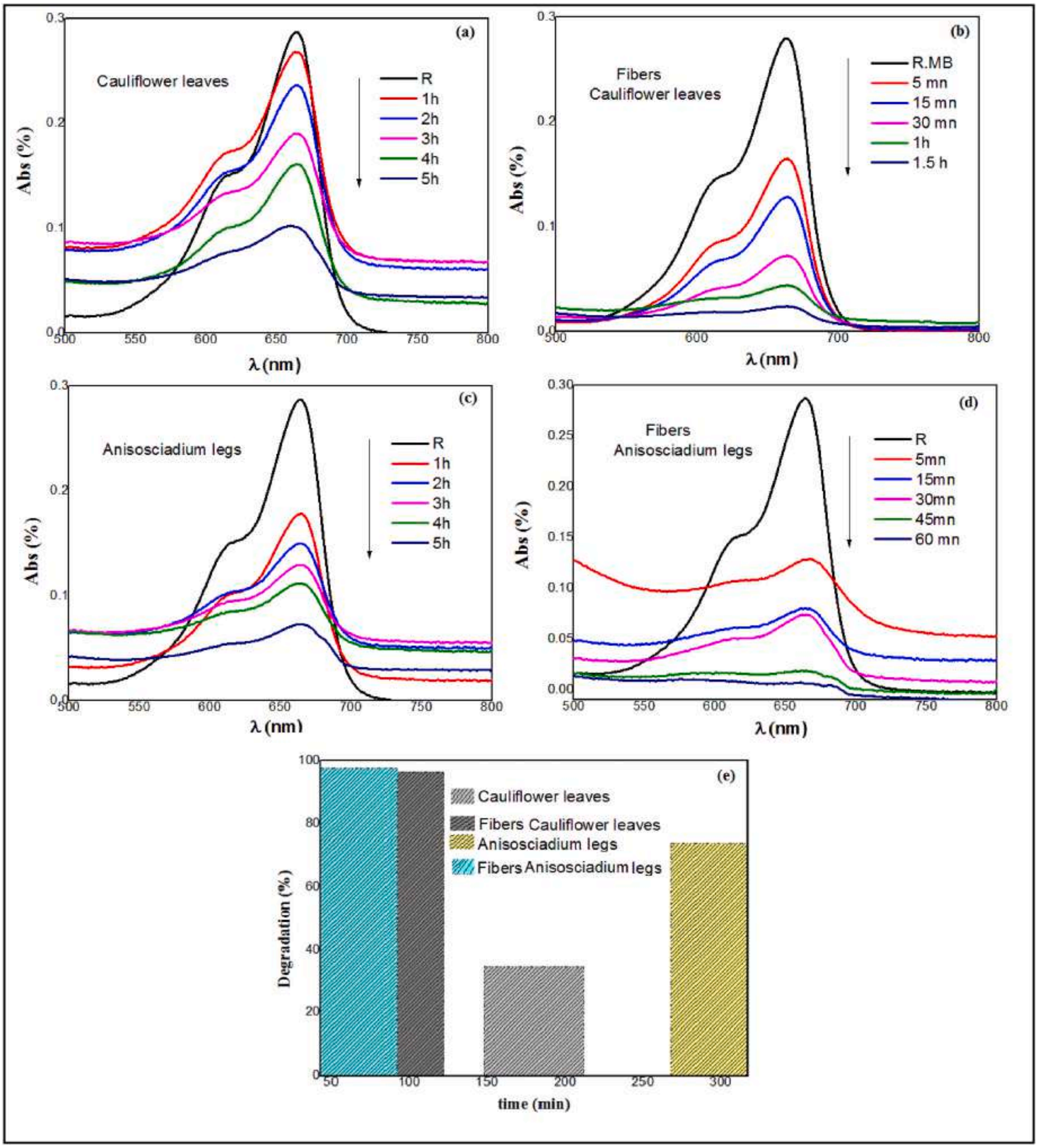

Fig. 10. Degradation of MB solution during the filtration process of (b) cauliflower leaves fibers, (d) anisosciadium leg fibers, (a) cauliflower leaves and (c) anisosciadium leg, with DD+ (Li/Mg) added.

55.45% and 76.25%, respectively (Fig. 8 a and c).

As for the orange II (OII) solution, the same observation was found for the first solution, where the best rate of degradation was 52.34% for cauliflower fibers during a period of 3 h (180 min), Fig. 9 illustrates this.

3.1.3. *Addition of DD3+(Li/Mg) to the raw materials*

In the case of the methylene blue solution (MB), within 1 h (60 min) only the solution was filtered when using anisosciadium and cauliflower fibers (Fig. 10 b and d), while it reached this stage after a period of 5 h (300 min) when using leaves and fibers (Fig. 10 a and c).

In the case of orange II solution (OII), when the powder was added to the plants used good results were achieved and the solution was completely filtered in all four cases. Where the fastest rate of degradation solution was OII again during the use of cauliflower fibers for a period of 2 h (120 min) (Fig. 11 b). Whereas, it reached the same percentage after 240 min while we used the anisosciadium fiber (Fig. 11 d and e).

The thing that is noticeable here is that the part of the anisosciadium leg was more effective than the cauliflower leaves, where the percentage of filtering was 84.05% for the first type, while the second type was filtering at a rate of 78.7% (Fig. 11 a - c and e).

3.2. *Analysis by infrared spectroscopy*

The obtained results were confirmed using infrared (IR) spectroscopy in Fig. 12. Where the solutions obtained after using the fibers of the two plants (anisosciadium legs and cauliflower leaves) were analyzed in the filtration process. From that we obtained a complete filtering of the solutions.

Figure (12 a and c) shows that the spectrum of MB solution is

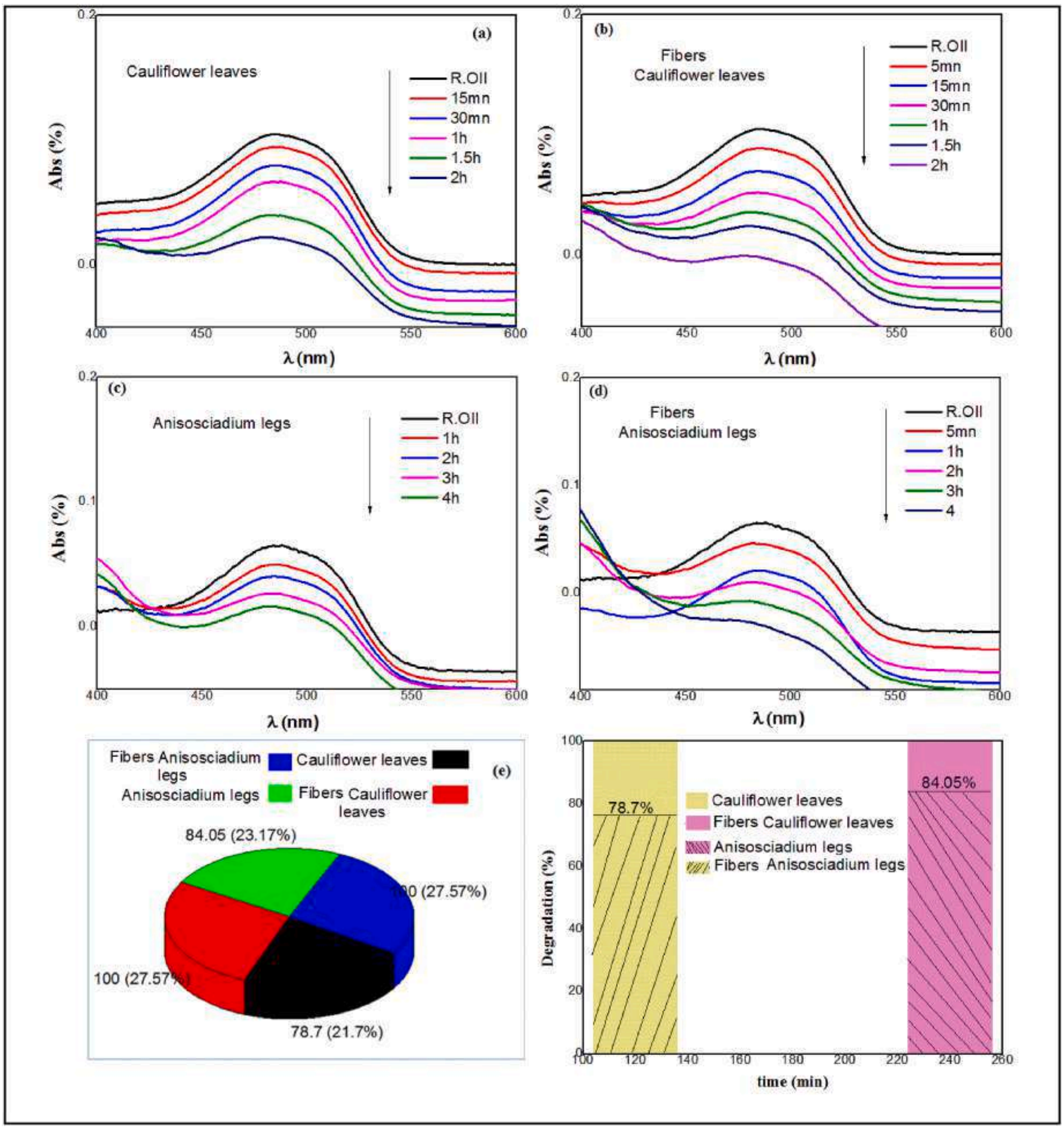

Fig. 11. Gradient ratio of OII solution during the filtration process of (b) cauliflower leaves fibers, (d) anisosciadium leg fibers, (a) cauliflower leaves and (c) anisosciadium leg, with DD+ (Li/Mg) added.

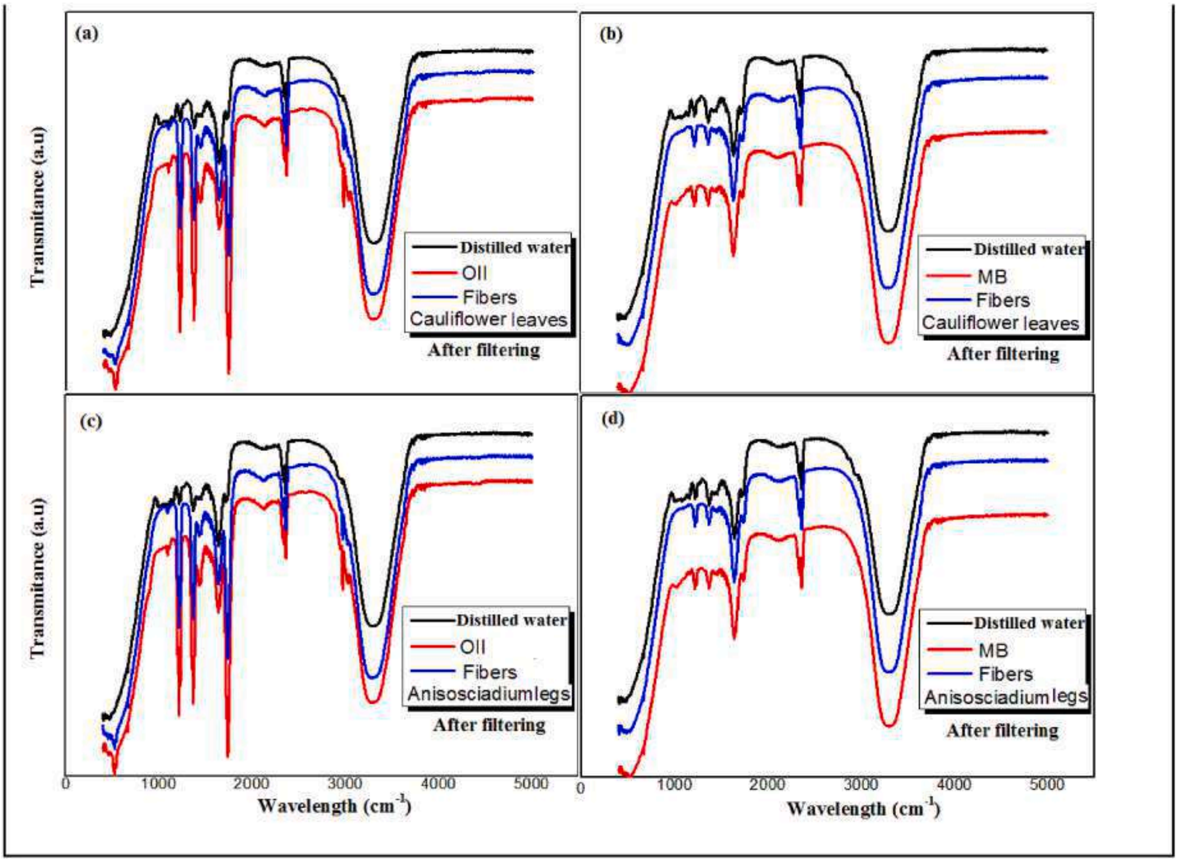

Fig. 12. Comparison between distilled water and the solution obtained after OII and MB filtration process using cauliflower leaves and anisosciadium leg fibers by IR spectra.

identical to that of distilled water after a time of 60 min in both types of fibers of the two plants, while the same behavior was found for OII solution (Fig. 12 b and d) where it was confirmed that the organic dye impurities were removed during Duration 120 min.

4. Conclusion

The aim of this work is to maintain the shape of the cohesive plant used from cauliflower and anisosciadium without damaging it or burning it. The samples were prepared using a very easy, simple and inexpensive method, with the addition of non-toxic and environmentally friendly materials to speed up the filtration process. The results obtained from the deposition of powder (Li/Mg) by adding the ceramic type DD3 to it on the used plant species gave greater effectiveness and improved the percentage of filtration in a shorter and faster time than the case where the powder was (Li/Mg) without addition. Also, the methylene blue solution is faster in the decomposition process than orange II, and the four species are legs or leaves or their fibers are effective during the filtering process without exception. After the impurities are extracted and absorbed by these types of plants, they can be disposed of by incineration at a temperature of 300 °C.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

[1] Shibaji Basak, Nibedita Nandi, Subir Paul, Ian W. Hamley, Arindam Banerjee, A tripeptide-based self-shrinking hydrogel for waste-water treatment: removal of toxic organic dyes and lead (Pb+2) ions, Chem. Commun. 53 (43) (2017) 5910–5913.
[2] M.A. Oturan, An ecologically effective water treatment technique using electrochemically generated hydroxyl radicals for in situ destruction of organic pollutants: application to herbicide 2, 4-D, J. Appl. Electrochem. 30 (4) (2000) 475–482.
[3] Imran Ali, V.K. Gupta, Advances in water treatment by adsorption technology, Nat. Protoc. 1 (6) (2006) 2661–2667.
[4] Ammar Houas, Hinda Lachheb, Ksibi Mohamed, Elimame Elaloui, Chantal Guillard, Jean-Marie Herrmann, Photocatalytic degradation pathway of methylene blue in water, Appl. Catal. B Environ. 31 (no. 2) (2001) 145–157.
[5] Dipa Ghosh, Krishna G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20 (6) (2002) 295–300.
[6] Fazle Subhan, Sobia Aslam, Zifeng Yan, Muhammad Yaseen, Muhammad Naeem, Muhammad Ikram, Asif Ali, Safia Bibi, Adsorption and reusability performance of hierarchically porous silica (MMZ) for the removal of MB dye from water, Inorg. Chem. Commun. (2022), 109380.
[7] Betul Tuba Gemici, Handan Ucun Ozel, Halil Baris Ozel, Removal of methylene blue onto forest wastes: adsorption isotherms, kinetics and thermodynamic analysis, Environ. Technol. Innovat. 22 (2021), 101501.
[8] Belal Bakheet, Yuan Shi, Zhaoxin Li, Huijiao Wang, Jiane Zuo, Komarneni Sridhar, Yujue Wang, Electro-peroxone treatment of Orange II dye wastewater, Water Res. 47 (16) (2013) 6234–6243.
[9] J. Herney Ramirez, Carlos A. Costa, Luis M. Madeira, Experimental design to optimize the degradation of the synthetic dye Orange II using Fenton's reagent, Catal. Today 107 (2005) 68–76.
[10] Chunli Zheng, Ling Zhao, Xiaobai Zhou, Zhimin Fu, Li An, Treatment technologies for organic wastewater, Water Treat. 11 (2013) 250–286.
[11] S.P. Nandi, P.L. Walker Jr., Adsorption of dyes from aqueous solution by coals, chars, and active carbons, Fuel 50 (4) (1971) 345–366.

[12] S.D. Lambert, N.J.D. Graham, C.J. Sollars, G.D. Fowler, Evaluation of inorganic adsorbents for the removal of problematic textile dyes and pesticides, Water Sci. Technol. 36 (2–3) (1997) 173–180.
[13] D. Bouras, A. Mecif, R. Barillé, A. Harabi, M. Rasheed, A. Mahdjoub, M. Zaabat, Cu: ZnO deposited on porous ceramic substrates by a simple thermal method for photocatalytic application, Ceram. Int. 44 (17) (2018) 21546–21555.
[14] Dikra Bouras, Abla Mecif, Abdelhamid Harabi, Régis Barillé, Abdel Hakim Mahdjoub, Mourad Zaabat, Economic and ultrafast photocatalytic degradation of orange II using ceramic powders, Catalysts 11 (6) (2021) 733.
[15] L. Keerthana, C. Sakthivel, I. Prabha, MgO-ZrO_2 mixed nanocomposites: fabrication methods and applications, Mater. Today Sustain. 3 (2019), 100007.
[16] Sol Yun, Young-Chul Lee, Ho Seok Park, Phase-controlled iron oxide nanobox deposited on hierarchically structured graphene networks for lithium ion storage and photocatalysis, Sci. Rep. 6 (1) (2016) 1–9.
[17] Xianfeng Zheng, Guofang Shen, Li Yu, Hanning Duan, Xiaoyu Yang, Shaozhuan Huang, Hongen Wang, Chao Wang, Deng Zhao, Bao-Lian Su, Self-templated synthesis of microporous CoO nanoparticles with highly enhanced performance for both photocatalysis and lithium-ion batteries, J. Mater. Chem. 1 (4) (2013) 1394–1400.
[18] Kamlesh V. Chandekar, Mohd Shkir, Badria M. Al-Shehri, S. AlFaify, Rajendra G. Halor, Aslam Khan, Khadijah S. Al-Namshah, Mohamed S. Hamdy, Visible light sensitive Cu doped ZnO: facile synthesis, characterization and high photocatalytic response, Mater. Char. 165 (2020), 110387.