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Adsorption of methylene blue dyes in aqueous medium by polylactic acid/olive husk flours biocomposites

Lisa KLAAI[1,*], Dalila HAMMICHE[1]

[1]*Université de Bejaia, Faculté de Technologie, Laboratoire des Matériaux Polymères Avancés (LMPA), Route de Targa-Ouzemmour, Bejaia 06000, Algérie*

Corresponding author: lisa.klaai@univ-bejaia.dz*

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Abstract

The dyes present in the waste from the textile industry represent a real danger for humans and their environment, due to their low biodegradability and their toxicity. For this, new eco-designed technologies for the treatment of polluted water. Several materials have been used in photocatalysis.

This work aims to degrade the dye Methylene Blue (BM) by photo catalysis-solar using polylactic acid /Olive husk flours biocomposites materials.

The degradation of this substance was followed by UV/Visible spectrophotometry, and the best result was obtained by the composite material loaded with 30% olive husk

Keywords: *Biocomposite, Dyes degradation, Methylene Blue (BM), Polylactic Acid, photo catalysis-solar.*

I. Introduction

Synthetic dyes represent a relatively large group of organic chemical compounds used in our daily life [1, 2]. Global production is estimated to be about 700,000 tons/year, of which 140,000 tons are released into effluents during various applications and manufacturing stages because of wrong or negligent discharges [3,4]. If not adequately treated, these effluents, composed of surfactants, biocide compounds, solid suspensions, dispersal and mooring agents, dyes, and metal traces, are toxic to most living organisms [5,6]. Their heterogeneous composition makes it difficult to reach pollution levels less or equal to those imposed by environmental standards when adopting the traditional treatments commonly used in municipal wastewater plants [7].

One of the primary concerns of water pollution is the dye contamination of wastewater from the textile industry, which is a significant chemical, physical, and aesthetical pollutant [8]. Eutrophication and disturbance of aquatic life (e.g., limiting access to sunlight and oxygen) presents a potential environmental danger. Possible bioaccumulation also represents a further threat, affecting human health and the environment. Several techniques can be used for pollution treatment, and adsorption has been commonly considered a reliable, versatile, and efficient option [9]. When applying this technique, the adsorbents that have been most adopted for use are commercial activated carbons, which are usually expensive despite their proven efficiency. In some cases, their use produces delayed pollution, representing an additional environmental threat [10, 11]. For these reason, in recent years different biodegradable polymers have been studied, to be used as media filters and applied at an industrial level depending on the manufacturing process [12–14]. Polymers such as polyurethane, polyacrylonitrile, polyvinylidene fluoride, polyvinyl chloride (PVC)/PU, polycarbonate, silk, polyimide and PLA poly (lactic acid) [15] have been used in the production of air filtration media, the latter having good biodegradable properties. Lactic acid is a precursor of poly (lactic acid) (PLA), with biodegradable characteristics [16].

Several studies have been carried out on the preparation of composites based on PLA for application as a water vapor barrier, antimicrobial properties [17], thermal properties [18] and mechanical properties [19–21].

The aim of this study is to determine the effect olive husk flours integrated to PLA in the adsorption of methylene blue, and the possibility to use this designed material to produce a new filter medium in health and environmental areas. For this purpose, to ensure flours dispersion, melt extrusion was used for the fabrication of poly (lactic acid) (PLA) and olive husk flours (10, 20, and 30 wt %) polymer biocomposites.

II. Material and methods

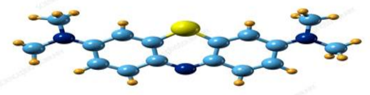
The PLA used is in the form of pellets, obtained by Nature Works in the grade of 2003D. It has a density of 1.24g/cm^3, Tg between 55 and 60°C and Tm between 145 and 210 °C.

Olive husk (OH) was collected at a modern oil mill in Bejaia, Algeria.

The vegetable filler used is common reed flour (OHF). Common reed flour obtained after sieving having an average particle diameter equal to 80µm.

The dye investigated in this work was methylene blue (MB: $C_{16}H_{18}N_3SC1$), its physico-chemical properties are detailed in Table 1.

Table 1: Physico-chemical properties of methylene blue (MB) [21].

Dye	Methylene blue
Structure	$C_{16}H_{18}N_3SCl$
Chemical formula	
Molar mass (g/mol)	319.85
Maximum wavelength λ_{max} (nm)	664

II.1. Preparation of composites

Composite samples of PLA/OHF was compounded by melt mixing using extrusion type 2005 micro-compounder DSM Xplore model (Screw temperature is set at 180°C; the speed of rotation is 100 rpm and a residence time of 8 min), followed by compression molding of the Carver type (Press temperature is at 180°C, first preheated for 5 min and pressed for 8 min under a load of 300 KN).
The proportions of the PLA/OHF mixtures used respectively are: 90/10, 80/20, 70/30.

II.2. Photo-catalytic evaluation

The mass concentration of aqueous solutions containing the molecule to be degraded was around 50 mg/L for MB. The rate of PLA/OHF photocatalyst degradation (10.20 and 30w% flours) under solar light irradiation is evaluated for the dye.
Practically, 25 mg of the powder of different composite materials are dispersed in an aqueous solution of volume 50 ml containing the dye. The mixture is put in a glass crystallizer covered with self-adhesive plastic film. Before the irradiation of the solution by the solar, the medium is placed under magnetic stirring in the dark for 50 minutes, in order to reach the adsorption equilibrium. After a time equal to 50 min, the concentration is almost stabilized regardless of the adsorption–desorption equilibrium couple. After 50 min of adsorption, the solution was exposed to the solar light and the chronometer starts counting time. During the photo-catalysis activity, samples of 2 ml were taken, at increasing time intervals, the sample was Centrifuged at 3000 rpm for 5 min and then filtered to remove the catalyst. The resulting filtrate was analyzed by the UV spectrophotometer.
The percentage of adsorption efficiency was calculated according to Equation (1):

% Adsorption = $((A_0-A_t)/A_0)*100$ (1)

Where, A_0 is the absorbance of initial MB; A_t is the absorbance of the solution after illumination at time t.

II.3. Characterization

The optical properties of prepared MB/Composites were investigated using UV–Visible absorption spectroscopy (UVmini-1240, SHIMADZU) at a maximum absorption wavelength of λmax = 664 nm.

The adsorption tests were repeated twice to assess the reproducibility of the results, with the average values considered.

III. Results and discussion

III.1. Photo catalytic activity

a. Photodegradation of methylene blue (MB)

Methylene Blue (BM) is a blue dye characteristic of textile pollutants. Its absorbance spectrum is shown in Figure I.

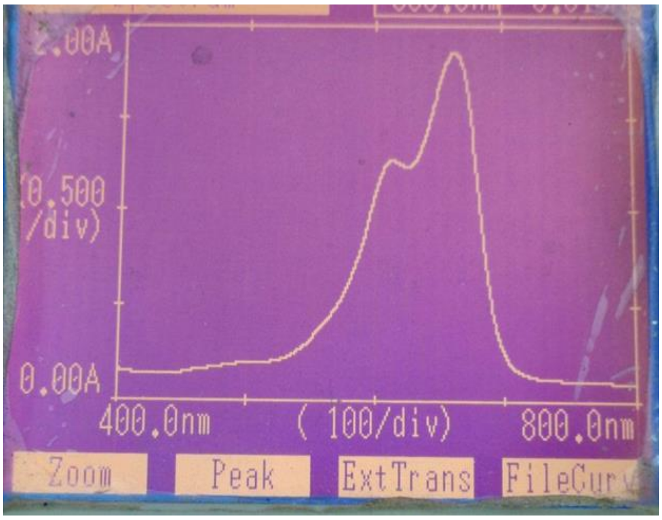


Figure 1: Absorption spectrum of photo-degraded methylene blue (MB) without catalyst

The evolution of the absorbance of the methylene blue (BM)/ PLA/OHF (10wt %), PLA/OHF (20wt %) and PLA/OHF (30wt %) solution as a function of the solar irradiation time are given in Figure 2. All photo-catalytic processes were carefully monitored by measuring the maximum absorption bands of this dye at predetermined time intervals. A reduction in the maximum absorption band in MB was noticed when the exposure time to solar irradiation was increased.
In the presence of photocatalyst PLA/OHF (10wt %), PLA/OHF (20wt %) and PLA/OHF (30wt %) show removal of MB to some extent which is attributed to fiber adsorption [22]. The porous fiber of OHF has proven to be effective, where the porous structure of fibers allows the contact of OHF with MB [23].
All composite fibers with OHF show higher MB removal, where the adsorption under dark condition resulted at MB removal of 10 %, 13.7 %, and 17.7 % for OHF(10 wt%)/PLA, OHF(20 wt%)/ PLA, and OHF(30 wt%)/PLA, respectively.
In this study, the usage of solar light source was performed to observe the maximum ability of synthesized photocatalyst composite. Under this condition, the composite of OHF (30 wt %) /PLA shows the excellent removal of MB, where 70 % MB was removed after 40 min irradiation, and 88 % MB removed after 50min of irradiation. While the composite of OHF (10 wt %) /PLA showed lower degradation of MB at 72.5 % removal after 50 min of irradiation.

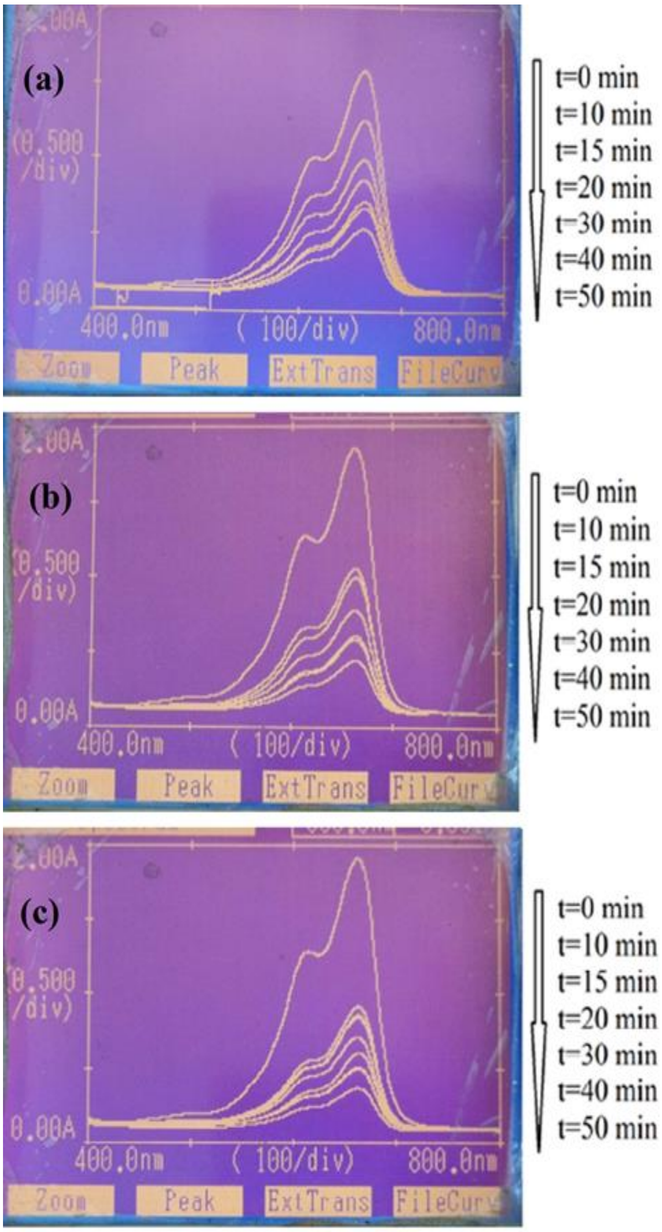


Figure 2: Absorbance profile of MB from sample taken at certain time interval by using: (a) PLA/OHF (10wt %), (b) PLA/OHF (20wt %) and (c) PLA/OHF (30wt %).

The results obtained at the end of study of Aarfane et al [24], made it possible to conclude that after 20 minutes of agitation, the BM elimination yield of aqueous solutions at 25 mg/L can reach 96% and 89% respectively during the use of the palm bark and the sugar cane bagasse. So these two plant substrates have proven to be natural supports with an affinity of significant adsorption with regard to MB. The abundance of these plant substrates can provide low -cost adsorption materials which can possibly contribute to the processing of textile effluents. In the study of Ho et al [25], porous polylactic acid (PLA) fibers were utilized as photocatalyst support using electrospinning technique to synthesis the fibers. The cadmium sulfide (CdS) was embedded in fibers at the amount of 1 wt%, 3 wt%, and 5 wt% as photocatalyst agent with absorption in visible light range. The photodegradation was performed under low-powered halogen lamp, with 90 % removal of methylene blue (MB) after 10 hours of irradiation using CdS (3 wt %) /PLA fibers. This result shows higher performance in comparison with PLA and CdS which could only remove 57 % and 65 % of MB, respectively.

IV. Conclusions

In this work, Olive Husk flours (10, 20, and 30 wt %) integrated to PLA was used to determine its effect in the adsorption of methylene blue under solar light irradiation, and the possibility to use this designed material to produce a new filter medium in health and environmental areas.

At predetermined time of solar irradiation, a reduction in the maximum absorption band in MB was noticed when the exposure time to solar irradiation was increased.

The composite of OHF (30 wt %) /PLA shows the excellent removal of MB, where 70 % MB was removed after 40 min irradiation, and 88 % MB removed after 50min of irradiation. While the composite of OHF (10 wt %) /PLA showed lower degradation of MB at 72.5 % removal after 50 min of irradiation.

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