Exploring a sustainable and economical biosorbent for organic pollutants remediation from real textile wastewater

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1. **Introduction** The Ficus benjamina is a widespread evergreen plant used in gardens and factories for landscape purposes. Although the advantages of the high speed of growth of the Ficus trees are great, there is a problem with getting rid of the fallen leaves due to their frequent trimming.. One of the most critical damages caused by the presence of these leaves randomly is that they greatly affect climate change, as intentionally or unintentionally burning of these leaves results in toxic gases that cause the black cloud and greenhouse gases that lead to climate change. Therefore, it was necessary to search for different ways to benefit from these sustainable natural resources to solve these environmental problems and avoid climate change (Abd El-Aziz et al., 2020).

   Another problem the world needs help with is the presence of dyes in industrial wastewater streams in many industries, such as textile, paper, leather, and cosmetics . About 5-10% of more than 700 Million kg/ year of different synthetic dyes are disposed of as unfavorable industrial effluents (El-sayed et al., 2020). Crystal violet is a kind of cationic dye that is more carcinogenic, mutagenic, and toxic than the other kinds due to their synthetic origin and aromatic ring structure with delocalized electrons however it has been utilized in many industries (Wu et al., 2022).

   This study aims to utilize the fallen Ficus leaves, as a biosorbent for CV removal after simple pyrolysis at 450 ˚C. The relationship between the FL450 characteristic, removal capacity in the biosorption, and removal mechanisms of dyes was investigated. Finally, the optimum operating condition was applied to real industrial wastewater to analyze its efficiency for color reducing .

2. **Materials and methods** The Ficus leaves utilized for the biosorption process were carefully selected. These leaves were washed, filtered, and oven-dried at 80˚C till obtained constant weight. Dried leaves were ground and sieved to get the fine powder and labelled as (WFL). A certain amount of WFL was placed in a crucible and calcined at 450 ˚C in a muffle furnace for 3 h and was labelled as (FL450).

3. **Result and discission** The surface morphology changes of the biosorbent before and after calcination were analyzed using SEM. As shown in Fig. 1a and b, the WFL has an almost bulky surface with a continuous massive cell wall without pores. However, after the calcination, a significant change occurred where the external surface became irregular with convexes and concaves and wrinkled with crevices and cracks in the well-performed porous structure which reflects the successful selection of the calcination temperature. The different sizes and shapes of the pores may enhance the biosorption process by allowing more dye attachment on the interior of the biosorbent beside the surface. The detected sizes of the pores are considered macropores (> 0.01 mm). These macropores may encourage the biosorption process by facilitating the internal mass transfer increasing the ability to trap the dye and increasing the proficiency of the material as a biosorbent.

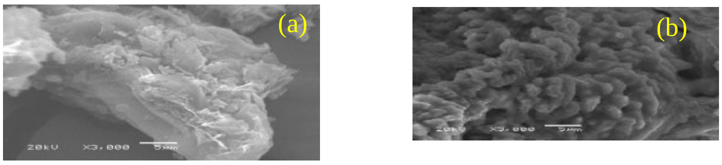
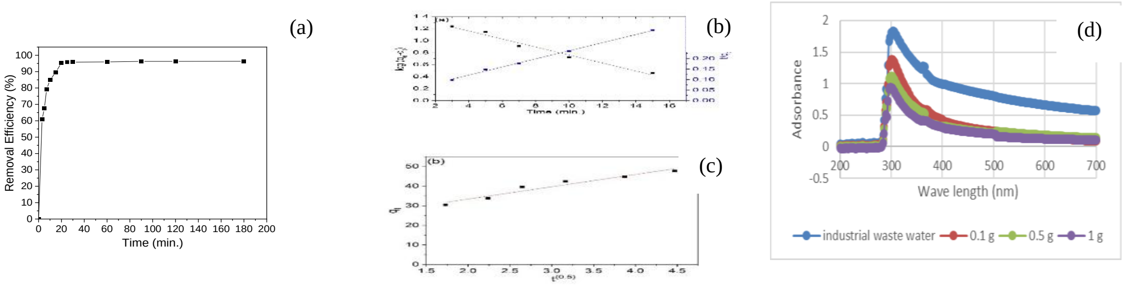


Figure 1. SEM images of (a) WFL and (b) FL450.

The effect of the calcination process on the WFL efficiency of the CV removal was evaluated. There is a large discrepancy between both WFL and FL450, as the CV removal percentages were 13 and 92.4 %, respectively under the same conditions. The practical experience indicated that the low efficiency of WFL is not only due to its smooth, nonporous surface morphology, and poor functional groups, but it was practically found that the Ficus in its natural form releases a pale brown-green colour in the wastewater during the biosorption process. The release of this colour may be due to the leaching of polyphenolic compounds (Hasan et al., 2022). Probably, this natural colour negatively affects the decolourization process. It has also been reported previously that composites provided more dye uptake capacity compared to native biomasses and enhanced biosorption capacity due to the favourable physicochemical properties of composites. Therefore, the biosorption process was studied using FL450 (Shoukat et al., 2017).

The contact time between the biosorbent and adsorbate is an important factor in determining the required time to attain equilibrium. As shown in Fig. 2a, the biosorption process was performed in two stages. In the first 20 min, the mass transfer limitation at the liquid-solid interphase can be overcome within this time frame and much of the dye molecules were biosorbed onto the active sites in the FL450. The variance of charges leads to attracting the positive ammonia group at CV to the negative groups attached on the FL450 surface such as –OH stretching vibrations of hydroxyl functional groups, the carboxyl group of conjugated carbonyl, and aryl –OH group. After 20 min, the biosorption rate slows down due to the reduction of surface area and binding sites and the concentration remains constant within the studied range. It can be concluded that 20 min is the optimum time for CV biosorption using FL450 to reach equilibrium. This result proved that FL450 has higher efficiency and activity than other adsorbents which attained equilibrium after 40 min like water hyacinth (Kulkarni et al., 2017a). This result revealed the strong interaction between the biosorbent and the CV molecules resulting in film diffusion as the predominant stage which surmised that the uptake process is quite rapid.

Figure 2. (a) Effect of contact time on CV biosorption using FL450 (initial CV concentration 100 ppm, agitation speed 150 rpm, and biosorbent weight 0.1 g / 25 ml at ambient temperature) **(b)**T Pseudo-first-order and Pseudo-second order, and **(c)** intra-particle diffusion kinetic models (d) Effect of initial biosorbent weight on colour removal from industrial wastewater dependent UV/V absorbance.



To determine the biosorption mechanism and the rate controlling step of the biosorption of CV on the FL450, Pseudo-first-order, Pseudo-second-order, and intra-particle diffusion models were tested. The linearization of the studied models were represented in Fig. 2 b and c. The Pseudo-second-order kinetic model fits well with the kinetic data over the entire contact time range. This reveals that chemical biosorption involving valence force induced by sharing or exchanging electrons between adsorbate and biosorbent is the rate controlling step. Similar trend was observed during CV removal using recovery cellulose (Wang et al., 2021). In Fig 2 c, the plot data has deviated from the origin, consequently intra-particle diffusion was not the only rate limiting step. Hence, CV biosorption onto FL450 is governed and limited by both, surface adsorption and intra-particle diffusion (Kulkarni et al., 2017b).

Most textile industries generate effluents with more than one dye. Thus, the biosorption performance of FL450 on the treatment of a real discharged wastewater contaminated with dyes mixture consists of different azo and sulfur dyes was evaluated to determine the dye competition at the substrate binding sites. A real dyeing textual wastewater, which collected from textile factory in Borg Al-arab, Egypt, was treated with the biosorbent. The effect of the biosorbent weight on the biosorption efficiency and the industrial wastewater treatment was investigated by comparing three different biosorbent weights (0.1, 0.5 and 1 g). Figure 2 d reveals that the biosorbent weight is proportional to the colour elimination. Utilizing 0.5 g of FL450 can remove about 50% of the industrial wastewater colour. Increasing this amount to 1 g led to close removal to that obtained from using 0.5 g. Hence, 0.5 g can be considered the optimum biosorbent weight for this dye mixture. The removal efficiency using real industrial wastewater is less than the studied efficiency of the synthesized dye which may be due to the presence of other dyes and organic compounds in wastewater effluent (Zein et al., 2022).

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