The removal of methylene blue and chemical oxygen demand by coagulation using cactus

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Abstract

In this study, we considered a cationic dye namely methylene blue, taken as a model pollutant in order to evaluate the performance of the prickly pear "cactus". In this context, the use of biomaterials which are both natural and eco-friendly, respectful of the environment less expensive could be a promising solution to be considered, possible to be implemented in the future, for the treatment of wastewater in containers dyes. The treatment process was conducted in conventional jar test. The FTIR spectrum values endorse the existence of various functional groups. The leverage of variables such as coagulant dose and initial pH were investigated in terms of dye and chemical oxygen demand (COD) removal efficiencies. The optimized value of the above-mentioned variables were examined and the values are 2 g of cactus to treat 1L of synthetic effluent under basic pH (pH=10). The maximum removal efficiencies were identified for initial concentration effluent of 50 mg.L^{-1}, were 57 % and 45 % of methylene blue and COD removal efficiencies, respectively. The adsorption and bridging mechanism played a major role rather than the hydrolysis process in methylene blue/cactus system.

Keywords: *Cactus, Coagulation-flocculation process, synthetic dye, methylene blue removal*

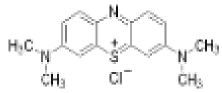
I. Introduction

Dyes are one of the most common contaminants in water. The textile industry is considered to be one of the water-intensive industries which produce a high volume of wastewater (200 to 350 L of wastewater per kg of finished product). In particular, processes such as fiber dyeing and washing release effluents which contain significant amounts of surfactants, fixing agents, oxidizing agents, recalcitrant chlorine compounds, dispersing agents, etc. smoothing agents, organic colorants (10% to 15% of the total colorant used in the process), additives, fine particles of starch and certain salts [1]. In most developing countries, these industrial effluents are generally discharged in large quantities into rivers or adjacent lands [2]. Due to their synthetic origin and complex aromatic molecular structure, dyes are difficult to biodegrade when released into the environment, and their incomplete degradation often produces toxic compounds [3]. In addition to their carcinogenic, mutagenic and toxic effects, the release of untreated colored effluents into the environment frequently causes colored bodies of water, resulting in chronic and acute toxicity. The re-oxygenating capacity of receiving waters could be limited by the untreated effluent, which could also cut off sunlight which in turn disrupts photosynthetic activities in the aquatic system. Therefore, environmental protection agencies consider it mandatory to treat dye bath effluents before discharging them into surrounding aquatic systems or planning their reuse [4]. The World Health Organization (WHO) has set safe limits for the discharge of tannery effluent into the environment. Wastewater treatment from tanneries has been studied using various analytical techniques, namely biological treatment [5], reverse osmosis [6], adsorption [7], electrochemical advanced oxidation [8] and coagulation processes [9].

As one of the most commonly used process in tannery wastewater treatment, the coagulation/flocculation process has the advantages of low investment, small land occupancy, fast processing, and suitability for batch treatment. Presently, coagulation process is used very widely in the wastewater treatment, but chemical agents are used in most cases, whereas biological coagulants are seldom used [10]. However, although synthetic coagulants show good performance in the coagulation/flocculation process, they have some disadvantages such as the production of large amounts of non-biodegradable sludge and high levels of toxicity [11,12]. Biocoagulants which are biodegradable, non-toxic, and produce very little residual sludge, are an alternative to overcome the main disadvantage of coagulation processes (which is the use of synthetic coagulants) [13,14].

In this research, it was considered a cationic dye namely methylene blue, taken as a model pollutant in order to evaluate the performance of our biomaterial; the prickly pear «cactus". In addition, although very interesting approaches have been proposed for efficient color removal, it is difficult to find a solution which works for the wide range of existing dyes and which is effective for complex mixtures of certain dye effluents. Therefore, several factors (constraints) must be taken into account such as the type and concentration of dyes present, the possible presence of other interfering substances, the pH and the operating temperature [15]. In this context, the use of biomaterials which are both natural and eco-friendly, respectful of the environment less expensive could be a promising solution to be considered, possible to be implemented in the future, for the treatment of wastewater in containers dyes and which falls within the framework of sustainable development. The objective of this study was to evaluate the potential of the prickly pear in the solid state biocoagulant for the depollution of the aqueous solution loaded with methylene blue. The experimental results showed that the pollution control was appreciable.

Table 1 Physicochemical characteristics of methylene blue

Name	Molecular structure	M_w ($g.mol^{-1}$)	λ_{max} (nm)
Methylene Blue		319.85	660

II. Material and methods

Synthetic effluent preparation

Methylene Blue (Analytical Reagents) was taken as a pollutant model. Its molecular structure is given in table 1. Stock solution was prepared by dissolving requisite quantity of dye without further purification in distilled water, and the concentrations used were obtained by dilution of the stock solution. The residual concentration was measured by UV– Visible spectrophotometry for dye concentration at the wavelength of 660 nm (UV–VIS spectrophotometer Shimadzu UV-160 A.

Biomaterial preparation

Cactus powder was prepared by cutting fresh cactus species (pads) into strips of 10^{-2} m width followed by drying at 48°C for 24 h, then ground and sieved followed by drying at 48°C for 24 h, then ground and sieved.

Coagulation/flocculation process

A standard jar test apparatus with digital feedback control system (JTM6C Model) was used in the coagulation/ flocculation tests. Samples of wastewater (500 mL) were stirred at a high speed of 160 rpm for 10 min and during this time the coagulant was added. The stirring speed was then lowered to 45 rpm for 20 min after which the samples were allowed to settle for 30 min. The pH value was adjusted to the desired value with HCl and NaOH before the coagulant/flocculent was added.

Analytical method

THE methylene blue removal efficiency (BM %) and The COD removal efficiency (COD %) were calculated using Eq. (1) and Eq. (2), respectively.

$$MB(\%) = \frac{[MB]_0-[MB]}{[MB]_0}\times 100 \quad (1)$$

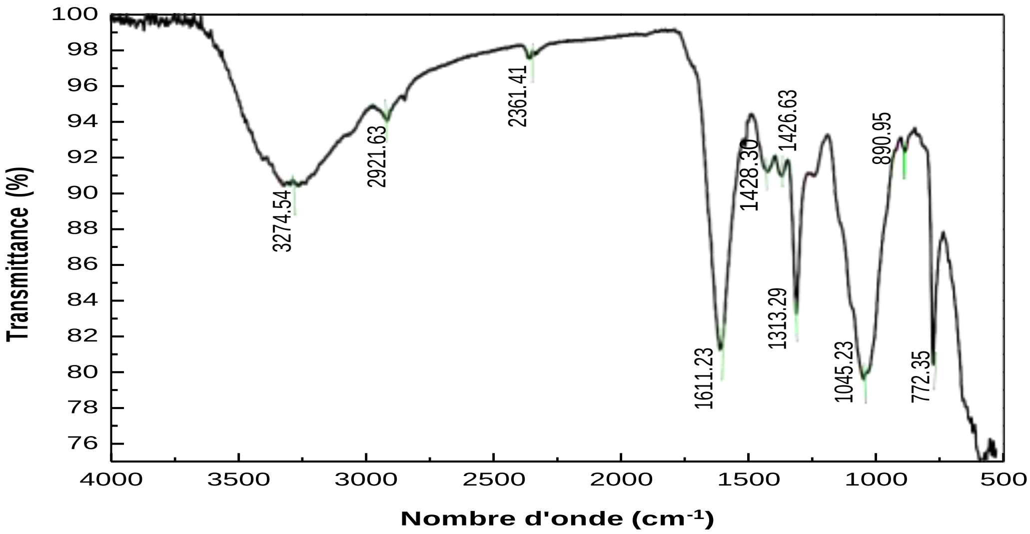


Figure 1. FTIR analysis of cactus powder.

Table 2 FTIR structural elucidation of cactus powder

Wave nomber (cm^{-1})	Compound	Vibration and bonds
890.94	Sulfoxides	S-O
1045.23	Chloro alcanes	C-Cl
1313.29	Polysacharides	C-O-C- or -OH
1428.02	Phenols	C-OH
1611.23	Aromatic	C=C
1740.44	Carboxylic acids, esters	C-O
2361.41	Nitrile	C≡N
2921.63	Aliphatic	CH_3, CH_2, CH
3274.54	Alcohols, phenols, acids and amines	O-H, H-N

Where $[MB]_0$ and [MB] represent the initial and final dye concentration, respectively.

$$C(\%) = \frac{COD_0 - \mathrm{COD}}{\mathrm{COD_0}} \times 100 \quad (2)$$

Where, COD_0 and COD represent the initial and final COD (mg O_2/l) of wastewater, respectively.

COD was determined in laboratory according to the methods given in the series of standard methods for the examination of water and wastewater [16].
Each experiment is carried out in triplicate and the average results are presented.

III. Results and discussion

Characterization of the biocoagulant

The possible chemical bonds in cactus were investigated by examining the FTIR characteristic peaks in the range of 4000–400 cm^{-1} for matching the corresponding chemical bonds. Fig. 1 shows the FTIR spectroscopy for cactus.

Figure 1 presents the FTIR of dried cactus was implemented to identify the presence of functional groups on the cactus powder. The peaks in the wave number region below 800 cm^{-1} could be attributed to biological ligands containing nitrogen. These results indicate that the dried cactus contains various functional groups such as carboxyl, hydroxyl, sulfate, phosphate, aldehydes, ketones and other charged groups. Table 2 shows the band assignments associated with the spectrum of cactus.

Effect of coagulant dosage

Figure 2 show that cactus powder has an appreciable flocculation and purification capacity. The effect of coagulant dosage on the MB removal efficiency was investigated. Figure showed that, as the biocoagulant dosage increased from 1 g.L^{-1} to 4.5 g.L^{-1}, there was an increase and a decrease in the level of MB (%) reduction and thus an increase in removal efficiency, whereas as the biocoagulant dosage increased further, the removal efficiencies decreased.

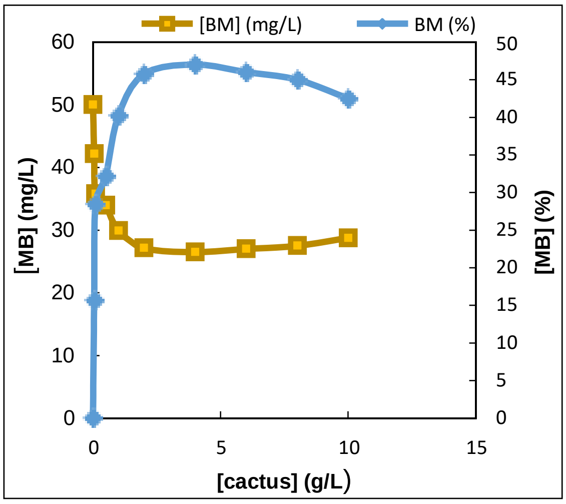


Figure 2. Effect of coagulant dosage on the methylene blue removal ([BM]$_0$ = 50 mg.L^{-1}, COD$_0$ = 1618 mg.L^{-1} (O_2), pH$_0$ = 8.04, T_0 = 16.8 ° C).

The main reason for the decrease was overdosing effect of cactus. There are two major mechanisms involved in the biocoagulation of charged particles, charge neutralization and adsorption and bridging mechanisms [17].

The adsorption and bridging mechanism suggested that the natural polymer could adsorb onto the surface of the colloids in water with its long chains where the tails and loops are extended far beyond its surface and can interact with other particles via bridging flocculation [18]. At lower dosages, there is an insufficient of natural polymer to form adequate bridging links between particles but with excess of natural polymer, there is no longer enough bare particle surface available for attachment of segments and the particles become destabilized. Therefore, there should be an optimum natural polymer dosage for coagulation–flocculation behavior [19,20]. It can be seen that the dye removal efficiency was 45.75 % by using 2 g.L^{-1} of the cactus powder. This result confirm the results obtained by Vishali and Karthykeyan [21].

The cactus powder as a natural coagulant showed very promising result above 45 % removal of COD (figure 3). This experiment also revealed that increase in dosage did not significantly increase the COD removal efficiency. The higher % removal efficiency was achieved at coagulant dose of 1.5 g.L^{-1} and a basic pH 8. From the results, it was clear that cactus powder show higher removal efficiency as compared to Moringa oleifera which is in accordance with the previous studies reported in the literature. Furthermore, cactus is non-toxic and non-corrosive in nature and it could be employed as a natural coagulant for water treatment [22].

Influence of initial pH

The influence of pH was examined in the range of 2–12. Figure 4 showed the removal of dye and COD as a function of pH for BM. the powder cactus has a significant effect at basic pH. It is observed that adsorption of MB dye increase from 10 % to 55 % as pH increases from 2 to 12 at optimum polymer dose of 2 g.L^{-1}.

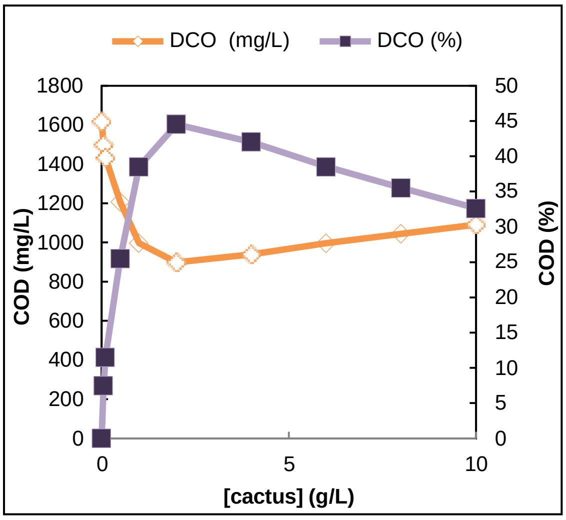


Figure 3. Effect of coagulant dosage on the COD removal ([BM]$_0$ = 50 mg.L^{-1}, COD$_0$ = 1618 mg.L^{-1} (O_2), pH$_0$ = 8.04, T_0 = 16.8 ° C).

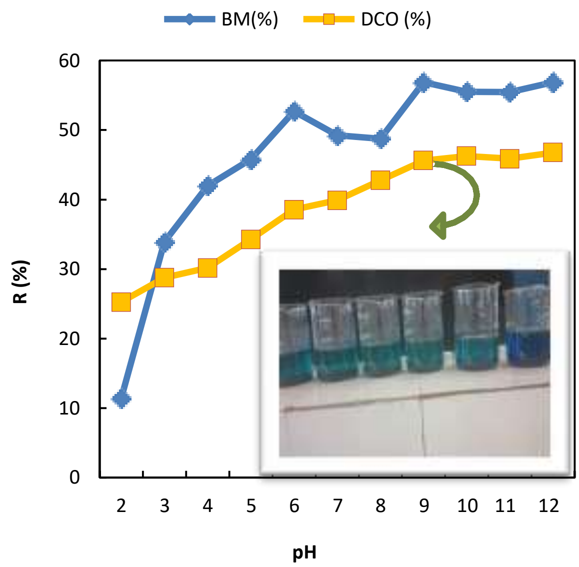


Figure 4. The effect of the pH value on the efficiency of the removal process ([BM]$_0$ = 50 mg.L^{-1}, COD$_0$ = 1618 mg.L^{-1} (O2), [cactus] = 2 g.L^{-1}, pH$_0$ = 8.04, T_0 = 16.8 ° C).

We noticed that dye removal efficiency reaches 57% and the COD removal exceeds 45% at pH of 10.

IV. Conclusion

The coagulation ability of the cactus was assessed and confirmed in the treatment of simulated dye effluent through color and COD removal. The natural coagulant keeps its coagulation power over the pH range of 8 to 10. Up to 55 % of dye removal and 45 % of COD reduction was achieved at 50 mg.L^{-1} of initial dye concentration, pH 10 and 2 g.L^{-1} biocoagulant dose. FTIR spectrum indicates that the dried cactus contains various functional groups such as carboxyl, hydroxyl, sulfate, phosphate, aldehydes, ketones and other charged groups. Concurrently, the biomaterial was managed and the treatment of synthetic dye effluent was also succeeded. Being a universally available, low cost, and abundant, wasted biomaterial, and based on its removal efficacy, this study concludes that cactus could be an alternate solution for the treatment of water-based paint effluent.

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