

Fixed-bed Column Packed with Low-Cost Spent Tea Leaves for the Removal of Crystal Violet from Aqueous Solution

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Abstract. Textile dyeing is considered as one of the large water consuming industries and produces large volumes of (color) wastewater in dyeing and finishing process. The effluents of such industry poses a serious environmental problem as it causes harm to the biota of receptor water. In this study, it is intended to conduct an experimental attempt to estimate the breakpoint and exhaustion times for a fixed-bed column packed with the low-cost and household waste product of Spent Tea Leaves (STL) while adsorbing Crystal Violet (CV) basic type of dyes. For optimizing the experimental conditions, the initial concentration of CV (10–30) mg l⁻¹, height of adsorbent bed (10–20) cm and flow rate (5–15) mlmin⁻¹ were investigated. Fourier transform infrared (FT-IR) spectroscopy and thermal analysis (TGA) of the raw material were also studied.

Keywords: Adsorption, crystal violet, fixed-bed column, spent tea leaves.

1. Introduction

Dyes are soluble organic compounds in the medium in which they are applied and different from pigments which are insoluble in application medium [1]. Dyes usually have synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade [2]. Dyes and their degradation products may be carcinogens and toxics if these effluents with dyeing waste materials are treated inefficiently before discharging to the streams; they could bring problems to human health and animals [3] and are not limited to themselves but also may be passed onto future generations by the way of genetic mutations, birth defects, inherited diseases [4]. Dyes are widely used in many industries such as textile, leather, pulp & paper and plastics in order to color their products. Over 7x10⁵ tones and 10,000 different types of dyes and pigments are produced world wide annually [5]. Crystal violet dye is widely used in textile manufactories for dyeing of cotton and silk and also in manufacturing of paints and printing inks [6].

In most coastal regions and cities of Libya, unfortunately the sea is usually used as the receptor water of not only the municipal wastewaters, but also industrial wastewater which in turn causes harms to the bio-aquatic forms as being severely toxic and can resist the natural biological degradation. As a result, this would definitely have a negative effect on the national economical resources. Therefore, it is environmentally very important to remove the synthetic dyestuff from the wastewater before discharging it into any natural receptor waters. In general, several difficulties are encountered in removal of dyes from wastewaters. By design, dyes are highly stable molecules, made to resist degradation by light, chemicals, biologicals and other exposures. Dyes vary widely in chemical composition. Basic dyes, to which CV belongs, are considered as one of the more problematic classes of dye which are generally consider as toxic colorants. As a result, improved or cost effective technologies are required to remove them from textile effluents [7].

Adsorption currently appears to be the best technique of choice in removing colors from wastewater [8]. Adsorption using activated carbon obtained from agricultural by-products/wastes such as cherry stones [9], coconut coir-pith [3] and palm ash [10] pommel peels [11] are inexpensive adsorbents, easily available and

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handled, and simply operated [12]. Spent tea leaves (STL), represent a good example of a low cost adsorbent and an agricultural waste, is found in abundance, and usually require little or no processing materials.

Tea is the dried and processed leaves of (*Camellia sinensis*) and is consumed by the largest number of people in the world. Only water is rated higher in the world consumption than tea. After hot water extraction of tea leaves, the residual mass is of no use and hence is disposed off [13]. In Libya in particular, tea as a beverage is second most consumed by all citizens after water. The crystal violet was selected as a model in this present study in order to evaluate the efficiency of the adsorbent spent tea leaves for its removal from its aqueous solution.

Most of the adsorption studies concerning dye remediation have been conducted in batch modes which are generally very easy to apply in the laboratory study and limited to the treatment of small wastewater quantities. The data obtained under batch conditions are generally not applicable to most treatment system, i.e. column operations, where contact time in batch mode is too short to attain an equilibrium state in column systems. In fact, it is very necessary to run a continuous flow mode when need to obtain basic engineering data [14]. Besides, the continuous flow process is very low in operation cost and has the ability to adapt to versatile processes [15].

2. Literature Review

Recently, the use of low cost materials to remove color has been reported by several workers. Spent coffee powdered residue from the soluble coffee industry was evaluated as an adsorbent for the removal of Methylene Blue (MB) from aqueous solution with 18.7 mg/g adsorption capacity [16]. Results from the utilization of *Acacia nilotica* leaves; it is native to Africa and the Indian subcontinent, show that it can be successfully used as adsorbents for the removal of CV and Rhodamine B (RHB) from their aqueous solution. The equilibrium adsorption is practically achieved in 120 min. The highest removal of CV and RHB was obtained at pH 6.0. Both CV and RHB dyes were found to be adsorb strongly on the surface of *Acacia nilotica* leaves [17]. Another study has focused on the use of carbonized green tea (CGT) as an adsorbent for the Remazol Brilliant Yellow (RBY) dye adsorption in a batch mode process. The results revealed that the spent tea have the potential to be used as a low-cost adsorbent for the removal of RBY. Based upon the experimental results of this study, the following conclusions were drawn: the equilibrium time period for removal of RBY onto CGT adsorbent was 7.0 hours, the maximum removal of the dye occurred at pH= 9.5, and the experimental data were better fit in Langmuir model [18]. Tea waste has been used as adsorbent for the removal of MB from its aqueous solution. The tea waste was incinerated and used as a cost effective adsorbent having 85.16 mg/g adsorption capacity [19]. Langmuir isotherm model with maximum monolayer adsorption capacities of rejected tea were found to be 147, 154 and 156 mg/g at 303, 313 and 323 K respectively [20]. STL was used as a new non conventional and low cost adsorbent for the MB adsorption in a batch mode process, at 303 K and the Langmuir isotherm monolayer adsorption capacity was found to be 300.052 mg/g [21].

The objectives of this study were to evaluate the adsorption of CV by STL in a continuous flow mode. The effect of operating conditions such as initial CV concentrations, bed height and flow rate were also investigated on the adsorption efficiency of CV dye. The results will enable us in a future part of this study to conduct a comparison study with alternative locally abundant and available adsorbents, i.e. activate carbon from date stones. Fixed-bed column experiments were conducted to optimize conditions for the adsorption process.

3. Materials and Methods

3.1. Preparation of Adsorbent

The type of tea leaves used in this study were produced originally from tea plantations from central high lands of Sir-lanka (100% Pure Ceylon Tea; Akbar Brothers (Pvt) Ltd); it is the most exporting counterpart to Libya. A spent cheap household black tea was collected from a local house. It was washed with boiling water to remove soluble and coloured components. The step was repeated until the filtrate was virtually colourless.

The boiled spent tea leaves were washed few times with distilled water and air dried 24 h. Then the dried spent tea leaves further oven dried at 90 °C until constant weight.

3.2. Preparation of Adsorbate Solutions

Crystal Violet is a triphenylmethyl cation ($C_{25}H_{30}N_3Cl$; molecular weight 408; λ_{max} 584 nm). It is used in this study as a model molecule for organic pollutants in general and basic dyes in particular. Crystal Violet was obtained commercially from B.D.H. Chemicals, Ltd. England and thus no further purifications were needed. The molecular structure of CV dye is illustrated in figure (1). CV dye stock solution (1000 mg/l) was prepared by dissolving accurately the weighed quantity of the dye in double distilled water. The working solutions of different concentrations were prepared thereafter by diluting the stock solution to give the appropriate concentrations. All chemicals used throughout this study were of analytical-grade reagents.

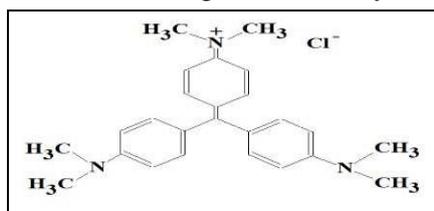


Fig. 1: Molecular Structure of Crystal Violet [17].

3.3. Fixed-Bed Column Studies

Adsorption tests were performed in a continuous flow system using CV as the compound to be adsorbed by STL. Figure (2) depicts the simple set up involved in the study, which consisted of a 30cm long column with 1.2 cm internal diameter (ID). The sorbent STL was packed with different quantities representing various heights in the column with two layers of glass wool at the top and the bottom. The CV dye solution of specific concentrations was charged from the top of the column in a down flow method (spontaneously) at fixed inflow rate using a controlling tank filled with CV solution. Prior to each experiment, distilled water was passed through the column to get rid of the column impurities and air bubbles. The CV dye solution of known concentration at neutral pH was inlet. The initial dye concentration of (10 - 30,) mg/l were used at room temperature, and sorption pH of (≈ 7.0), a flow rate of (5-15) ml/min and in conjunction with a bed height of (10-20) cm. The percent removal of dye was calculated using the following equation:

$$\% \text{ of Removal} = (C_i - C_o / C_i) \times 100 \dots (1)$$

where

C_i = initial concentration of CV dye solution (mg/l)

C_o = final concentration of CV dye solution (mg/l)



Photo1: Spent Tea Leaves.

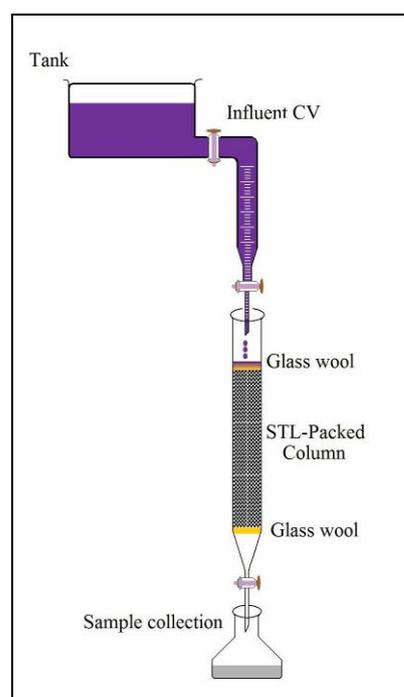


Fig. 2: Set up involved in the study.

A number of equipments were used in this study: (i) A Tensor 27 Bruker, USA Fourier Transform Infrared Spectroscopy (FT-IR) for the characterization of the STL functional groups at the range of 500 - 4000 cm^{-1} ; (ii) a TGA instrument was used for the study of STL thermal analysis, SDT Q 500 operating under nitrogen with a flow rate of 100 ml/min through a furnace of a temperature range of (30–800) $^{\circ}\text{C}$; (iii) a UV-visible spectrophotometer (Specord 205, UV-Analytikjena, Germany) at $\lambda = 586 \text{ nm}$ for the determination of the CV concentrations. Most tools and instruments involved in this study were locally supplied in Libya. However, FT-IR Spectroscopy and TGA analyzer were supplied by Gdansk University of Technology in Poland.

4. Results and Discussion

4.1. Characterization of Spent Tea Leaves

4.1.1. FTIR spectroscopy analysis

Fourier transform infrared (FTIR) spectroscopy was used to measure the carbons of the STL sorbent within the range of 500-4000 cm^{-1} wave number [22]. Fig. 3 shows the spectra of the studied STL with indications of a mini broad band around 3332 cm^{-1} assigned to isolated $-\text{OH}$ groups [23]. Another weak peak with a shoulder at 2920 cm^{-1} and 2852 cm^{-1} assigning the $-\text{CH}$ stretching mode from the aliphatic. The absorbance peaks of STL at 1609 cm^{-1} is due to the presence of $\text{C}=\text{O}$ stretching of amide group (I), and at 1731 cm^{-1} assigns to the $\text{C}=\text{O}$ of the carboxylic groups and at formation of oxygen functional groups like a highly conjugated $\text{C}=\text{O}$ stretching in carboxylic moieties [24]. Furthermore, the figure indicates the presence of a small peak at 1514 cm^{-1} due to the presence of N-H bending types of bonds of amide (II). Finally, the band appeared at 1034–1156 cm^{-1} probably assigned to C-O stretching in alcohols. The IR spectral study thus revealed that the sorbent STL contain mainly $-\text{OH}$ and $\text{C}=\text{O}$ functional groups which are mainly responsible for the sorption of CV through chemical bonding.

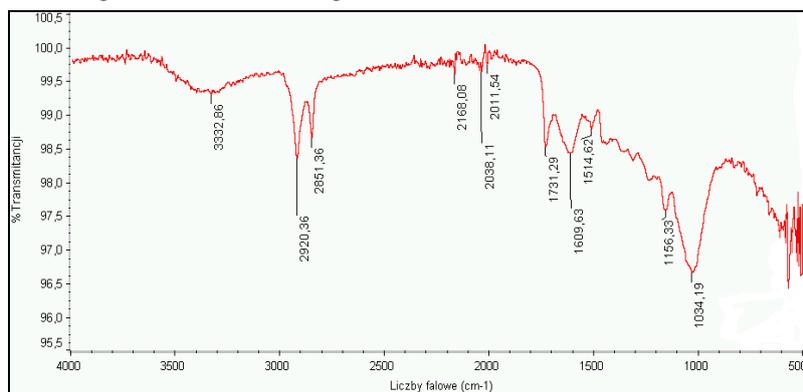


Fig. 3: FTIR Spectra of repeatedly water-washed STL before adsorption process.

4.1.2. Thermal Analysis (TGA)

Thermo-gravimetric analysis of the STL was performed by heating the sample up to 600 $^{\circ}\text{C}$ under nitrogen flow rate of 100 ml min^{-1} through a furnace of a temperature range of (30–800) $^{\circ}\text{C}$. It can be observed from figure (4) that there has been a very little drop in STL weight of approximately a total of 3.0% between initial temperature and 200 $^{\circ}\text{C}$ in relation to the elimination of hygroscopic water, and some volatile matters from the sample which were determined gravimetrically in a separate part. Beyond this point, increasing temperature has led to a semi sharp drop in weight to almost 65% representing the degradation of the main components by dehydration, decarboxylation and decarbonizations [25].

Therefore, at the oven drying temperature; that was 90 $^{\circ}\text{C}$, there would be neither chemical nor structural modifications to occur by heating. Degradation of lignin and cellulose responsible probably for the adsorption of CV would be avoided. In particular, in addition to the aforementioned peak, the derivative weight curve displays two main endothermic peaks; one sharp peak at about 300 $^{\circ}\text{C}$ attributed to the degradation of cellulose, another peak as a shoulder at 450 $^{\circ}\text{C}$ attributed to degradation of lignin as indicated elsewhere [26].

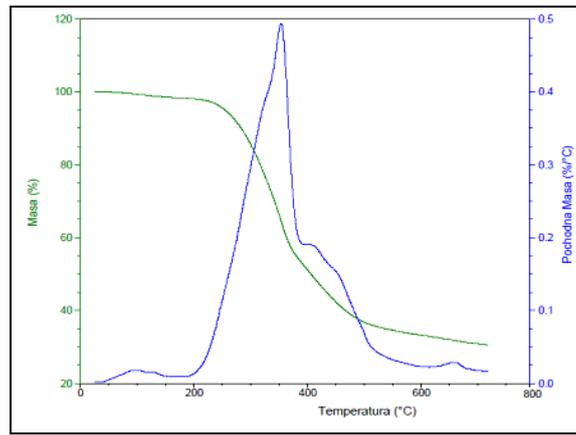


Fig. 4: TGA experiment at 650 °C, initial weight of adsorbent 10 mg.

4.2. Effect of Initial dye Concentrations

The effect of initial influent CV concentration for bed height of 10 cm and solution flow rate of 5 ml/min is demonstrated by the breakpoint time curve in figure (5). At the interval of 60 min. at most, the value of C_t/C_0 reached its highest values of 0.92 for all the influent initial concentration of 10, 20 and 30 mg/l. The higher the CV influent initial concentration, the steeper is the slope of breakpoint curve and the higher the exhaustion time. From the figure, it can also be observed that the breakpoint time decreased from 30 min. to 7 min. and the exhaustion time decreased from 70 min. to 30 min. Similar findings were obtained in literatures dealing with the removal of basic Red 46 by granular activated carbon [27] and removal of CV by *Citullus Lanatus Rind* [28]. The findings were attributed to the increase in driving force made by the increase of the influent CV concentration leading to quick saturation of the adsorbent active sites, which in turn lead to fast breakpoint and exhausted times, as corroborated with the clarification made by J. Goel *et al.*, [29], Kandaswamy and SirKrishna [14] and Abass *et al.*, [30].

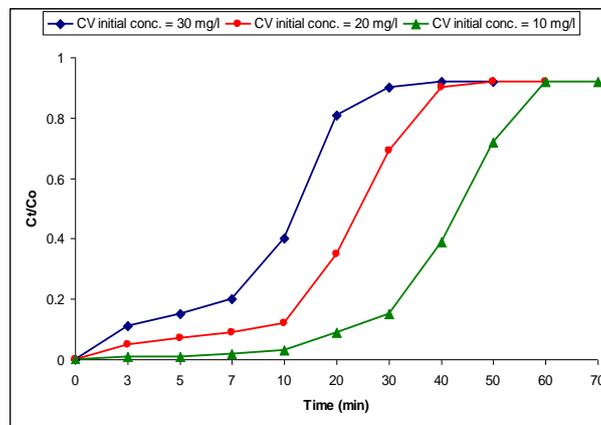


Fig. 5: Breakthrough curve for CV sorption onto STL at different CV initial concentrations (Bed height = 10.0 cm, flow rate = 5.0 ml/min.)

4.3. Effect of Bed Height

In order to estimate the effect of bed height on the breakpoint time curve, an initial CV influent concentration of 30 mg/ml (proved in previous section as the best of three) and a flow rate of 5.0 ml/min were kept constant, while varying the bed height from (10–20) cm. From figure (6), it can be observed that the breakpoint time increased from about 3 min. to 7 min. and the exhaustion time increased from 20 min. to 30 min. with the increase of bed height from 10 cm to 20 cm. As the bed height increased, the adsorbate material, (i.e CV molecules) would have more time to contact with the adsorbents (i.e STL) which in turn would result in a higher CV removal efficiency in the column. The increase in bed height from (10 – 20) cm leads to a decrease in adsorbate material concentration (i.e. CV concentration) in the effluent at the same time [31]. The slope of the breakpoint curve was slightly decreased with increasing bed height, which resulted in a broadened mass transfer zone. Hamdaoui (2006) [32] and Vijayaraghavan *et al.*, (2004) [33] have both stated that with the increase in bed height, the mass of the adsorbents increase and thus the surface

area would also increase which in turn provide an increase in the active binding site numbers leading to a larger adsorption capacity.

4.4. Effect of Flow Rate

When dealing with optimizing the conditions of the continuous treatment of wastewater on industrial scale, the flow rate of such influent wastewater is a very essential factor to evaluate [14]. The effect of the flow rate on the sorption of CV is shown by the breakpoint curve in figure (7). The adsorbent bed height and the influent CV initial concentration were kept constant at 20 cm and 30 mg/l respectively. From the figure, it is clear that rapid uptake is noticed in the initial stages of flow rate and the rate of uptake starts to decrease thereafter and finally reaches saturation. As increasing the flow rate of the CV influent solution from 5 to 15 ml/min, the breakpoint curves becomes steeper and reaches the breakpoint time faster from almost 7 min. to 3 min. or less. This is attributed to the fact that as the flow rate becomes higher, the contact between the adsorbate solutes and the adsorbents is minimized in time which become insufficient for the solutes to diffuse into the pores of the adsorbents, causing the adsorbate solutes to leave the column before equilibrium to occur and breakpoint time to be reached earlier. These results were corroborated with a number of reported findings [34]-[36].

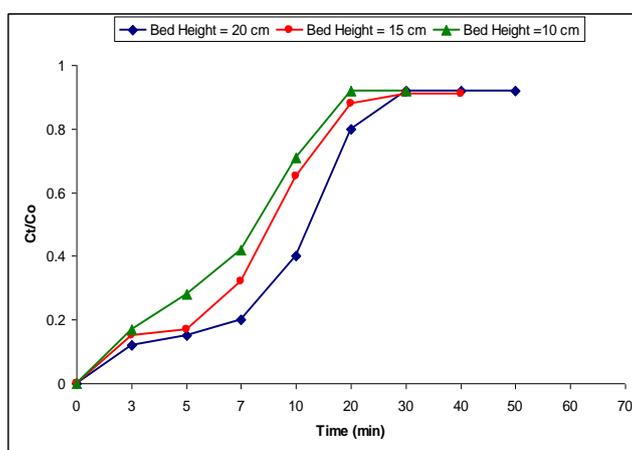


Fig. 6: Breakpoint curve for CV adsorption onto STL at different bed heights (CV initial concentrations = 30 mg/l, flow rate = 5.0 ml/min).

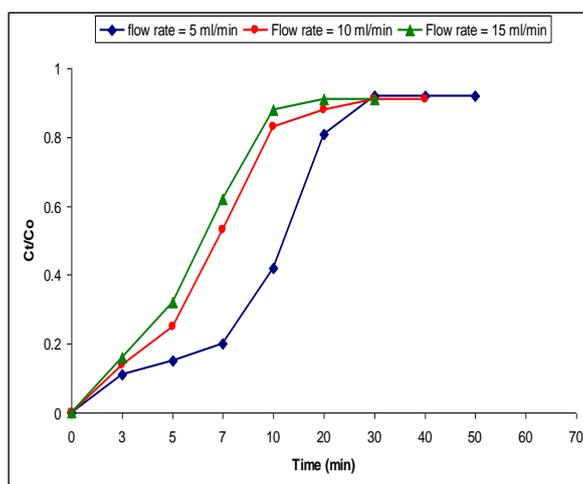


Fig. 7: Breakpoint curve for CV adsorption onto STL at different Flow rates (CV initial concentrations = 30 mg/l, Bed height = 20 cm).

5. Proposed of Column Design Connected to a Single Basin

5.1. The Idea

At some scientific laboratories such as medical, microbiological and pharmaceutical ones, dyes are usually involved in research. After research termination and dyes become waste, these waste dyes find their

way drained to the sink. These substances are considered the most hazardous organics due to their complicated structure which make them more stable and difficult to biodegradable. So, their removal from wastewater before discharging to environment and from raw wastewater before offering it to public use is very essential for the protection of health and environment.

5.2. The Way out

For that reason, we think that it would be a great endeavor to propose a simple design for a column packed with an efficient sorbing material made of an agricultural by-product such as leaves of plants. spent tea leaves good example for the adsorption of crystal violet basic dye from aqueous solution using a fixed bed column method. The attempt has been successful leading to very satisfactory results. This proposal of using the agricultural by-products as raw materials in treatment of wastewater represent a great example of the so-called “Green chemistry”.

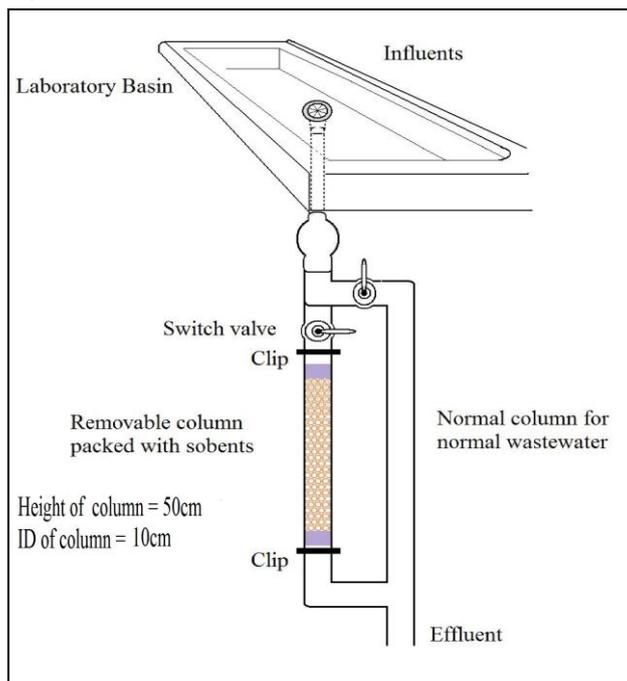


Fig. 8: Set up of column design.

A number of effluent water can latter be connected all together through a network with additional “Removable column packed with sorbents”

6. Conclusion

The study confirmed that STL, the locally and freely abundantly available material, could be utilized in removing Crystal Violet from its aqueous solution. According to the data obtained, the removal of CV was possible by STL and very efficient up to the breakpoint time of about 7 min where the percentage accounted for 68%, when the concentrations of the dye, bed height, and flow rate were optimized at 30 mg/l, 20cm and 5 ml/min. respectively. CV is used as a basic dye model and its adsorption by STL is dependent on the (i) Bed height, (ii) flow rate, and (iii) the initial concentrations of the influent CV.

The STL requires almost no cost, no further treatment, and more important very effective in removing CV from aqueous solution as well as it may be useful for wastewater treatment i.e. textile industries, tanning industries and even at some scientific laboratories such as biological, pharmaceutical, medical, and also chemical laboratories at universities where dyes are involved in research.



Photo 2: flasks with the influent CV (left), and effluent CV (right).

7. Acknowledgements

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