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REMOVAL OF DYES (DIRECT RED 80 AND LEVAFIX BRILLANT BLUE) BY USING VINE STEM WASTE AS A BIOSORBENT

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Abstract: *Synthetic dyes, which are commonly used in textile, paper, leather and plastic industries, pose a significant risk to the environment. This means that the wastewater from industrial sources mixes with groundwater, surfacewater or rivers, affecting aquatic life, water quality and food chain in negatively. Vine stem is an agricultural side product and has no economic value. Every year hundreds thousands of tons vine stem come out as a waste by trimming or pruning and destroyed by burning. In the present study, grinded vine stem was investigated as a biosorbent for the removal of dyes from the aqueous solution. To identify the functional groups of the biosorbent, attenuated total reflectance spectra (ATR-IR) were used. The zeta potential of vine stem was measured as a function of pH for investigating the surface charge. It was found negativity for all the pH. The batch biosorption method (BBM) was used for the study. The analysis of the pH functioning, biosorbent amount, and contact time of the biosorption process have been made. The Langmuir model was found to fit well with the experimental data for the biosorbent. The maximum adsorption capacities were found as 53.5 and 45.5 for Direct Red 80 and Levafix Brillant Blue, respectively. The optimization study revealed that the grinded vine stem can be an effective and economically feasible biosorbent for the removal of dye.*

Keywords*: Biosorption, vine stem, dye Direct Red 80, Levafix Brillant Blue*

1. INTRODUCTION

Synthetic dyes, which are commonly used in textile, paper, leather and plastic industries, pose a significant risk to the environment. This means that the wastewater from industrial sources mixes with groundwater, surfacewater or rivers, affecting aquatic life, water quality and food chain in negatively [1]. Varied methods such as chemical precipitation and filtration, chemical reduction and oxidation, electrochemical purification, ion exchange, reverse osmosis are used for the removal of dyes. Adsorption techniques are preferred today because of the advantages of the adsorption process which are more economical, simple design and independence from high concentration.The toxic chemicals can be removed without degrading the quality of the water and without releasing any reduced toxic substances. Most effective adsorbent is active carbon, but it is quite expensive [2]. For this reason, the researches were focused on alternative low-cost adsorbents to active carbon and explored the substances which is cheap and obtained easier [3]. Bentonite, clay, fly ash, chitosan, chitin etc. substances were used as an alternative to the active carbon. In addition, lignocellulosic biomass is also used as biosorbent because of the negative surface charge of the outer surfaces [4]. It is thought that the use of the wastes will make an economical contribution to the environment. Vine-stem waste was used as an adsorbent in the present study. In Turkey, an area of 560.000 hectares produces approximately 3.500.000 tons of grapes per year and generates approximately 300,000 tonnes of vine stem wastes emerge annually after pruning, which is destroyed by incineration or various methods.

The purpose of the study is to investigate the removal capacity of the vine stem on theaqueous solution containing Direct Red 80 and Levafix Brillant Blue dyes. The analysis of the pH functioning, biosorbent amount, and contact time of the biosorption process have been made.

2. MATERIALS AND METHODS

2.1 Materials

The vine-stem wastes were collected from the vineyards in the Manisa/Turkey region and separated into small pieces, then washed with pure water until the color of the washing water was clear. Then, it was dried under the daylight and re-milled having a 0.25 mm particle sized sieve. After milling step, the grinded substance was oven dried at 110 ^{o}C till constant weight was obtained for the study.

2.2 Dyes

Structures of the dyes are given in the Figures.

Fig. 1: *Direct Red 80*

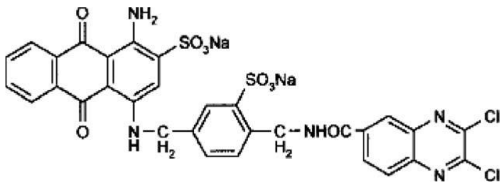

Fig. 2: *Levafix Brilliant Blue E-B*

2.3 Adsorbent characterization

The electrophoresis method was used to determine the zeta potential of the vine stem by using a Zeta-Meter. The zeta potential of the particles was measured as a function of pH between 2 and 10. Attenuated total reflectance infrared (ATR/IR) spectra of biosorbents and activated carbon were taken by using a spectrophotometer (Spectrum 100, Perkin-Elmer)

2.4 Methods

The adsorption experiments were carried out for specific time intervals with 100 mL of known dye concentration. A certain amount of the biosorbent and known concentration of dye solution were shaked with the orbital shaker (150 rpm) at 25 ± 2 °C. Prior to mixing, the pH of the solution was adjusted using with pH-meter with glass electrode. At the end of the each experiment, the biosorbent was carefully removed by filtration with the aid of filter paper and the absorbance of dye in the filtrate was measured by UV spectrophotometer. All experiments were repeated 3 times and mean results were given.

3. RESULTS AND DISCUSSION

3.1 Surface properties

3.1.1 FT-IR spectra

The Fig. 3 shows the FT-IR analysis of vine-stem. The bands;1023–1030 cm^{-1} corresponding to C-O deformation vibrations in cellulose, 3000 and 3600 cm^{-1} attributed to the associated OH- functional group of phenols, alcohols, and carboxylic acids. 2923 cm^{-1} and 1734 cm^{-1} can be assigned to the C-H bonds of aliphatic acids and C-O stretching band of aromatic ethers, esters, respectively and phenols appearing at 1232 and 1234 cm^{-1}.

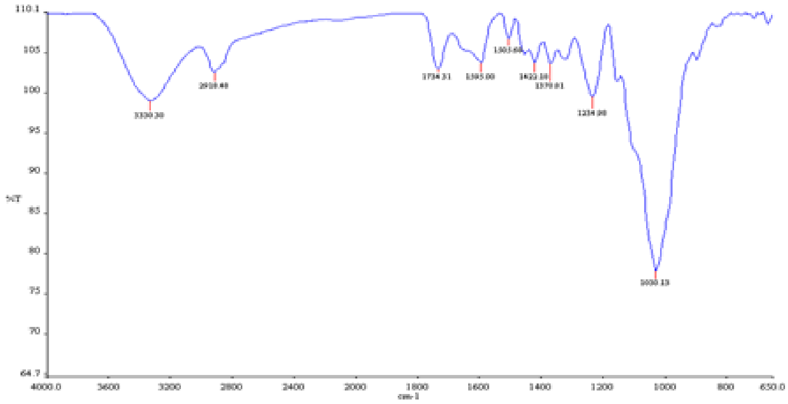

Fig. 3: *FT-IR spectra of vine-stem waste.*

The bands at 1705 and 1575 cm^{-1} can be attributed to the C-O stretching in ketones and esters, respectively. The wide band between 1500 and 900 cm^{-1} may be attributed to ether groups and the band at 878 and 753 cm^{-1} show the aromaticity [5].

3.1.2 Zeta Potential

The surface charge of adsorbents was investigated by measuring zeta potential. The zeta-potentials of vine-stem in a pH range of 2–10 were measured. Fig. 4 shows the variation of zeta potential (z) of adsorbents as a function of pH. The surface of biosorbent exhibited an increasing negativity as the pH of the solution increased slightly from 2 to 10 and indicated negative charge values that should be favorable to the attraction between active sites and positive charges of dyes, resulting in an electrostatic interaction [5].

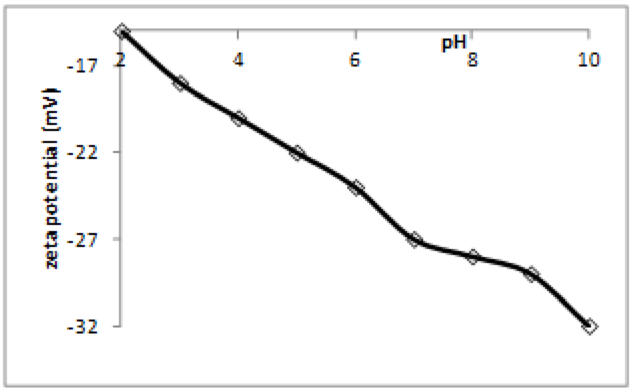

Fig. 4: *The effect of pH on the zeta potential of vine-stem.*

3.2. Direct Red 80

3.2.1 The Effect of Contact Time

50 ppm Direct Red 80 (pH 2) and 0.1 g biosorbent were mixed with orbital shaker for 2, 4, 6 and 24 hours. There was no significant effect on the adsorption capacity after 4 hours, so the contact time was chosen as 4 hours.

3.2.2 The Effect of pH

50 ppm Direct Red at different pHs and 0.1 gram of biosorbent were stirred in the shaker for 4 hours. No removal was observed at pH >2 so pH was selected as 2. This is compatible with the work of Ardejani et al. (2008) using a different adsorbent with same dye [6,7]. The biosorbent is lignocellulosic and consists of negative groups on its surface. Since the dye has a negative charge, it is not observed to be removed at higher pH due to the repulsion between the dye and the adsorbent due to increased OH^- groups at high pH [5].

3.2.3 The Effect of Biosorbent Amount

50 ppm Direct Red 80 and different amounts of biosorbent (0.05, 0.1, 0.2, 0.5) were mixed for 4 hours in a shaker. As it can be seen from the Fig. 5, the highest removal of dye was obtained by using 0.05 gram biosorbent.

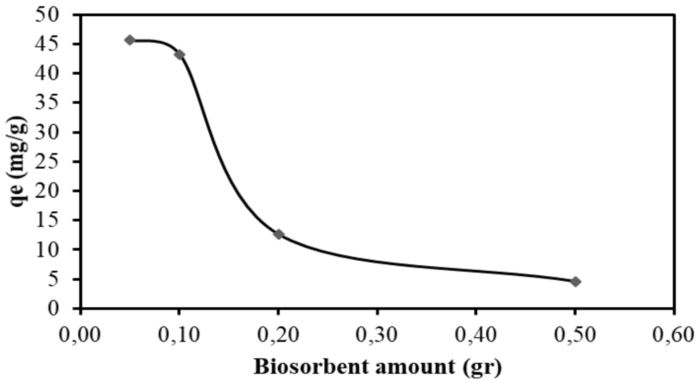

Fig. 5: *The effect of biosorbent amount on the adsorption capacity of Direct Red 80 Dye*

3.2.4 The Adsorption Isotherm

Adsorption isotherms were obtained by mixing 100 mL dye (pH 2) ranging from 30-130 ppm in concentration at optimum conditions. Langmuir and Freundlich isotherms which are commonly used for adsorption have been tested and the adsorption is coincided with the Langmuir ishoterm. The maximum adsorption capacity was found to be 53.48 mg/g and the Langmuir constant (K_L) was calculated as 0.000855 L / g. The maximum adsorption capacity was found to be 28.50 mg /g by the researchers working on the same dyes [6]. In another study, the maximum adsorption capacity was calculated as 21.052 mg /g using the orange shell for the same dye. In another study using soy bran, the maximum adsorption capacity for the same dye was calculated to be 178.57 mg /g [6]. Langmuir isotherms suggests that adsorption was a single layer. Potential binding sites are thought to be phenols, alcohols, and carboxylic acids in the biosorbent.

3.3. Levafix Brillant Blue

3.3.1 The Effect of Contact Time

100 ppm Levafix Blue Brillant (pH 2) and 0.1 g biosorbent were mixed with orbital shaker for 2, 4, 6 and 24 hours. There was no significant effect of the contact time on the adsorption capacity. So, the contact time was chosen as 2 hours.

3.3.2 The Effect of pH

50 ppm Levafix Blue Brillant at different pHs and 0.1 gram of biosorbent were stirred in the shaker for 2 hours (Fig.6). The best removal observed at pH 2 and decreased as pH increase, so pH was selected as 2. It is not observed to be removed at higher pH due to the repulsion between the dye and the adsorbent due to increased OH^- groups at high pH [5].

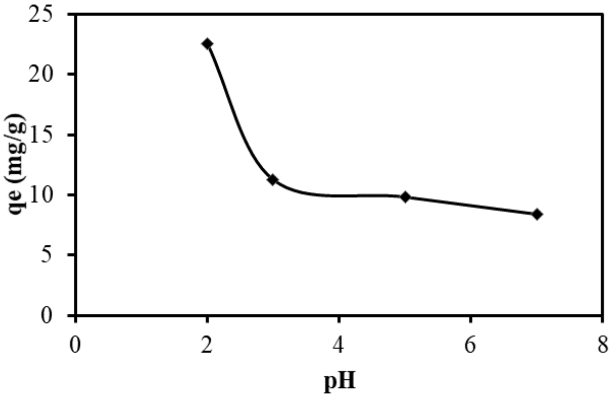

Fig. 6: *The effect of pH on the adsorption capacity of Levafix Blue Brillant Dye*

3.3.3 The Effect of Biosorbent Amount

50 ppm Levafix Blue Brillant (pH 2) and different amounts of biosorbent (0.05, 0.075, 0.1, 0.5) were mixed for 2 hours in a shaker. The highest removal was at 0.05 grams.

3.3.4 The Adsorption Isotherm

Adsorption isotherms were obtained by mixing 100 mL dye ranging from 20-110 ppm in concentration at optimum conditions. Langmuir and Freundlich isotherms have been tested and the adsorption is coincided with the Langmuir ishoterm. The maximum adsorption capacity is found to be 43.48 mg /g and the Langmuir constant (K_L) is calculated as 0.003128 L/g. In the study of Erkut et al. (2012) using Aspergillus oryzae to investigate the removal of Levafix Blue Brillant dye, the maximum adsorption capacity was found to be 61 mg/g [8]. Yavuz and Aydın (2005) calculated the maximum adsorption capacity of 26.22 and 48 mg/g, respectively, using activated carbon, kaolinite and montmorillonite from coconut shell for the same dye [9]. In another study using the fibers of the banana tree, the maximum adsorption capacity for the same dye was calculated to be 4.42 mg/g [10].

4. CONCLUSIONS

In this study, vine stem was investigated as a biosorbent for the removal of textile dyes (Levafix Blue Brillant and Direct Red 80) from aqueous solution. The biosorption data conformed best with the Langmuir model for Direct Red 80 and Levafix Brillllant Blue. The maximum adsorption capacities were found as 53.5 and 45.5 for Direct Red 80 and Levafix Brillllant Blue, respectively. The results showed that vine stem can be used as low-cost biosorbent in treating colored dye effluents.

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