THE WASTES OF VINE STEM AND TURKISH RED PINE AS AN ALTERNATIVE BIOSORBENT FOR THE REMOVAL OF LEATHER DYES

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The use of high amount water in the industries such as leather, textile and paper causes hazardous wastewater for the environment due to the contents of organic compounds and heavy metals. Discharging high amount of leather dyes such as acid and metal complex to ecosystem pose a problem due to their resistance to biological treatments. Vine stem and Turkish red pine sawdust are agricultural wastes and could be an alternative bio-sorbents for the leather industry due to their cost effectiveness. For this purpose, it was aimed to determine the removal efficiencies of the dyestuff Acid Brown 282 SGR by the use of vine stem and Turkish red pine sawdust. The batch adsorption technique was used for the study and the effect of the pH, biosorbent amount and contact time was investigated. The functional groups of the bio-sorbents were determined by attenuated total reflectance spectra (ATR-IR). The biosorption data showed that Langmuir model was the best fitted model for the sorption of Acid Brown 282 SGR. The maximum adsorption capacities were found as 25.91 and 26.67 for vine stem and Turkish pine sawdust respectively. The results revealed that vine stem and Turkish red pine sawdust could be used as low-cost biosorbents for the removal of dyestuff remaining after the dyeing process of leathers.

Keywords: biosorption, vine stem, red pine sawdust.

INTRODUCTION

Synthetic dyes used in various industries such as textile, chemistry and leather industries, pose an important risk for the environment if they are discharged to groundwater, surface water or rivers without any removal process. Due to the harmfulness of many synthetic dyes to human beings and environment, the removal of dyes becomes a very important topic for the researchers (Chiou and Li, 2002). Various types of dyestuffs are used in leather industry and their removal from the dyeing baths constitutes a major problem due to the treatment methods difficulty. Adsorption, chemical reduction and oxidation, ion exchange, reverse osmosis, chemical precipitation and filtration techniques etc. are well known for the use of dye removal (Allen *et al.*, 2005). Active carbon is an effective adsorbent, but it is quite expensive (Sanghi *et al.*, 2002). The adsorption process is more economical and effective (Ferrero, 2007). So, up to now different adsorbents such as clay (Kashif Uddin, 2017), peat (Allen *et al.*, 2004), fly ash, walnut shell (Nazari Moghaddam *et al.*, 2010), chitin (Wawrzekiewicz *et al.*, 2017) and leather shaving waste (Zengin *et al.*, 2010) have been investigated due to their low-cost. Turkish red pine sawdust and vine stem are lignocellulosic biomasses. They have negative surface charge of the outer surfaces (Nethaji *et al.*, 2010) and they are endemic to Turkey.

In Turkey, approximately 300.000 tons of vine stem wastes are emerging annually in pruning. In 2011, 17.5 million m³ industrial woods were consumed and lumber production was one of the biggest subdivision of industrial wood production which was produced 2.3 million m³ annually (Annon, 2010). After the production of lumber, high

amount of sawdust were generated as a waste. Although there were a couple of study on red pine sawdust such as additional substance for pyrolysis of wood-plastic composite (Vaisanen *et al.*, 2016), sintering performance (Findorak *et al.*, 2014), and usage for biocomposite derived substance (Das *et al.*, 2016), these waste are widely used for solid fuel, animal bedding material. Although various adsorbents were used for removal of the dyestuffs, there has not been any study about the use of the non-modified vine-stem and Turkish red pine sawdust on the remaining dyestuff after the dyeing process of leather industry.

For this purpose, the aim of this study was to investigate the adsorption properties of vine stem and Turkish red pine sawdust as cheap adsorbents. The adsorption properties of the vine stem and Turkish red pine sawdust on the removal of anionic dyestuff (Acid brown 282 SGR) were investigated with the use of batch adsorption technique.

MATERIALS AND METHODS

Materials

The vine stem was collected from the vineyards of Manisa, Izmir and Turkish red pine sawdust was obtained from a timber company in Torbalı, Izmir. These biosorbents were milled and washed with pure water until the color of the washing water became clear. Then, the biosorbents were dried at room temperature and re-milled until having a particle size of less than 0.2 mm. Later, they were dried in the oven at 110°C and stored in a sealed box. Acid Brown 282 SGR (CAS 12219-65-7) anionic dyestuff that has been widely used in dyeing process of leather manufacturing was used for the absorption experiments.

Methods

The batch adsorption technique was used in the experiments. A certain amount of the biosorbent and known concentration of dye solution (100 mL) were shaken with an orbital shaker at room temperature at certain time intervals. The rate of the shaker was 150 rpm. The pH of the solution was adjusted using pH-meter with glass electrode before mixing. The biosorbents were removed by Whatman filter paper at the end of each experiment. Then the absorbance of dye in the filtrate was measured by UV spectrophotometer. Triplicate experiments were performed and the mean values were given as a result.

Characterization of adsorbents was determined by attenuated total reflectance Fourier transform infrared (ATR/FTIR) spectra (Spectrum 100, Perkin-Elmer).

RESULTS AND DISCUSSION

Characterization of Biosorbents

The FT-IR analysis of vine stem and Turkish red pine sawdust used as biosorbents are shown in Figure 1 and 2. The figures are representing the most important bands that are observed in an infrared spectrum of vegetable sources such as woods, barks and their assignment to functionality.

Figure 1. FT-IR spectra of vine stem waste

Figure 2. FT-IR spectra of Turkish red pine sawdust

The bands of C—O deformation vibrations are the region of 1023–1030 cm^{-1} (1024 cm^{-1} for TPS and 1030 cm^{-1} for VS). 3000 and 3600 cm^{-1} bands attributed to the associated OH- functional group of phenols, alcohols, and carboxylic acids for each biosorbent. For vine stem, the bands at 2923 cm^{-1} and 1734 cm^{-1} can be assigned to the C—H bonds of aliphatic acids and C—O stretching bonds of aromatic ethers, esters respectively. The bands 2926 cm^{-1} and 1602 cm^{-1} can be assigned to C-H bond of aliphatic acids, and aromatic C=C sym stretching bands for TPS, respectively. The band 1509 cm^{-1} can be assigned to the ring in-plane bending. Phenol bands appear at 1232 and 1234 cm^{-1} . The C—O stretching of ketones and esters give band at 1705 and 1575 cm^{-1} , respectively. The ether groups are in the 1500-900 cm^{-1} region. The bands at 878 and 753 cm^{-1} show the aromaticity (Mavioglu Ayan *et al.*, 2011).

The Adsorption of Vine Stem

The Effect of Contact Time

80 ppm of Acid brown SGR 282 (pH 2) and 0.1 g biosorbent were mixed and shaken at an orbital shaker for 2, 4, 8 and 24 hours. The contact time was chosen as 4 hours because no significant effect on the adsorption capacity was found for the contact time after 4 hours (Figure 3).

Figure 3. The effect of contact time on the biosorption of Acid brown SGR 282 with vine stem

The Effect of pH

80 ppm of dyestuff solution was prepared at different pH values (2, 4, 7, and 10). Then the dye solutions were mixed with 0.1 gram of biosorbent for 4 hours at the orbital shaker. The best removal was determined at pH 2. The biosorption of each sorbent was decreased with the increased pH value as expected from the anionic dyes. There is not any study about the adsorption of Acid brown SGR 282 which is in the group of anionic dyestuffs. This is compatible with the adsorption studies with anionic dyestuff (Mavioglu Ayan *et al.*, 2011; Balarak *et al.*, 2015). The vine stem is lignocellulosic material and has negative groups on its surface. Since the dye has a negative charge, there is repulsion between the dye and vine stem at higher pH due to the increased OH⁻ groups (Nethaji *et al.*, 2012).

The Effect of Biosorbent Amount

80 ppm of dyestuff solutions (pH 2) and different amounts of vine stem and Turkish red pine sawdust (0.05, 0.1, 0.2, 0.5, 1.0g) were mixed for 4 hours at a shaker, separately. The highest removal was obtained for 0.1 g for each sorbent.

The Adsorption Isotherm

100 mL of dyestuff solutions (pH 2) at different initial concentration ranging from 20-100 ppm were shaken with 0.1 g vine stem and Turkish red pine sawdust for 4 hour. Langmuir and Freundlich isotherms were tested and found that the biosorption is belonging to the Langmuir isotherm. A Langmuir isotherm suggests that adsorption is a single layer. The maximum adsorption capacity was found to be 25.91 mg/g and the Langmuir constant (K_L) was calculated as 0.003721 L / g. Potential binding sites in the biosorbent are phenols, alcohols, and carboxylic acids.

The Adsorption of Turkish Red Pine Sawdust

The Effect of Contact Time

100 ppm of dyestuff solutions (pH 2) and 0.1 g biosorbent were mixed with orbital shaker for different contact time (2, 4, 8 and 24 hours). As seen in Figure 4, after 4 hours there is not significant effect of the contact time on biosorption of anionic Acid brown SGR 282. Therefore, the optimum contact time was 4 hour.

Figure 4. The effect of contact time on the biosorption of Acid brown 282 SGR with Turkish pine saw dust

The Effect of pH

100 ppm of dyestuff solutions were mixed with 0.1 gram of biosorbent at the shaker for 4 hours. The biosorption of Turkish red pine sawdust was decreased with the increased pH value of the solution as expected from the acidic dyes and the best removal was observed at pH 2. There is not any study about the adsorption of acid brown 282 SGR with any other adsorbent.

The result was found compatible with the biosorption studies of acidic dyes (Mavioglu Ayan *et al.*, 2011; Balarak *et al.*, 2015). Turkish red pine is lignocellulosic material. As seen in the results of vine stem, biosorption was decreased with pH increase.

The Effect of Biosorbent Amount

100 ppm of dyestuff (pH 2) and different amounts of Turkish red pine sawdust (0.05, 0.1, 0.2, 0.5, 1.0) were mixed for 4 hours at a shaker. The highest removal was obtained for 0.1 g biosorbent.

The Adsorption Isotherm

100 mL of dyestuff solutions (pH 2) at different initial concentration (20-100 ppm) were shaken with 0.1 g Turkish red pine for 4 hour. Langmuir and Freundlich isotherms were tested to obtain the adsorption capacity. The results showed that the biosorption belongs to the Langmuir isotherm. The maximum adsorption capacity is found to be 26.67 mg /g and the Langmuir constant (K_L) was calculated as 0.017618 L/g. Potential binding sites in the biosorbents are phenols, alcohols, and carboxylic acids.

CONCLUSIONS

In this study, the adsorption properties of vine stem and Turkish red pine sawdust were investigated as cheap adsorbents and following conclusions have been drawn;

- The results are important because no any other study on the removal of Acid brown 282 SGR dye was found in literatures.
- The adsorption capacity of the biosorbents was found good.
- The results indicated that the biosorbents had significant effect on the adsorption of the Acid Dyestuff.
- After the adsorption, dyestuff enriched biosorbent could be a composite substance for the clay bricks.
- Moreover they can also be used as a solid fuel due to their high calorie.

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