

Stabilized Protein Waste as a Source for Removal of Color from Wastewaters

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ABSTRACT: Seeking solution to pollution problems is a prime concern of many researchers today. The waste from one industry can be judiciously used to treat another waste. This concept has been used in this study, wherein, the fleshing, a solid waste (biopolymer) emanating from leather industry has been used as an adsorbent for removal of dyes from wastewater. Fleshing has been cross-linked with glutaraldehyde to stabilize it against degradation. The various parameters like effect of pH, role of salt concentration, adsorbent dosage, and initial concentration of dye have been standardized. About 90% dye removal has been achieved by treating 100 mg/L dye solution with 12 g/L of glutaraldehyde-crosslinked flesh-

ing. The dye removal has been found to follow Langmuir type of adsorption isotherm. The optimized parameters of batch adsorption studies have been applied to treat sectional wastewater from a commercial tannery. The study also explores the possibility of reusing the dye loaded fleshing as a reductant in the manufacture of a tanning salt, which is used in leather industry for tanning of leathers. Thus, a holistic solution to both solid and liquid waste has been presented in this work. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1397–1402, 2011

Key words: dyes; tannery fleshing; isotherms; adsorption; solid waste; water pollution

INTRODUCTION

Leather is one of the oldest commodities in today's world market. Leather manufacturing is a by-product industry, which existed from the day man hunted animals and will exist until man consumes animal as food. Nevertheless, it also exists as an independent industry because of the unique properties of the leather itself. This industry is also synonymous with pollution. Every step in leather processing generates waste either in solid or liquid form. Fleshing, which is integral part of a hide/skin, is removed during leather processing as it is an unwanted material in the final leather. For every ton of leather processed, about 100–150 kg of fleshing is generated.¹ This shows the quantum of fleshing waste generated by tanneries. This also depicts the enormity of the solid waste disposal problem, which arises because of this fleshing.

The presently followed disposal techniques are not economical. For instance, the widely followed

disposal method for fleshing is glue manufacture.² This method is highly noneconomical in terms of initial capital costs and maintenance costs. Hence, the need of the hour is to develop cost effective disposal methodologies for fleshing emanating from tanneries.

On the other hand, there is another problem, which is grabbing the attention of environmentalists worldwide, namely dyes. This pertains not only to leather industry but also to many other industries such as textiles, paper etc. Dyes not only color the wastewater but also cause various health hazards.³ Although various dye removal techniques are available, adsorption scores over many owing to its efficiency.^{4–6} The uptake of the diazo dye Acid Blue 113 by hydrotalcite and calcined hydrotalcite, fly ash was studied recently.^{7,8} Activated carbon is the most widely used adsorbent; however, there are drawbacks like high initial cost and regeneration cost associated with it. Hence, there is a look out for low-cost adsorbent for dye removal. A number of low-cost adsorbents from steel and fertilizer industries wastes have been prepared and investigated for the removal of anionic dyes such as ethyl orange, metanil yellow, and acid blue 113 from aqueous solutions.⁹ Use of seaweeds and calcium alginate beads for dye removal has been studied recently.^{10,11} Tannery fleshing contains proteins like collagen, elastin, reticulin, and fats.¹² This leads to the presence of

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many functional groups and hence, it can act as a good adsorbent. Use of iron crosslinked fleshing for removal of chromium(VI) has been established earlier.¹³ Because fleshing is a biodegradable material, glutaraldehyde crosslinking has been done to provide stability to the adsorbent. In this study, the use of glutaraldehyde-crosslinked fleshing as an adsorbent for removal of dyes has been investigated. Thus, this study explores the possibility of a holistic solution to both solid waste and liquid waste problem. Also, the dye-loaded fleshing has been used in the manufacture of a tanning salt, thereby, providing complete solution to the aforementioned problems.

EXPERIMENTAL METHODS

Preparation of biosorbent

Raw fleshing was collected from the soaking yard of a tannery located in Chennai, India. The raw fleshing was washed thoroughly using distilled water and stabilized using glutaraldehyde as per standard procedure.¹⁴ These stabilized fleshing were then dried, powdered, and sieved through a mesh size of 500 μ . The glutaraldehyde treatment prevents the putrefaction of fleshing against bacteria and stabilizes the same.

Dye removal experiments

The dye solution was prepared by dissolving the acid blue 113 dye in deionized water to produce a stock solution of 1000 mg/L (pH 6.0). This stock solution was diluted in accurate proportions to produce solutions of different initial concentrations. The effect of pH on discoloration was studied using 100 mL of 100 mg/L dye solution taken in stoppered conical flask containing 12 g/L of fleshing. The pH of the solution was varied from 3.0 to 9.0 using 0.1N H₂SO₄ and 0.1N NaOH. The solution at the respective pH was agitated for a period of 3 h in a rotary mechanical shaker (75–85 strokes per minute) at constant temperature (30 \pm 2°C). The reduction in color was estimated by measuring absorbance at 564 nm using Perkin-Elmer Lambda 35 UV-Vis spectrophotometer. To determine the time required for complete removal of color and the effectivity of the adsorbent against various initial concentrations of the dyes, 100 mL of five different concentrations of dye viz., 50, 100, 200, 300, and 400 mg/L were taken into five stoppered conical flasks containing 12 g/L of fleshing each and the flasks were agitated in a mechanical water bath shaker. The absorbance was measured at various time intervals ranging from 5 min to 3 h. The effect of the fleshing dosage on the dye removal was studied by varying the adsorbent dosage as 1.2, 3.0, 3.6, 9.0, and 12 g/L with a dye

concentration of 100 mg/L. The role of neutral salt concentration on the discoloration of the dye was studied by taking 12 g/L of adsorbent along with 0.5, 1, 1.5M of sodium chloride and formate concentration of at pH 5 \pm 0.2 and added to 100 mg/L of 100 mL dye solution.

Studies on dye removal from commercial tannery wastewater

Sectional dye wastewater of volume 20 L from a commercial tannery near Chennai, India using the same dye used in this study was collected. The wastewater was quantified for the dye present using UV spectrophotometer. Parameters optimized in batch study viz. the pH and adsorbent dosage were used to treat the commercial wastewater.

Preparation of tanning salt and tanning experiments

Dye-loaded adsorbent were collected by filtration and used as a reductant in the preparation of a tanning salt, basic chromium sulfate (BCS). Sodium dichromate was dissolved with equal proportion of water to which sulphuric acid was added in ratio of 1 : 0.96 and heated. To the heated mixture, the various ratio of adsorbent was added in slow manner to facilitate the reduction of Cr(VI) to Cr(III). Throughout the reaction, the temperature was maintained 90 \pm 5°C. The BCS prepared using fleshing as a reducing agent was used for tanning experiments. Delimed goat skins were used as raw material. The delimed skins were conventionally pickled to a pH of 2.8 to 3.0 and chrome tanned using modified BCS.¹² A conventionally tanned wet blue was used for the comparison of leather properties.

RESULTS AND DISCUSSION

This study explores the potential of glutaraldehyde-crosslinked fleshing for removal of dyes from wastewater. Fleshing contains proteins like collagen, elastin, reticulin, and fats.¹² These proteins are rich in functional groups like carboxyl, amino, hydroxyl etc. Hence, they have greater potential for adsorption of pollutants and also have high crosslinking density. Glutaraldehyde crosslinking is known to stabilize collagen and thus helps in providing the required enzymatic, thermal and mechanical stability to the adsorbent.¹⁵ This study also attempts to determine if a confluence between solid and liquid waste will lead to a holistic solution to pollution problem.

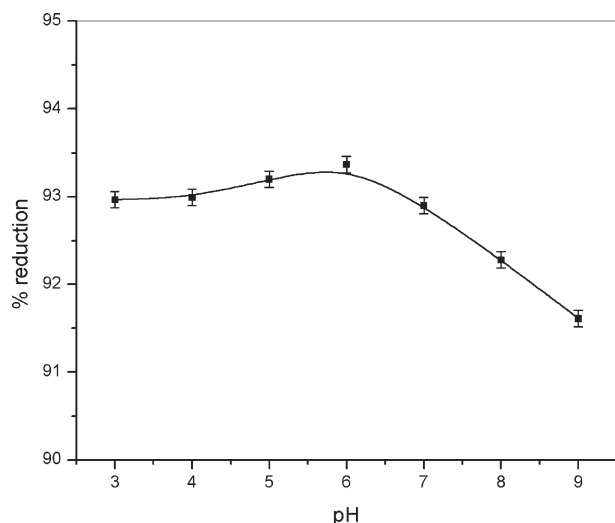


Figure 1 Effect of pH on % dye removal by fleshing at an initial concentration of dye 100 mg/L and fleshing dose of 12 g/L.

Effect of pH on dye uptake

The pH of the solution plays an important role in sorption studies. The effect of pH on the uptake of dye by aldehyde-treated fleshing was studied by varying the pH from 3 to 9. Figure 1 gives the % removal of dyes with increasing pH values. It is seen that the adsorption of dye by glutaraldehyde-treated fleshing is higher in the pH range of 3 to 6 above which a decrease in the percentage removal observed. This is because the amino groups present in the collagenous fibers are protonated in acidic pH (NH_3^+) and can bind the anionic dyes effectively. A uptake of about 93% was observed around pH 5.0 and 6.0 for an initial concentration of 100 mg/L solution. However, the pH was maintained at 5.0 as the real life wastewater from a tannery has a pH of about 5.0. Hence, a pH of 5.0 ± 0.2 was taken as optimum for further experiments.

Effect of time and effect of initial dye concentration on uptake

To determine the equilibrium time for removal of dye by glutaraldehyde-crosslinked fleshing, time vs. uptake study was carried out. Figure 2 shows the uptake of dye for time intervals ranging from 0 to 180 min. It can be seen that the equilibrium is reached after 3 h. Figure 2 also shows the effect of initial dye concentration on uptake of dyes. The dye concentration was varied from 50 to 400 mg/L. It can be seen from the figure that there is more uptake of dye at high initial concentration as against low initial concentration. This increase in uptake could be attributed to the fact that higher initial concentration provides an important driving force to overcome all mass transfer resistances of the dye

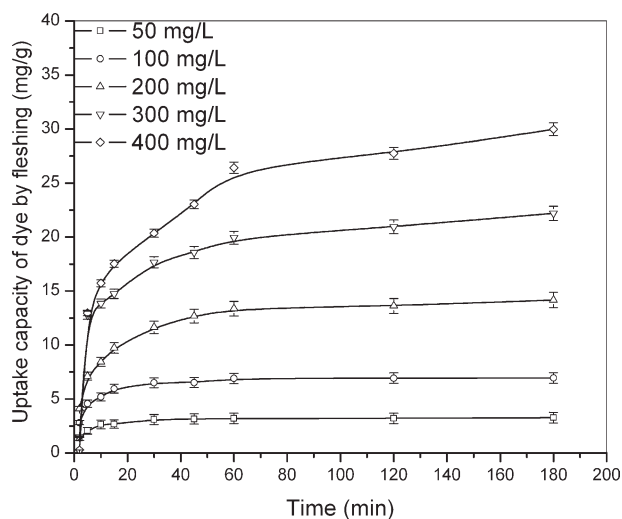


Figure 2 Effect if initial concentration of dye on uptake of dye at 12 g/L dosage of fleshing.

between the aqueous and the solid phases, thus increasing the uptake. In addition, increasing initial dye concentration increases number of collisions between dye anions and sorbent, this enhances the sorption process. The uptake increased from 3.3 to 30 mg/g when the initial concentration increased from 50 to 400 mg/L with an adsorbent dose of 12 g/L.

Effect of adsorbent dosage

The amount of adsorbent used influences the uptake of dyes. Hence, experiments varying the adsorbent dosage were carried out. The effect of adsorbent dosage on the dye uptake capacity of fleshing and % removal of dye is given in Figure 3. It is observed from the figure that the percentage reduction of dye

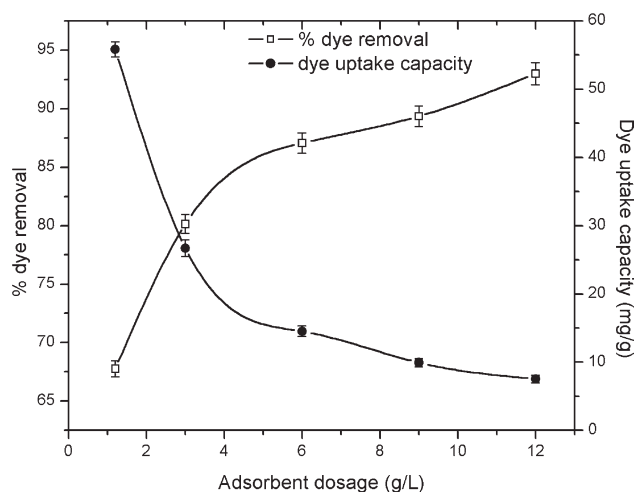


Figure 3 Effect of quantity of aldehyde-treated fleshing on dye uptake capacity % dye removal at an initial concentration of 100 mg/L of dye.

increased from 67 to $93.01\% \pm 0.94\%$ on increasing the initial dosage of glutaraldehyde-treated fleshing from 1.2 to 12 g/L. With an adsorbent dosage of 12 g/L and a dye concentration of 100 mg/L, the maximum uptake capacity was found to be about 7.53 ± 0.58 mg/g. The decrease in uptake capacity may be due to splitting effect of concentration gradient between sorbate and sorbent with increasing fleshing concentration causing a decrease in amount of dye adsorbed on to unit weight of fleshing. On the other hand, an increase in % removal of dye has been observed for increase in fleshing dosage. This could be due to the fact that as the adsorbent dosage is increased, more biosorption sites are available for the dye, enhancing the uptake.

Adsorption isotherm studies

The experimental data obtained have been analyzed using Freundlich and Langmuir isotherm. The Freundlich isotherm assumes that the adsorbent consists of a heterogeneous surface composed of different classes of adsorption sites. The Freundlich constants n and k were obtained from the linear regression analysis of the equation

$$\log q_e = \log k + 1/n \log C_e \quad (1)$$

where q is the maximum uptake capacity (mg/g) and C_e is the equilibrium concentration of dye (mg/L). Plot of $\log q$ vs. $\log C_e$ should give a straight line with a slope of $1/n$ and an intercept of $\log k$.

The Langmuir adsorption isotherm model assumes that the adsorbed layer will be only one molecule thick. The Langmuir model is given as,

$$q = b q_o C_e / 1 + b C_e \quad (2)$$

where, q_o is adsorption capacity (mg/g) and b is energy of adsorption (L/mg). The maximum sorption capacity is useful tool in accessing the uptake capacity of a given sorbent. Langmuir constants q_o and b can be determined from the linear plot of C_e/q vs. C_e which has a slope of $1/q_o$ and intercept of $1/q_o b$.

For both Freundlich and Langmuir isotherm models, a linear relation has been observed among the plotted parameters at 12 g/L of the adsorbents. The calculated isotherm constants for the adsorption of dye by glutaraldehyde-crosslinked fleshing have been provided in Table I. The value of Freundlich constant $1/n$ has been observed to be 0.343. " n " value, which is related to the distribution of bonded ions on the sorbent surface, is greater than unity, indicating that dyes are favorably, adsorbed under all the examined experimental conditions. The value of " n " between 1 and 10 also represents beneficial adsorption. Based on the observed low-adsorption

TABLE I
Isotherm constants for the adsorption of dye by glutaraldehydecrosslinked fleshing

| Freundlich constants | | | Langmuir constants | | |
|----------------------|-------|-------|--------------------|------------|-------|
| k_f | $1/n$ | R^2 | q_o (mg/g) | b (L/mg) | R^2 |
| 10.74 | 0.343 | 0.884 | 70 | 0.032 | 0.993 |

intensity values ($1/n < 1$), it can be said that the glutaraldehyde-crosslinked fleshing has identical adsorption energy in all sites and the adsorbed dye interacts only with the active site but not with other sites. It can also be said that as $1/n$ value of glutaraldehyde-crosslinked fleshing is less than 1, chemical rather than physical adsorption seems to be dominant. Thus, it is very clear that fleshing have good affinity for the dye. This result was also confirmed by the higher k value. The sorption capacity (q_o) and the energy of adsorption (b) for fleshing have been calculated as 70 mg/g and 0.032 L/mg, respectively using Langmuir isotherm equation. Although the plots of Freundlich and Langmuir isotherms for the adsorption of dye onto glutaraldehyde-treated fleshing appeared linear (Figures not shown), the correlation coefficient for Freundlich model (0.884) is lower than that of Langmuir model (0.993). The best fit of equilibrium data in Langmuir isotherm expression confirm monolayer adsorption of dye onto glutaraldehyde-crosslinked fleshing. The fact that the Langmuir isotherm fits the experimental data very well may be due to homogenous distribution of active sites on the surface of glutaraldehyde-crosslinked fleshing; since the Langmuir equation assumes that the surface is homogenous.

Effect of neutral salts

The role of neutral salts on the uptake of dye was studied, and the same is given in Figure 4. It is clearly observed that the dye uptake capacity of the fleshing has been slightly affected by the addition of neutral salt. The uptake capacity decreased from 7.85 mg/g to 6.96 and 7.21 mg/g when 0.5M of sodium chloride and sodium formate were added. This uptake capacity reached 6.53 and 6.94, mg/g, respectively, when 1.5M of sodium chloride and sodium formate were added. It has earlier been reported by Niu and Volesky that a decrease in sorption with increase in ionic strength is possible if the sorption process involved electrostatic attraction between the sorbent and the sorbate.¹⁶ The increased amount of electrolyte swamps the sorbent surface, decreasing the interaction of dyes to the surface for sorption, and therefore, the dye sorbed may be significantly decreased. Thus, the decreased uptake of dye by glutataldehyde-treated fleshing in the presence of neutral salts could be due to the masking of the surface of the fleshing by excess neutral salts. This is further substantiated by the subsequent

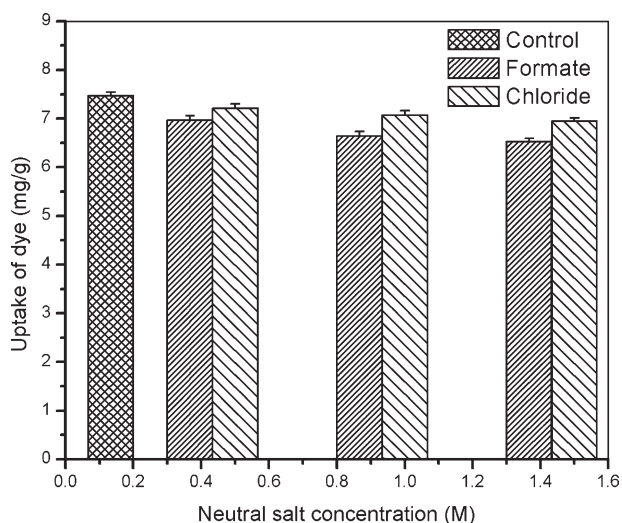


Figure 4 Effect of various concentrations of formate and chloride ions in % dye removal from 50 mg/L of dye solution using 12 g/L of fleshing.

present could compete for the same available sites. Wastewater from a sectional stream using acid blue 113 dye was collected from a tannery. The concentration of dye in the wastewater was estimated to be around 200 ppm. The optimized parameters from batch experiments viz. 12 g/L of fleshing, pH 5.0 were used for the treatment of commercial wastewater. The % reduction of dye from the commercial wastewater was found to be 87% when compared with 90% dye reduction in the case of synthetic dye solution under optimum conditions. From the results, it could be seen that the % reduction of dye has not been significantly affected. This result is in concurrence with the results from studies in the presence of neutral salts. The slight reduction in the uptake could be attributed to the presence of neutral salts and other constituents in the commercial wastewater. Also, the uptake of dye from the commercial wastewater was found to be 14.16 mg/g for 12 g/L of the adsorbent.

reduction in the dye uptake capacity with increasing neutral salt concentration.

Experiment with commercial wastewater

To study the potential of the prepared adsorbent on the removal of dyes from real world wastewaters, studies using commercial wastewater from a tannery were carried out. This study is essential as it would throw light on the feasibility of the stabilized fleshing to perform in conditions where other chemicals (syntans and fatliquors used in leather manufacture)

Utilization of dye-loaded adsorbent

The aforementioned studies prove the efficiency of fleshing as a potential adsorbent for dye removal from wastewaters. However, the disposal of dye-loaded fleshing poses a similar solid waste disposal challenge. And hence, unless a solution is presented to the disposal of dye-loaded fleshing, this method will not be practicable. In this study, the dye-loaded adsorbent has been used as a reducing agent in the manufacture of a tanning salt, basic chromium sulfate (BCS), which is the most widely used tanning

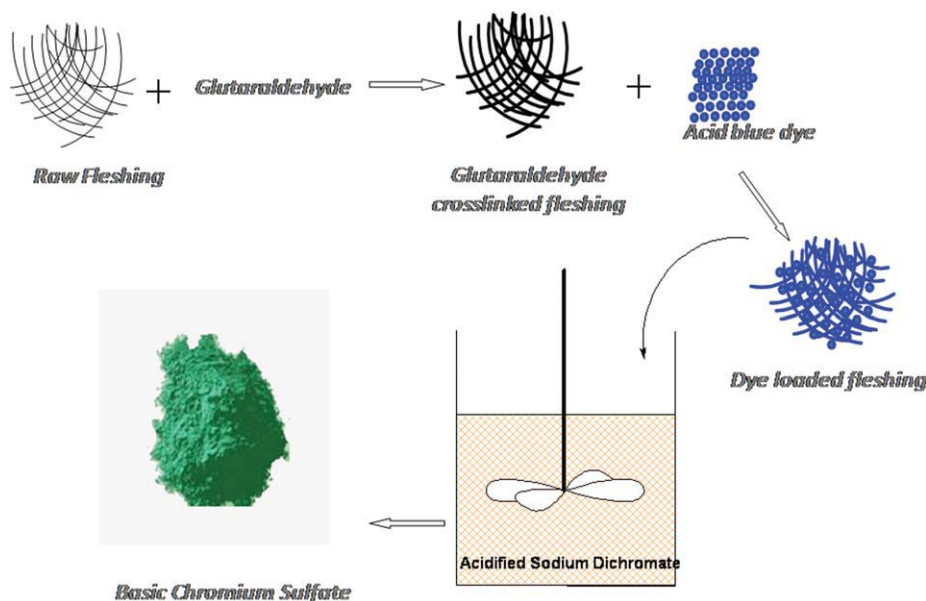


Figure 5 Scheme showing various steps involved in the use of raw fleshing for the removal of acid blue dye from aqueous solution and the utilization of same for the preparation of basic chromium sulfate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

agent in leather industry. The scheme showing the utilization of raw fleshing for the adsorption of dye from aqueous solution and using the same for the preparation of basic chromium sulfate is depicted in Figure 5. Three trials were carried out with varying dichromate to adsorbent ratios viz. 1 : 0.7, 1 : 1, and 1 : 2. As complete reduction of chromium was observed with all three ratios, the lower ratio of 1 : 0.7 (dichromate:adsorbent) was chosen. The pH of the prepared BCS was adjusted to 2.8 to 3.0 using sodium carbonate and tanning experiments were carried out. The chrome content of the fleshing-reduced BCS was estimated to be 21%. The shrinkage temperature of leathers is found to be above 110°C. There is slight increase in the exhaustion of chromium in the case of fleshing-reduced BCS when compared with control at similar offer of metal oxide. The chromic oxide content in the wet blue leathers is in the range of $2.85 \pm 0.5\%$. The color of the wet blue made from fleshing-reduced BCS is comparable to commercial tanned leathers. This shows that the dye-loaded adsorbent could be effectively reused in the same industry.

CONCLUSIONS

This investigation explored the potential of glutaraldehyde-crosslinked fleshing as an adsorbent for removal of dyes from colored wastewater. Various parameters required for maximum removal efficiency have been optimized. The adsorption isotherm studies reveal that dye removal using fleshing follows Langmuir type of adsorption. The efficiency of fleshing for dye removal in real life conditions has been

tested by carrying out trails on commercial wastewaters. Also, the disposal problem related to the dye-loaded adsorbent has been tackled by using it as a reductant in manufacture of a tanning salt. Thus, this study offers glutaraldehyde-crosslinked fleshing as a potential adsorbent for removal of dyes.

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