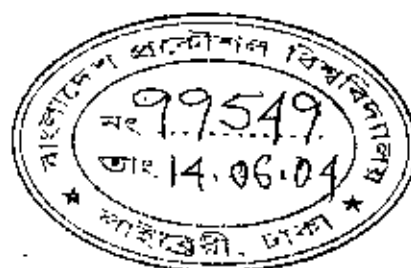


**Design and Fabrication of Column  
Filtration Reactor for the Removal of  
Dissolved Dyes from Tannery  
Wastewater**

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**A Project Thesis**

**By**

**Muhammad Bozlur Rahman**

**Department of Industrial & Production Engineering  
Bangladesh University of Engineering & Technology  
Dhaka-1000**



**June, 2004**

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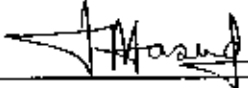

Submitted to the Department of Industrial & Production  
Engineering, Bangladesh University of Engineering & Technology,  
Dhaka, in partial fulfillment of the requirements for the degree of  
**MASTER OF ENGINEERING** in Industrial & Production  
Engineering.

**Department of Industrial & Production Engineering  
Bangladesh University of Engineering & Technology  
Dhaka-1000**

**June, 2004**

The thesis titled **Design and Fabrication of Column Filtration Reactor for the Removal of Dissolved Dyes from Tannery Wastewater**, submitted by Muhammad Bozlur Rahman, Roll No. 040208019F, session April 2002, has been accepted as satisfactory in partial fulfillment of the requirement for the degree of **MASTER OF INDUSTRIAL & PRODUCTION ENGINEERING** on June 6, 2004.

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## **Declaration**

I do hereby declare that this work has been done by me and neither this thesis nor any part of it has been submitted elsewhere for the award of any degree or diploma except for publication.

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June, 2004

Author

## **Abstract**

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The presence of color in many industry effluent streams is esthetically undesirable. Color organic effluent produced in the textile, paper, plastic, leather, food and mineral processing industries are high volume, hazardous and toxic waste. Color removal requires five to twelve times the concentration of dye that is normally used for flocculation, making it an expensive and inefficient process. Thus there is a clear need for more cost effective and environmentally friendly processes for removal of color from wastewater.

Adsorption techniques have proven successful in removing colored organic compounds. Saw dust is an excellent low cost adsorbent of colored organic anions and may have significant potential as a color removal from tannery wastewater. As a result, sawdust is now being considered as low cost adsorption alternatives because they are easily prepared and found every where. Acid activated sawdust (ACSD) was prepared from dried sawdust with concentrated HCL that can be easily synthesized by co-precipitation of dilute aqueous solutions of dyes. The effectiveness of acid activated sawdust in absorbing Lurazol Brown PH (LBP) dye from aqueous solutions has been studied as a function of agitation time, adsorbent dosage and initial dye concentration. The rate constants were calculated using Lagergren equation and found to be 0.01512, 0.02003 and 0.02217 for initial concentrations 100, 300 and 500 mg/l. The experimental data were also fitted to Langmuir and Frundlich isotherm and found that adsorption process follows both the isotherm. The values of Langmuir and Frundlich constants indicate favorable and beneficial adsorption.

# **Contents**

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Acknowledgements	v
Abstract	vi
Contents	vii
List of Figures	viii
List of Tables	ix
<b>Chapter-1 Introduction</b>	<b>1</b>
1.1 Leather Tanning & Finishing Operation	3
1.1.1 Pre-Tanning Operations	5
1.1.2 Post-Tanning Operations	11
1.1.2.1 Crusting Operations	11
1.1.2.2 Finishing Operations	17
1.1.2.3 Coating	19
1.2 The Effluent of Different Stages and Bangladesh Context	23
1.3 The Dyes and Dyeing of Leather	28
1.4 Environmental Problems	31
1.5 Objectives of the Present Work	34
<b>Chapter-2 Experimental Investigation and Procedure</b>	<b>35</b>
<b>Chapter-3 Results and Discussions</b>	<b>44</b>
<b>Chapter-4 Conclusions</b>	<b>61</b>
<b>Chapter-5 References</b>	<b>64</b>

## ***List of Figures***

---

<b>Figure 1.1</b>	Soaking Operation	7
<b>Figure 1.2</b>	Un-hairing Operation	7
<b>Figure 1.3</b>	Baling Operation	9
<b>Figure 1.4</b>	Splitting Operation	12
<b>Figure 1.5</b>	Retanning Operation (Neutralization Operation)	13
<b>Figure 1.6</b>	Drying Operation	13
<b>Figure 1.7</b>	Buffing Operation	19
<b>Figure 1.8</b>	Residues of dyestuffs and large quantities of auxiliary chemicals	24
<b>Figure 1.9</b>	Rest treated hides and skins are cooked in open air to obtain glue for the local market	26
<b>Figure 1.10</b>	Schematic diagram of tanning operations	27
<b>Figure 2.1</b>	Photographic view of acidify of sawdust with magnetic stirrer	36
<b>Figure 2.2</b>	Sample of filtered solution	39
<b>Figure 2.3</b>	Photographic view of centrifugal machine used to remove the suspended particles from the solution	40
<b>Figure 2.4</b>	Photographic view of Spectrophotometer used for monitoring absorbance	40



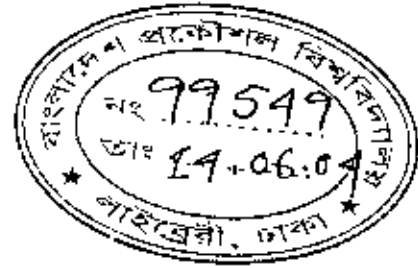
<b>Figure 2.5</b>	Photographic view of the experimental set up for removal of dyes from wastewater by two stages	42
<b>Figure 3.1</b>	Schematic diagram of a simple spectrophotometer $P_0$ is the power of the radiation entering the sample cell and $P$ is the transmitted power	46
<b>Figure 3.2</b>	UV-Vis Spectrum of Lurazol Brown PH at different concentrations ( $\lambda_{max} = 443$ nm)	47
<b>Figure 3.3</b>	Adsorption calibration curve for Lurazol Brown PH	49
<b>Figure 3.4</b>	Rate of dye sorption by sawdust at 25 <sup>o</sup> C	50
<b>Figure 3.5</b>	Amount of dye sorption by sawdust at equilibrium	51
<b>Figure 3.6</b>	Plot for Lagergren rate constant for adsorption of Lurazol Brown pH dye by sawdust	52
<b>Figure 3.7</b>	Variation of rate constant ( $k_1$ ) with initial Concentration	53
<b>Figure 3.8</b>	Rate of dye uptake by sawdust	54
<b>Figure 3.9</b>	Langmuir plot for Lurazol brown pH adsorption by sawdust	56
<b>Figure 3.10</b>	Freundlich plot for the adsorption of Lurazol Brown pH by sawdust	57
<b>Figure 3.11</b>	Enhancement of dye removal by two-step column filtration system	58
<b>Figure 3.12</b>	Left: treated raw water; Right untreated raw water	60

## ***List of Tables***

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<b>Table-1.1</b>	Common acid dyes and their color in water	23
<b>Table-3.1</b>	Concentration vs. absorbance of Lurazol Brown PH at $\lambda_{\text{max}} = 443 \text{ nm}$	48
<b>Table-3.2</b>	Characteristics of Lurazol Brown PH	48
<b>Table-3.3</b>	Variation of rate constant with initial concentration	52
<b>Table-3.4</b>	Variation of $R_L$ with initial concentrations	56
<b>Table-3.5</b>	Shape of the isotherm with respect to $R_L$	56
<b>Table-3.6</b>	Equilibrium concentration in stage filtration system	59

# Chapter-1



## ***Introduction***

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Leather industry in Bangladesh is a highly potential sector. But this could not prosper much because of proper planning and patronization. Its history and background is vast and vivid what intended to be explained here in brief and attempts have also been made to explain how leather industry of Bangladesh has developed in the post liberation period.

In the pre liberation period the Bangladesh tannery owners mainly sold their home made leather to non-locals for various reason. But after liberation around later part of 1972 the Bangladesh entrepreneurs organized themselves and started wet blue export on co-operative basis. This leather industry was in fact the first foreign exchange earner sector for the newly born Bangladesh. The entrepreneurs of this tanning sector faced lot of complications while exporting wet blue of international standard. They didn't have proper technological and infrastructure support to meet the demand of international market. Yet they continued their wet blue / export ignoring the odds they were facing and saved the way for earning more foreign exchange from easily decomposable raw hides and skins. In the year 1974-75 the

government first introduced duty draw back system to encourage the exporters and this was a positive step towards export earning. Our leather in the meantime became popular in the world market. But unfortunately the duty draw back system for wet blue export did not last long. The government in 1976-77 had withdrawn the system from wet blue export and imposed 15% custom duty thereon which was subsequently reduced to 10%.

Leather is produced from skins of different types of wild and domestic animals. The structure of the skin is based on interlaced bundles of micelles and fibrils, the collagen. Respectively, three peptide-chains form a triple alpha-helix structure. Five of them form microfibril units, which in turn form higher fibric structures. These structures are stabilized internally and laterally (cross linked) by hydrogen bonds between the peptide groups of the amino acids. In the tanning process substances like chromium sulphate, alum or vegetable tanning agents replace the hydrogen bonds. Leather production belongs to the natural product industry. It comprises:

- Tanning of the skin to stabilize the material against microbial proteolytic enzymes in the wet environment, prevention of fracture in the dry environment and of gluing in hot surrounding.
- Giving properties and fashion effects to the leather, which are requested, by the market.

Production of leather goods is characterized by intermittent mechanical and chemical (batch) treatments, often high in number. Depending on the desired

type of the final product the hides undergo a wide variety of processing steps. The wastewaters arising from the individual steps are sometimes separately pre-treated, but in most cases are mixed before discharge in order to make use both of dilution and neutralization effects.

In leather processing, the animals are slaughtered in butcher shops then flayed to hides and skins to reach the tannery. By using chrome tanning, the following processes are used to get finished leather from animals.

**Animal**→Slaughtering→Flaying→Curing→Soaking→Liming→Un-hairing→Fleshing→Deliming→Bating→Pickling→Chrome-tanning→Basicification→Sammying→Splitting→Shaving→Washing&Neutralization→Retanning, fatliquoring & dyeing→Setting→Vacuum-drying→Drying & moistening→Vibration-staking→Toggle-drying→Buffing (if necessary)→Polishing (if necessary)→Finishing-coats→Hydraulic-pressing→Ironing & embossing→Measuring→**Finished leather**

## **1.1 Leather Tanning & Finishing Operations**

Bangladesh is a country of cultivation. She grows a lot of animals likes cow, buffalo, goat, sheep etc from which huge quantities of hides and skins are obtained and then raw hides and skins are turned into leather by tanning. Without tanning it cannot be used, because very soon raw hides and skins are started to putrefy. If the raw hides and skins are dried by means of any

process, it lost its flexibility and softness and became very hard and brittle, which cannot be used in any application. To overcome these problems, raw hides and skins are tanned. Tanned leather does not putrefy. Even after drying and wetting. It does not become hard and brittle, but remains flexible and workable in all respects.

Tanning may be of different types like vegetable tans, mineral tans, synthetic tans, etc. Their applications depend on the types of hides and skins and the requirements on the production of quality leather. Most of the heavy-duty machinery used in the tanneries is operated with hydraulic system. Medium and small duty machinery are operated with pneumatic system. Some machinery is also operated with both the hydraulic and pneumatic system or in combine. The controlling systems of these machinery are either electrical or electronics or both the electrical-electronics in combine. Electric power is supplied to this machinery from an A.C source. Inverter is used to some machinery to control the rotations.

For the production of quality leather accurate pH value and concentration of chemicals for different operations of every stage of a complete operation must be maintained. Exact rotation of machine element and appropriate temperature and pressure of the chemicals using in different operations must be controlled to get the desired production. Safety control for all stage or every section of a complete operation must be maintained. Appropriate plant layout, factory layout, machine layout must be followed during the construction of factory building and installation of machinery. Proper motion

study, work-study and time study must be applied in every stage of production. Taking proper statistical report from man, materials, machines, power supply, transportation, etc a resultant methodical specific production schedule should make, which will yield the smooth and continuous production of quality leather in time. So, proper ergonomic study and its controls is a must for quality production.

In the tanneries, the raw materials go through different chemical and mechanical operations and finally come out as finished leathers. Tannery operations can be broadly divided into three categories, which are illustrated in the following headings.

### **1.1.1 Pre-Tanning Operations**

Tanning may be performed in many ways, like vegetable tans, chrome tans, oil tans, etc. The pre-tanning operations of different tans are not similar but vary a little bit. The pre-tanning operations (in a normal sequence) are discussed in the following ways [1-3].

**Flaying:** This is known as removing the skin or hide from the animal. Proper methods and more attention should be given in this operation. The animal should be in a clean, dung-free, healthy condition and the slaughter rapid and efficient. Bruising should be avoided. It is then bled to remove blood from the carcass and also from the small arteries and veins of the skin. If this is not done quickly, the blood clots therein, readily putrefies, giving rise to

blue-black markings in the skin and areas of putrefaction in these regions. It is usual to hang the beast up by the hind shanks on a transporter rail for this purpose.

**Curing:** It is a temporary preservation of hides and skins during transportation or storage. It is not always possible to send the hides and skins during transportation or storage. It not always possible to send the hides and skins to tanneries immediately after flaying because the source of collection and the tanneries are not generally located in the same area. The time gap between the flaying operation and the start of tanning operations vary from one or two months. If hides and skins are not cured just after flaying, they get completely putrefied within 2/3 days. Curing may be done in many ways like curing by controlling temperature, pH value, using toxic materials, sun drying, salting-wet salting, brining and dry salting, etc.

**Soaking:** Soaking is a treatment with water to restore 'cured' hides and skins to a natural raw condition. This is actually the first tannery operation. During curing hides and skins lose large quantity of its physiological content of water and unless the former regains this water during soaking operation good quality leather cannot be produced. Fig.1.1 shows the soaking operation [4].

**Unhairing:** This part is conventionally done in liming operation. Additional unhairing process (Fig.1.2) likes like sweating, enzymeing, painting or using in an unhairing machine also do unhairing. In this operation, the hides and



skins are treated with milk of lime with the addition of sharpening agents like sulfide, etc. The objects of this operation are mainly to,

- remove the hairs, nails, hooves, and other keratinous matters
- remove natural grease and fat
- swell up and to split up the fibers to desired extent and
- bring the collagen to a proper condition for satisfactory tanning.



Fig.1.1 Soaking operation [4]

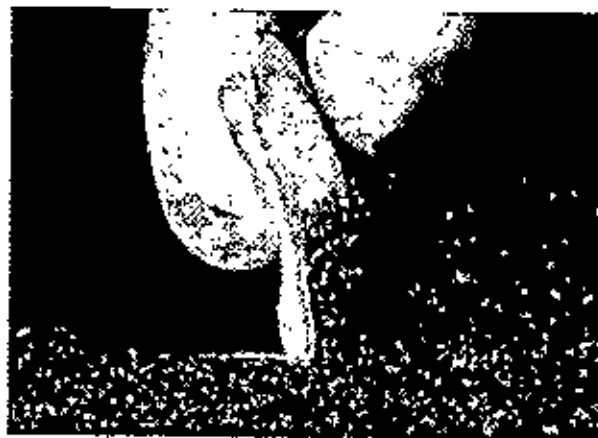


Fig. 1.2 Unhairing operation [6]

**Fleshing:** This is the next operation where unwanted fat and flesh from the hides and skins are cut away. This operation may be done by hand with the help of a knife or using a rubber roll fleshing machine. After liming the unhaired and fleshed hides and skins are known as pelts.

**Deliming:** Pelts are taken for the next operation called deliming. The object of deliming is to remove lime and other alkalis from the limed pelt by chemical treatment. The removal of alkalis from the pelts before tanning is important and essential for the production of good quality leather.

**Bating:** Limed and partially delimed pelts sometimes required additional treatment known as bating as shown in Fig.1.3. According to the class of leather it is intended to make. In this operation pelts are treated with a solution of proteolytic enzymes derived from different sources. The hides or skins are delimed to a pH of 8.0-8.5 and washed. This is the degree of alkalinity at which most enzymes show greatest digestive power. The goods are then usually padded or drummed in 300-500% water at 37°C with a 1-2% addition of the powdered enzyme mixture. It is important to maintain the pH and temperature accurately, as slight variations give a great loss of bating power. During bating operation of different classes of leathers temperature, duration of bating, strength and pH value of bating liquor must be considered as important factors for the production of quality leather.



Fig.1.3 Bating operation [7]

**Pickling:** The use of liquors containing acid and salt is referred to as pickling, which is commonly carried out in the usual wooden paddles and drums or processors. The salt stage of pre-tanning operation is the Pickling. In this operation delimed or bated pelts are again treated with a solution of acid and salt. This is the most important and essential operation, which bring the hides of skins to the right acidity for the next operation tanning.

**Tanning:** The tanning process converts the protein of the rawhide or skin into a stable material, which will not putrefy and is suitable for a wide variety of purposes. There is a vast array of tanning methods and materials and the choice depends chiefly on the properties required in the finished leather, the cost of the alternative materials depends on the plant available, and the type of raw material. Tanning may be done in many ways like mineral tanning (Chrome tanning, Alum tanning, Iron tanning, Zirconium tanning etc.), Non-mineral tanning (Aldehyde tanning, Oil tanning, Resin tanning, Synthetic tanning, Combination tanning etc. actually). Tanning is a best technology, on

which the quality leather productions are widely depended. During tanning the  $p^H$  value, concentration and temperature of using chemical or its mixture must be seriously controlled. But to get the leather of good quality chrome and vegetable (as used in large scale) tanning materials are not sufficient such as chrome tanning materials can produce leather shrinkage temperature but not the fullness of leather. On the other hand, vegetable tanning materials produce leather with good fullness handle and excellent buffing property but at the cost of grain tightness, light & colorfastness and elasticity. In this operation proper penetration of tanning materials,  $P^H$  Value and fixation or basification is maintained.

**Wet-blue:** Freshly tanned chrome leather which has not been dried out, etc., is referred to as being "in the blue" (from the color, which goes much paler on drying). It is very important to remember that all blue leather develops acidity on standing or ageing.

Blue chrome leather has a very strong affinity for many dyes, fat-liquors and vegetable tans, but this becomes much less after drying, owing to changes which occur in the chrome sulphate complex during drying or ageing.

## 1.1.2 Post-Tanning Operations

Post tanning operations may be divided into two major classes like crusting operations and finishing operations, which are illustrated in the following ways.

### 1.1.2.1 Crusting Operations

**Sammying:** The next operation is sammying where excess water is removed from the hides and skins, passing through the roller of the hydraulic or mechanical operated sammying machine. Setting out—where wrinkles are removed and flatten the leather. Oiling—where, to make the leather grains flexible and have good color.

**Splitting:** In splitting operation (Fig.1.4) the leather may be split into different layers (If the hide or skin is thick enough e.g. 3mm may be split into two layers—a grain layer of 2mm and a flesh layer of 1mm.). The band knife splitting machine is almost universally used today.

**Shaving:** Shaving operation makes even thickness from the uneven thickness of hides or skins. The quality of finished leather depends to a great extend on the degree of uniformity in shaving. If the thickness of the leather is not uniform throughout the area; the mechanical effects during finishing operation like staking, glazing, ironing pressing etc. will be non—uniform on

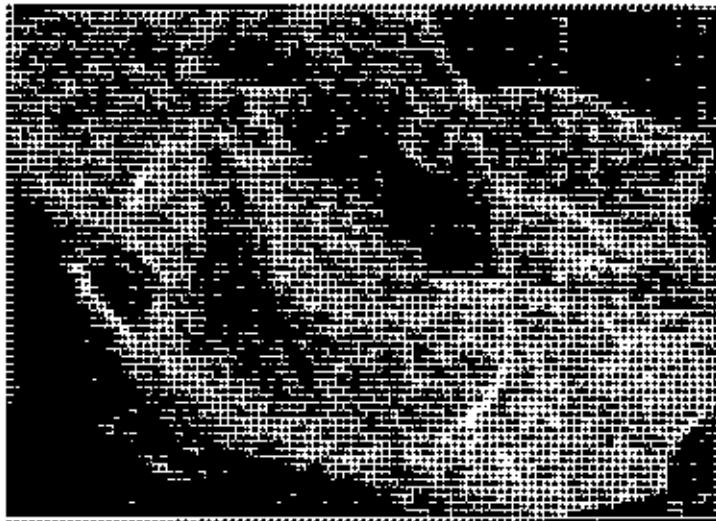
the leather surface and the total absorption of season by different portions of the leather surface will be different



**Fig.1.4** Splitting operation [8]

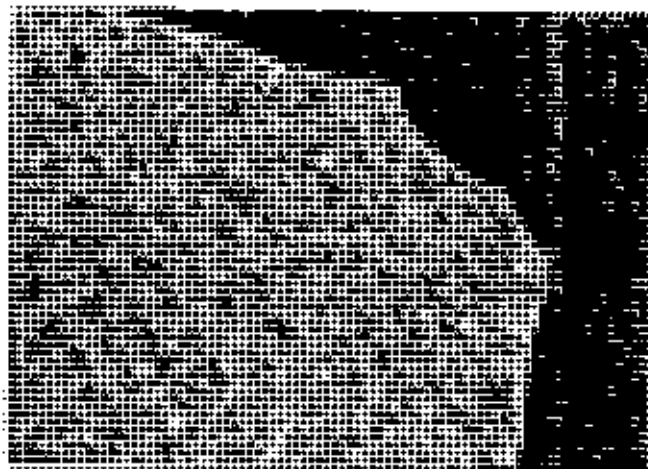
**Washing and Neutralization:** This is a tanning step (Fig.1.5). The pH is raised 4.0 to 6.5 by removing free acids that are present in the wet blue. This step determines many of the properties of the leather when processing is ended. Vegetable extracts and syntans can be added to give the leather its desired feel when made into the final product. Retanning can make the leather softer or firmer.

**Sammying-Setting:** In this operation where the rollers of this machine compressed the leather and make it firm and flat. Sometimes sammying and Setting are done together in a single machine.



**Fig.1.5** Neutralization operation [7]

**Drying:** The final step of crusting operation is drying (as shown in Fig.1.6). Drying of leather means removal of water from settled leather by thermal means at a temperature far below the boiling point of water. It may broadly be classified into two categories like (i) evaporating (vacuum) drying and (ii) convective drying (tunnel drying).



**Fig.1.6** Drying operation [8]

**Vacuum Drying:** The normal atmosphere exerts a pressure of about 14 lb per square inch when water boils at 100°C. If the pressure is reduced the boiling point and can be evaporated more easily and quickly in a vacuum. Here vacuum pressure created is 53 mm of mercury. At this low pressure the water in the leather readily evaporates with the heat, and the water vapour is sucked through the porous felt into the vacuum systems. Here drying may be completed in two or three minutes, when the vacuum is stopped, and the head assembly rose usually by a preset time switch. The evaporative temperature would be 70-80°C. In case of evaporating drying leathers are kept in a leak proof closed room and the air pressure of the room is reduced by means of pumping to maintained a certain negative pressure (vacuum). For creating vacuum in the room boiling temperature of water remains in leather reduced and evaporated from its surface; Vacuum dryer works on this principle. Besides this, some alternative methods of drying like radiant heat drying, high frequency drying, heat pump drying, fluid bed drying, high velocity air drying, solve drying, etc are used in different cases.

**Tunnel Drying:** In convection drying, leathers are hanged in a room and the air temperature of the room is always maintained at a certain degree higher than the temperature of the leather by means of ventilating fans or opening louvers Tunnel drying. Where the only control on a drying plant is the dry bulb temperature of the inlet air, it is often found that the drying is faster, or the leather drier, in winter, with cold external air may be 30°C and either 25% RH or 90% RH giving either very good drying or very poor drying.



During drying, the leather tends to shrink in area, particularly after the water content has dropped below about 25%, and these shrinkage forces can be quite strong. Vegetable-tanned leather usually shrinks less than the other types. Normally, higher drying temperatures produce greater shrinkage and crust leather. If temperatures on the wet leather are too high, they can cause "burning" or permanent shrinkage to a hard, cracky state. Vegetable-tanned leather is usually dried below 50° C, chrome leather below 70° C and chamois below 45° C.

**Vibration-Staking:** vibration-staking is the softening operation, which jacks the leather flex and soften in many ways like hand staking, using slocomb staking machine, Svit Molissa system, Vibrating Staking, etc. This system is the pummeling and flexing action of a series of tools, which vibrate vertically against the horizontal skin. The skin is conveyed through the system by laying it (sandwich-wise) between the upper and lower elastic conveyor bands. The speed of throughput can be controlled by the speed of these conveyors. The vibrating tools then act externally on the conveyor bands holding the skin between them. The pressure and working action of the tools can be adjusted to suit different skins and even different parts of skins (e.g. differences between flank and backbone). Once the machine has been adjusted it is capable of a very high output with unskilled labor.

A variation of this vibrates the tools horizontally as well as vertically, giving a more vigorous two dimensional action less prone to leaving small round tool

marks on the leather. Care must be taken in adjustment to avoid excessive wear in the expensive transport bands.

**Toggle Drying:** After staking the leather is dried under stretched condition, so that the fiber bundles, which have been separated from each other by staking, may not stick together again. It is done by toggle dryer. The simplest method is to set out the skin well and then nail it out flat on boards. This enables it to be stretched out and the shape adjusted to some extent. It gives flat leather but there is a tendency for shrinkage strains to make the skin thinner and harder and to distort or weaken the looser flank areas. It is commonly used for vegetable-tanned light leathers and skivers. Drying tends to be slow and limited to one side, the board inhibiting drying on the other side. Toggling is similar in principle but the wooden board is replaced by toggling frames, either of heavy gauge wire meshes or perforated metal. Toggles hold the skin which "spring clip" on to the skin and peg into the holes in the frames.

A major merit of tension drying systems is that the leather can be stretched out to give maximum area yield, which is the basis on which most leathers are sold. Tension drying can, in some cases, increase the area by 15%. Errors in judging the amount of tension needed, without losing handle, etc., are of prime financial importance. A significant factor can be the loss of area caused by the necessity to trim off the toggle or nail marked areas of the leather.

**Jaw Staking:** This operation is done on some special cases. This machine flexes and softens the skin of leather. The two jaw arms open as the crank moves them forward. The skin is laid between them and is held by the clamp against the clamping bar. In some designs of this machine is omitted and the operator holds the skin against a bolster bar with his body. On the outward stroke the arms close and the skin is trapped between the roller on the top jaw and the blades on the bottom jaw. As the arms move back, the skin is stretched and flexed at an acute angle over these blades. The degree of staking given may be increased by depressing treadle, which raises the bottom arm and jaw. This machine can give a very vigorous softening action. It requires skill to get the best results, e.g to avoid pleating, tearing or bagging and is more commonly used for the softer types of mineral tannage, e.g. glace kid and, particularly, gloving leather.

### 1.1.2.2 Finishing Operations

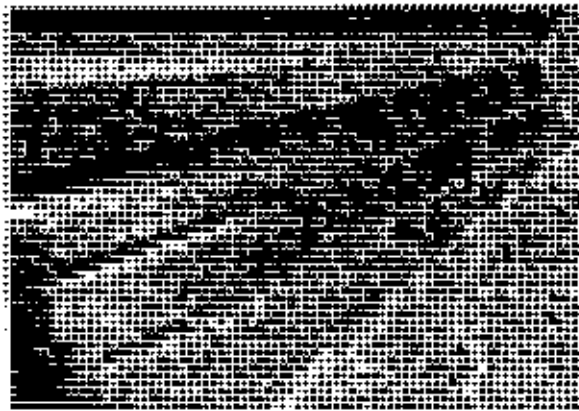
Finishing operation of leather are performed in many ways and varied on different factors like types of leather, requirement of the leather goods, etc. The most common finishing operations are illustrated below.

**Finishing or Seasoning:** This is the operation, which improves the appearance of the leather surface. In many cases a transparent film or coating may be applied which modifies the skin. The mixture of water with a very small amount of egg albumen, lined mucilage or cellulose ethers abate

most common seasoning solutions. The other seasoning additives are oil addition, wax, etc.

**Buffing:** Buffing is the best operation, which consists of grinding the leather surface with an abrasive, and is akin to sandpapering which is shown in Fig.1.7. It is used on the grain to remove surface blemishes and thus provide a more uniform surface, to which pigment and other finishers can be applied. It may be performed using a number of machines like throat type buffing machine, lightening type-buffing machine etc.

The buffing cylinder is of metal about 7-9 inches diameter and may be of various widths from 10-24 inches. It rotates at about 1000 rpm. In case of all buffing machines the surface of the cylinder is covered with buffing paper (coated with abrasive grit) clamped tightly and uniformly in position. It is important to keep the paper free from accumulations of leather buffing dust. A revolving brush below the cylinder does this. The cylinder is encased and a fan draws a strong blast of air past it, carrying the dust along ducting to a dust collecting system. In most cases the rotating cylinder is also given a small, sideways, oscillating movement to prevent long scratch lines being formed on the nap. Normal Swedes are buffed on the flesh side, while Ooze and Nubuck or velvet Swedes are buffed on the grain side with finer papers. "Snuffing" is a term, which denotes finer buffing on the grain side, while "fluffing" denotes removal of surplus flesh. For coarse, heavy work buffing papers of 80 grit sizes are used. 220 or 320 are common for shoe Swedes, whilst 400 is for the finest work.



**Fig.1.7** Buffing operation [6]

**Polishing:** Polishing is used to polish the surface of the leather before and after spraying of pigments as necessary. Here a roller and polishing brush rotary type.

### **1.1.2.3 Coating**

Coating is done by three methods like; pad coating, spray coating and curtain coating Pad coating and spray coating are generally used in combination with one another; whereas recently developed curtain coating is an independent system, which is suitable in a tannery where daily production is very high.

**Spraying:** In this technique the season or finish solution is fed to a spray gun by gravity or compressed air where it is ejected from a fine nozzle or orifice by pressure as a spray of fine atomized droplets which are blown onto the leather surface. Spraying are two types like hand-spray and rotary spray

**Hand spraying:** Hand-spraying is the operation used for small-scale production. It is desirable that these droplets should then flow together to give a continuous wet film on the leather before drying. Failure to flow out may result in poor anchorage, poor rub-fastness, and loss of gloss, poor film strength or non-smooth film surfaces, e.g. "orange-peel" effects.

Here the compressor supplies compressed air to the reservoir at pressures between 40-70 lb per square inch. From here it passes through a pressure regulator and filter, which removes any trace of compressor oil or water, and thence to the spray gun. The finish is fed into the gun by gravity or by pressure and is projected from the nozzle as a fine, "atomized" spray on to the leather. The leather is normally hung or laid on a frame. An exhaust fan behind the frame removes surplus spray.

**Auto spraying:** Auto-spraying is the operation used for bulk production. Here the guns are mounted on the arms of a rotor, which rotates above the conveyor band. Once again the spraying of the guns is limited to the period of time when leather is actually beneath them, by mounting sensing elements on the rotor arms so that they will sense the incidence of leather beneath them just before it comes beneath the adjacent spray gun. These sensing elements may be of the photoelectric eye type or the ultrasonic beam type.

Uniform dosage of the leather surface is important and this can depend not only on the amount being sprayed from the gun, which is adjustable by needle and air settings on the gun, but also on the spray pattern of the guns

and the speed of the conveyor moving at 11 meters per minute, an overlap pattern is obtained.

**Glazing:** Glazing is a high pressure polishing, done in rolling machine. Kid and calf leather, whose finishing mixture are always prepared with protein binders, are glazed under a glazing machine for a high degree of glaze. Glazing produces a high gloss and also smoothes out and flattens the grain surface. The friction momentarily produces a very high temperature on the jack, and the machine is used in conjunction with specially compounded finishes, which are designed to give a high gloss under these conditions.

**Rotary ironing:** Rotary ironing is a process where the leather is passed over a polished and heated steel cylinder, thermostatically controlled at a pre-set temperature, producing an ironing effect. The Finiflex machine resembles a setting out machine, the leather surface being pressed against a smooth top cylinder heated internally to a pre-set temperature. This gives a smooth, glossy surface by the combination of pressure, heat and friction which is caused between the faster moving periphery of the heated cylinder and the slower moving leather surface. It also has some softening action on the leather, in contrast to plating.

**Embossing and hydraulic-press plating:** In this operation leather is placed in the embossing die setting tangible of the hydraulic press. Pressure is applied through the ram on the leather and the fiber structure of the leather surface becomes distorted so that on release, it retains the mirror image of

the hard surface. For the better result the leather is little bit heated and some times moist. The art of tooling leather by hand with hot tools has been used for many decorative purposes. There are certain obvious precepts, the softer the leather the easier it is to emboss but the less permanent the emboss to subsequent flexing or handling of the leather. It is known that the leather at the normal 14% moisture content becomes more plastic at higher temperatures, embosses better and retains the imprint better than when the leather is cold. At higher moisture contents the effect is even more pronounced. These damp, thermoplastic properties have been exploited not only by the hand tooled but also by the shoemaker in shaping the sole and lasting the upper. If moisture and heat are used in lasting the shoe toe and heel, a reversal of the phenomena may occur, i.e. the embossed pattern of the leather may be lost. Traditionally, vegetable-tanned leather was chosen for ease of embossing and retention of pattern as opposed to the more elastic nature of full chrome leather, which requires higher pressure and temperature, greater humidity and longer dwell time to achieve equivalent.

**Measuring:** Measuring is the operation to measure the square feet of leather. It is a light-scanning process measuring by computer.

**Dyeing:** Dyeing is an important finishing operation. It may be done by different methods like drum dyeing, paddle dyeing, tray dyeing etc. Dyeing performance mostly depends on the theory of color production. Dyes may be classified according to their chemical nature (Sulfur-dyes. Nitro-dyes etc.) or

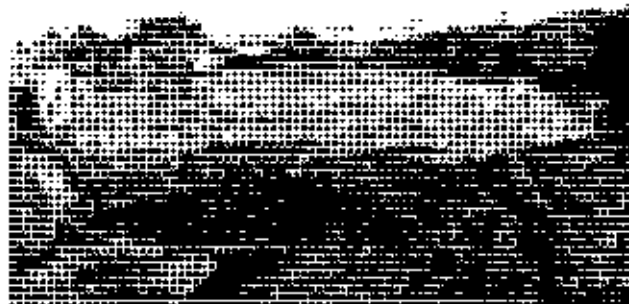


according to their application (Acid dyes, Basic dyes, Vat dyes etc.). The quality production of leather mostly followed the resultant of the finishing operation. So, in the competitive market, all the leather manufacturing industry should be taken special attention on this operation for selling or exporting their goods.

## **1.2 The Effluent of Different Stages and Bangladesh Context**

The operation in tanning which give rise effluents may be categorized into pre-tanning and post-tanning processes. Pre-tanning is employed mainly for the removal of impurities from the raw materials. These consist largely of protein (blood, hair, etc.) and the process chemicals employed include salts, lime and sulphides. The tanning processes themselves are used to alter the characteristics of skin or hide and their effluents contain chromium and vegetable or synthetic tanning. Post-tanning process includes coloration and produce effluents typical of these addition processes; that is, containing residues of dyestuffs or pigments and larger quantities of auxiliary chemicals (as shown in Fig.1.8).

The process chemicals employed are a variety of inorganic and organic materials, affecting total solids, pH, COD and of particular importance are the applicable quantities of sulphide and of heavy metals.



**Fig.1.8** Residues of dyestuffs and large quantities of auxiliary chemicals

Hazardous chemicals for leather and dyes treatments are Ammonium Bicarbonate, Chromic Acetate, Ethylene Glycol Monoethyl Ether, Methylamine, o-Nitrophenol, Toulene Diamine, 2,4,5-Trichlorphenol, Zinc Hydrosulfite, Zinc Sulfate, tert-Butylamine, Cadmium Nitrate, Cadmium (II) Acetate, Copper (2) Nitrate, 1,4-1,8 Dichloronaphthalene, Nickel Sulfate, o-Xylene, Zinc Nitrate etc. For example Chromic Acetate shows the following characteristics (Sax, 1986):

- Potential for Accumulation: Positive
- Food Chain Contamination Potential: Positive, can be concentrated in food chain
- Etiologic Potential: Chrome ulcer
- Carcinogenicity: Potential, higher occurrence of lung cancer
- Acute hazard Level: Extremely toxic if ingested or inhaled. Corrosive to living tissue.

- Degree of Hazard to Public Health: Highly toxic material via ingestion or inhalation. Corrosive to skin and mummy; potential carcinogenic.

At present in Bangladesh the tanner's basic wet process technique is to treat the stock with increasing concentrations of process chemicals using water as the carrier. In order to ensure full penetration of the thickest hide or skin in the batch, these concentrations are in excess of what is needed and the unabsorbed chemicals are discharged in the effluent, where they are a waste and cause expensive treatment problems.

While the Chemical companies in the Federal Republic of Germany, the United States, the United Kingdom, Switzerland, Spain and Italy provide short term training on the application of their chemicals, Whereas they do not provide any assistance how to treat toxic effluents that increasingly contaminate surface and ground water. Consultant provides technological transfer and management either on arm's length fee paying basis on assignment or financed by the World Bank, UNIDO, ITC or other United agencies.

The small cottage tanners of Hazaribagh producing sandal leather out of cow heads are probably the only tanning group in the world using waste tanning liquor from the modern tanners as their process liquor. But after using these wastes are eventually discharged, as are all other tannery discharges in the Hazaribagh tanning effluents into the streets, gutters and sewers, which ultimately enter surface and ground water.

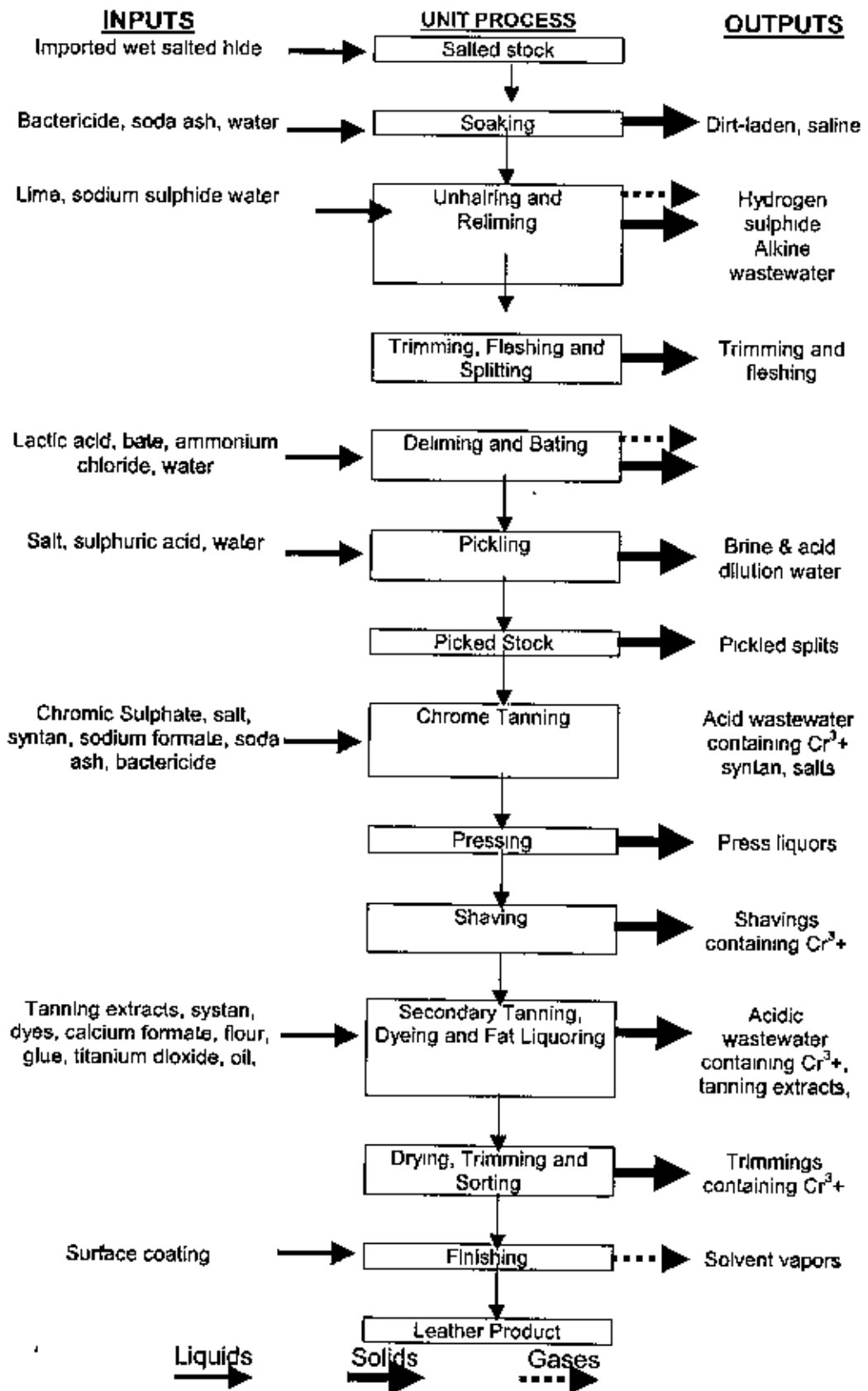
According to Dittfurth and Röhring (1987) about 250 different toxic chemicals and heavy metals like cadmium, chromium, arsenic, zinc etc are used by the leather industry. When the local industry was basically a vegetable-tanning complex, this effluent might have been high in BOD and unpleasant but particularly dangerous.

There is, in addition, extremely hazardous air pollution occur in Hazaribagh, which is not known in any other places of the world. The rest treated hides and skins are cooked in open air to obtain glue for the local market (Fig.1.9). They burn treated leather pieces instead of coal or wood, as it is cheaper. The smog and the smell like a witch cooking pot and it is terrible. The most hazards occur when the poorer group uses poisonous treated leather pieces as an alternative fuel to cook regular meals.



**Fig.1.9** Rest treated hides and skins are cooked in open air to obtain glue for the local market

No body knows how much harm and potential carcinogen diseases will occur to the slum inhabitants. There is no warning from the Government or aid giving agencies or their representatives. This is the vicious circle that the poorest groups are the worst victims of the foreign currency earning schemes.



**Fig.1.10** Schematic diagram of tanning operations

Now the Government has recently taken a measure to relocate the tanneries from Hazaribagh area to Savar with in a short period of time and the process will be finished by the year 2005. In this new location the Govt. will setup a joint waste treatment plant so that the environment of the surrounding area could not hamper and the pollution by leather industries could not occur. A flow diagram was prepared to illustrate the interrelationship between the various units operations i.e. the input, process and output as can be seen in the Fig.1.10.

### **1.3 The Dyes and Dyeing of Leather**

A colored substance is known as dye when that can be fixed up to the fabric and when fixed, is not fugitive i.e. fast to light and not washable by water, dilute acid or alkali. Many natural dyes had been known and they were obtained from either vegetable or animal sources. Today, however, practically all dyes re synthetic and are prepared from aromatic compounds, the only source of which, until recently, was coal Tar, hence the name Coal tar dyes.

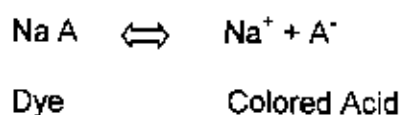
A substance looks colored when that absorbs all the waves from white light except that what can produce that particular color of the substance. If only a single band of the spectrum is absorbed, the substance has the complementary color of the absorbed light. If the absorption of light is towards the band of shorter wave length of the spectrum the color of the

substance is pale and latter becomes more and more deep as the absorption maximum approaches from band of shorter to band of longer wavelengths.

Dyes are classified either according to their chemical nature or according to their application. The chemical constitutions of dyes are so varied that it is difficult to classify them into groups and the generally accepted dyes are Nitro dyes, Nitroso dyes, Azo dyes, Diphenyl methane dyes, Triphenyl methane dyes, Xanthen dyes, Diphenyl amine dyes, Heterocyclic dyes, Sulphur dyes, Pthalocyanin dyes and Anthraquinoid dyes etc. On the other hand, according to their application different types of dye are used in tannery industry which are Acid dyes, Basic dyes, Direct dyes, Vat dyes, Developed dyes and Sulphur dyes etc.

Tanners are generally interested with acid, basic and direct dyes and sometimes with Sulphur and developed dyes.

**Acid Dyes:** these dyes are generally sodium or potassium salts of organic colored acids and ionize in solution as follows:



It is the negatively charged acid portion  $\text{A}^-$  that imparts color to the fabric. For full and uniform shades the dyes are completely ionized in solution by the addition of acids.

The solubility of the acid dyes in water is generally increased by the introduction of sulphonic acid groups ( $-HSO_3$ ) in the molecules. Table-1.1 shows the different acid dyes and their color in water.

Table-1.1 Common acid dyes and their color in water

Common acid dyes used in leather tanneries (Company)	Color in water
Lurazol Brown PH (BASF)	Brown
Luganil Dask Green N (BASF)	Green
Leather Black VM Liquid	Black
Lurazol Black HS (BASF)	Black
Luganil Black NT (BASF)	Black
Fast Red (HODGSON)	Red
Derma Carbon AF (CLARIANT)	Black
Black TS (BASF)	Black
Derma Brown HG (CLARIANT)	Brown

Through the first day of a tanner is to convert putrescible protein to non-putrescible leather by treating the former with some tanning material. The job is not finished unless the products become attractive and usable. Dyeing is thus the first step of operation, which makes leather attractive and suitable for use and the fact is good finish cannot be expected from undyed leather.

The nature of tanning actually determines the type of dye to be used for leather. Acid dye for example can react with both chrome and vegetable



tanned leather, but the basic dye can only react or impart color to vegetable, not to chrome tanned leather. Similarly direct dye can dye chrome and not vegetable tanned leather. If chrome tanned leather are to be dyed with basic dye, they must be mordanted with some suitable mordant or vegetable tannin. Semi chrome leather, which is treated with chrome liquor after vegetable tanning, can be dyed with direct dyestuffs. Before dyeing with certain dyes, therefore the leather are to prepare according to the dye to be used.

Since the intensities of color of basic dyes are much more than that of the acid dye and since the basic dye make the defective portion prominent the selection of dye are largely depends upon the physical condition of the leather and the nature of the leather to be manufactured.

## **1.4 Environmental Problems**

The presence of color in many industry effluent streams is esthetically undesirable. Color organic effluent produced in the textile, paper, plastic, leather, food and mineral processing industries are high volume, hazardous and toxic waste. About 634900 metric tons of dyes are produced worldwide each year and nearly 10-15% of them are discharged as effluent [5]. Developing countries like Bangladesh, India discharges the effluents to surface water without any treatment or sometimes little treatment due to technological and economical limitations. Colors affect the nature of water

and inhibit sunlight penetration and reduce the photosynthetic action. Some of the dyes cause rapid depletion of dissolved oxygen affecting aquatic life adversely [6]. Again, some of the dyes especially Benzodrine based dyes are toxic, carcinogenic [7,8]. Thus uses of dye-contaminated water without any treatment may cause adverse effect on human health, domestic animals, and wildlife and in environment. So it is very much essential to treat dye contaminated wastewater before discharging it to surface water and to develop simple and economical methods to treat the stream suitable for the developing countries.

The general public assumes that visible color pollution from expended effluent indicates the presence of toxicants [5]. Hence, there is increasing pressure on governments to tighten or introduce regulations for effluent color levels.

Traditionally both biological and chemical methods have been employed for dye removal, but these techniques have not been very successful due to the essential non-biodegradable nature of most dyes. That is, biological-chemical reactions do not work for color removal due to the presence of large organic molecules and their very stable nature under microorganisms.

The conventional methods of removal of dye using alum, ferric chloride, activated carbon, lime etc. are not economical. Adsorption is a physiochemical treatment process, which has gained lot of attraction for the removal of dyes from wastewater since it produces a high quality treated

effluent [8,9]. In adsorption process dissolved molecules are attracted to the surface of the adsorbent and this interactions may be expressed both in terms of adsorptive characteristics and physical properties. The most widely used adsorbent for industrial application is activated carbon [10-12]. But the cost of the activated carbon is high and it increases with its quality. Considerable amount of research works have been carried out for the search of low cost adsorbents suitable to remove dyes from wastewater. Agricultural solid waste such as coir pitch [13], banana pitch [14], coconut husk [15], biogases residual slurry [16], rice hulls [17], biogases and paddy straw [18], sawdust [19] etc have been investigated for the removal of dyes from wastewater. Hardwood sawdust is a very cheap and easily available materials in developing countries like Bangladesh has not been investigated with much attention for its possibility as an adsorbent. Though Asfour et al [19] has reported the application of hardwood sawdust for the removal of some basic dyes from wastewater and their results give positive indication of use of sawdust as an effective and economical adsorbents but so far our knowledge goes no works are available for the removal of acid dyes and reactive dyes from wastewater stream using sawdust. It seems that the extensive work is still required especially for acid dyes and reactive dyes before using it as a practical adsorbent. Thus the aim of the present study was evaluate the prospect of using acid activated sawdust as an adsorbent for the removal of an acid dye Lurazol Brown PH (LBP) used in leather dyeing.

## **1.5 Objectives of the Present Work**

Adsorption is a physicochemical treatment process, which has gained a lot of attraction for the removal of dyes from wastewater since it produces a high quality treated effluent. In adsorption process dissolved molecules are attracted to the surface of the adsorbent and these interactions may be expressed both in terms of adsorptive characteristics and physical properties. The most widely used adsorbent for industrial application is activated carbon. But the cost of the activated carbon is high and it increases with its quality. Considerable amount of research works have been carried out for the search of low cost adsorbents suitable to remove dyes from wastewater. Agricultural solid waste such as coir pitch, banana pitch, coconut husk, biogas residual slurry, rice hulls, biogas and paddy straw, red mud, orange peel etc have been investigated for the removal of dyes from wastewater.

In the present investigation a low adsorbent suitable for developing countries like Bangladesh will be searched and the practical application of this adsorbent will be carried out. The main objective of the present work is to

- design and development of an economical column filtration reactor and
- make a thorough and systematic investigation on the role of low cost adsorbents (acid activated sawdust) on the removal of dissolved dyes from tannery wastewater and overall benefits of column filtration reactor.

# Chapter-2

## ***EXPERIMENTAL INVESTIGATION AND PROCEDURE***

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**Adsorbent preparation:** Hardwood Sawdust was collected from sawmills and dried in air for one day. Then larger particles of it were removed with a sieve of hole size 200 $\mu$ m and only the fine particles were taken for acidify.

**Acidify:** To make the saw dust acidify 20(twenty) gm of sieved saw dust was taken in a jar and mixed with 400 ml water of pH value  $1.0 \pm 0.05$  which was previously prepared by adding Hydro Chloric Acid (HCL). The pH value was ensured by the pH meter (Denver Instrument. model-b000512006, Germany) in the lab. Then the mixer was stirred for one hour at  $80^{\circ}\text{C} \pm 2^{\circ}\text{C}$  in a magnetic stirrer with hot plate (STUART SCIENTIFIC, serial-R000100370, Germany). The temperature rises up to that level within 30 min. The sawdust was then filtered and dried in air carefully. Now it becomes Acid Activated Saw Dust (AASD). During the activation it imparted an orange color to the water. Fig.2.1 shows the acidifying the sawdust with magnetic stirrer

During acidify the hardwood saw dust was mixed with HCL acid for one hour so it become cationic in properties. As our dye Lurazol Brown pH (LBP) is acid dye so sawdust become active with the dye. Also the organic compound present in the sawdust removed and the porosity of the sawdust increases. So the surface area increased and the adsorbent capacity become higher as more dye particles comes in contact with the sawdust.



**Fig. 2.1** Photographic view Acidify of saw dust with magnatic stirrer

**Preparation of dye solution:** The dye we used, Lurazol Brown PH (LBP) (collected from BASF) is an acid dye. The CI number and the chemical formula are not available for the dye. At first 1 gm of dye was mixed with 1 liter of distil water to make a mother solution and the concentration becomes

1 gm/l. From the mother solution, three different solutions of 100 mg/L, 300 mg/L and 500 mg/L concentrate were prepared in three different jars.

**Adsorption studies:** Lambert and Bouger independently discovered the relationship between the relative intensity of the radiant energy emerging from a solution and the depth of the solution. They found that the intensity of the transmitting energy decreases exponentially as the depth increases. This can be express as  $A = \log P_0/P = -\log P/P_0 = \log 1/ T = kb$

Where A is the absorbance, P and  $P_0$  are the respective powers of the transmitted and incident beams, T is the transmittance, k is constant for the chemical system, and b is the path length of the light.

Beer discovered the relationship between the concentration of an absorbing species in a solution and the transmission of radiant energy through the solution in 1852. Concentration, like depth, is a reciprocal exponential function of transmittance and a linear function of absorbance. This can be expressed as

$$A = -\log P/ P_0 = -\log T = k'c$$

Where P and  $P_0$  are the respective energy powers of the emerging and incident beams,  $k'$  is a constant for the chemical system, and c is the concentration of the absorbing species. Absorptivity, a, is defined as  $a = A / bc$ .

It is a fundamental physical constant for a specific chemical species at a specific wavelength. Unlike depth and concentration, the operator cannot vary it.

Since the fraction of radiation absorbed depends upon the three factors: Absorptivity, path length, and concentration. These parameters are mostly combined to yield the Beer-Bouguer-Lambert law, more commonly known as Beer's Law. It states that  $A = abc$

Where  $A$  is the absorbance,  $a$  is absorptivity in liters (gram centimeter),  $b$  is the path length or depth of the solution in centimeters, and  $c$  is the concentration in grams/liter.

Alternately, the combined law is express as

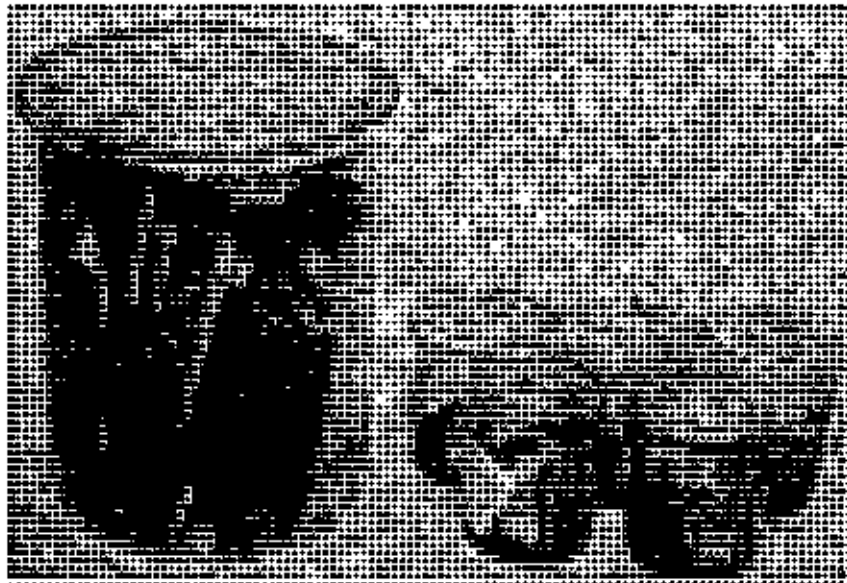
$$A = \epsilon bc.$$

Again,  $A$  is absorbance but  $\epsilon$  (molar absorptivity) now has the units of liters /mole centimeter) and  $b$  still possesses units of centimeter. The concentration,  $c$  is now expressed in molarity.

Batch sorption studies were carried out by 40 ml of desired concentration dye solution (100 mg/L, 300 mg/L and 500 mg/L) with 1 gm of Acid Activated Sawdust (AASD). The mixer was agitated in a 250 ml beaker at room temperature (25<sup>0</sup>C) in a magnetic stirrer (Magnetic Stirrer Hotplate, SM6,

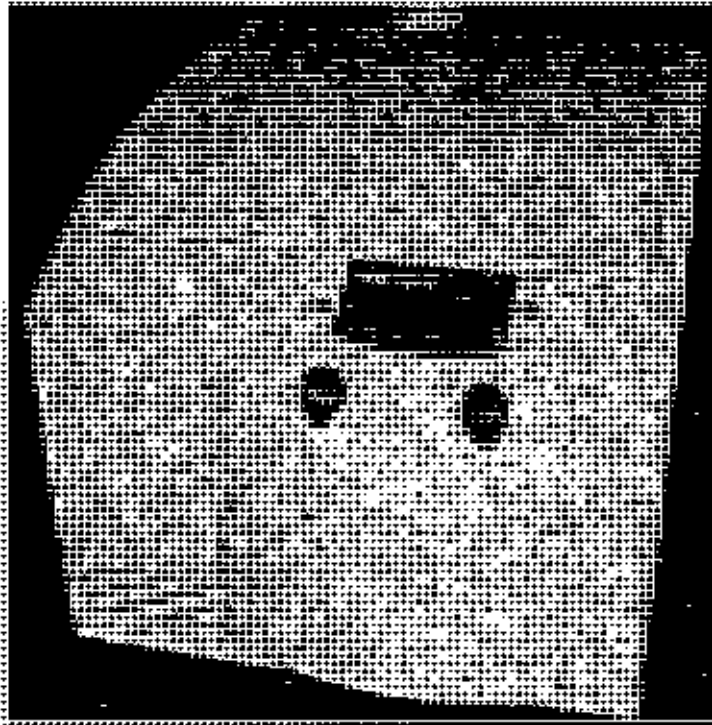


Stuart Scientific, UK) at the time intervals of 1, 2, 4, 8, 10, 20, 30, 40, 50, 60, 80, 100 and 120 min using no hot plate. The pH of the solution was  $2.65 \pm 0.05$  level, which is, determine by the pH meter. After desired time the solution filtered in a two-steps sieve and was collected in small beaker as can be seen in Fig2.2.

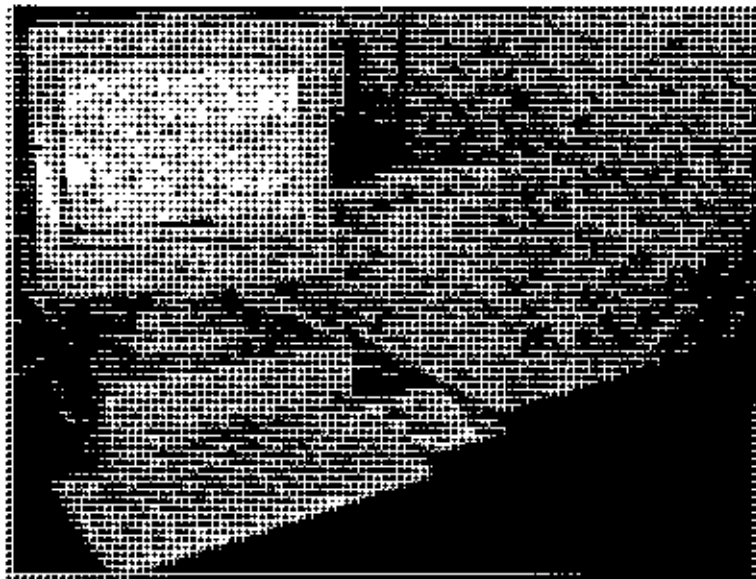


**Fig. 2.2** Sample of filtered solution

Then to remove the suspended particles from the collected solution it is centrifuged at 2000 rpm for 10 min in a SIGMA 2-5 (Germany) centrifuged machine (Fig.2.3). So the remaining saw dust (adsorbent) deposited and we get the sawdust separated dye solution for analysis.



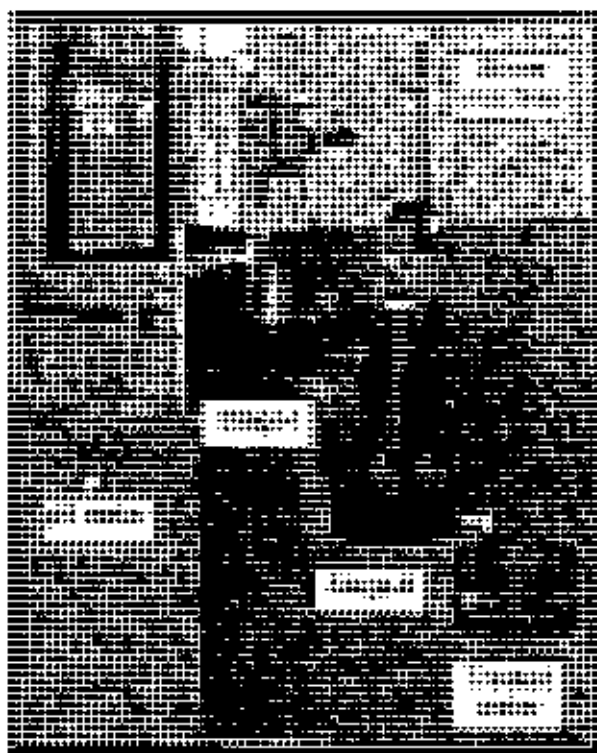
**Fig. 2.3** Photographic view of centrifuged machine used to remove the suspended particles from the solution



**Fig. 2.4** Photographic view of Spectrophotometer used for monitoring absorbance

Then the dye removal of the solution is determined spectrophotometrically by monitoring absorbance change at wavelength of maximum absorption (443 nm). All the absorbance measurements were carried out in a Perkin Elmer Lamda 35 UV/VIS (USA) spectrophotometer (Fig.2.4).

Adsorption is a physiochemical treatment process, which has gained lot of attraction for the removal of dyes from wastewater since it produces a high quality treated effluent. In adsorption process dissolved molecules are attracted to the surface of the adsorbent and this interactions may be expressed both in terms of adsorptive characteristics and physical properties. The most widely used adsorbent for industrial application is activated carbon. But the cost of the activated carbon is high and it increases with its quality. Considerable amount of research works have been carried out for the search of low cost adsorbents suitable to remove dyes from wastewater. Column filtration reactor was designed and fabricated to remove the dyes from tanneries wastewater by using low cost adsorbent like acid activated sawdust (AASD). The photographic view of the column filtration reactor is shown in Fig.2.5. The dye removal operation has been investigated by (a) single stage operation and compare it with the previous results and (b) double stage operation and compare it with the previous results.



**Fig. 2. 5** Photographic view of the experimental set up for removal of dyes from wastewater by two stages

In the single stage operation, 10 liter container containing 5 liter of 500 mg/L concentrate dye solution, mixed with 125 gm of AASD and stir it for 2 (two) hours with a fan at 716 rpm. In this stage the pH remains  $1.2 \pm 0.05$  and was determined by the pH meter. For every 10 minutes, the sample was collected and centrifuged it at 2000 rpm for 10 minutes and then the dye removal of the solution is determined spectrophotometrically by monitoring absorbance change at wavelength of maximum absorption (443 nm).

In the double stage operation, the total operation was performed in two stages. In the first stages 5 liter of 500 mg/L concentrate dye solution was mixed with half of the AASD i.e. 62.5 gm for one hour at 720 rpm. Then the

solution after 1 hour transferred through filter to another stage or the container, where the remaining saw dust i.e. 62.5 gm added and stir at 716 rpm for another one hour. During the operation the sample has been taken for every 10 minutes and after centrifuged the dye removal of the solution is determined in spectrophotometer. Here also in both the stages the pH remains  $1.2 \pm 0.05$  levels. The treatment procedure allows 81% reduction in color from tannery wastewater.

# Chapter-3

## *Results and Discussions*

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Ultraviolet spectroscopy deals with the recording of absorption of light in the visible and ultraviolet regions of the spectrum. Light of wavelength between  $4000 \text{ \AA}$  and  $7500 \text{ \AA}$  (400-750 nm) is visible. Just beyond the red end of visible spectrum (wavelength is more than 700 nm) starts the infrared region and just beyond the violet end of the visible spectrum (wavelength less than 400nm) lies the ultraviolet region. Thus, ultraviolet region starts at the blue end of the visible light (about  $4000 \text{ \AA}$ ) and ends at  $2000 \text{ \AA}$  (200 nm)

The region is further sub-divided into near ultraviolet region (200-400 nm) and far or vacuum ultraviolet region (region below  $2000 \text{ \AA}$ ).

When radiant energy impinges upon a solution it may be absorbed, transmitted, reflected, or refracted. In spectrophotometry the absorbed light is determined. However, because of the difficulty of directly measuring the absorbed energy, the transmitted energy is measured and the amount absorbed is indirectly determined by subtracting the transmitted from the initial energy. The relationship  $E = h\nu$ .

Where  $E$  is the transition energy from a stable to excited state,  $h$  is Planck's constant, and  $\nu$  is the frequency. The energy of ultraviolet and visible radiation corresponds to that required for electronic transitions of the outer electrons. Since these are the valence electrons of the molecules or ions, absorption spectra reflect the bonding characteristics of these particles.

The absorbance at various wavelengths is determined with a spectrophotometer. This instrument in its simplest form consists of

- a radiant energy source
- a means of obtaining monochromatic or nearly monochromatic light
- a cell for the sample or blank
- a detection and readout assembly.

Actually, more sophisticated instruments are generally used. In order to obtain a broad overview of the instrument, to establish nomenclature, and to define system parameters, the schematic diagram (Fig.3.1) shown below will be considered in more detail.

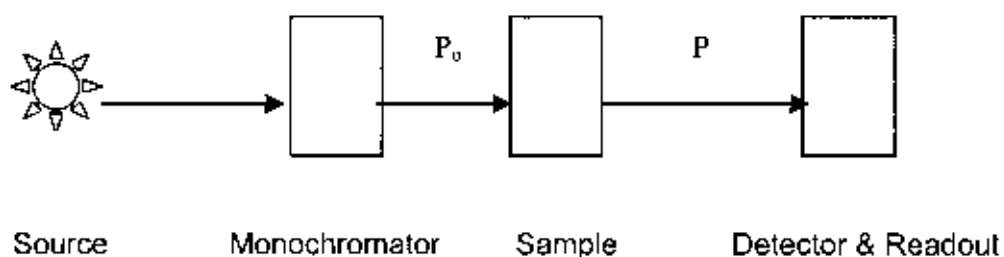


Fig.3.1 Schematic diagram of a simple spectrophotometer.  $P_0$  is the power of the radiation entering the sample cell and  $P$  is the transmitted power.

After originating at the source and passing through the monochromator system the radiant energy,  $P_0$  enters the sample where a portion of it is absorbed. The remainder of energy,  $P$ , i.e., that which is transmitted, strikes the detector and a quantitative readout is obtained.

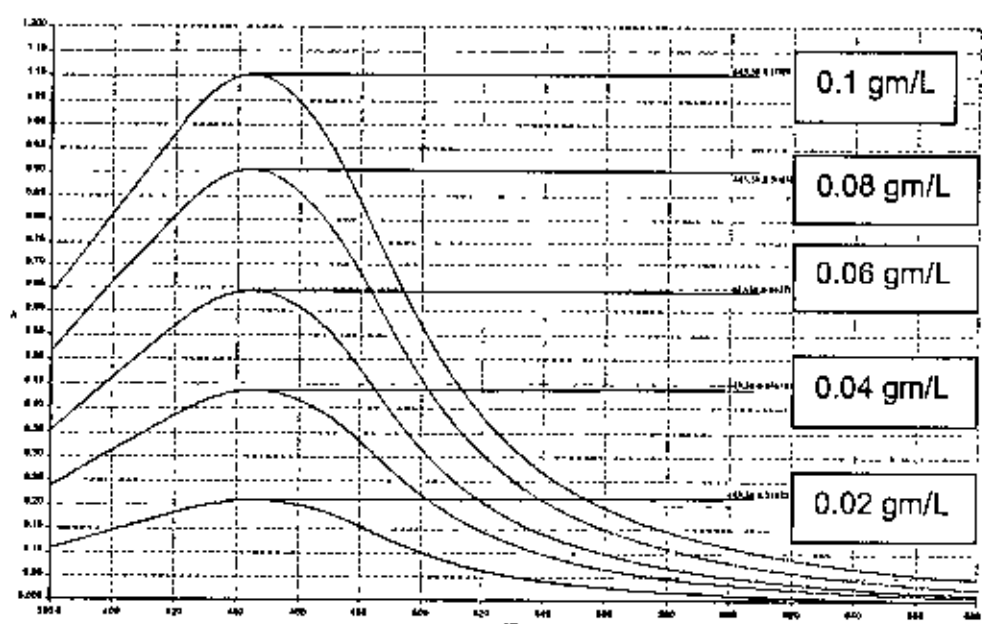
The radiant power,  $P_0$ , which is striking the sample, is reduced in intensity while passing through the sample and the emerging power,  $P$ , is measured. Transmittance,  $t$ , is the ratio of the radiant power,  $P$ , transmitted by a sample to the radiant power,  $P_0$ , entering the sample and percent transmittance is this ratio multiplied by 100, i.e.  $T = P/P_0$  and  $\%T = 100T = 100 (P/P_0)$

Absorbance,  $A$ , is the logarithm to the base 10 of the reciprocal of the transmittance:  $A = \log_{10} (1/T) = \log_{10} (P_0/P)$

The  $\lambda_{max}$  and molar extinction coefficient of a particular dye are constant parameters. In the present investigation the  $\lambda_{max}$  and molar extinction co-



efficient of Lurazol brown PH were measured by preparing 0.02, 0.04, 0.06, 0.08 and 0.10 mg/L concentrated solution. The UV-Vis spectrum was taken for each solution. Fig.3.2 represents the UV-Vis spectrum of Lurazol brown PH at different concentrations within the range 320nm–720nm. It is observed from the figure that each curve shows the peak at 443 nm, which is the  $\lambda_{max}$  for this dye. The absorbance obtain at different concentration are shown in Table-3.1. The concentration vs. absorbance plot has been shown in Fig.3.2. It is interesting to mention that the plot shows the straight-line nature and can be represented by the equation  $A = 0.011 c$ . Comparing this equation with Lambert-Beers equation  $A = \epsilon b c$  and taking the cell dimension  $b = 1$ , the value of  $\epsilon$  becomes equal to 0.011 which is the molar extinction co-efficient. That is, the Lurazol Brown PH (LBP) can characterize as (Table-3.2):



**Fig.3.2** UV-Vis Spectrum of Lurazol Brown PH at different concentrations ( $\lambda_{max} = 443$  nm).

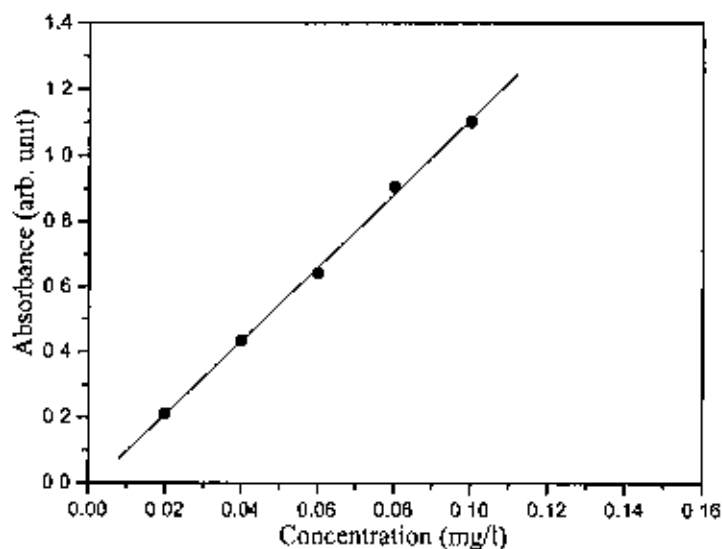
**Table-3.1** Concentration vs. Absorbance of Lurazol Brown PH at  $\lambda_{max}=443\text{nm}$ 

Concentration (g/L)	Absorbance (arb. Unit)
0.02	0.210
0.04	0.436
0.06	0.643
0.08	0.906
0.10	1.102

**Table-3.2** Characteristics of Lurazol Brown PH (LBP)

Lurazol Brown PH, BASF	
Characteristic wavelength, $\lambda_{max}$	443 nm
Molar Extinction Coefficient, $\epsilon$	$0.011 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$

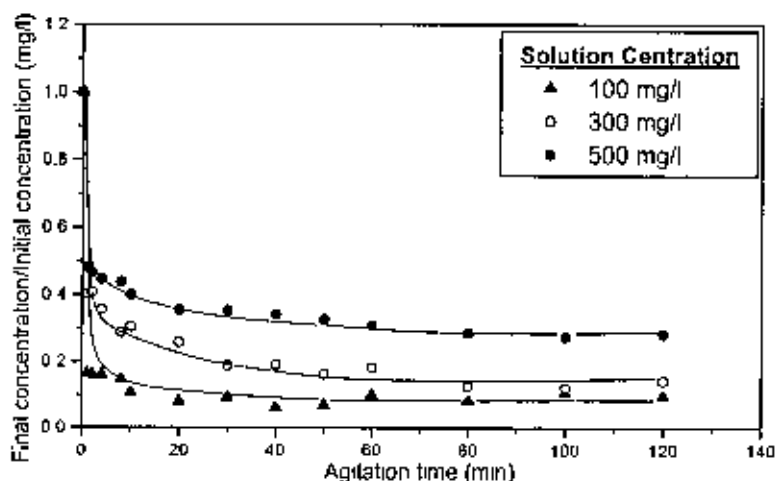
Based on the calibration curve (Fig.3.3) the concentrations of the dye solutions were determined using Lambert-Beer's law in different stages. The experimental data were analyzed for kinetics studies, Langmuir isotherm and Freundlich isotherm. The calibration curve, which is the plot between absorbance vs. different concentration, gives the linear relationship. The value of molar extinction co-efficient is obtained from this curve, which is 0.011053.



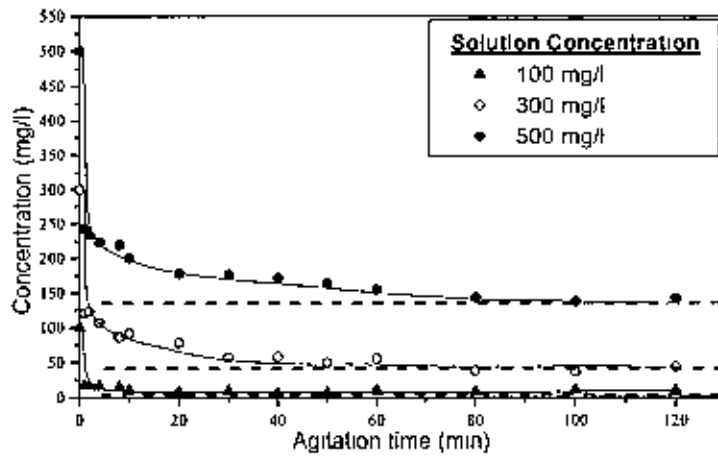
**Fig.3.3** Adsorption calibration curve for Lurazol Brown PH

Fig.3.4 and Fig.3.5 represent the sorption of Lurazol Brown PH (collected from BASF) by acid activated sawdust (AASD) with variation of agitation time. It is observed that the removal of dye is rapid in the initial stages of agitation time and gradually decreases and finally reaches at equilibrium. The equilibrium time is the time taken for the maximum adsorption of the dye on to the adsorption surface, above which adsorption remains constant. The equilibrium time is observed to be 50 min. for 100, 300, and 500 mg/L dye concentrations. It is also observed the sorption of LBP depends on the initial concentration of LBP and the rate of LBP uptake by activated sawdust decrease with the increases in initial concentration. The similar relationship also observed by McKay in case of sorption CI Direct Orange 39 and Victoria Blue by activated carbon [20], Tusi et.al. in case of sorption of CI Reactive

Red 2 by compost [21], Sivaraj et. al. in case of sorption of Acid Violet 17 by Orange peel [22]. Tusi et. al. explain that decrease of sorption kinetics with increase of concentration may have been the results of steric interactions between the anionic molecules in the solutions. According to McKay some sorbents may be more efficacious for waste streams that contain smaller concentrations of dyes because of the more rapid kinetics.



**Fig.3.4** Rate of dye sorption by sawdust at 25°C



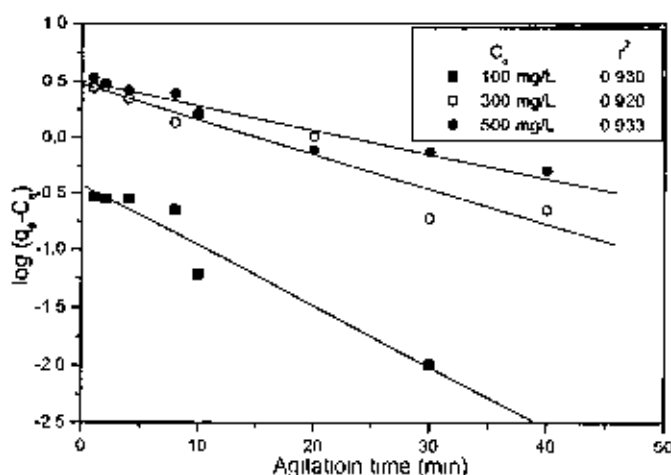
**Fig.3.5** Amount of dye sorption by sawdust at equilibrium

In order to design an effective sorber having the knowledge on the rate at which the adsorption takes place by the adsorbent is an important factor. However, adsorption Kinetics largely depends on the physical and chemical characteristics of the adsorbent material, which influences the adsorption mechanism. Thus the constants of sorption of dye were determined using the following first order Lagergren equation [23].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \dots\dots\dots (3.1)$$

Where  $q_e$  is the amount of dye sorbed at equilibrium (mg/g) and  $q_t$  is the amount of dye sorbed at time  $t$ , (mg/g) and  $k_1$  is the equilibrium rate constant of pseudo-first order sorption ( $\text{min}^{-1}$ ). In order to obtain the rate constants, the straight-line plot for  $\log (q_e - q_t)$  against  $t$  (agitation time) has been

analyzed (Fig.3.6). The rate constants,  $k_1$  and the correlations coefficients,  $r^2$  were calculated from these plots. The values have been shown in Table-3.3.



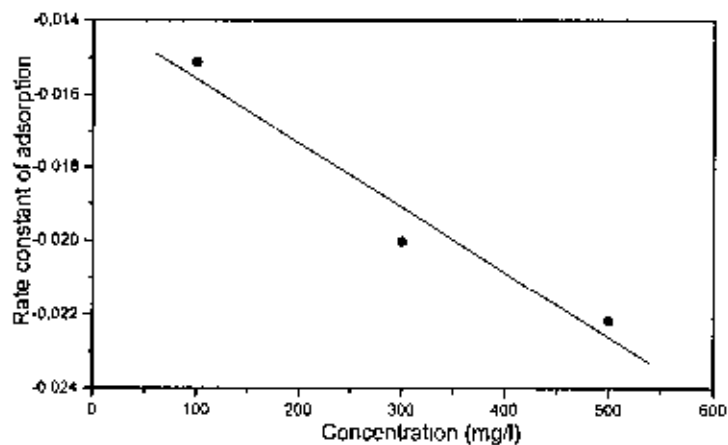
**Fig.3.6** Plot for Lagergren rate constant for adsorption of Lurazol Brown PH dye by sawdust

**Table-3.3** Variation of rate constant with initial concentration

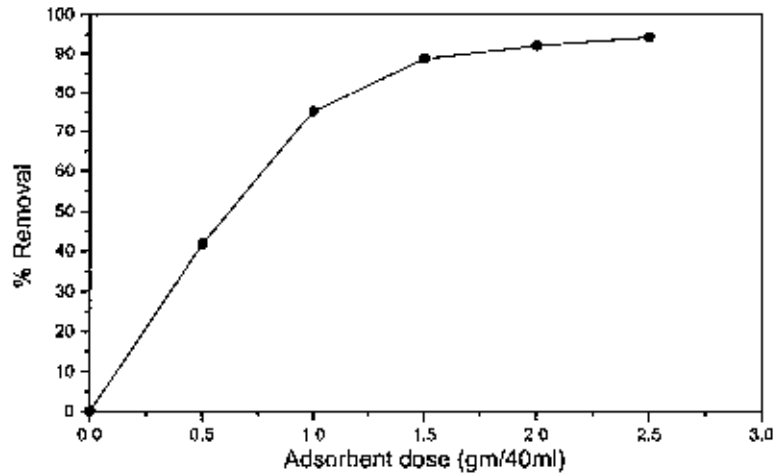
Initial concentration ( $C_0$ )	Rate constant ( $k_1$ )	Correlation coefficient ( $r^2$ )
100	0.01512	0.8196
300	0.02003	0.9622
500	0.02217	0.9257

It is observed that the value of rate constant decreases with the increase of the initial concentration. The rate constant for the adsorption of dyes Congo red, rhodamine-B and acid violet by biogas residual slurry were 0.026, 0.024, 0.014 l/min respectively at 50 mg/L dye concentration [16]. The

corresponding values for waste banana pitch were reported to be 0.106, 0.048 and 0.037 l/m respectively [23]. The rate constants for the orange peel of removal acid violet 17 (acid dye) is 0.0691, 0.0553, 0.0353, 0.0419 l/min at the initial concentration 10, 20, 30 and 40 mg/L respectively [22]. From Fig.3.7, It is very interesting to mention that in this investigation the initial concentration vs. rate constant follows a linear relation having the equation,  $K_1 = -0.01382 - 1.7625 \times 10^{-5} C_0$  with the regression co-efficient,  $r^2 = 0.9510$ .



**Fig.3.7** Variation of rate constant ( $K_1$ ) with initial concentration



**Fig.3.8** Rate of dye uptake by sawdust

Fig.3.8 shows the removal of dye as a function of adsorbent dosage. It is observed that initially the increase in adsorbent dose increased in percentage removal of dye and finally become saturated. It is observed that only 2.5 gm of saw dust is capable of removing 94% dye from an initial concentration of 300 mg/L of 40 ml solution.

The data were also fitted to the following Langmuir and Freundlich adsorption isotherm equations respectively.

$$\frac{C_c}{q_c} = \frac{1}{Q_o b} + \frac{C_c}{Q_o} \dots\dots\dots(3.2)$$

$$\log_{10} \frac{x}{m} = \log_{10} k_f + \frac{1}{n} \log_{10} C_c \dots\dots\dots(3.3)$$



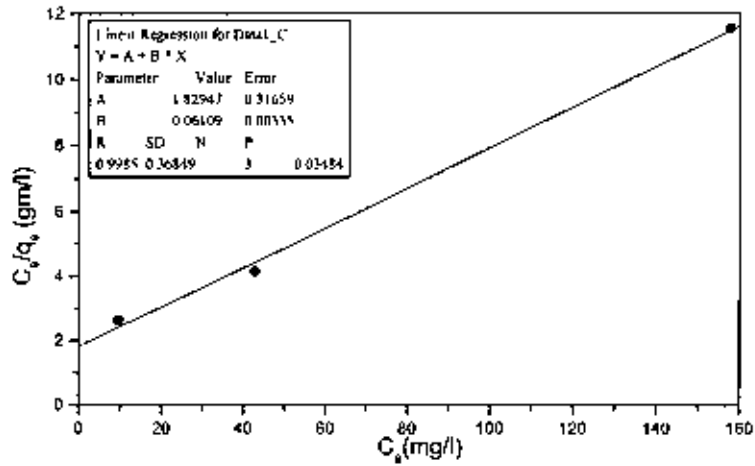
Where  $C_e$  is the equilibrium concentration mg/L,  $q_e$  is the amount of dye adsorbed at equilibrium mg/g, and  $Q_0$  and  $b$  is Langmuir constants related to adsorption capacity and energy respectively.

The linear plot of  $C_e/q_e$  vs.  $C_e$  shows that the adsorption obeys Langmuir isotherm model (Fig.3.9). The values of  $Q_0$  and  $b$  are determined from the slope and intercept of the plot and presented in the Table-3.4.

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter,  $R_L$  which is defined by

$$R_L = \frac{1}{(1 + bC_o)} \dots\dots\dots(3.4)$$

According to Hall et al it has shown using mathematical calculation that  $R_L$  indicates shape of the isotherm as indicated in the Table-3.5. The  $R_L$  value obtained in the present studies for different initial concentration indicates favorable adsorption of LBP by AASD.



**Fig.3.9** Langmuir plot for Lurazol brown pH adsorption by sawdust

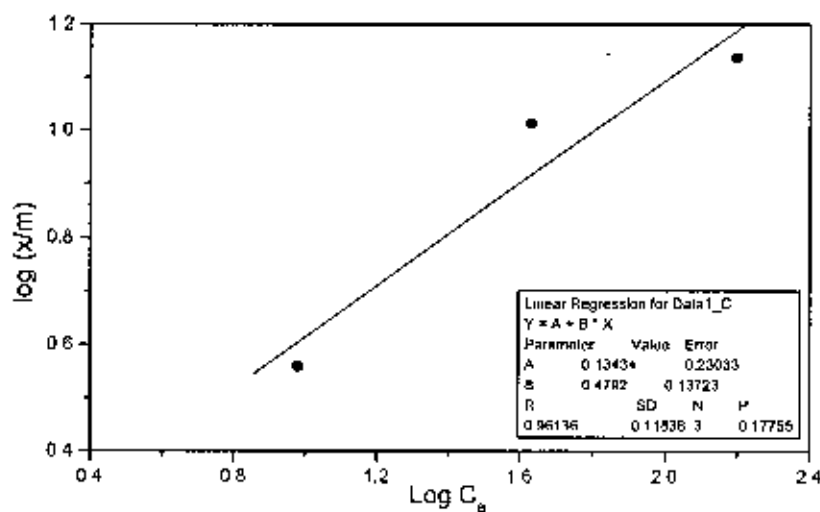
**Table-3.4** Variation of  $R_L$  with initial concentrations

Langmuir Constant	Initial Concentration ( $C_0$ )	$R_L$
$Q_0 = 16.37$	100	0.2304
$b = 0.0334$	300	0.0907
	500	0.0565

**Table-3.5** Shape of the isotherm with respect to  $R_L$

$R_L$ value	Type of Isotherm
$R_L > 1$	Unfavorable.
$R_L = 1$	Linear.
$0 < R_L < 1$	Favorable.
$R_L = 0$	Irreversible.

Fig.3.10 represent the variation of  $\log_{10} (x/m)$  with respect to  $C_e$ . The linear nature of the plot indicates that the present observations follow the Freundlich isotherm as well. The values of Freundlich constants were calculated from the intercept and slope of the plot and found to be  $n = 2.12$  and  $K_f = 0.134$ . According to Treybal [23] it has been shown that if the value of  $n$  is between 1 and 10, then it represent beneficial adsorption.

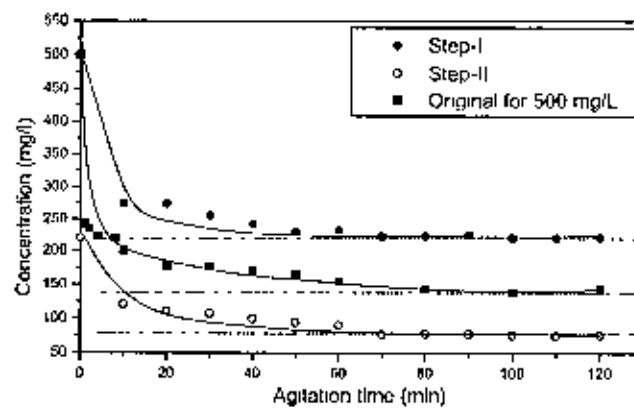


**Fig.3.10** Freundlich plot for the adsorption of Lurazol Brown pH by sawdust

As observed in the Fig.3.10 and Fig.3.7 that the amount of dye adsorbs at equilibrium and the time required for it depend on the initial concentration. Thus in the present study a two-stage filtration were carried out. Initially, 5 liter of solution having 500-mg/L dye concentrations was taken and 125gm of sawdust was used. The mixer was agitated and concentrations were measured in different time intervals. At next step the sawdust was divided in equally two portions and the process was repeated with the one portion (62.5

gm) of sawdust. After completion the process the filtered solution was taken to the second column and another portion of sawdust was added and agitated the mixer accordingly and concentration was measured at certain time intervals.

Fig.3.11 shows the comparative studies of removal of dyes between one-stage and two-stage filtration system. Table-3.6 represents the equilibrium concentration and time in two systems.



**Fig.3.11** Enhancement of dye removal by two-step column filtration system

**Table-3.6** Equilibrium concentration in slage filtration system.

<b>Initial Concentration, <math>C_0</math></b> <b>(mg/L)</b>	<b>Step</b>	<b>Equilibrium Concentration,</b> <b><math>C_e</math> (mg/L)</b>	<b>Time</b> <b>(min.)</b>
500	Original	150	80
500	Step-I	221	80
221	Step-II	96	60

It is observed that one stage filtration system can lower the concentration from 500 mg/L to 150 mg/L at equilibrium, which is equivalent to 70% removal. But if the same concentration of dye is used and the same amount of adsorbent is applied in two step the final equilibrium concentration become 96 mg/L, which is equivalent to 81% removal. It indicates that two-stage filtration system can enhance the dye adsorption in 11% when the initial concentration is 500 mg/L. It is also observed from the Fig.3.11 and Table-3.6 that the time required to reach the equilibrium for two-stage system is 60 min. but that of one-stage is 80 min, which indicates that the two-stage system improves the rate of uptakes of dye, by the adsorbent. In conclusion it can be mentioned that two-stage system can provide two-way benefits by removing more amount of dyes in lesser time with compare to one-slage system. Fig.3.12 shows both untreated and treated wastewater.

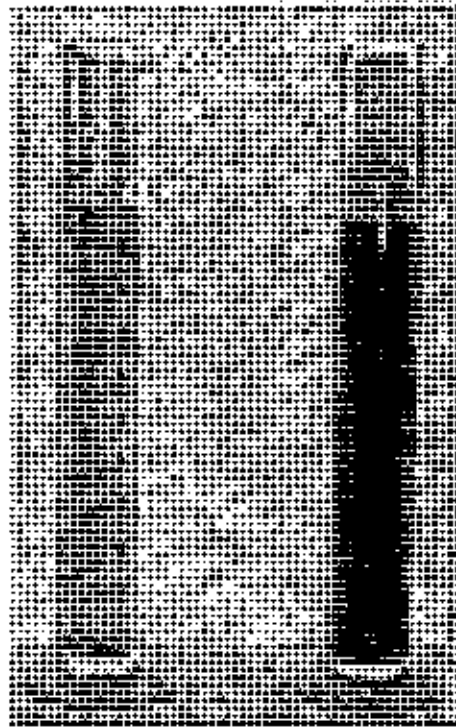


Fig. 3.12 Left: treated raw water, Right: untreated raw water

# Chapter-4

## ***Conclusion and Recommendation***

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### **Conclusion:**

Adsorption is a physiochemical treatment process, which has gained lot of attraction for the removal of dyes from wastewater since it produces a high quality treated effluent. In adsorption process dissolved molecules are attracted to the surface of the adsorbent and this interactions may be expressed both in terms of adsorptive characteristics and physical properties. The most widely used adsorbent for industrial application is activated carbon. But the cost of the activated carbon is high and it increases with its quality. Considerable amount of research works have been carried out for the search of low cost adsorbents suitable to remove dyes from wastewater. Agricultural solid waste such as coir pitch, banana pitch, coconut husk, biogases residual slurry, rice hulls, biogases and paddy straw, red mud, orange peel etc have been investigated for the removal of dyes from wastewater.

The study of removal of dyes from tannery wastewater by activated sawdust to serve as low cost effective adsorbents was bounded by the limitation that only a few experiments had been undertaken in the field. Despite the minimal amounts of data and experimental procedures pertaining to this study being found in literature, the study has been remarkably successful. It was found that sawdust was highly effective for removing up to 70% of the dyes from tannery wastewater. But, our experimental filtration process, the removal of dyes from wastewater up to 81%. The study was remarkably successful with good experimental results being obtained despite the lack of experimental protocols found in literature. The adsorption obeyed both Langmuir and Freundlich isotherms.

A better understanding into the pertinent properties and kinetics that explain the mechanics of the adsorption process was obtained. In addition to acquiring data on the adsorption capacity of these activated saw dust, kinetic curves and adsorption isotherms were established.

### **Recommendation:**

With the lack of experimental protocols found in literature there was no starting knowledge of the optimal experimental parameters, such as starting dye concentration and adsorbent mass, needed to undertake effective experiments. Hence, a large amount of effort and experimental work was needed to acquire publishable kinetic curves and adsorption isotherms.



Further studies can be undertaken using an optimal starting dye concentration and adsorbent mass. For example, the screening tests could be refined to better reveal the differences in adsorption capacities for dye and activated saw dust. Using 1gm of sawdust (adsorbent) and 40mL of dye diluted to 100mL is recommended.

Follow up projects could now provide the basic data on the effects of various parameters such as the mass of sawdust, pH, and agitation time, stirring speed and temperature on various adsorbent properties. The impact of these parameters on the properties of surface area, ion-exchange capacity and color removal efficiency is needed.

11/24/11

# Chapter-5

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