

Effect of Water Pollution on
Selected Dye Effluents

BY

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Introduction

I INTRODUCTION

Ever since the advent of Industrial Revolution, there have been greater changes in the attitudes and vision of all those reaping the benefits of mechanisation and mass production; much emphasis has been made especially on the disposal and management of waste and effluents (both biochemical and industrial) that cause greater amount of pollution of water, noise, air and environment. With the ever-growing urbanisation and industrialisation all over the world, the fear of pollution, is taking rapid strides into being. And, separate studies are conducted to tide over the alarming situation for effective control and management of all parameters of pollution.

Of all types of pollution, water pollution is more immediate and dangerous to human and animal living and therefore a study of which is of paramount importance. This is derived from the simple fact that water needs no introduction and is an invaluable gift of the bounteous nature, prevalently found in all organisms, raw-materials and other industrial inputs.

Sewell (1975) says that water is a liquid of hydrogen-oxygen molecules. Water is never pure in nature. Gases including oxygen, carbon-di-oxide and nitrogen, are dissolved in between the water molecules. Salts such as

nitrates, chlorides, and carbonates, also become part of the liquid solution, solids, dust and sand, can be carried as suspended solids. Other chemicals give water colour and taste. Ions may cause a chemically alkaline or acid reaction.

'Pollution' is, "any degree of contamination of air, water or land which is likely to produce a significant adverse health effect to a significant number of persons in a foreseeable period of time opines Barbour (1983).

Environmental pollution problem has become pressing both in developed and developing countries. It is posing a challenge to scientists, technologists, ecologists, planners and academicians. Industry, transport and domestic sectors are the major contributors to pollution. Pollution of various kinds are water, land, noise and air.

Pollution of water resources can be caused by one or more of the following factors viz. (i) atmosphere dissolved gases (ii) weathering of soil, and rock minerals (iii) decomposition of animal and vegetable materials and (iv) industrial effluents, sewage and municipal wastes.

Kumar (1983) views that water is "polluted" when it changes its quality directly or indirectly as a result of discharge of the various toxic chemical pollutants so that it becomes less suitable for drinking and agricultural purposes. Water is one of the most important solute used

in the textile industry. Millions of gallons of water are used everyday in textile mills.

The industry is the major offender for creating water pollution. Untreated industrial effluents with toxic elements are polluting the water resources in our country. Thus most of the industrial waste water find its way into water courses without treatment rendering the water stream unfit for use.

Textile industries are classified as Dry Process industries and wet process industries. Production of yarn from raw cotton includes steps like opening and cleaning, picking, carding, drawing, spinning, winding and warping. These dry operations do not contribute to the liquid waste of the mill. The entire liquid waste from the textile mills come from the operations of slashing, scouring, desizing, bleaching, mercerizing, dyeing and finishing. All these sequences are wet processes.

In dyeing industries, water is a vital raw material not only for the dyeing processes but also for the boilers supplying steam for heating and drying purposes.

Doshi and Pillai (1982) point out, in textile industries, the wet processing of textiles consume 70 per cent of the total water. The wet process involves the use of various dyes and chemicals depending upon the constituent

chemical treatments, yields, different types of effluents.

The disposal of dye waste water is a major problem, because such effluents contain a number of contaminants including acid or alkali, dissolved solids, toxic compounds and colour. Of all these, colour is the first contaminant to be recognised because it is visible to the human eye. It is essential to treat the colour waste by suitable process.

The discharge of highly coloured effluent is not only aesthetically displeasing, but also impedes light penetration, thus upsetting biological processes. In addition, many dyes may be toxic to aquatic organisms and may cause direct destruction of aquatic communities.

According to Pramod Singh (1985), water for human consumption must be free from organisms and concentration of chemical substances that may be hazardous to health. Absence of turbidity, colour, disagreeable taste are of utmost importance in public supplies of drinking water.

The main objective in the treatment of industrial dye effluent is to eliminate, remove the offending pollutant to a desirable safe limit.

The specific objectives of this study are given below:

1. To assess the pollution load of selected dyes.
2. To suggest ways to reduce pollution
3. To recommend ways of efficient and economical treatment of dye effluent.

Reviews of Literature

II REVIEW OF LITERATURE

The literature pertaining to the study is dealt under the following headings:

1. Water, its classification, uses and its qualities
2. Sources of water pollution
3. Characteristics and properties of industrial waste effluent
4. Water pollution through industrial effluents
 - (a) Problems of water pollution
 - (b) Effect of water pollution
5. National policies and objectives
6. (a) Pollution control in textile industry
 - (b) Method of pollution control
 - (c) Purpose and treatment of waste effluent
7. Dyes
 - (a) Classification of dyes
 - (b) Theory of dyeing
 - (c) Selected dyes and its properties

1. Water

Doshi and Pillai (1982) opine, water is the basic necessities of life. It is an essential raw material in almost all chemical oriented industries (Ganu, 1982).

Kumar (1983) says, water is one of the important and most precious of natural resource used by us. Man is the most important member of the ecosystem consisting of air, water, land and living and non-living elements expresses Roy (1980).

Chanlett (1973) states that water is a raw material, which must be of a quality fitted to use. Regular and plentiful supply of clean water is essential for the survival and health of most living organisms. Life could not exist without water says Carpenter et al. (1947).

Classification of water

According to Pramod Singh (1985), water for practical purposes can be classified as clean, polluted and contaminated in the following order:

- (i) A clean water is one which is free from all contamination and safe for human consumption.
- (ii) A polluted water is one which is impaired of physical qualities through addition of substances causing turbidity, colour, odour and taste.
- (iii) A contaminated water is one which may carry infection by the addition of human or animal wastes or which has been rendered in wholesome by poisonous chemical compounds.

Manivasakam (1985) says, water can be classified according to mineral constituents as "Hard" or "Soft" according to the concentration of calcium and magnesium ions. These ions when present in high concentration, the capacity of the water to lather with soap is reduced and such waters are termed as "Hard waters". A soft water is one which produces lather easily with the soap. The degree of hardness is indicated by the terms, "moderately hard", "Hard" and "very hard".

Water uses

Sewell (1975) views that uses of water can be divided into four broad categories:

- (i) Direct physical use by man and his domesticated animals. Water must appear clean, tasty, pure, free from dangerous and debilitating micro organisms.
- (ii) Direct use in industry and agriculture as a factor in production. Industries are the largest consumers, nearly 40 per cent being drawn for cooling by the electric utilities. Another 17% is classified "industrial and miscellaneous and includes manufacturing, mining and construction. Irrigation accounts for 33%.
- (iii) Psychological use as part of our esthetic and cultural environment.

(iv) Ecological use as a vital component in the earth's life support system.

Nordell (1956) points out that the water used for any manufacturing plant, mill, institution or municipality should be (i) abundant enough to take care of present and future needs (ii) available at sufficient flow rates and pressures to meet all peak demands and provide adequate fire protection (iii) of suitable quality for its various end uses.

Water quality requirements for wet processes

The availability of water suited to need is a consideration in plant siting, water used in textile dyeing is nearly distilled water in quality views Chanlett (1973).

Nordell (1956) opines that the quality of water required depends on its end use. As the tolerances for various impurities vary according to these uses, the quality of water required in each case may differ greatly.

Doshi and Pillai (1982) expressed the quality of water used for wet processing of textiles assumes considerable importance from the point of the quality of textiles processes. The quality of water required in the various sections of a process depend upon the type of processing involved.

The textile industry is confronted with three main problems connected with water says Parikh (1979). They are as follows:

- (a) Production of water of suitable quality for processing of textile products
- (b) Supplies of water suitable for boiler
- (c) Prevention of corrosion of metal tanks, pipe lines etc.

Thus it is a matter of considerable importance that water be of a high grade quality.

2. Sources of water pollution

World Health Organization (1972) opines that the uncontrolled disposal of sewage and other liquid wastes resulting from domestic uses of water, industrial wastes containing a variety of pollutants, agricultural effluents from animal husbandry and drainage of irrigation water. The addition of chemicals to water to control undesirable organisms is another cause of pollution.

The available sources of water supply are fast getting polluted with the industrial wastes, which contain different water-borne germs, organic matter, oils, detergents, radio-active substances and sewage on account of the unrestrained urbanisation and industrialisation says Hara Prasad (1980).

Hari and Rajeshwari (1985) explain, water pollution comes from three major sources are (i) sewage (ii) industrial waste and (iii) Agricultural waste. Today industry contributes more water pollution than do household users.

3. Characteristics and properties of Industrial waste effluent

Characteristics of waste effluent:

The waste water discharged from dyeing and finishing mills varies with the form of enterprise, the processes to be carried out, the installations and the kind of textiles to be processed. Waste water to be discharged from one and the same dye works varies every hour in concentration, draining quantity etc. Waste water is characterized in that the dyeing waste water is tinted and absorbs sunlight and as a result may hinder the existence of microbes which contribute to the purification of rivers states Uejima (1973).

Narayana Rao and Datta (1987) point out, the characterization of the raw waste is essential in the planning for effective and economical methods of water pollution control. Due to varying nature of the industrial wastes, the raw waste characteristics and the effluent characteristics as established. Suspended Solids (SS) and Biochemical Oxygen Demand (BOD) after five days 20°C (BOD₅) are the usual parameters of pollution. As the pollution load varies according to the dilution offered by the water used,

it is a common practice to express suspended solids and BOD₅ in terms of per capita contribution.

Textile waste characteristics

The pollutional features of textile wastes differ widely among various segments of the industry, and each type of waste presents a special treatment problem. Organic substances such as dyes, starches, and detergents in textile waste undergo chemical and biological changes which consume dissolved oxygen from the receiving stream and destroy aquatic life. Colours from dyes vary and, although not toxic, are esthetically objectionable for drinking and recreational water. Chemical carriers used in dyeing such as phenols may add taste and odor, opines Gurnham (1965).

According to Manivasakam (1987), the characteristics of the dye effluent are the intense colour, residual dyes, presence of acids or alkalies and excess salts. They are combination of inorganic and organic wastes and possess high BOD, COD and suspended solids, which mineralise the receiving stream.

The character and quantity of wastes from different industries vary, depending on the nature of the products, raw materials and processes used and by-products recovered and size of the plant states Roy (1980).

Kumar (1983) feels that Textile industry waste originate from the manufacture of specific products in the form of liquid, solid or gaseous wastes. Industrial wastes are commonly more concentrated and require extensive treatment as compared to municipal wastes.

Properties of polluted water

Varshney (1983) stresses that the physical and chemical properties of water can be estimated by standard methods. Important water quality characteristics are explained as follows:

(i) Biological oxygen Demand (BOD): It is the amount of oxygen which is needed to oxidize the organic material by micro-organisms anaerobically and the test period is five days.

(ii) Chemical Oxygen Demand (COD): It is a measure of oxygen consumed to oxidize organic matter by boiling potassium dichromate and concentrated sulphuric acid for two hours. COD is taken as indicative of the total amount of carbonaceous organic matter present in water but it indicates a part of organic matter oxidized.

(iii) Permanganate value (PV): It is a chemical oxidation using acid potassium permanganate solution for four hours at 27°C.

(iv) Dissolved Oxygen (DO): It is of great use to assess survivability of life, particularly of fish which require atleast 5mg/l DO. While the maximum dissolved oxygen in water is only 9.1mg/l at 20°C.

4. Water pollution through industrial effluents

Vaidya and Datye (1982) say, pollution is the discharge of the material and energy residues into the environment. Some of these residues are raw materials which are unconverted, some are not fully recovered and some are by-products. All these are waste.

Water resources have been the most exploited natural system. The deterioration in the chemical, physical and biological properties of water brought about mainly by industrial wastes. The addition of an organic waste will not only influence the chemical characteristic, but also the colour, odour, and biological properties simultaneously. Pollutants such as heavy metals and various organic products, which are not biodegradable have been found at certain levels to be injurious to human health explains Varshney (1983).

According to Vakil (1984), the reduction in environmental quality caused by the disposal of residuals from the industry. Industrial effluents are actually more serious,

they may include organic material and inorganic compounds like sulfuric acid, arsenic and cyanides, which are difficult to remove and highly poisonous. Industry is responsible for more than twice as much pollution as is domestic sewage. The change in the physico-chemical and biological equilibrium of the environment caused by industrial wastes says Ananthakrishnan and Viswanathan (1976).

Mahajan (1985) feels that water pollution occurs due to the presence of dissolved inorganic materials such as free chlorine, ammonium hydrogen sulphide and other sulphides, organic materials such as proteins, fats, carbohydrates and other substances found in industrial water and physical factors such as turbidity, colour, temperature of effluent associated radioactivity etc.

The industrial wastes usually contain traces or larger quantities of the raw materials, intermediate products, final products, co-products and by-products and processing chemicals used. The composition and amount of pollutants discharged into the water are likely to create nuisances and are not suitable for all functions and purposes stresses World Health Organization (1972).

The addition of industrial waste effluents and sludge containing organic matter and many inorganic salts and metals to water which changes its natural qualities.

Industrial effluents are produced with a wide range of potential pollutants says Dix (1981).

Noguchi et al. (1974) opine, the discharge of dye effluent containing relatively large amounts of suspended solids, sulfide, high bio-chemical oxygen demand value into water courses which is less suitable for highest uses and for human consumption.

The quantity of dye used depends on the characteristics of the fiber, the colour and the desired finish. Synthetic textiles require the use of special carriers to achieve satisfactory penetration of dye into the fiber. These carriers are very strong and present a major source of pollution, says Environmental Protection Agency (1978).

(a) Problems of water pollution

Dix (1981) points out that the existence of pollution in the environment, as a national and a world problem. It is increasingly being appreciated that in general effects of pollution produce a deterioration of the quality of the environment.

The pollution is not a problem affecting only industrialized countries. India has many localized areas where water pollution already creates situations not only dangerous to health but also injurious to the economy in many ways says Varshney (1983).

Stephens (1967) and Sapru (1987) opine, water borne diseases of cholera, and typhoid are directly and indirectly caused by polluted water. They are carried in the wastes from infected people, which means down the drains and into streams and rivers explains Holum (1977).

The more densely the area is populated the greater the problem of industrial waste treatment and disposal. The problem of industrial wastes and their treatment is affected by the volumes of dilution water available and the permissible use of streams views Rudolfs (1953).

According to Hari and Rajeshwari (1985), pollution problem in the country has reached tremendous dimensions and the major reasons for increasing pollution are the increase in population. Size and advances in technology and the application of energy to limited productive purposes.

Vakil (1984) feels that pollution of water is probably a more acute problem in developing nation like India than air pollution. India is poised for a significant and rapid industrial growth, and in future the pollution load will increase manifold unless proper care is taken states Roy (1980).

(b) Effect of water pollution

Dix (1981) points out that the effect of water pollution may be as follows:

- (a) Physical effects such as suspended particle solids that cause water turbidity, cooling water that raises water temperature and oily surface films that resist the reoxygenation of water.
- (b) Oxidation effects caused by bacterial action or chemical oxidation of inorganic and organic substances, both of which significantly reduce the dissolved oxygen content of water.
- (c) Toxic chemical effects caused by a range of substances that cause intermediate or cumulative physiological changes in plants, animals and humans.
- (d) Chemical nutrient effects resulting from high concentrations of nitrates and phosphates.
- (e) Pathogenic effects caused by microorganisms, where bacteria and viruses are present in sufficient numbers to cause a health hazard.
- (f) Radio nuclide effects caused by the accumulation of radio active substances in food organisms, which produce human body changes.

According to Narayana Roa and Datta (1987), the effect of water pollution is classified as follows:

- (a) Organic substances that deplete the oxygen contents of the receiving streams and impose a great load on the biological units of the sewage ^treatment plant.
- (b) Inorganic substances like carbonates, chlorides, nitrogen etc. that render the water body unfit for further use and some times encourage the growth of some undesirable micro-plants in the body of water.
- (c) Acids or alkalies which make the receiving stream unsuitable for the growth of fish and other aquatic life.
- (d) Toxic substances like cyanides, sulphides, acetylene, alcohol, petrol etc. which cause damage to the flora and fauna of the receiving water, affect the municipal treatment processes.
- (e) Colour producing substances like dyes, which though not toxic, are aesthetically objectionable when present in the water supplies.
- (f) Oil and other floating substances, which not only render the streams unsightly, but interfere with self-purification of the same, and the operations of sewage treatment plants.

Raghavan (1986) states that effect of pollution can be categorised as follows:

(a) pH (Hydrogen ion concentration)

High alkalinity of waste waters have an adverse effect on aquatic life. This will also cause incrustation on sewers. If waste water is used for irrigation, it has an adverse effect on growth of crop and soil loses its productivity.

(b) Suspended solids: Colloidal organic matter will increase turbidity of water and along with colours, dyes and oily scums will produce an unsightly appearance, oily layer also interferes with oxygen transfer at air/water interface.

(c) Biochemical Oxygen Demand (BOD)/Chemical Oxygen Demand (COD)

Organic matter in wastes like starches, dextrin, as well as inorganic matters like sulphides, hydrosulphides, and nitrites will exert, an oxygen demand resulting in septic condition of receiving waters.

(d) Chemicals

Toxic chemicals like chlorine, chromium and aniline dyes affect aquatic life.

5. National Policies and objectives

Patel (1977) says that as a policy, water intensive industries may have to be located in areas where water is available in plenty taking into consideration sites for discharging of effluents and the treatment of effluents. The treated effluents can be used for agricultural and other purposes. The policy has to lay down norms for preservation and enhancing the value of waters and for creating better environment.

According to Hara Prasad (1980), Indian Standards Institution had published many criteria and tolerance limits for different types of waste waters which can be disposed of by different methods.

In developing country, assessment of water sources both surface flows and ground water supplies is essential for development of irrigation, industrial and domestic needs states Ramakrishnan (1978).

Manivasakam (1987) expresses that in India, Pollution Control Act is being in force and each state has Pollution Control Board for implementing pollution control measures, to monitor the quality of water and air, to protect the environment from pollution. Each State Pollution Control Board has fixed tolerance limits for effluents to be

discharged. These tolerance limits are almost the same as those prescribed by Bureau of Indian Standards.

6. (a) Pollution control in Textile industry

The solid waste collection and disposal methods have to be improved by proper methods of waste disposal, reuse, recycling, greater control of pollution at the source, and better location of pollution generating activities, proper treatment and monitoring of pollutants inside the factory will be helpful in controlling pollution from industries say Hari and Rajeswari (1985).

According to Haraprasad (1980), for effective water pollution control, it is essential to have a system of adequate collection, treatment and disposal of community wastes. A sound system of water pollution control results in the preservation of the aquatic organisms; lower water treatment costs.

Pai (1980) and Sandoz (1979) view, the waste water should be free from sludge deposits, unnatural colours, oil films, and toxic substances before it can be discharged into the receiving stream. It should have P^H of 5.5 to 9.0. The dissolved oxygen in the receiving water should be at least 5 parts per million (ppm).

Warty (1980) opines that the physio-chemical treatment is only appropriate for the purification of effluents which are highly coloured. The effluent treatments are essential to produce water of a standard satisfactory quality to discharge into sewage system or into a river views East (1971).

The textile industry water effluents must meet the requirements for BOD₅, COD, PH, suspended solids, total solids, heavy metals, colour, toxic non-degradable chemicals, solvents, temperature, oil and grease, turbidity etc. stresses Benisek (1979).

Mckay and Otterburn (1980) state, suitable dyes are used where the amount of water will be negligible. The insoluble colour bodies are readily treated by processes collectively named as coagulation explains Herbert Noble (1973).

Goodman and Porter (1980) point out, before a process waste water is recycled for reuse in a textile process, the impurities in the water must be reduced to a level that is suitable for use in that process.

(b) Method of Pollution control

Raghavan (1986) describes that the pollution control can be achieved as follows:

(a) Reduction in waste volume: This can be achieved by proper management of water in the mills, avoiding wastages and wherever possible by recycling the water, by using counter current system of washing. In a cotton textile mill it is possible to reduce water consumption by 20 to 40 per cent.

(b) Recovery of chemicals: The recovery of synthetic sizing agents, caustic from mercerizing by concentration and evaporation, and kier wastes by dialysis help in reducing the strength of effluent.

(c) Substitution of chemicals: (i) use of carboxy methyl cellulose and polyvinyl alcohol in place of starch used in sizing of cloth (ii) use of mineral instead of acetic acid (iii) use of non-degradable detergents instead of soap. The reduction is possible by proper chemical substitution to the maximum extent of 50%.

(d) Effluent treatment: When all the means of reduction of quality and quantity of effluents are adopted, then the effluent can be treated for either disposal or re-use.

Jasdeep Singh (1981) opine that the waste water effluent is subjected to a number of physical and chemical treatments so as to render it free from any harmful element and only then it is supplied to the consumers.

Mahajan (1985) prescribes two basically important measures for effective waste water treatment, viz.

1. The preventive steps are made up (i) volume reductions of waste water: It can be achieved by (a) conservation of water used in process (b) segregation of different streams in process (d) changing the production schedule to decrease waste water produced and (e) avoiding batch discharges.

(ii) Strength reduction: It can be achieved by (a) equipment modifications and process changes (b) Segregation, equilization and proportioning and (c) recovery of important by-products from waste streams.

The preventive measures mentioned above are general and one or more of them may be applied depending on the specific application.

(2) Curative measures deal with the actual treatment of liquid effluents by physical, chemical and biological methods of^r their combination, depending on the nature of the pollutants in the waste and the extent to which they are to be removed.

Uejima (1973) says that there are different methods for treating waste water as follows:

(i) Physical method: This method is employed for separating solids from waste water. It consists of screening, sedimentation, filtration, centrifugal separation systems.

(ii) Chemical method:

This method is used for the chemical reaction to change contaminative matters into harmless matters. It consists of the neutralization reaction, the oxidation reduction reaction. The ion-exchange reaction, the addition condensation reaction etc.

(iii) Physical chemical methods:

This method is used for treating matters dissolved in waste water. It utilizes^t coagulation, adsorption, evaporation, dialysis etc.

(iv) Biological method:

This methods includes natural purification of contaminative matter dissolved in waste water by utilizing the action of bacteria. It is the effective method for treating waste water in which organic matters are dissolved. This method employes either aerobic bacteria or anaerobic bacteria. It consists of activated sludge system, trickling filter system, anerobic digestion system.

Rudolfs (1953) states that the basic principles of industrial waste treatment are based upon:

- (i) Separation of solids from the liquid
- (ii) oxidation of organic and oxygen demanding materials

(iii) Neutralization

(iv) Removal of poisonous substances

(v) Disposal of Residues

The methods used are physical, chemical and biological in nature or may constitute combinations of various methods.

C. Purpose of examination and treatment of waste water

Manivasakam (1985) opines that the major reason for examining the waste water is to decide their pollution potential and to design a perfect treatment plant.

Different types of examinations (physical, chemical, biological and micro biological) of water are necessary for the following reasons:

- (a) To assess its quality to provide a pure water to the public for drinking and other domestic purposes.
- (b) To assess its suitability for the specific industrial purpose.
- (c) To assess the pollution load in a water course and to trace the origin and extent of pollution and suggest a possible remedy.
- (d) Determine the efficiency towards purification of industrial wastes discharged into water courses.
- (e) Check the efficiency, uniformity and consistency of treatment and purification processes.

The purpose for treating waste water has been directed to the reuse of some parts of waste by employing a recycling system or by using advanced waste water treatment system. The importance of waste water treatment is to remove or collect the contaminating factors found in waste water, this involves not only the purification and reuse of water but also the effective utilization of the collected matters views Uejima (1973).

According to Dix (1981), the aim of Industrial waste treatment is to separate the suspended solids and dissolved substances from the liquid fraction. The primary objective in the treatment of industrial waste is to eliminate the pollutant to a desirable safe limit or the standards laid down by the authorities stresses Mahabal (1979).

7. Dyes

According to Wingate (1976), Dyeing is a means of applying colour to fibers, yarns or fabrics. Dyeing is the art of colouring textiles in such a manner that the colour may be fast or may not be ordinarily removed by such operations as washing, rubbing, sunlight, and others to which the textiles are usually subjected.

(a) Classification of Dyes

Joseph (1980) points out that dyes can be classified in several ways according to hue produced, chemical class, method of application and types of fibres to which they are successfully applied.

The dyestuffs employed in the process of dyeing may be divided into two classes namely natural colouring matters and artificial colouring matters. Natural colouring matters such as logwood, turmeric, fustic, orchil, catch. Artificial colouring matters such as direct, acid, basic, disperse, mordant, vat, ^Yreactive, and sulphur dyes, opines Othmer (1965).

According to Hall (1955), a classification of synthetic dyes according to chemical composition and structure is very useful to the manufacturer, but the dyer refers one that is based on the dyeing behaviour of the dyestuff.

The dyes are classified according to their chemical constitution and also on the basis of their dyeing properties explains Cowan and Jungerman (1969) as

Nitroso, Nitro, Monoazo, Disazo, Triazo, Polyazo,
Diphenyl methane, Trianyl methane, Thiazole, Indamine,
Indophenol, ^Zisoic, Thiazine, sulphur, Lactone, Amino-quinones,
hydroxy ketone, Indigold, Anthraquinone, Phthalocyanine,
chloro and Dichloro Triazinyl and Remazol.

Potter and Corbman (1954) classified dyes into natural dyes such as:

Vegetable dyes (Alizarin, Logwood, and Indigo, Saffron, Madder, henna)

Animal dyes (Tyrian purple and cochineal, squid sepia, lac)

Mineral dyes (Iron buff, Chrome yellow, Prussian blue)

Synthetic dyes such as: Basic, Acid, direct, sulphur, Azoic, vat, Reactive, Acetate, chrome, Developed, Pigment, mordant, Azo, metallised and dispersed dyes.

According to Rupp (1955), as the art of dyeing came under the scrutiny of chemists, the synthetic production of coloured substances suitable for dyeing fabrics increased. These replaced the natural dyes entirely owing to their cheapness, purity and reliability regards Welford (1966).

Labarthe (1964) has stated that there are approximately 4000 chemical colourants produced which present a new challenge to the ingenuity by the dyer.

(b) Theory of Dyeing

Lynn and Press (1977) observe that from the time of the introduction of synthetic dyes until the present day various attempts have been made to formulate a theory

of dyeing. It is generally accepted that dyestuffs and fibers go together in chemical relationship and according to the solubility function which the fiber exerts over the dye in the dyebath to draw it from the dye bath and absorb it.

The three ways of coloring may be distinguished by adsorption of a soluble molecule by virtue of the physical forces which operate between the dye and fibre molecules, an insoluble pigment is formed in the fibre by the adsorption of a soluble molecule which is then insolubilized by oxidation or any other chemical reactions and by formation of a chemical bond between dye and fibre explains Leene (1972).

According to Baker and Baker (1920), the simplest process of dyeing a fabric consists of submerging, it in a solution of dye, known as a "dye bath" and allowing it to extract or exhaust the colour from the bath.

Srivastava (1972) states that the absorption theory is advanced by those who claim that colour is produced on cotton fibre by adhesion of molecules of the dissolved dyestuff to the surfaces of the fibres as solid bodies, the whole resulting in such a relatively high concentration of the molecules as to produce a colour of intensity desired.

Giles (1971) points out the chief factors affecting the rate of dyeing are liquor to goods ratio, temperature, type of yarn, concentration of electrolytes in the dyebath and depth of shades.

All parts of the textile substrate should be given equal opportunity to extract the dye in order that a uniform colour or level dyeing be obtained. Thus in theory of dyeing colour play an important role and the dyeing process is a very complex phenomenon in which several reactions take place simultaneously in a heterogenous system states Mathews (1947).

(c) Selected dyes and their properties
Vat Dyes:

The vat dyes are organic compounds that are insoluble in water, dilute acids and alkals but which on being reduced, form a 'colour base' soluble in alkaline media, and exposure of material dyed with such a colour base produces the original colour compound by oxidation says Ellis (1940).

Considine (1974) points out that dyes are one of the best known types of dyestuff which were used in Egypt prior to 2000 BC. A synthetic vat dye was developed in 1987 and since then a great number of vat dyes have synthesized and these have replaced natural vats. India has produced vat colours from Indigo by cheap labour cost from plant and at

the end of the 19th century the annual output was amount to one billion. It was therefore called "King of Dyestuff" states Keenihiro (1977).

According to Gale (1968), vat dye includes Indigo and tyrian purple. Indigo was one of the oldest naturally occurring dye and is widely used on cotton, viscose rayon, linen and other vegetable fibres. The colours are brilliant and almost any shade can be obtained and are characterised by good fastness to laundering and sunlight.

Vat colours is the fastest variety of all dyes chiefly used in cotton dyeing. It is not soluble in water unless formed into leuco compound with the help of strong alkali and reducing agents. Vat dyes are among the most resistant dyes in the market to both washing and sunlight opines Basu (1964).

Properties of vat dyes

Wolfe (1941) and Monaghan (1935) view, vat dyes are water insoluble coloured compounds which cannot be applied on fibres as such but have to converted into their water soluble leuco form having affinity for the fibres. Oxidation of the leuco compound by air on an oxidizing agent reproduces the original compound.

Their acceptance in dyeing has been progressing at a rapid rate because of their ease of application and relatively good fastness properties. These are only class of dyes that actually form a chemical bond with textile fibers to produce bright colours states Lyle (1977).

Shanai and Shab (1979) view the reactive dyes are the first synthetic dye which was introduced in the year 1956 for cotton. As the name reactive indicates these dyes chemically react with the fibre to form a covalent link. The presence of this type of link imparts good wash and other fastness properties. These dyes have made possible, the production of bright and attractive shades of varied colour and high fastness.

Procion dyes are the new class of dyes which was introduced by the I.C.I. in 1956 and gives brilliant fast shade on cellulosic fibres. Fixation is achieved by direct chemical linkage so that the dye molecules become an integral part of the cellulosic molecules. These dyes are anionic in character and possess good solubility in cold water is employed for the dyeing opines Marsh (1979).

Properties of Reactive Dyes

Trotman (1970) points out that procion dyes are readily soluble in water, the dyes react with alcohols, amines and water. These dyes are stable in water solution,

low substantivity to cellulose has high degree of fixation on cellulose and compatible with disperse and pigments state Whitaker and Wilcock (1942).

The procion dyes has two chlorine atoms left unsubstituted and this two atoms when react with hydroxyl groups of cellulose forms colour and due to this property reactive dyes has got a extremely good light and wash fastness. These dyes react chemically with the fibre to form a covalent link and presence of this link, the dye produces a good wash and other fastness properties explains Carter (1971).

Sulfur dyes

Hess (1958) views that sulfur dyes have become important for producing fast shades on cotton and other cellulose fibers including regenerated cellulose. It is excellent fastness to washing.

These colours are used almost entirely on vegetable fibers because of the difficulty of applying them to textiles in a strong alkaline bath. If glue is added to the dye bath, sulfur dyes can be applied to silk and wool states Wingate (1953).

Woolman and McGowan (1943) expressed, they are applied in reduced form with sodium sulfide and soda ash, then oxidized in the fiber with sodium perborate or with

copper or chrome salts. Sulfur dyes are increasing in importance because of their application to army needs in tenting material, khaki, work fabrics and similar uses.

These dyes are widely used on cotton goods for fast colours mostly blacks, browns, and deep blues. These dyes are insoluble or only ^aspringly soluble in water opines Giles (1974).

Properties of sulfur dyes

Lee (1953) feels that these dyes are applied on cellulose fibers. It has good fastness to washing and light. Blacks, browns, and navies are found in sulfur colour state Woolman and McGowan (1943).

The dye molecule contains sulfur and is insoluble in water but is soluble in sodium sulfide or other alkaline reducing agents. The strongly alkaline bath prohibits their being used for protein and acetate fibers. The dyes are fast to light, alkalies and perspiration opines Hess (1958).

Experimental Procedure

III EXPERIMENTAL PROCEDURE

The experimental procedure pertaining to the study is as follows:

1. Selection of Dye
2. Selection of colour
3. Desizing the material
4. Equipment used for Dyeing
5. Preparation of Dye solution
6. Method of Dyeing
 - a. Vat Dye
 - b. Reactive Dye
 - c. Sulphur Dye
7. Collection of Dye Effluent
 - a. Vat Dye Effluent
 - b. Reactive Dye Effluent
 - c. Sulphur Dye Effluent
8. Laboratory Experiments
 - A. Before Treatment
 - a. General parameters
 - (i) Colour Intensity
 - (ii) Potentia Hydrogenii (pH)
 - (iii) Biochemical Oxygen Demand (BOD)
 - (iv) Chemical Oxygen Demand (COD)
 - (v) Total Suspended Solids (TSS)
 - (vi) Total Dissolved Solids (TDS)

b. Chemical parameters

- (i) Chloride
- (ii) Residual chlorine
- (iii) Phosphate
- (iv) Sulphate

B. After Treatment

- 1. Neutralization
- 2. Coagulation

Coagulants used for the treatment

- (i) Treatment with Alum
- (ii) Treatment with Lime
- (iii) Treatment with Ferrous Sulphate

3. Decolourisation

- (i) Treatment with chlorine
- (ii) Treatment with charcoal

1. Selection of Dye

The type of dyestuff used for dyeing any particular fabric depends on the nature of the fabric and the fastness or other qualities required in the finished goods (Birrell, 1959).

According to Marks (1959) and Basu (1964), vat dye is the fastest variety of all the dyes chiefly used in cotton dyeing. It is the most resistant dye for both washing and sunlight.

Dolby (1976) says that reactive dyes offer more benefits to the dyers. Further Marsh (1979) points out that reactive dyes give more brilliant shades of great brightness and excellent fastness to the cotton fabrics.

Shenai (1983) opines that sulphur dyes plays an important role in the development of the correct shades of their optimum fastness properties. Lee (1953) feels that it is used on cellulose fibers and is most resistant to washing and light.

Vat, Reactive, Sulphur dyes were selected for the study mainly because of their suitability to cotton material (Hess, 1978).

2. Selection of colour

Hess (1958) points out that olive D colouring matter known as Novatic is one of the vat dye, which is largely used as a standard of fastness.

Butterworth (1967) opines that procion brilliant Red has shown that the dye reacts with both primary and secondary hydroxyl groups. This is excellent colour for dyeing cotton.

Woolman and McGowan (1943) feel that the use of Sulfast Violet B Brown colour are increasing in importance because of their excellent fastness properties. These dye

compounds have affinityⁿ to cellulose fibers opines Shenai (1983).

3. Desizing the material

Ishida (1977) opines that desizing is to dissolve the sizing agents by using suitable chemicals because if not completely removed, the sizes can become fixed, which will hinder the dye absorption (Tattersall, 1975).

According to Saroja and Savitry (1968) desizing can be done easily by soaking the material in cold water for one hour and rinsing it in fresh water.

4. Equipment used for Dyeing

According to Chitrangada Krishna (1977), the following equipment are used for dyeing purpose:

1. Hand jigger machine (Plate I)
2. Thermo meter
3. Physical balance
4. Small beakers to mix dyes
5. Dyes and chemicals
6. Glass measures
7. Plastic spoons
8. Heater

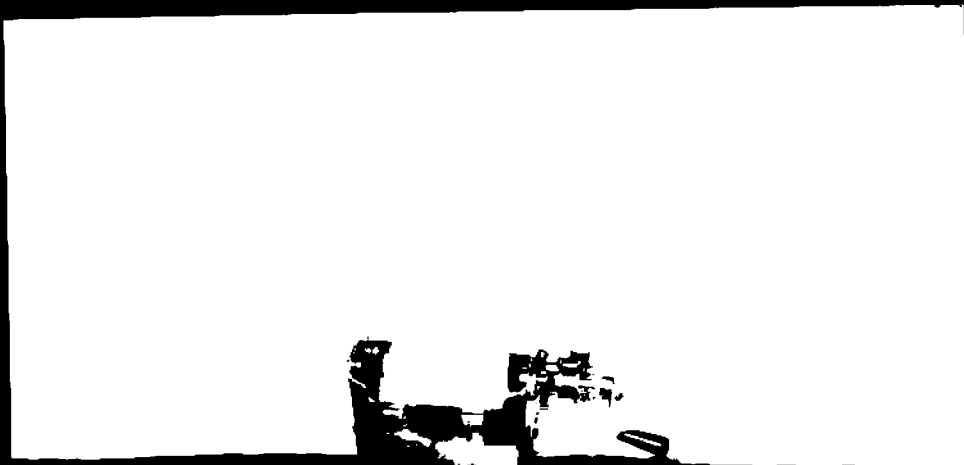


PLATE I--HAND JIGGER

of colour 1.9 grams of soda ash was added to the dye bath, stirred thoroughly and dyeing was continued for thirty minutes. Then the material was washed thoroughly (Sample given in Appendix IIb).

c. Sulphur Dye

The desig^zed material was wound on the hand jigger machine and the prepared dye solution was poured in the hand jigger container and the machine was operated till the temperature reaches to 60°C. 1.9 grams of salt dissolved in 50cc of water was added in the dye bath and the process was continued for ten minutes at 80°C. Then the material underwent in the cold wash, hydros wash, and hot wash thoroughly and oxidation treatment was given. For oxidation 1.14 grams of dichromate and 1.5cc of acetic acid were added to 140cc of water. This solution was poured in the jigger container and the work was continued for five minutes at 60°C. Finally the material was washed thoroughly. (Sample given in Appendix IIc). The methods suggested by United Bleachers Limited.

7. Collection of Dye Effluents

The dye effluents were collected in the following ways:

a. Vat Dye effluent

Before oxidation, after treating the material in the dye bath	.. 300ml
Cold wash	.. 380ml
After oxidation	.. 250ml
After rinsing the material in the solution (3cc of soap solution in one litre of water and boil the solution for five minutes)	.. 1000ml
Final wash	.. 1000ml

Totally 2930ml of dye effluent was collected and kept aside.

b. Reactive Dye Effluent

After dyeing the material, the dye solution from the jigger container	.. 250ml
Cold wash	.. 250ml
After rinsing the material in the soap solution (3cc soap/litre for 5 minutes)	.. 250ml
Final wash	.. 250ml

Totally 1000ml of dye effluent was collected and kept aside.

c. Sulphur Dye Effluent

Before oxidation, after treating the material in the dye bath	.. 300ml
Cold wash	.. 140ml
Hydros wash	.. 140ml
After oxidation	.. 140ml
Cold wash	.. 140ml
After rinsing the material in the soap solution (3cc soap/litre for five minutes)	.. 1000ml
Final wash	.. 1000ml

Totally 3000ml of dye effluent was collected and kept aside.

8. Laboratory experiments

A. Before treatment:

(a) General parameters:

1. Colour intensity

The intensity of colour is directly proportional to the optical density and indirectly proportional to the transmittance. The optical density of the sample is measured before and after the treatment^{en} and the reduction in the colour intensity is observed.

Procedure

The colour intensity of the sample before treatment was measured in the photoelectric colorimeter using the filters of 530m μ and 660m μ (Plate II). The filter range to be used for the sample was known from the values of the optical densities given by different filters. The filter which shows higher optical density was taken as the correct range.

The filter range for the three samples were found out as:

For Reactive dye effluent	..	530m μ
For vat dye effluent	..	530m μ
For sulphur dye effluent	..	530m μ

The optical density of the sample before treatment and after treatment was measured using the above filter and the reduction in the colour was noted (The method suggested by United Bleachers Limited).



PLATE-II--PHOTOELECTRIC COLORIMETER

(ii) Potentia Hydrogenii (p^H)

p^H is the measure of the intensity of acidity or alkalinity and measures the concentration of hydrogen ions in water. The normal acidity or alkalinity depends upon excess H⁺ or OH⁻ ions over the other, and measured in gram equivalents of acid or alkali. If free H⁺ are more than OH⁻ ions, the water is acidic. If free OH⁻ ions are more than H⁺ ions, the water is alkaline say Trivedy and Goel (1984).

p^H is the negative log₁₀ of the hydrogen ion concentration in a solution, measured by calorimetric methods using various indicators. For accurate measurement of p^H, electro-metric methods are used employing the hydrogen ion sensitive electrodes.

Description

p^H meter employ^s 2 electrodes, an indicator glass electrode, and a calomel reference electrode, while others may have combined glass and reference electrodes, operated by battery. p^H scale ranges from 0 to 14 with 7 as neutral, below 7 being acidic and above 7 as alkaline (Plate III).

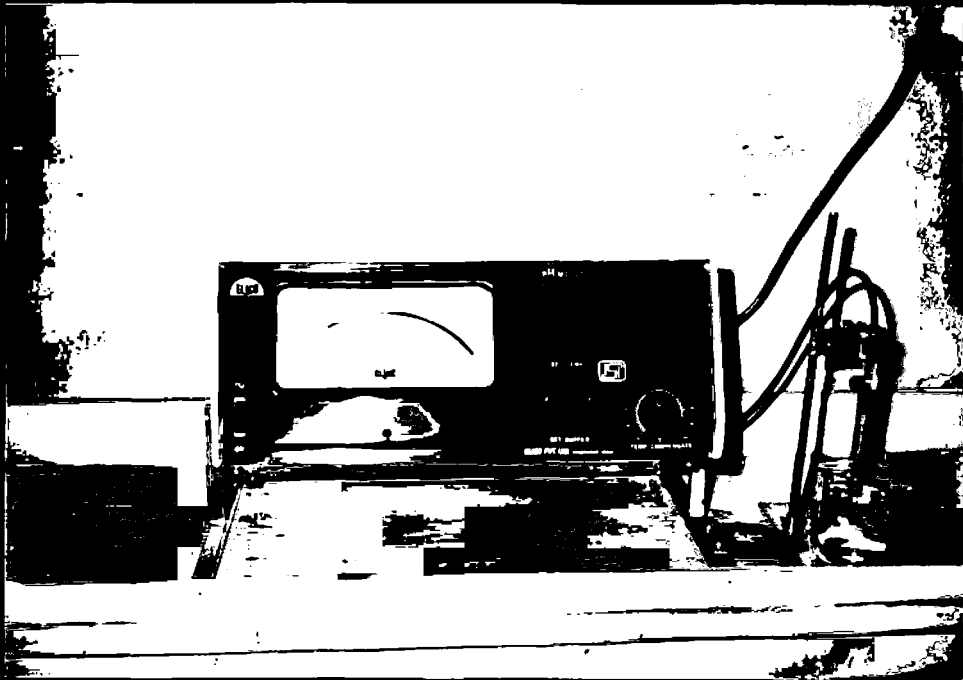


PLATE III--pH METER

Procedure

An essential aspect to use all the pH meters was to calibrate it with suitable buffers. Ready glaxco buffer tablets of known pH value (Buffer solution 4) are available in the market. pH meter with a buffer value was checked. The required quantity of samples were tested to find out the pH values.

(iii) Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand is the measure of the degradable organic material present in a water sample. It is defined as the amount of oxygen required by the micro-organisms in stabilizing the biologically degradable organic matter under aerobic conditions opine Trivedy and Goel (1984).

The method involves, measuring are differences of the oxygen concentrations between the sample and after incubating it for five days at 20°C.

Requirement

1. BOD bottles (350ml)
2. BOD incubator (Plate IV)
3. Phosphate buffer
4. Magnesium sulphate
5. Calcium chloride

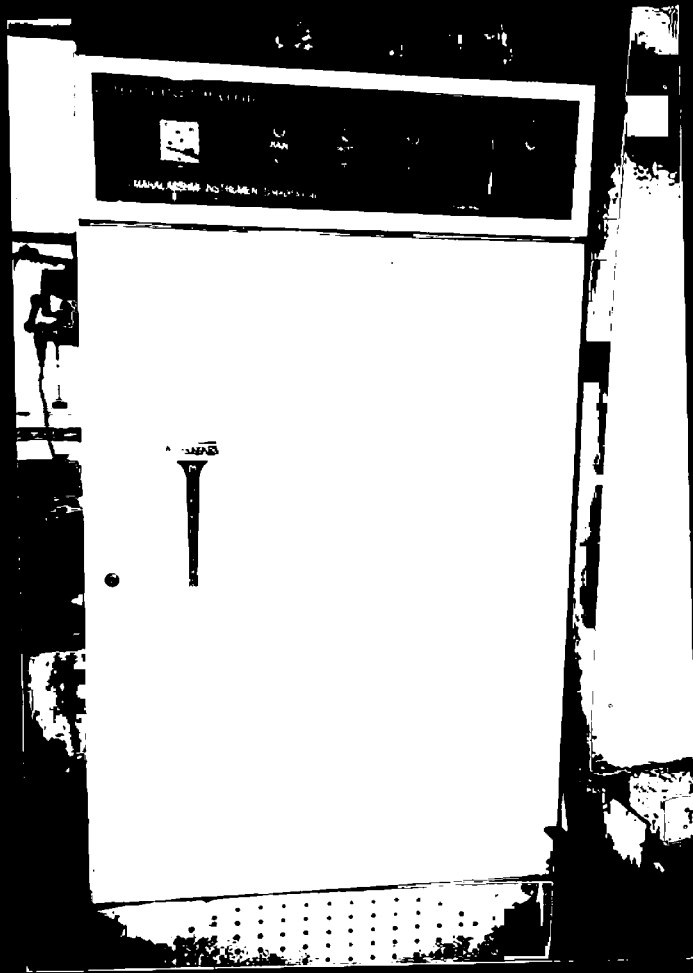


PLATE IV--BOD INCUBATOR

6. Ferric chloride
7. Sodium sulphite solution (0.025N)
8. Seeding

The procedure for preparing the reagents and the formula for calculating Biochemical Oxygen Demand are given in Appendix III.

Procedure

In one litre of water, 1ml of each reagent was added and mixed thoroughly. Neutralized the required amount of sample by using H_2SO_4 to pH around 7.0. Since dissolved oxygen in the sample was likely to be exhausted, it was necessary to prepare a suitable dilution of the sample to the expected BOD range (Table given in Appendix IV). Required dilutions were prepared in a large glass t \ddot{h} rough and filled two sets of BOD bottles. One set of sample was kept in incubator at 20°C for five days, and the other set of sample was used to determine the dissolved oxygen content immediately. The same procedure was repeated to get concordant values.

Dissolved Oxygen (DO)

Winkler's Iodometric Method

According to Trivedy and Goel (1984), Dissolved Oxygen is one of the most important quality assessment and reflects the physical and biological processes

prevailing in the water. Its presence is essential to maintain the higher forms of biological life in the water; and the effects of a waste discharge in a water body are largely determined by the oxygen balance of the system. Low oxygen concentrations are generally associated with heavy contamination by organic matter. In such conditions oxygen, some times totally disappears from the water.

The manganous sulphate reacts with the alkali (KOH or NaOH) to form a white precipitate of manganous hydroxide which in the presence of oxygen, gets oxidized to a brown colour compound. In the strong acid medium manganic ions are reduced by iodide ions which get converted to iodine equivalent to the original concentration of oxygen in the sample. The iodine can be titrated against thio sulphate using starch as an indicator.

Requirement

1. Sodium thio sulphate, 0.025N
2. Alkaline potassium iodide solution
3. Manganous sulphate solution
4. Starch solution
5. Sulphuric acid

The procedure for preparing the reagents and the formula for calculating Dissolved Oxygen are given in Appendix V.

Procedure

350ml of diluted sample was taken in a glass stoppered bottle (BOD bottle) without any air bubbles. 2ml of manganous sulphate and alkaline potassium iodide solutions were added well below the surface from the walls. Immediately precipitate was formed. The contents were shaken well by inverting the bottle repeatedly and then the precipitate was allowed to settle down. This was dissolved completely by adding 2ml of concentrated sulphuric acid. A part of the content was removed to a conical flask, and it was titrated against sodium thiosulphate solution using starch as an indicator, within an hour. As a result, initial dark blue colour changes to colourless. The reading was noted. The same procedure was repeated to get concordant values.

(iv) Chemical Oxygen Demand (COD) Dichromate Reflux Method

The chemical oxygen Demand is a measure of the oxygen which is equivalent of the organic matter content of a sample, i.e. susceptible to oxidation by strong chemical oxidants.

Most of the organic matter are oxidized by a boiling mixture of chromic and sulphuric acid. The sample is refluxed in strongly acid solution with a known excess of

potassium dichromate. The amount of potassium dichromate consumed is determined and the amount of oxidizable organic matter is calculated in terms of oxygen equivalent. (Trivedy and Goel, 1984)

Description

Reflux apparatus consisting of 500ml of 250ml Erlen Meyer flask with ground glass 24/40 neck and 300mm condenser and a hot plate having sufficient power to produce atleast $1.4w/cm^2$ of heating surface.

Requirement

1. Standard potassium dichromate solution
2. Sulphuric acid
3. Ferrion Indicator
4. Ferrous Ammonium Sulphate (0.25N)
5. Mercuric sulphate
6. Silver sulphate

The procedure for preparing the reagents and the formula for calculating the Chemical Oxygen Demand are given in Appendix VI.

Procedure

In a 500ml refluxing flask, 20ml of sample was taken. 1 gram of mercuric sulphate, 3-4 glass beads and 10ml of

potassium dichromate solution (0.25N) were added. A pinch of silver sulphate was added to the content of the flask and mixed thoroughly. While mixing to dissolve the mercuric sulphate, 30ml of sulphuric acid was added slowly. A flask was attached to the condenser (Plate V). Distilled water was allowed to flow to cool down the condenser. This was to reflux the mixture for two hours and then it was disconnected. The mixture was diluted by adding 100ml distilled water. This was titrated against excess potassium dichromate with Ferrous ammonium sulphate using ferroin indicator. As a result the first sharp colour changes from blue green to reddish brown. The reading was noted. Like wise same procedure was followed and noted down the reading for blank also. To get concordant values same procedure was repeated.

(v) Total suspended Solids (TSS)

The undissolved matter present in water is usually referred as suspended solids. It is one of the valuable parameter in judging the pollution potential of an effluent.

The suspended matter is determined by filtering the sample, drying the residue and determining its weight by subtracting the initial weight from the final weight of the gooch crucible. This gives the weight in mg of the suspended matter (Indian Standards Institution, 1967).

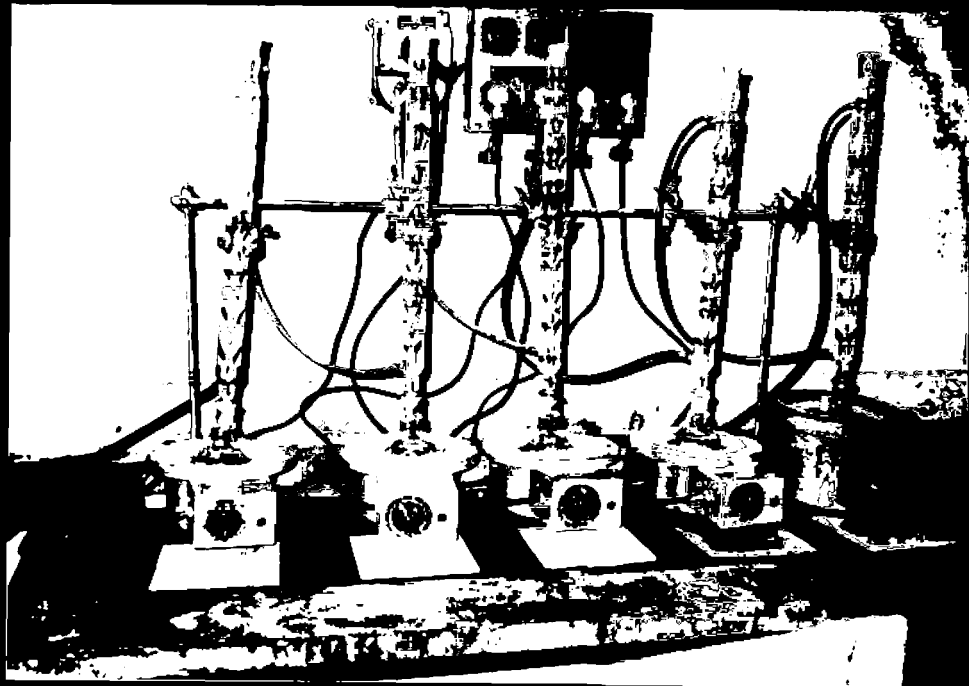


PLATE V--COD CONDENSER



PLATE VI--OVEN

was noted, this gives the value of the total suspended solids. The same procedure was repeated to get concordant values.

The formula used for calculating the Total Suspended Solids is given in Appendix VII.

(vi) Total Dissolved Solids (TDS)

Dissolved solids denote mainly the various kinds of minerals present in the water. Dissolved solids do not contain any gas and colloids etc. Concentration of dissolved solids is an important parameter in water quality standards.

Total Dissolved Solids are determined as the residue left after evaporation of the filtered sample and determining its weight by subtracting the initial weight of the dish from final weight of the dish, gives the weight in mg of the dissolved matter (Trivedy and Goel, 1984).

Requirement

1. Whatman filter paper (Whatman No.30)
2. China dish

Procedure

Required volume of sample was filtered through a filter paper and this was evaporated in a China dish on a

water bath. The residue was dried in an oven at 105°C. The increase in weight of the dish was noted, this gives the value of the total dissolved solids. The same procedure was repeated to get concordant values.

The formula used for calculating the Total Dissolved Solids is given in Appendix VIII.

(b) Chemical parameters

(i) Chloride

Chlorides occur naturally in all types of water. In fresh water, its concentration remains quite low and is generally less than that of sulphates and bicarbonates. The most important source of chlorides in the water is the discharge of industrial waste. The chloride concentration serves as an indicator of pollution.

Silver nitrate reacts with chloride to form silver chloride in the form of white precipitate. At the end point all the chlorides get precipitated, free silver ions react with chromate to form silver chromate of reddish brown colour.

Requirement

1. Erlenmeyer flask
2. Silver nitrate, 0.02N
3. Potassium chromate, 5%

The procedure for preparing the reagents and the formula for calculating the chlorides are given in Appendix IX.

Procedure

In an Erlenmeyer flask 50ml of the sample was taken with 2ml of potassium chromate solution. This was titrated against 0.02N silver nitrate until a persistent red tinge appeared. The reading was noted. The same procedure was repeated to get concordant values.

(ii) Residual chlorine

Chlorine is primarily added in water for destroying the harmful micro-organisms. Presence of excess chlorine intensifies the taste and odour of many other compounds. It may also be harmful to many aquatic organisms in combination with ammonia. Chlorine is a strong oxidizing agent and liberates iodine from potassium iodide. The liberated iodine is equivalent to the amount of chlorine and can be titrated against sodium thio sulphate using starch as an indicator.

Requirement

1. Erlenmeyer flask
2. Acetic acid
3. Potassium iodide

4. Sodium thio sulphate

5. Starch indicator

The procedure for preparing the reagents and the formula for calculating the residual chlorine are given in Appendix X.

Procedure

50ml of the sample was taken in an Erlenmeyer flask. with 5ml acetic acid. The pH of this was adjusted between 3 and 4. 1 gram of potassium iodide crystals was added and mixed thoroughly or about fifteen minutes. This was titrated against 0.025N sodium thiosulphate with a few drops of starch as an indicator. As a result the contents turned into colourless from blue. The end point was noted. The same procedure was repeated to get concordant values.

(iii) Phosphate

Phosphorus is an important constituent of biological systems is present mostly in both organic and inorganic form. The higher concentration of phosphorus is an indicative of pollution.

The phosphates in water react with ammonium molybdate and form complex heteropoly acid (molybdophosphoric acid), which gets reduced to a complex of blue colour in the

presence of stannous chloride. The absorption of light by this blue colour can be measured at 660 m μ to calculate the concentration of phosphate.

Requirement

1. Erlenmeyer flask
2. Ammonium molybdate
3. Stannous chloride
4. Standard phosphate

The procedure for preparing the reagents and the formula for calculating the phosphate are given in Appendix XI.

Procedure

In an Erlenmeyer flask, 50ml of the filtered sample was taken. A spoonful of activated charcoal was added to remove the colour and colloidal impurities. Then it was filtered. 2ml of Ammonium molybdate was added followed by five drops of stannous chloride solution. Appearance of blue colour was noted. Readings were taken down for blank solution with the use of spectrophotometer at 660m μ . Then the reading for the sample was taken after five minutes but before twelve minutes of the addition of the last reagent. The concentration was found out with the help of the standard curve (given in the Appendix XIII). The same procedure was repeated to get concordant values.

Preparation of standard curve

Made various dilutions at the interval of 0.1mg phosphate/litre from the standard phosphate solution according to Table given in Appendix XII. 50ml of each dilution was taken and added 2 ml of ammonium molybdate and five drops of stannous chloride solution. The readings were noted at 660m μ and plotted a graph between 'transmittance' and 'concentration'.

(iv) Sulphate

Gravimetric method

It is naturally occurring anion in all kinds of natural water. Biological oxidation of reduced sulphur to sulphate also increase its concentration. Discharge of industrial wastes in water tends to increase its concentration.

Sulphate is precipitated as barium sulphate in the hydrochloric acid medium by addition of barium chloride solution. The reaction is carried out near the boiling temperature. The precipitate is filtered, washed to remove the chlorides, dried and weighed as Barium sulphate.

Requirement

1. Whatman filter paper No.42
2. Hydrochloric acid

3. Barium chloride
4. Silver nitrate-nitric acid
5. Methyl red indicator

The procedure for preparing the sample and the formula for calculating the sulphate are given in Appendix XIV.

Procedure

100ml of sample with few drops of methyl red was taken and the p^H was adjusted to 4.5--5 by adding Hydrochloric acid. The content was boiled by adding slowly the warm solution of barium chloride in excess until the precipitation process completes. Then this was heated at 80-90°C for two hours. Finally filtered the precipitate through filter paper and was washed thoroughly with distilled water until the filtrate was free from chloride. This was checked by using silver nitrate solution. Otherwise silver nitrate gives a white turbidity. Finally the content was dried and weighed. The readings were noted. The same procedure was repeated to get concordant values. The method followed for chemical parameters was suggested by Trivedy and Goel (1984).

B. After Treatment

1. Neutralization

According to Ganu (1982), methods of Neutralization of waste water includes equalization and Direct p^H Control.

Equalization: Mixing acidic and alkaline waste streams available in the plant to get uniformity, before it is subjected to treatment Raghavan (1986).

Direct p^H control: Rudolfs (1953) and Ashkenazi (1983) point out that neutralization of alkaline wastes with Hydrochloric acid or sulfuric acid is carried out under certain conditions.

2. Coagulation

Kudesia (1985) describes that the principle of coagulation involves two aspects:

(i) Floc formation: When coagulant is added to water and thoroughly mixed, a thick insoluble gelatinous precipitate called floc is formed. It has the property of arresting the suspended impurities in water and removes fine and colloidal particles quickly. This process removes colour and taste. In this process, a non-ionic coagulant as poly-electrolyte is used to remove nearly 90 per cent of the colour from dye effluent Uejima (1973).

(ii) Electric charge: The floc ions are electrically charged (+ve) while the colloidal particles have negative charge. Therefore floc attracts the colloidal particles and removes easily by settlement process.

Little (1975) and Fair et al., (1971) opines that the objective of chemical coagulation by adding flocculants is to produce large, stable flocs, which enmesh solid particles to form rapidly settling and filterable flocs. So that these can be filtered easily. The commonly used coagulants are Alum, Lime and Ferrous sulphate.

Coagulants used for the treatment

(1) Alum

According to Environmental Protection Agency (1978), when alum is added to waste effluent, it reacts with available alkalinity and phosphate to form aluminium salts. The combination of alum with alkalinity or phosphate are competing reactions that are p^H dependent.

Alum is the most commonly and successfully used coagulant, on a large scale, says Choudhury (1984). It is an off-white crystal form which when dissolved in water produces acidic conditions (100 grams of alum dissolved in 1 litre of water) states McKay (1981).

Narayana Rao and Datta (1987) opine that the optimum range of p^H for alum treatment is 6.5 to 8. Alum has been used for the reduction of turbidity and BOD in water treatment.

Polyelectrolyte or Polymer

Rishabh metals and chemicals states that polyelectrolytes are high molecular weight compounds when added to waste effluent, it increases the efficiency of solid-liquid separation process. It has the characteristic of both polymer and electrolyte. Polyelectrolyte is water soluble flocculant (1gm of polyelectrolyte dissolved in 100ml of water). Polymers are made from acrylamide, and are available in cationic, non-ionic and Anionic. As a coagulant aid, polymers reduce a charge repulsion between colloidal and dispersed floc particles and increasing settling velocities. The application of smaller concentrations of polymers in conjunction with alum improves the removal of suspended solids and reducing BOD and COD and finally effluent clarifies and its quality improves.

(ii) Lime

According to Manjunath and Indumehrotra (1981), it is a chemical coagulant, when added to waste effluent they will form calcium salts, being an hydroxide, it should form flocs and the suspended solids would adhere to them and would settle down.

(iii) Ferrous sulphate

It is a chemical coagulant which when added to dye effluent reacts with alkalinity and phosphate forms an insoluble iron salts states Pandit and Mayadea (1985).

3. Decolourisation

Kazutomo Mizumoto (1974) views that chlorine is highly effective for decoloration as well as the decomposition of BOD and COD. In addition, the use of granular activated carbon having high BOD and COD adsorption rates, enables to carry out a more economical and effective waste water treatment.

Activated carbon processes is an absorptive method by which powdered carbon is added to dye effluent in the coagulation process to remove organic materials says Rich (1973).

Mckay (1981) points out that chemical decolourisation of the effluent is usually by chlorine treatment, chlorine is fed directly into the effluent. The dye molecules are attracted by chemical forces to the surfaces of the adsorbent. Decolorisation with chlorine is fairly successful at a p^H of 4.0, but COD reduction was minimal and substituted chlorinated hydrocarbons were formed.

Absorption appeared to be the most logical method to remove the soluble colour (Herbert Noble, 1973).

C. Treatment method

The suitable and the required concentration of coagulant for the treatment of dye effluent was found out by pilot study.

For Alum treatment, first a dye effluent was taken in 5 different 100ml measuring jars, and adjusted the p^H to around 7.36 by using Hydrochloric acid. By adding 200, 400, 600, 800 and 1000 ppm coagulant in each jar, approximate range of coagulant was found out.

For Lime treatment, first a dye effluent was taken in three different 100ml measuring jars, and adjusted the p^H to around 7.36 by using Hydrochloric acid. By adding 100, 300 and 500 ppm coagulant in each jar, approximate range of coagulant was found out.

For Ferrous sulphate treatment, first a dye effluent was taken in four different 100ml measuring jars, and adjusted the p^H to around 7.37 by using Hydrochloric acid. By adding 200, 400, 600 and 800 ppm coagulant in each jar, approximate range of coagulant was found out. The jar tests were made for each dye effluent.

For neutralization, dye effluent was taken in 500ml measuring jar. The pH was adjusted between 7.3 to 7.6 by adding Hydrochloric acid. The coagulant was added in the optimum range, which was found out from the pilot study. The content was mixed thoroughly. To increase the rate of floc formation the polymer was added. The sludge was settled down completely.

For decolourisation, the chlorine or activated charcoal was used suitably for different dye effluents. The removal of pollutants were found after treatment.

Results and Discussion

IV RESULTS AND DISCUSSION

The findings of the present study are discussed under the following headings:

1. General parameters
2. Chemical parameters
3. Pilot study
4. Colour intensity
5. Potentia hydrogenii
6. Biochemical oxygen Demand
7. Chemical oxygen Demand
8. Total suspended solids
9. Total Dissolved solids
10. Chloride
11. Phosphate
12. Sulphate

1. General parameters

The values of general parameters in selected dye effluents are given in Table I.

TABLE I
GENERAL PARAMETERS IN SELECTED DYE EFFLUENTS

S.No.	General parameters	Vat dye effluent	Reactive dye effluent	Sulphur dye effluent
1.	Colour intensity (Optical Density)	0.70	1.20	0.68
2.	Potentia Hydrogenii (p ^H)	11.90	10.30	8.50
3.	Biochemical oxygen Demand (BOD) (mg/lit)	245.0	285.7	110.0
4.	Chemical Oxygen Demand (COD) (mg/lit)	23,000	23,000	20,000
5.	Total Suspended Solids (TSS) (mg/lit)	0.27	0.09	0.27
6.	Total Dissolved Solids (TDS) (mg/lit)	8.08	5.97	3.93

The above table reveals clearly that the colour intensity for the vat dye effluent was 0.70 O.D. whereas 1.20 and 0.68 O.D. for reactive and sulphur dye effluents.

The p^H value for Vat dye effluent was found to be high (11.90) when compared to Reactive and Sulphur dye effluents (10.30, 8.50) respectively.

The value of BOD for vat dye effluent was 245.0mg/lit, where as 285.7 and 110.0mg/lit for Reactive, and sulphur dye effluents respectively.

The COD values of Vat, Reactive and Sulphur dye effluents were found to be 23,000, 23000 and 20,000mg/lit.

There was not much difference between TSS values for Vat, Reactive and Sulphur dye effluents as 0.27, 0.09 and 0.27 mg/lit respectively.

The value for TDS was found to be 5.97 mg/lit for Vat dye effluent, 8.08 mg/lit for Reactive dye effluent and 3.93 mg/lit for Sulphur dye effluent.

2. Chemical parameters

The values of chemical parameters in selected dye effluents are given in Table II.

TABLE II

CHEMICAL PARAMETERS IN SELECTED DYE EFFLUENTS

S.No.	Chemical parameters	Vat dye effluent	Reactive dye effluent	Sulphur dye effluent
1.	Chloride (mg/lit)	184.6	5908.6	198.6
2.	Residual chlorine (mg/lit)	Nil	15.97	Nil
3.	Phosphate (mg/lit)	120.0	120.0	390.0
4.	Sulphate (mg/lit)	0.69	2.84	0.70

The above table shows the chloride values of vat, Reactive and Sulphur dye effluents. The presence of chloride value was very high (5908.6 mg/lit) when compared to Vat and Sulphur dye effluents (184.6, 198.9 mg/lit).

Residual chlorine was present only in Reactive dye effluent. That too only 15.97 mg/lit. This was completely removed with Alum treatment (Table is given in Appendix XV).

Presence of Phosphate was found to be 390.0mg/lit in sulphur dye effluent, whereas 120.0 mg/lit was present in Vat and Reactive dye effluents.

The sulphate values for Vat, Reactive and Sulphur dye effluents were found to be 0.69, 2.84 and 0.70mg/lit respectively.

3. Pilot study

It was found out from the pilot study that during the effluent treatment, there was coagulation only with Alum whereas there was no such precipitation with lime and ferrous sulphate. Hence the investigator selected only Alum for effluent treatment. (Tables are given in Appendix XVI, XVII and XVIII).

4. Colour intensity

The results of the colour intensity for the selected dye effluents are given in Table III.

TABLE III
COLOUR INTENSITY VALUES IN OPTICAL DENSITY (O.D.)

Selected dye effluents	Before treatment Mean \pm S.D.	After Alum treatment Mean \pm S.D.	Difference Mean \pm S.D.	Groups compared	't' value
Vat dye Effluent	0.70 \pm 0.158	0.05 \pm 0.005	0.65 \pm 0.159	a vs b a vs c	2.28NS 1.33NS
			a		
Reactive dye effluent	1.20 \pm 0.200	0.02 \pm 0.002	1.18 \pm 0.201	b vs a b vs c	2.28NS 9.04**
			b		
Sulphur dye effluent	0.68 \pm 0.056	0.31 \pm 0.010	0.37 \pm 0.021	c vs a c vs b	1.33NS 9.04**
			c		

NS - Not significant

** - Significant at 1% level

The above table shows the value of the colour intensity before treatment for Vat dye effluent was found to be 0.70 \pm 0.158 O.D., 1.20 \pm 0.200 O.D. and 0.68 \pm 0.056 O.D. for Reactive and Sulphur dye effluents.

After treatment, the colour intensity values for Vat, Reactive and Sulphur dye effluents was found to be 0.05 \pm 0.005 O.D., 0.02 \pm 0.002 O.D. and 0.31 \pm 0.010 O.D. respectively.

It was found out that colour intensity was reduced with Alum treatment. Statistically there was no significant difference in colour removal between Vat and Sulphur, Vat and Reactive dye effluents. But there was significant difference in colour removal between Reactive and Sulphur dye effluents at 1 per cent level. So Reactive dye effluent has significant effect in colour removal.

5. Potentia Hydrogenii

Table IV and Fig.I presents the potentia Hydrogenii values of Vat, Reactive and Sulphur dye effluents.

TABLE IV
POTENTIA HYDROGENII VALUES (p^H) IN UNITS

Selected dye effluents	Before treatment Mean _± S.D.	After Alum treatment Mean _± S.D.	Difference Mean _± S.D.	Groups compared	't' value
Vat dye effluent	11.90 _± 0.187	5.00 _± 0.187	6.90 _± 0.283	a vs b a vs c	11.55** 18.70**
Reactive dye effluent	10.30 _± 0.158	5.50 _± 0.187	4.80 _± 0.292	b vs a b vs c	11.55** 7.05**
Sulphur dye effluent	8.50 _± 0.187	5.00 _± 0.255	3.50 _± 0.292	c vs a c vs b	18.70** 7.05**

**Significant at 1% level

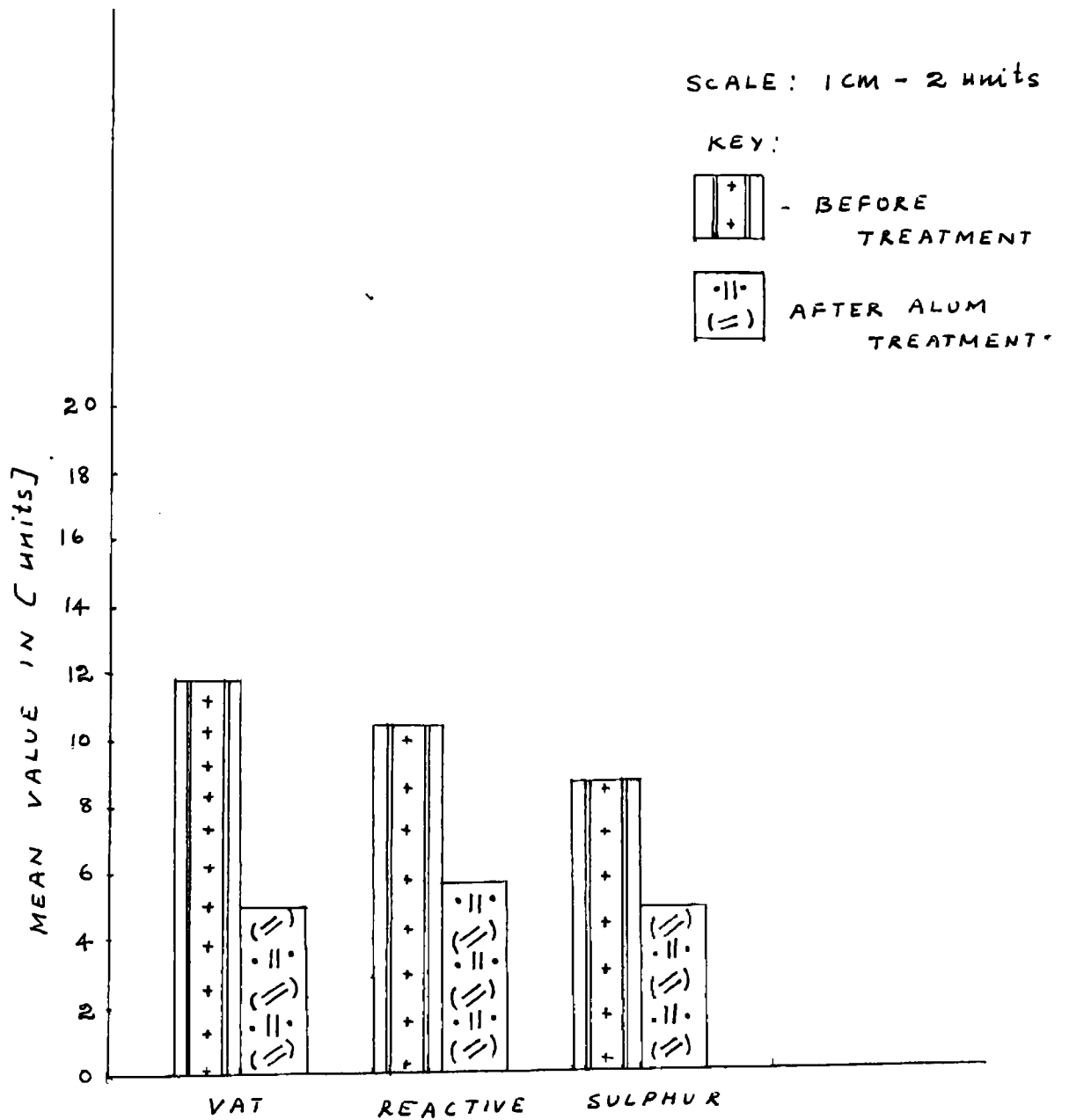


FIGURE - 1

POTENTIA HYDROGENI]

From the above Table it was clear that the value of the Potentia Hydrogenii before treatment for Vat dye effluent was 11.90 ± 0.187 and 10.30 ± 0.158 , 8.50 ± 0.187 for Reactive and sulphur dye effluents.

After treatment, Potentia Hydrogenii values for Vat, Reactive and Sulphur dye effluents were 5.00 ± 0.187 , 5.50 ± 0.187 and 5.00 ± 0.255 respectively.

The study shows that potentia Hydrogenii value was reduced with Alum treatment. The reduction in the potentia Hydrogenii value was found to be statistically significant among the selected dye effluents at 1 per cent level.

6. Biochemical Oxygen Demand

The values of Biochemical Oxygen Demand in selected dye effluents are given in Table V and Fig.II.

TABLE V
BIOCHEMICAL OXYGEN DEMAND VALUE IN Mg/lit

Selected dye effluents	Before treatment Mean \pm S.D.	After Alum treatment Mean \pm S.D.	Difference Mean \pm S.D.	Groups compared	't' value
Vat dye effluent	245.0 \pm 19.987	25.0 \pm 4.123	220 \pm 16.325	a vs b	5.14**
				a vs c	24.44**
Reactive dye effluent	285.7 \pm 0.406	28.0 \pm 1.581	257.7 \pm 1.692	b vs a	5.14**
				b vs c	105.20**
Sulphur dye effluent	110.0 \pm 5.874	75.0 \pm 3.082	35.0 \pm 4.416	c vs a	24.44**
				c vs b	105.20**

**Significant at 1% level

The above table indicates the Biochemical Oxygen Demand values of Vat, Reactive and Sulphur dye effluents before treatment was found to be 245.0 \pm 19.987 mg/lit, 285.7 \pm 0.406 mg/lit and 110.0 \pm 5.874 mg/lit respectively.

The value of Biochemical Oxygen Demand in Vat dye effluent after treatment was 25.0 \pm 4.123 mg/lit, whereas 28.0 \pm 1.581 mg/lit and 75.0 \pm 3.082 mg/lit for Reactive and Sulphur dye effluents.

It was found that the Biochemical Oxygen Demand value decreases with Alum treatment. The decrease in the Biochemical Oxygen Demand value was proved statistically significant among the selected dye effluents at 1 per cent level.

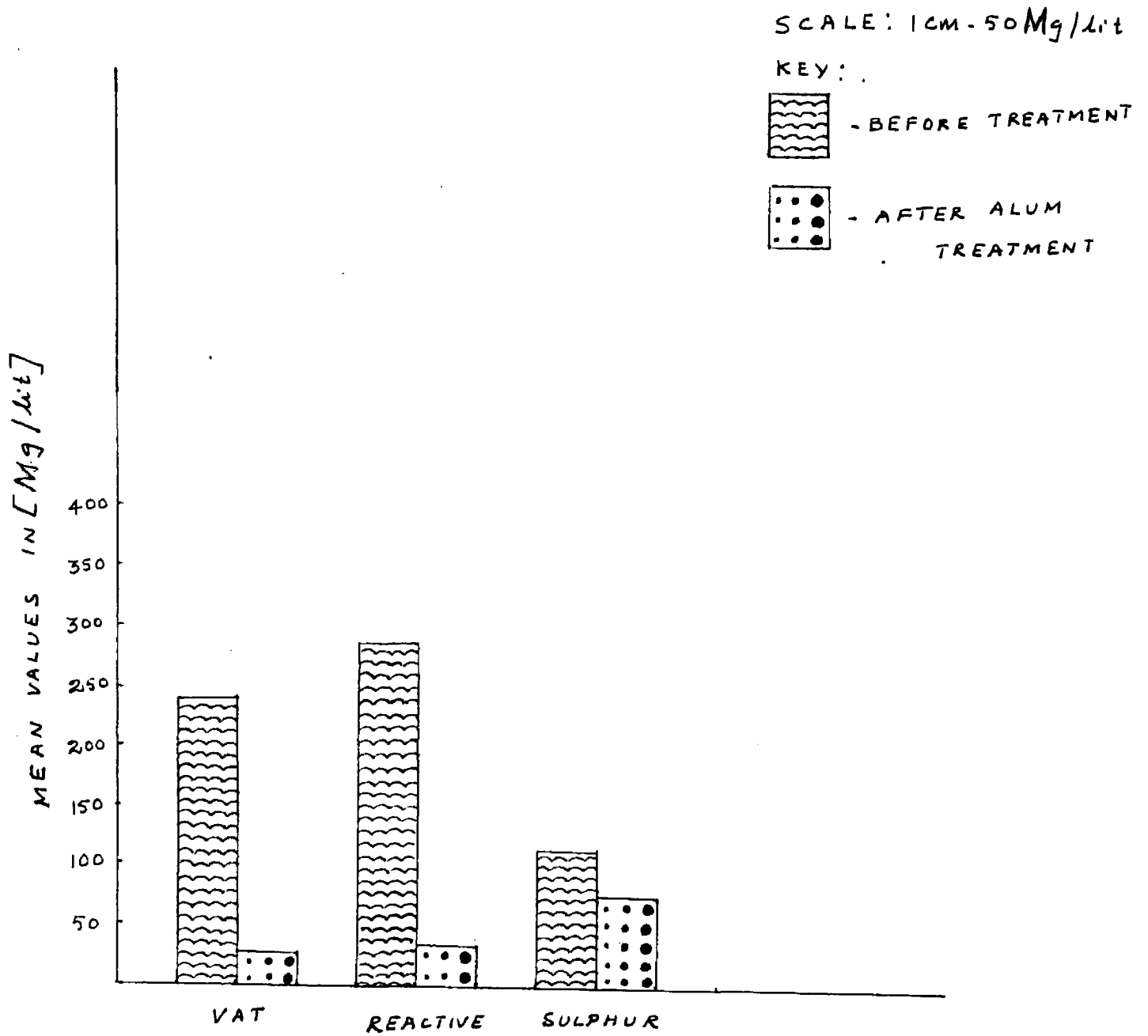


FIGURE - II

BIOCHEMICAL OXYGEN DEMAND

7. Chemical Oxygen Demand

Table VI and Fig.III shows the Chemical Oxygen Demand values of Vat, Reactive and Sulphur dye effluents.

TABLE VI
CHEMICAL OXYGEN DEMAND VALUES IN Mg/lit

Selected dye effluents	Before treatment Mean \pm S.D.	After Alum treatment Mean \pm S.D.	Difference Mean \pm S.D.	Groups compared	't' value
Vat dye effluent	23,000 \pm	13,000 \pm	10,000 \pm	a vs b	33.05**
	227.930	316.180	499.460	a vs c	11.14**
			a		
Reactive dye effluent	23,000 \pm	5000 \pm	18,000 \pm	b vs a	33.05**
	227.930	93.541	207.240	b vs c	23.23**
			b		
Sulphur dye effluent	20,000 \pm	18,000 \pm	2000 \pm	c vs a	11.14**
	1044.030	984.890	1524.790	c vs b	23.23**
			c		

**Significant at 1% level

From the above table it was clear that the value of Chemical Oxygen Demand in Sulphur Dye effluent before treatment was found to be 20,000 \pm 1044.030 mg/lit whereas 23,000 \pm 227.930 mg/lit was present in Vat and Reactive dye effluents.

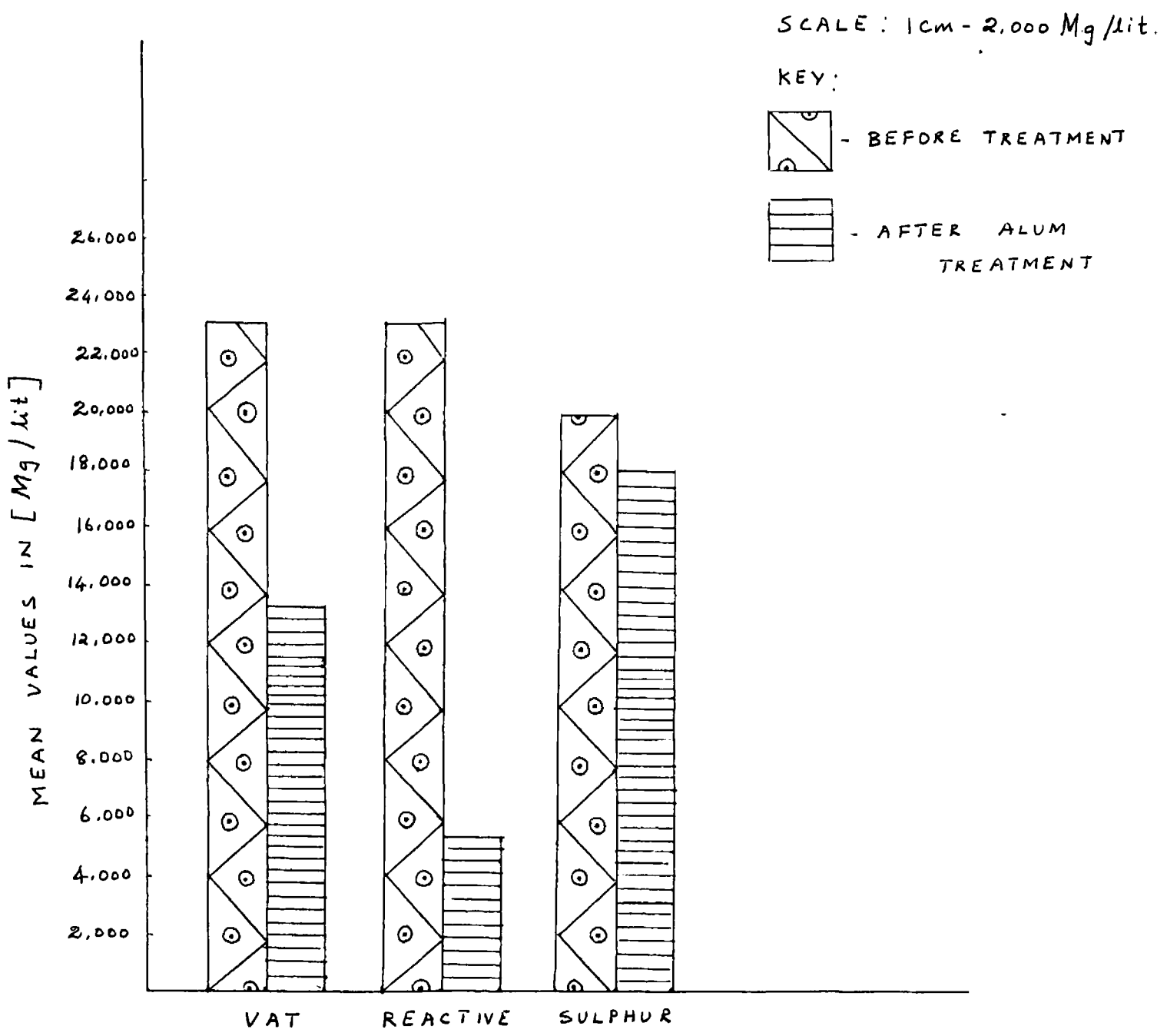


FIGURE - III

CHEMICAL OXYGEN DEMAND

The Chemical Oxygen Demand values of Vat, Reactive and Sulphur dye effluents after treatment was found to be 13,000 \pm 316.180 mg/lit, 5000 \pm 93.541 mg/lit and 18,000 \pm 984.890 mg/lit respectively.

The study shows that the Chemical Oxygen Demand value reduces with Alum treatment. Statistically there was significant difference at 1 per cent level in Chemical Oxygen Demand reduction among the selected dye effluents.

8. Total Suspended Solids

Table VII indicates the values of total suspended solids for selected dye effluents.

TABLE VII

TOTAL SUSPENDED SOLIDS VALUE IN Mg/lit.

Selected dye effluents	Before treatment Mean \pm S.D.	After Alum treatment Mean \pm S.D.	Difference Mean \pm S.D.	Groups compared	't' value
Vat dye	0.27 \pm 0.013	0.07 \pm 0.002	0.20 \pm 0.015	a vs b	14.33**
				a vs c	17.95**
Reactive dye effluent	0.09 \pm 0.012	0.08 \pm 0.004	0.01 \pm 0.007	a	
				b vs a	14.33**
Sulphur dye effluent	0.27 \pm 0.013	0.25 \pm 0.009	0.02 \pm 0.017	b vs c	0.78NS
				b	
Sulphur dye effluent	0.27 \pm 0.013	0.25 \pm 0.009	0.02 \pm 0.017	c vs a	17.95**
				c vs b	0.78NS
			c		

NS - Not significant

** - Significant at 1% level

The above Table shows that the value of Total suspended solids in Vat, Reactive and Sulphur dye effluents before treatment was 0.27 ± 0.013 mg/lit, 0.09 ± 0.012 mg/lit and 0.27 ± 0.013 mg/lit respectively.

After treatment the value of Total suspended solids for vat dye effluent was found to be 0.07 ± 0.002 , whereas 0.08 ± 0.004 mg/lit and 0.25 ± 0.009 mg/lit for Reactive and Sulphur dyes.

It was found out from the study that the value of Total suspended solids decreases with Alum treatment. Statistically there was no significant difference in total suspended solid reduction between Reactive and Sulphur dye effluents. But there was significant difference in the reduction of Total suspended solids between Vat and Reactive, Vat and Sulphur dye effluents, at 1 per cent level. So Vat dye effluent has significant effect in reducing the amount of Total suspended solids.

9. Total Dissolved solids

The values of Total dissolved solids for Vat, Reactive and Sulphur dye effluents are given in Table VIII and Fig.IV.

TABLE VIII

TOTAL DISSOLVED SOLIDS VALUE IN Mg/lit

Selected dye effluents	Before treatment Mean \pm S.D.	After Alum treatment Mean \pm S.D.	Difference Mean \pm S.D.	Groups compared	't' value
Vat dye effluent	5.97 \pm 0.055	6.14 \pm 0.009	0.17 \pm 0.063	a vs b	6.91**
				a vs c	0.54NS
a					
Reactive dye effluent	8.08 \pm 0.593	10.07 \pm 0.016	1.99 \pm 0.584	b vs a	6.91**
				b vs c	6.96**
b					
Sulphur dye effluent	3.93 \pm 0.053	3.78 \pm 0.086	0.15 \pm 0.097	c vs a	0.54NS
				c vs b	6.96**
c					

**Significant at 1% level

NS - Not significant

From the above table it was clear that the value of the Total Dissolved Solids in vat dye effluent before treatment was found to be 5.97 \pm 0.055 mg/lit and 8.08 \pm 0.593 mg/lit, 3.93 \pm 0.053 mg/lit for Reactive and Sulphur dye effluents.

The Total Dissolved solid values for Vat, Reactive and Sulphur dye effluents after treatment was 6.14 \pm 0.009mg/lit 10.07 \pm 0.016 mg/lit, 3.78 \pm 0.086 mg/lit respectively.

SCALE: 1 cm - 1 Mg / lit

KEY:



- BEFORE TREATMENT



- AFTER ALUM TREATMENT

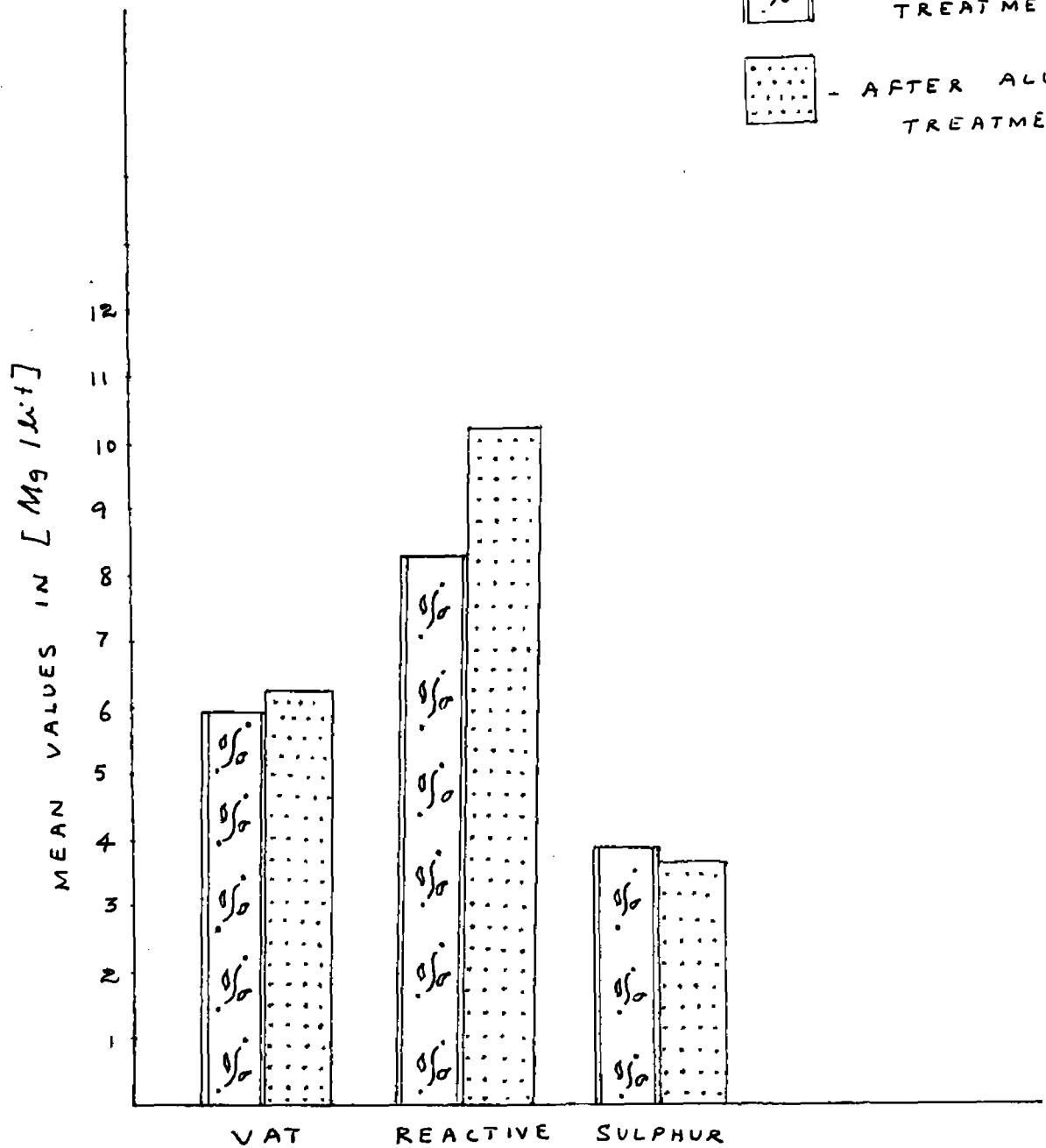


FIGURE - IV
TOTAL DISSOLVED SOLIDS

The study has shown that the value of Total Dissolved Solids increases with Alum treatment in Vat and Reactive dye effluents, but it was found to be decreased in Sulphur dye effluents.

Statistical analysis has proved that the value of Total Dissolved Solids increases significantly at 1 per cent level between Vat and Reactive dye effluents.

10. Chloride

Table IX reveals clearly that the chloride values of selected dye effluents.

TABLE IX

CHLORIDE VALUES IN Mg/lit

Selected dye effluents	Before treatment Mean \pm S.D.	After alum treatment Mean \pm S.D.	Difference Mean \pm S.D.	Groups compared	't' value
Vat dye effluent	184.6 \pm 0.255	99.4 \pm 0.846	85.2 \pm 0.778	a vs b a vs c	7.02** 12.79**
			a		
Reactive dye effluent	5908.6 \pm 84.634	5254.0 \pm 123.857	654.6 \pm 181.237	b vs a b vs c	7.02** 7.47**
			b		
Sulphur dye effluent	198.9 \pm 0.654	156.2 \pm 0.187	48.4 \pm 6.352	c vs a c vs b	12.79** 7.47**
			c		

**Significant at 1% level

The above table shows the chloride value of Vat, Reactive and Sulphur dye effluents before treatment was 184.6 ± 0.255 mg/lit, 5908.6 ± 84.634 mg/lit and 198.9 ± 0.654 mg/lit respectively.

The value of chloride in Vat dye effluent after treatment was found to be 99.4 ± 0.846 mg/lit whereas 5254.0 ± 123.857 mg/lit and 156.2 ± 0.187 mg/lit for Reactive and Sulphur dye effluents.

It was found out from the study that Alum treatment reduces the value of chloride in the dye effluents. Statistical analysis proves that there was significant difference in chloride value among the selected dye effluents at 1 per cent level.

11. Phosphate

Table X and Fig.V presents the phosphate values of Vat, Reactive and Sulphur dye effluents.

TABLE X
PHOSPHATE VALUES IN Mg/lit

Selected dye effluents	Before treatment Mean±S.D.	After Alum treatment Mean±S.D.	Difference Mean ± S.D.	Groups compared	't' value
Vat dye effluent	120.0±5.138	70.0±1.871	50.0±6.058	a vs b a vs c	2.79* 32.90**
			a		
Reactive dye effluent	120.0±5.138	60.0±0.707	60.0±5.248	b vs a b vs c	2.79* 43.52**
			b		
Sulphur dye effluent	390.0±5.766	200.0±7.906	190.0 ± 4.123	c vs a c vs b	32.90** 43.52**
			c		

**Significant at 1% level

*Significant at 5% level

The above table reveals clearly that the value of phosphate before treatment for Vat and Reactive dye effluent was found to be same 120.0 ± 5.138 mg/lit, whereas 390.0 ± 5.766 mg/lit for sulphur dye effluent.

After treatment, the phosphate value of Vat, Reactive and Sulphur dye effluents was 70.0 ± 1.871 mg/lit, 60.0 ± 0.707 mg/lit and 200.0 ± 7.906 mg/lit respectively.

SCALE : 1cm - 50 Mg / lit

KEY :



- BEFORE TREATMENT



- AFTER ALUM TREATMENT

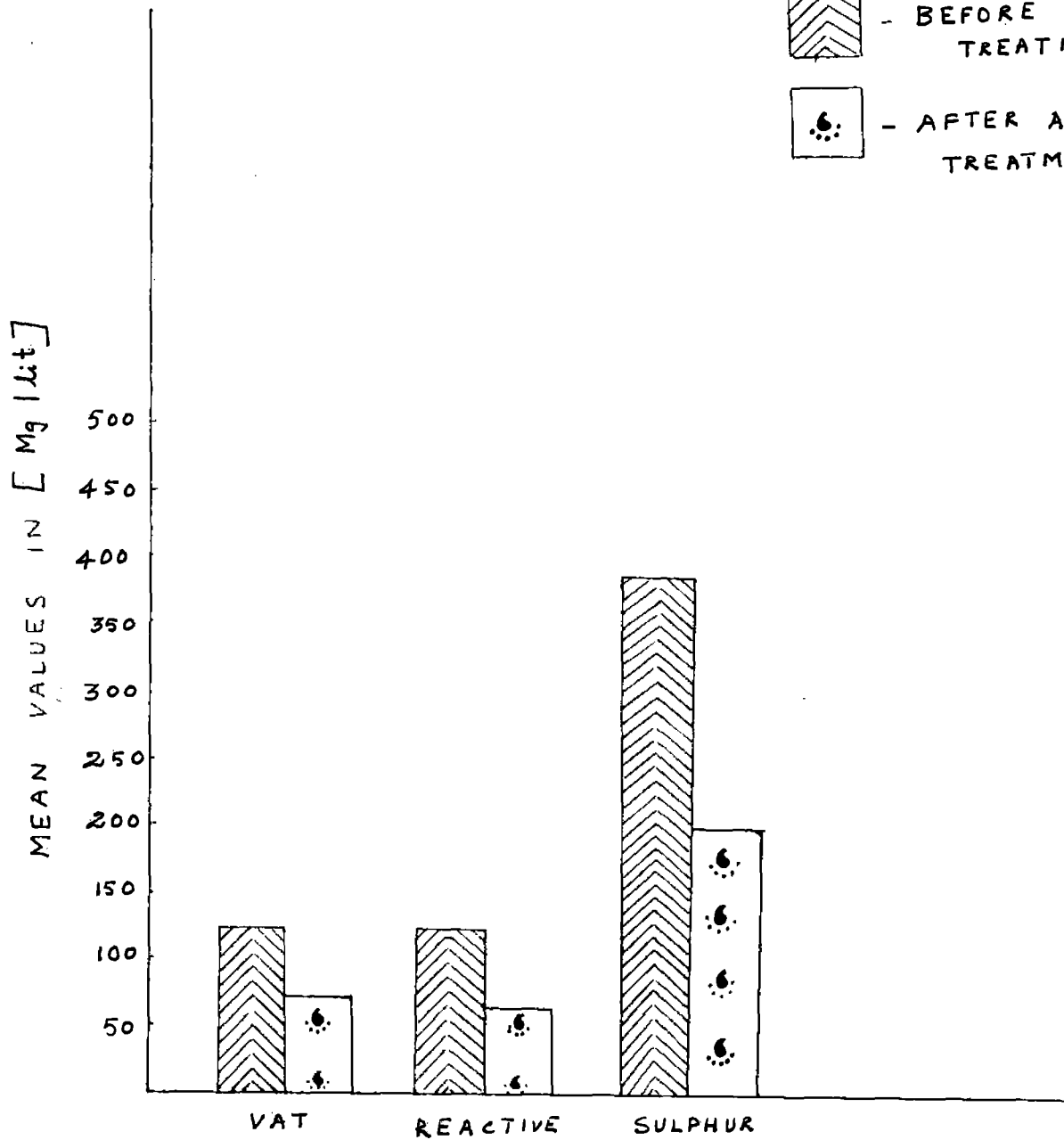


FIGURE - V
PHOSPHATE

The study has shown that the phosphate value decreases with Alum treatment. The decrease in phosphate value was found to be statistically significant between Vat and Sulphur, Reactive and Sulphur dye effluents at 1 per cent level and also at 5 per cent level there was significant difference in phosphate reduction between vat and Reactive dye effluents. So sulphur dye effluent has significant effect in reducing the concentration of phosphate.

12. Sulphate

Table XI and Fig.VI indicates the sulphate values in selected dye effluents.

TABLE XI

SULPHATE VALUES IN Mg/lit

Selected dye effluents	Before treatment Mean±S.D.	After Alum treatment Mean ± S.D.	Difference Mean± S.D.	Groups compared	't' value
Vat dye effluent	2.84±0.109	3.89±0.181	1.05±0.091	a vs b	18.39**
				a vs c	3.29*
			a		
Reactive dye effluent	0.69±0.006	0.94±0.034	0.25±0.033	b vs a	18.39**
				b vs c	63.17**
			b		
Sulphur dye effluent	0.70±0.005	1.90±0.0005	1.2± 0.005	c vs a	3.29*
				c vs b	63.17**
			c		

**Significant at 1% level

*Significant at 5% level

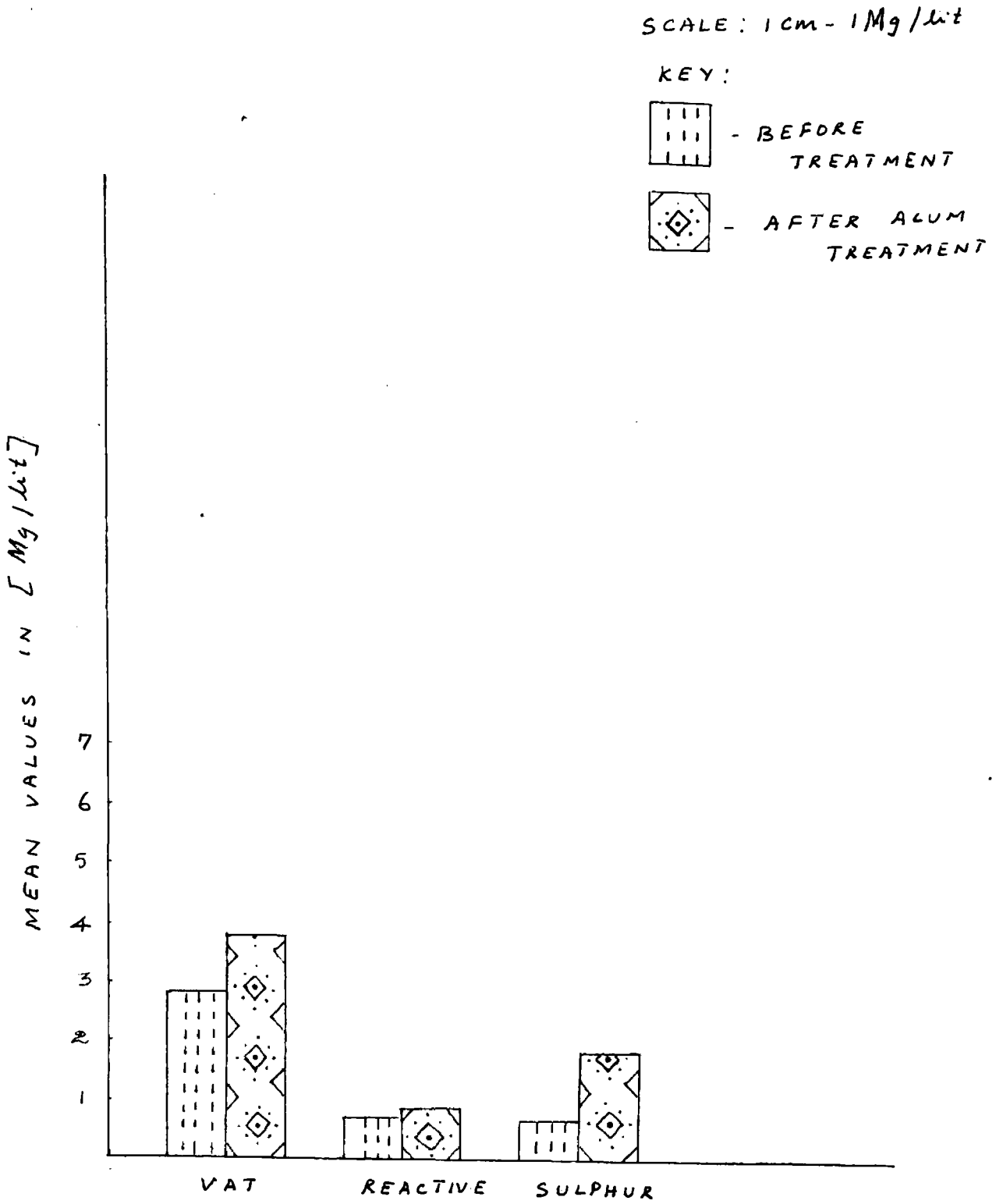


FIGURE - VI
SULPHATE

The above table presents the sulphate values of Vat, Reactive and Sulphur dye effluents before treatment were found to be 2.84 ± 0.109 mg/lit, 0.69 ± 0.006 mg/lit and 0.70 ± 0.005 mg/lit respectively.

The sulphate value of vat dye effluent^e after treatment was 3.89 ± 0.181 mg/lit and 0.94 ± 0.034 mg/lit, 1.90 ± 0.006 mg/lit for Reactive and Sulphur dye effluents.

It was found out from the study that the sulphate value increases with Alum treatment. The increase in sulphate value was found to be statistically significant at 1 per cent level between Vat and Reactive, Reactive and Sulphur dye effluents and significant at 5 per cent level between Vat and Sulphur dye effluents.

Summary and Conclusion

V SUMMARY AND CONCLUSION

Pollution is a major attribute to inhealthiness and inhygiene and it provides for a wide scope of study in the developing and developed countries in as much as it is associated both with the industry and animal kingdom as a whole. Wherever we find dense clusters of either industrial units or tenements, there are ample chances of getting the eco-system polluted. A thing that is the most common and basically essential in all walks of life is water, the purity of which is always advocated for consumption while, with or without our knowledge, maximum exertions are being laid to pollute the same. The ill-effects of water pollution are largely caused by industrial effluents and other chemical matters discharged into the running stock of good water, where it loses its dissolved oxygen level.

Textile industry takes in large quantities of water as a raw material for cleaning, conditioning and chemically processing the fibres, with the result that strong chemical effluents are discharged into consumable water. Several aspects of such water pollution caused by dyes and chemicals used in the manufacture of textile goods have been focussed in this study with the sole aim of suggesting means for effective treatment of waste water, especially in reducing pollution loads in it.

The experimental procedure consisted of

- (i) Collection of selected dye effluents; and,
- (ii) Conducting laboratory tests; and,
- (iii) Evaluating the results before and after treatment studies.

Findings of the study are summarised as under:

1. Colour Intensity

(a) Before alum treatment: Reactive dye effluent had more colour intensity than vat and sulphur dye effluents.

(b) After alum treatment: The colour intensity reduced

2. Potentia Hydrogenii (pH)

(a) Before alum treatment: Vat dye effluent had more alkaline pH than Reactive and Sulphur dye effluents.

(b) After alum treatment: pH was brought to standard level in all the three dye effluents.

3. Biochemical Oxygen Demand (BOD)

(a) Before alum treatment: The BOD was higher in Reactive dye effluent than in Vat and Sulphur dye effluents.

(b) After alum treatment: The BOD was reduced maximum in Reactive dye effluent.

4. Chemical Oxygen Demand (COD)

(a) Before alum treatment: The COD was higher in Reactive and Vat dye effluents than in sulphur dye effluents.

(b) After alum treatment: The COD could be reduced maximum in Reactive dye effluent.

5. Total Suspended Solids (TSS)

(a) Before alum treatment: The value of Total Suspended Solids was higher in Vat and Reactive dye effluents than in sulphur.

(b) After alum treatment: The value of Total Suspended Solids could be reduced greatly in Vat dye effluent.

6. Total Dissolved Solids (TDS)

(a) Before alum treatment: The value Total Dissolved Solids was higher in Reactive dye effluent than in Vat and Sulphur dye effluents.

(b) After alum treatment: The value of Total Dissolved Solids was increased in Reactive and Vat dye effluents whereas in Sulphur dye effluents it was found to be reduced.

7. Chloride

(a) Before alum treatment: The value of Chlorides was higher in Reactive dye effluent than in Vat and Sulphur dye effluents.

(b) After alum treatment: The value of chlorides was reduced greatly in Reactive dye effluent.

8. Residual chlorine

(a) Before alum treatment: Residual chlorine was present only in Reactive dye effluent.

(b) After alum treatment: The Residual chlorine in Reactive dye effluent was completely removed.

9. Phosphate

(a) Before alum treatment: The value of phosphate was higher in sulphur dye effluent than in Vat and Reactive dye effluents.

(b) After alum treatment: The value of phosphate was greatly reduced in sulphur dye effluent.

10. Sulphate

(a) Before alum treatment: The value of sulphate was higher in vat dye effluent than in Reactive and Sulphur dye effluents.

(b) After alum treatment: The value of sulphate increased more in vat dye effluent than in Reactive and Sulphur dye effluents.

From the study, it is concluded that Reactive dye effluents have the best effect in reducing the pollutants after the alum treatment; next to Reactive dye effluents, Vat dye effluent is found to have better effect in reducing pollutants (after the alum treatment) than the Sulphur dye effluent because it has more BOD, COD, TSS when compared to Vat dye effluent.

Suggestions

Based on the results and discussion of this study the following suggestions are made:

1. The problem of reducing waste water load was thus to be tackled by different aspects such as modification of dyeing techniques to use less water, selection of dyes with less pollutants and auxiliaries and to reduce their pollutants through effective treatment.
2. The removal of pollutants may be enhanced by the application of physico-chemical method of conventional coagulation system with alum as coagulant.
3. The alum was found to be best in the point of view of high reduction in pollution and in the point of view of the economy.

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Appendices

APPENDIX I

5. Preparation of Dye solution

The procedure suggested by United Bleachers Limited, (UBL) was followed for dyeing the samples in one per cent shade. The preparation of Vat, Reactive and Sulphur dyes are given below:

Vat Dye Bath

Weight of the material	.. 76 grams
Material liquid ratio	.. 1:5

Recipe

For 1% vatting

Novatic Olive D. (P/F)	.. 760mg
Turkey red oil	.. 0.5cc
Water	.. 50cc
Sodium hydroxide	.. 1.52 grams
Hydros (Sodium hydro sulphite)	.. 1.52 grams
Duration	.. 15 mts
Temperature	.. 60°C

Dye bath

Sodium hydroxide	.. 6.08 grams
Hydros	.. 5.32 grams
Temperature	.. 60°C

Water	..	250cc
Duration	..	30 mts

Developing bath

Hydrogen peroxide	..	1.5cc
Water	..	250cc
Temperature	..	60°C to 70°C
Duration	..	10mts

Method

The required amount of vat dye was taken and mixed with turkey red oil. Boiled water was added and stirred well. This was vatted (reduced and sulubilised) by adding required amount of sodium hydro-sulphite (Hydros) and sodium hydroxide (caustic) at a temperature of 60°C for 15 minutes. Now vat dye solution was ready for dyeing the fabric.

Reactive Dye Bath

Recipe

For 1% shade

Procion Red M _g B	..	760 mg
Water	..	300cc
Temperature	..	cold
Duration	..	10 mts
Sodium hydroxide	..	11.4 grams
Duration	..	20 mts

Fixation

Soda ash	..	1.9 gms
Duration	..	30 mts

Method

The required amount of Reactive dye and water was made into a paste form, with this add sodium hydroxide: After 20 minutes add soda ash, and stirred thoroughly.

Sulphur Dye Bath

Recipe

For 1% shade

Sulfast violet Brown 765	..	760 mg
Turkey red oil	..	0.5cc
Hot water	..	10cc
Sodium sulfide (60%)	..	2.85gm
Soda ash	..	950 mg
Water	..	40cc

}Boiled
} for
} 10mts
}

Dyestuff and the boiled chemical solution were again boiled for 3 mts.

Dye bath

Water (cold)	..	200cc
dextrose	..	950mg
Temperature	..	60°C

At 60°C Add

Salt	..	1.9gm
Water	..	50cc
Temperature	..	80°C
Duration	..	10 mts

Developing bath

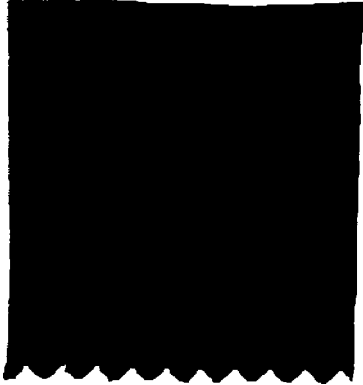
Water	..	140cc
Dichromate	..	1.14gm
Acetic acid	..	1.5cc
Temperature	..	60°C
Duration	..	5mts

Method

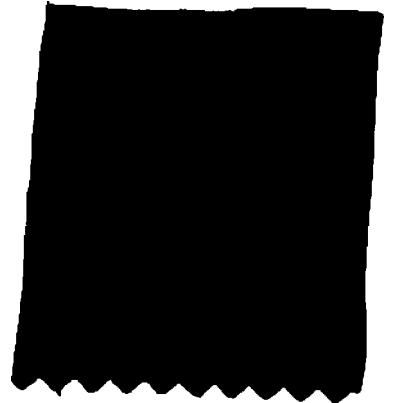
The required amount of sulphur dye was taken and mixed with turkey red oil. Boiled water was added and stirred well. The boiled chemical solution was added to the dye solution and boiled for 3 minutes. Then add dextrose mixture. At 60°C add salt solution, and boiled for 10 minutes at 80°C.

APPENDIX II

DYED SAMPLES



IId. VAT DYE



IIf. REACTIVE DYE



IIf. SULPHUR DYE

APPENDIX III

PROCEDURE FOR PREPARING THE REAGENTS AND THE FORMULA FOR CALCULATING THE BIOCHEMICAL OXYGEN DEMAND (BOD)

Preparation of Reagents

1. Phosphate Buffer

Dissolved each 8.5g potassium bi phosphate, 21.75g Dipotassium hydrogen phosphate, 33.4g Di sodium hydrogen phosphate and 1.7g Ammonium chloride. Adjusted pH to 7.2.

2. Magnesium sulphate

Dissolved 82.5g magnesium sulphate in distilled water and diluted it to 1 litre solution.

3. Calcium chloride

Dissolved 27.5g anhydrous calcium chloride in distilled water and prepared 1 litre of solution.

4. Ferric chloride

Dissolved 0.25g Ferric chloride in distilled water and prepared 1 litre of solution.

5. Sodium sulphite solution (0.025N)

Dissolved 1.575g sodium sulphite in distilled water and diluted it to 1000ml solution.

Formula used for calculating BOD:

$$\text{BOD, mg/l} = \frac{(D_1 - D_2) - (B_1 - B_2)}{P}$$

Where,

D_1 = Dissolved oxygen content in diluted sample immediately

D_2 = Dissolved oxygen content in diluted sample after 5 days, incubation at 20°C.

B_1 = Dissolved oxygen of seed control before incubation

B_2 = Dissolved oxygen of seed control after incubation

P = Decimal volumetric fraction of sample used

APPENDIX IV

PREPARATION OF DILUTIONS FOR VARIOUS RANGES OF BIOCHEMICAL OXYGEN DEMAND IN THE SAMPLES

Range of BOD mg/1 O ₂	Dilution (%)	Sample volume in 1 litre of mixture
0-6	No dilution	1000
4-12	50	500
10-30	20	200
20-60	10	100
40-120	5	50
100-300	2	20
200-600	1	10
400-1200	0.5	5
1000-3000	0.2	2
2000-6000	0.1	1
Above 6000	0.05	0.5

APPENDIX V

PROCEDURE FOR PREPARING THE REAGENTS AND THE FORMULA FOR CALCULATING THE DISSOLVED OXYGEN (DO)

.....

Preparation of Reagents

1. Sodium thio sulphate, 0.025N:

Dissolved 24.82g of sodium thio sulphate in boiled distilled water and made up in to 1 litre. Add few pellets of sodium hydroxide as stabilizer. This was 0.1N stock solution. Diluted it to 4 times with boiled distilled water and prepared 0.025N solution.

2. Alkaline potassium iodide solution:

Dissolved 100g of potassium hydroxide and 50g of potassium iodide in 200ml of boiled distilled water.

3. Manganous sulphate solution:

Dissolved 100g of manganous sulphate in 200ml of boiled distilled water and filtered.

4. Starch solution:

Dissolved 1g of starch in 100ml of warm distilled water (80°C - 90°C) and added a few drops of formaldehyde solution.

5. Concentrated sulphuric acid

Formula used for calculating Dissolved oxygen:

$$\text{Do, mg/l} = \frac{(\text{ml} \times \text{N}) \text{ of Titrant} \times 8 \times 1000}{\text{Volume of sample taken for titration}}$$

Where,

M1 = Volume of sodium thio sulphate used
for the sample

N = Normality of sodium thio sulphate

APPENDIX VI

PROCEDURE FOR PREPARING THE REAGENTS AND THE FORMULA FOR CALCULATING THE CHEMICAL OXYGEN DEMAND (COD)

.....

Preparation of Reagents

1. Standard Potassium di chromate solution (0.25N)

Dissolved 12.259g of potassium dichromate in distilled water and diluted it to 1000ml.

2. Sulphuric acid:

Added 25g silver sulphate in 2.5 litres of concentrated sulphuric acid.

3. Ferroun Indicator

Dissolved 1.48mg 1.10 phenanthroline monohydrate and 695mg ferrous sulphate in distilled water and diluted it to 100ml.

4. Ferrous Ammonium sulphate Titrant (0.25N)

Dissolved 98gm Ferrous Ammonium sulphate in distilled water and added 20ml of concentrated sulphuric acid and diluted it to 1000ml.

Standardisation of Ferrous Ammonium sulphate:

Diluted 10ml standard potassium dichromate to 100ml, added 30ml concentrated sulphuric acid and titrated it with

Ferrous Ammonium sulphate using ferroin indicator.

5. Mercuric sulphate

6. Silver sulphate

Formula for calculating COD:

$$\text{COD, mg/l} = \frac{(\text{A}-\text{B}) \times \text{N} \times 8000}{\text{ml of sample}}$$

Where,

- A = Volume of Ferrous Ammonium sulphate used for the blank**
- B = Volume of Ferrous Ammonium Sulphate used for the sample**
- C = Normality of Ferrous Ammonium Sulphate**

APPENDIX VII

FORMULA USED FOR CALCULATING THE TOTAL SUSPENDED SOLIDS
(TSS)

...

$$\text{TSS, mg/l} = \frac{1000 \times W}{V}$$

Where,

W = Weight in mg of the dissolved matter

V = Volume of sample taken in ml

APPENDIX VIII

**FORMULA USED FOR CALCULATING THE TOTAL DISSOLVED
SOLIDS (TDS)**

.....

$$\text{TDS, mg/l} = \frac{\text{A} - \text{B} \times 1000}{\text{V}}$$

Where,

A = Final weight of the dish in mg

B = Initial weight of the dish in mg

V = Volume of sample taken in ml

APPENDIX IX

PROCEDURE FOR PREPARING THE REAGENTS AND THE FORMULA FOR CALCULATING THE CHLORINE

.....

Preparation of Reagents

1. Silver Nitrate (0.02N)

Dissolved 3.400g of dried silver nitrate in 1 litre of distilled water.

2. Potassium chromate (5%)

Dissolved 5g of potassium chromate in 100ml of distilled water.

Formula used for calculating the chlorides:

$$\text{Chlorides, mg/l} = \frac{(\text{ml} \times \text{N}) \text{ of titrant} \times 1000 \times 35.5}{\text{ml of sample}}$$

Where,

ml = Volume of silver nitrate used for the sample
N = Normality of silver nitrate

APPENDIX X

PROCEDURE FOR PREPARING THE REAGENTS AND THE FORMULA FOR CALCULATING THE RESIDUAL CHLORINE

.....

Preparation of Reagents:

1. Acetic acid, concentrated (glacial)

2. Potassium iodide:

Potassium ⁱodide crystals

3. Sodium thio sulphate, 0.025N:

Dissolved 24.82g of sodium thio sulphateⁱⁿ boiled distilled water and made up the volume to one litre. Added few pellets of sodium hydroxide as stabilizer. This was 0.1N stock solution. Diluted it to 4 times with boiled distilled water and prepared 0.025N (250 → 1000ml).

4. Starch indicator:

Dissolved 1g of starch of 100ml of warm distilled water (80°C - 90°C) and added a few drops of formaldehyde solution.

Formula used for calculating the Residual chlorine:

$$\text{Residual chlorine, mg/l} = \frac{(\text{ml} \times \text{N}) \text{ of titrant} \times 1000 \times 35.5}{\text{ml of sample}}$$

Where,

ml = Volume of sodium thio sulphate used for the sample

N = Normality of sodium thio sulphate

APPENDIX XI

PROCEDURE FOR PREPARING THE REAGENTS AND THE FORMULA FOR CALCULATING THE PHOSPHATE

....

Preparation of Reagents

1. Ammonium molybdate solution:

(a) Dissolved 25g of Ammonium molybdate in 175ml of distilled water. (b) Added 280ml of concentrated sulphuric acid to 400ml of distilled water and cooled. Mix these two solutions (a) and (b) and diluted to 1 litre.

2. Stannous chloride solution:

Dissolved 2.5g of stannous chloride in 100ml glycerol by heating on a water bath for rapid dissolution.

3. Standard phosphate solution:

Dissolved 4.388g of dried anhydrous potassium hydrogen phosphate in 1 litre of distilled water. Diluted this solution to 100 times (10 → 1000ml). This was standard solution containing 10mg phosphate/litre. (1ml = 0.01mgP).

Formula used for calculating the phosphate:

$$\text{Phosphate, mg/l} = \frac{\text{Concentration} \times 1000 \times \text{dilution factor}}{\text{Vol of sample}}$$

APPENDIX XII

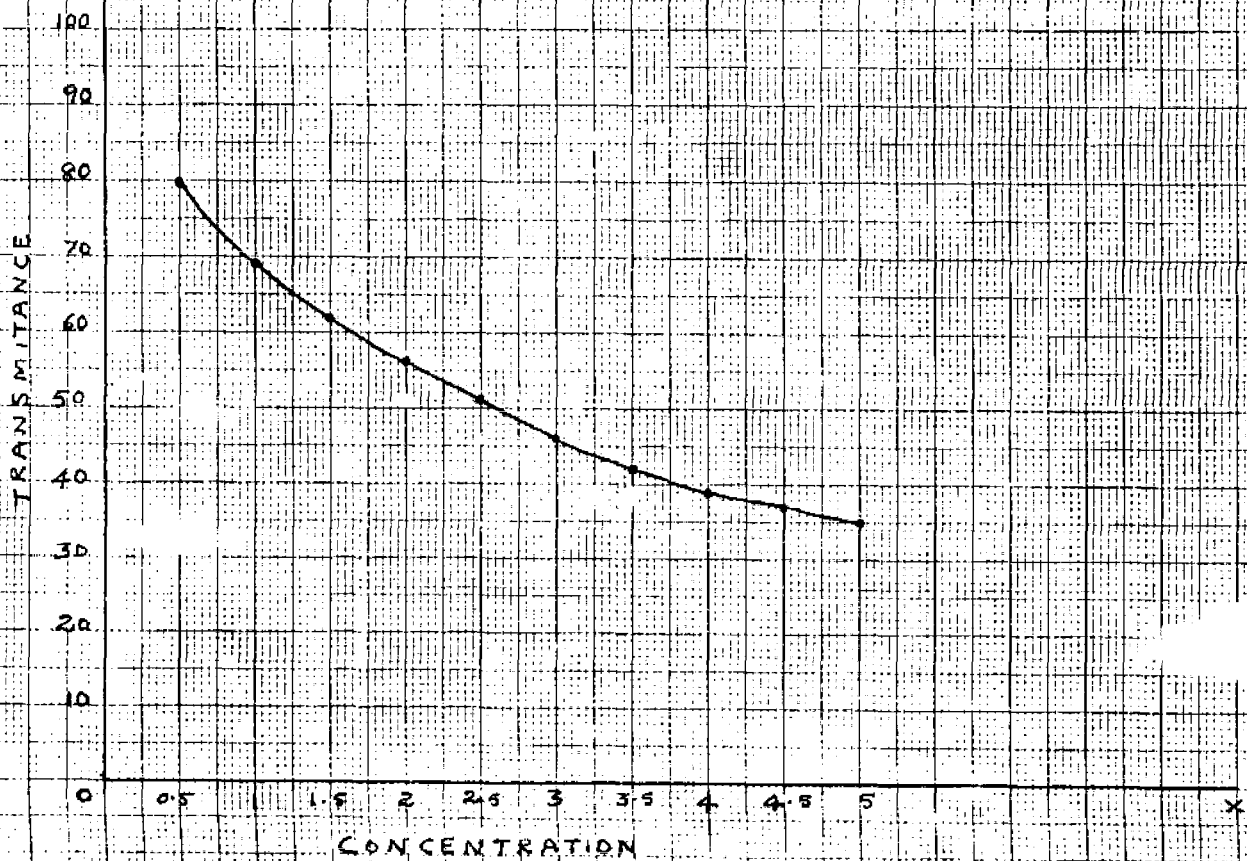
PREPARATION OF VARIOUS DILUTIONS OF PHOSPHORUS
FOR THE STANDARD CURVE

ml of standard solution	Diluted to ml	Concentration of PO ₄ -P mg/l
5.0	50	1.0
4.5	50	0.9
4.0	50	0.8
3.5	50	0.7
3.0	50	0.6
2.5	50	0.5
2.0	50	0.4
1.5	50	0.3
1.0	50	0.2
0.5	50	0.1

APPENDIX - XIII

SCALE:

X Axis - 1 cm - 0.5 units
Y Axis - 1 cm - 10 units



PHOSPHATE STANDARD CURVE

APPENDIX XIV

PROCEDURE FOR PREPARING THE REAGENTS AND THE FORMULA FOR CALCULATING THE SULPHATE

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Preparation of Reagents:

1. Hydrochloric acid (1+1)
2. Barium chloride solution:

Dissolved 100g Barium chloride in 1litre of distilled water. Filtered the solution through a filter paper before use.

3. Silver nitrate - nitric acid reagent:

Dissolved 8.5g of silver nitrate and 0.5ml concentrated nitric acid in distilled water and prepared 500ml reagent.

4. Methyl red indicator

Dissolved 100mg methyl red sodium salt in 100ml of distilled water.

The formula used for calculating the sulphate:

$$SO_4, \text{ mg/l} = \frac{\text{mg of Barium sulphate} \times 411.5}{\text{ml of sample}}$$

Where,

mg = Weight of the barium sulphate precipitate

APPENDIX XV

RESIDUAL CHLORINE IN SELECTED DYE EFFLUENTS

S.No.	Selected Dye Effluents	Before treatment (mg/lit)	After treatment (mg/lit)
1.	Vat Dye effluent	Nil	Nil
2.	Reactive Dye Effluent	15.97	Nil
3.	Sulphur Dye Effluent	Nil	Nil

APPENDIX XVI

COAGULANT TREATMENT WITH VAT DYE EFFLUENT

Coagulants used	Dosage in ppm	Observation	Non-ionic polyelectrolyte in ppm	Settling time in hours	Sludge in ml	Final pH
1. Alum	200	No coagulation	-	-	-	-
	400	No coagulation	-	-	-	-
	600	Slight coagulation but slow settling	-	4	20	-
	800	Coagulation occurs with rapid settling	3	1	14	5.0
2. Lime	1000	Coagulation dispersed	-	-	-	-
	100	No coagulation	-	-	-	-
	500	No coagulation	-	-	-	-
3. Ferrous sulphate	500	Colloidal gel is formed	-	-	-	-
	200	Very slight coagulation but no settling	-	-	-	-
	400	Very slight coagulation but no settling	-	-	-	-
	600	Very slight coagulation but no settling	-	-	-	-
	800	Colloidal condition with H ₂ S smell	-	-	-	5.5

APPENDIX XVII

COAGULANT TREATMENT WITH REACTIVE DYE EFFLUENT

Coagulants used	Dosage in ppm	Observation	Non-ionic Polyelectrolyte in ppm	Settling time in hrs.	Sludge in ml.	Final pH
1. Alum	200	No coagulation	-	-	-	-
	400	Slight flocs are developed	-	-	-	-
	600	Coagulation occurs but slow settling	3	4	20	-
	800	Coagulation occurs with rapid settling	3	1	15	5.5
2. Lime	1000	Coagulation disturbed-discrete particles occurs but no settling	-	-	-	-
	100	Very slight coagulation	-	5	20	11.5
	300	No coagulation	-	-	-	-
3. Ferrous sulphate	500	No coagulation	-	-	-	-
	200	Very slight coagulation builds up turbidity	-	-	-	4.5
	400	Very slight coagulation builds up turbidity	-	-	-	-
	600	Very slight coagulation builds up turbidity	-	-	-	-
800	Colloidal solution	-	-	-	-	-

APPENDIX XVIII

COAGULANT TREATMENT WITH SULPHUR DYE EFFLUENT

Coagulants used	Dosage in ppm	Observation	Non-ionic Polyelectrolyte in ppm	Settling time in hrs.	Sludge in ml.	Final pH
1. Alum	200	Discrete particles occurs	-	-	-	-
	400	Discrete particles occurs	-	-	-	-
	600	Slight coagulation but very slow settling	-	4	35	-
	800	Coagulation with rapid settling	3	1	26	5
2. Lime	100	Slight coagulation but no settling	-	-	-	-
	300	Slight coagulation but no settling	-	-	-	-
3. Ferrous sulphate	500	Coagulation dispersed	-	-	-	11.5
	200	No coagulation	-	-	-	-
	400	Discrete particles appears	-	-	-	-
	600	Turbid solution with revolution of H ₂ S	-	-	-	-
800	Colloidal solution occurs	-	-	-	-	4.5

APPENDIX XIX

FORMULA USED FOR STATISTICAL ANALYSIS OF THE DATA OBTAINED IN THIS STUDY

Statistical Analysis of the results obtained in the laboratory tests was done according to the method recommended by Gupta (1986) as follows:

't' tests were conducted whenever necessary to check if the results were significant using the formula:

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s} \times \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

Where,

\bar{x}_1 = mean of the first sample

\bar{x}_2 = mean of the second sample

s = Combined standard deviation

n_1 = Number of observations of the first sample

n_2 = Number of observations of the second sample

$$s = \sqrt{\frac{(x_1 - \bar{x}_1)^2 + (x_2 - \bar{x}_2)^2}{n_1 + n_2 - 2}}$$