Treatment of Dyestuff Wastewater

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PASSION FOR CHEMISTRY

History

Prior to the middle of the 19th century, dyes were made from natural sources (minerals, vegetables/roots, animals or insects) like beet root, Madder and the Murex shell. They are generally less allergenic and toxic than synthetic dyes and generate wastewater that can be treated by biodegradation/coagulation/settling unlike synthetic dyes.

History of Modern Dyes

- Early industrialization of dyes was conducted by J. Pullar and Sons in Scotland. The first synthetic dye, mauve, was discovered serendipitously by William Henry Perkin in 1856. The discovery of mauveine started a surge in synthetic dyes and in organic chemistry in general. Other aniline dyes followed, such as fuchsine, safranine, and induline. Many thousands of synthetic dyes have since been prepared.
- Many of the earliest chemical companies in the UK, Japan, USA and Europe had their start in the dyestuff industry: ICI, I G Farben, CIBA, Geigy, BASF, Bayer, AGFA, Hoechst, Du Pont, Dow, Solvay, Nippon, Mitsui, Sandoz, Hoffman La Roche, etc.

The Problem

- Textile processing wastewater is rich in chlorine, acids, salts/heavy metals and man-made organic compounds such as **dyes**, **pigments**, **colorants**, surfactants, waxes, and other substances used to colour clothes and make them resistant to physical, chemical, and biological agents. These chemicals have an adverse effect on receiving waters/human health if not removed/recovered.

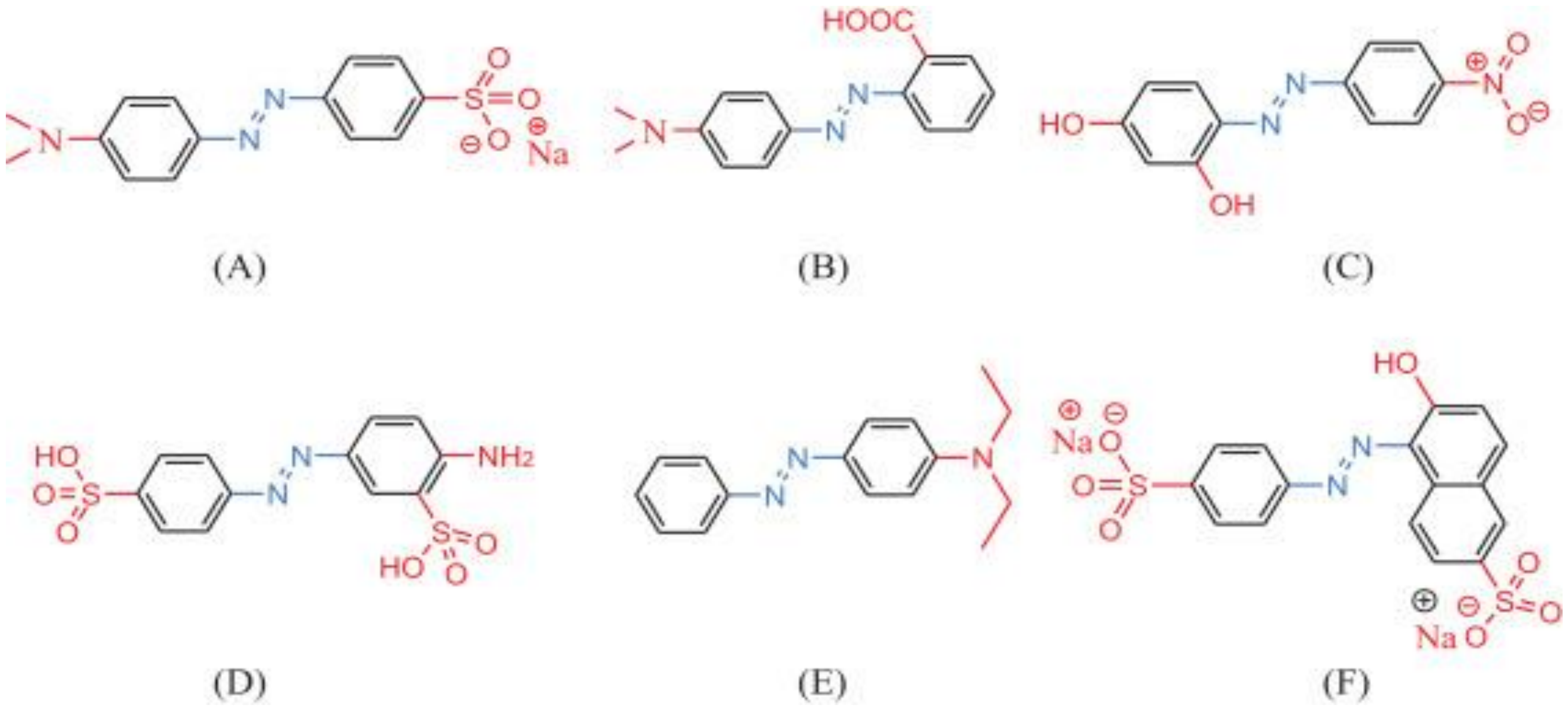
Source: Industrial Water Treatment Process Technology, 2017.

Note: Some Azo dyes break down during use and release chemicals known as aromatic amines, some of which are carcinogenic. The EU has banned the use of these azo dyes that release cancer-causing amines in any textiles that come into contact with human skin.

Chemistry

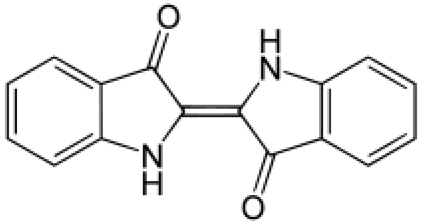
- Dyes are organic compounds with three essential groups in their molecules: the **chromophore**, the **auxochrome** and the **matrix**. The active site of the dye is the chromophore, it can summarize the spatial localization of atoms absorbing light energy. Chromophore-containing molecules feature also in surgical practice, with synthetic dyes gaining popularity over endogenous optical adjuncts.
  An auxochrome is a functional group of atoms with one or more lone pairs of electrons when attached to a chromophore, alters both the wavelength and intensity.
- The chromophore consists of groups of atoms, the most common of which are nitro (–NO_2), azo (–N═N–), nitroso (–N═O), thiocarbonyl **(**–**C═S**), carbonyl **(**–**C═O**), as well as the alkenes **(**–**C═C**–**).** The absorption of electromagnetic waves by the chromophore is due to the excitation of the electrons of a molecule. The molecule that contains them becomes chromogenic. The chromogenic molecule has dyeing possibilities only by the addition of other groups of atoms called “auxochrome”. These auxochromic groups allow the fixation of the dyes and can modify the colour of the dye. They may be acidic (**COOH, SO_3** and **OH**) or basic (**NH_2, NHR** and **NR_2**). The rest of the atoms of the molecule correspond to the matrix, the third part of the dye.

Sample Dye Molecules

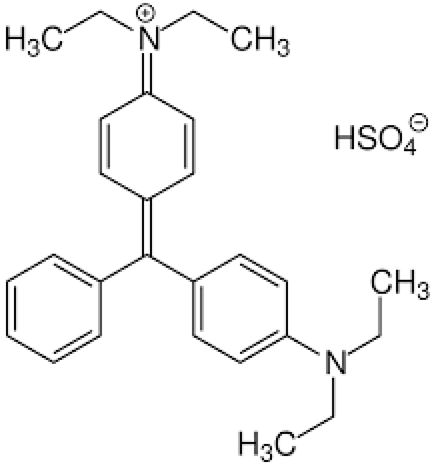


Molecular structure of azo dyes: (A) methyl orange; (B) methyl red; (C) azo violet; (D) fast yellow B; (E) oil yellow DE; and (F) sunset yellow FCF. The blue color represents the chromophore group and the red color represents the auxochrome group.

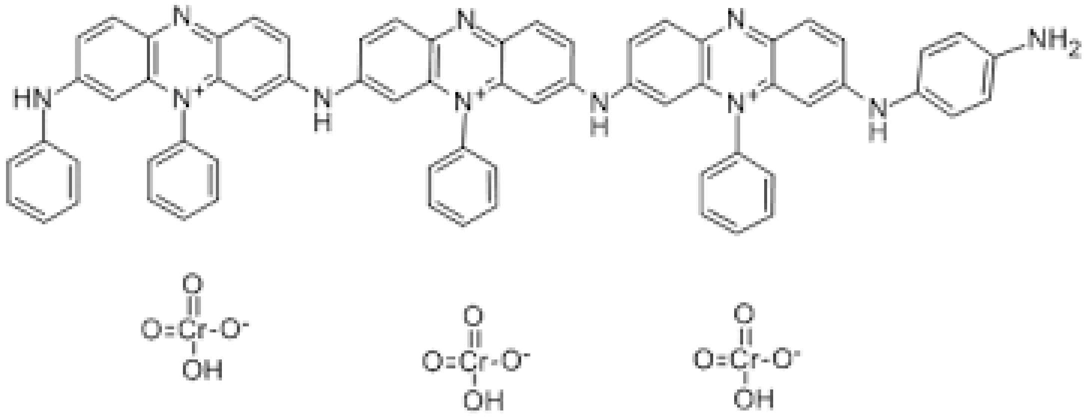
Dye Chemical Structures



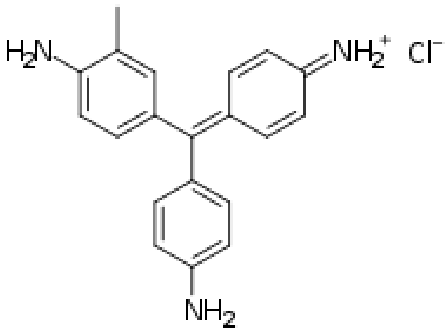
Indigo



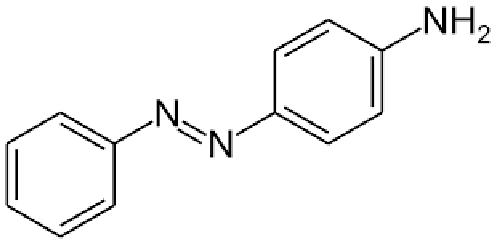
Brilliant Green



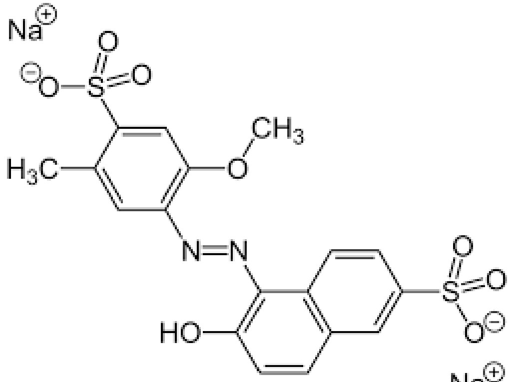
Aniline Black



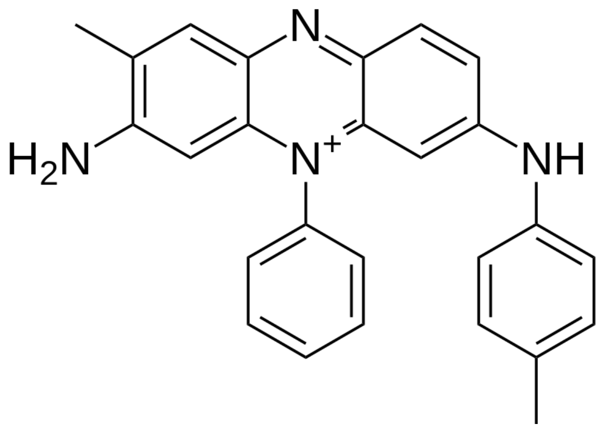
Fuschine



Aniline Yellow



Allura Red



Mauveine A

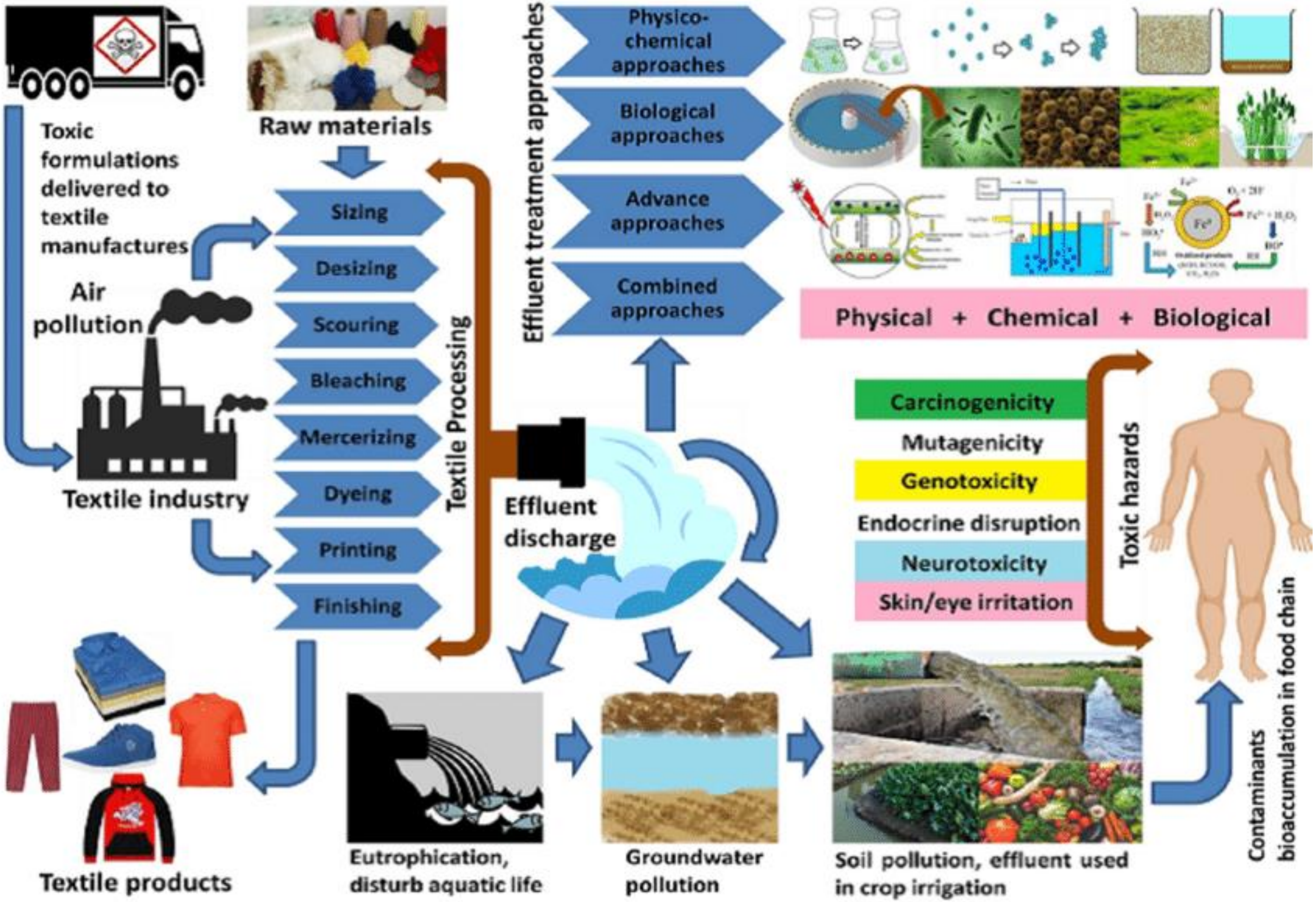
Impact On Air Pollution

- The textile industry, while contributing to economic development, also brings about atmospheric pollution in addition to water pollution. In the textile industry, the heat setting machine plays an important role in the pre-treatment process of textiles. During heat setting, various dye and coating auxiliaries on the textile are released into the air, resulting in the emission of a large amount of volatile organic compounds (**VOC's**). These organic gases mainly include formaldehyde, polycyclic aromatic hydrocarbons, and other organic gases.

Water Pollutants

- High COD and Colour
- High fibre content
- Sometimes waxes are used
- Many salts/heavy metals are used as mordants
- High BOD
- High SS
- Aniline (Endocrine Disrupting Chemical)
- High or Low pH

Graphic Summary



Types of Dyes

1. Acid dyes: Primarily suitable for protein fibres, nylon, and silk, among others. They are known for their vibrant colours but have poor color fastness to water washing. However, they exhibit excellent dry-cleaning fastness and are widely used in natural dyeing.

2. Cationic dyes (Basic dyes): Suited for acrylic, polyester, nylon, cellulose, and protein fibres. These dyes offer bright colours and are well-suited for synthetic fibers. However, they have poor colour fastness to water washing and light, especially when used on natural cellulose and protein fabrics.

3. Direct dyes: Ideal for cellulose fibre fabrics. They have relatively poor color fastness to water washing and varying light fastness. However, modified direct dyes can significantly improve their colour fastness to water washing.

4. Disperse dyes: Suitable for viscose, acrylic, nylon, polyester, and similar fibres. They exhibit varying colour fastness to water washing, with better results on polyester and poorer results on viscose.

Types of Dyes - II

5. Azo dyes (Naphthol dyes): Suitable for cellulose fabrics, offering bright and vibrant colours.

6. Reactive dyes: Mostly used on cellulose fibre fabrics and less commonly on protein fibres. They are known for their bright colours, good light fastness, and excellent water washing and rubbing fastness.

7. Sulphur dyes: Suitable for cellulose fibre fabrics, these dyes provide dull and dark shades such as navy blue, black, and brown. They exhibit excellent light and water washing fastness but poor chlorine bleaching fastness. Prolonged storage of fabrics dyed with sulphur dyes can cause fibre damage.

8. Vat dyes: Suited for cellulose fibre fabrics, these dyes offer excellent light and water washing fastness, as well as resistance to chlorine bleaching and other oxidative bleaching agents.

The Chemistry of Mordants

- Organic Mordants include acetic, tannic acid and oxalic acid.
- Metal mordants include salts of aluminium (Al), chromium (Cr), iron (Fe), copper (Cu) and tin (Sn) are also used to fix colours to the substrate. Some of the important metallic mordants are alum, potassium dichromate, ferrous sulphate, copper sulphate, stannous chloride and stannic chloride.
- Mordants are also knows as dye fixatives because they bind the dye on the fabric. They do this by forming coordination complexes with the dye which then attaches chemically to the fabric.

Other Chemicals/Biochemicals Used

- dyeing auxiliaries (acid/alkali donors)
- wetting agents (surfactants)
- swelling agents (dyeing accelerators)
- anti-migrating agents
- sequestering agents
- levelling agents
- dispersing agents
- soaping agents
- fixing agents
- anti-foaming agents
- crack mark inhibitors
- Flame retardants
- enzymes

Application of Dyes

- **Acid** dyes work well on silk, wool, and nylon while **reactive** dyes are ideal for cotton, linen, and rayon. **Disperse** dyes are suitable for polyester and acetate while **pigment** dyes can be applied to various fabrics using different techniques like hand painting or screen printing.
- The principal dye used in anti-infective procedures in the 21st Century is the phenothiazine (phenothiazinium) derivative of methylene blue.
- BactoView™ Live, RedDot™1, DMAO, Thiazole Orange, and Hoechst are cell membrane permeant nucleic acid binding dyes. SynaptoGreen™, SynaptoRed™, and CellBrite™ Fix are all cell membrane/cell periphery stains.
- Indigo appears to be licensed for use as a food dye in the U.S., and most food dyes are also synthetic and of broadly similar chemical structures to those used as textile dyes.

Top Textile Dyestuff Companies in the World

- Allied Industrial Corp. Ltd.
- LanXess.
- Sumitomo Chemical.
- Huntsman Corporation.
- Kiri Industries.
- BASF SE.
- Bozzetto Group.

Kiri Industries Limited
Future Full of Colours.....

LANXESS
Energizing Chemistry

BOZZETTO GROUP
OVER 100 YEARS OF ADVANCED CHEMISTRY

HUNTSMAN
Enriching lives through innovation

SUMITOMO CHEMICAL

BASF
We create chemistry

Water Treatment Methods

- pH Correction of acidic waste waters
- Precipitation
- Removal/neutralization of Chlorine/bleaches
- Textile wastewater is often treated with physiochemical methods: Coagulation, Flocculation and Settling.
- Sometimes DAF is needed if the fibres don’t settle well
- UF can help remove fibres and SS
- NF can remove colour molecules
- Photocatalytic decomposition
- Biological treatment
- MFC’s = Microbial Fuel Cells

Water Treatment Methods - II

- ACF can also remove COD and colour molecules
- AOP can also remove residual COD and persistent organic molecules
- Anaerobic Digestion can remove COD/recover methane from Sludge
- RO can remove high TDS/recover water
- Weak Ion exchange can trap organic molecules
- Vegetable Oil + Magnetite = Ferromagnetic Microplastics/fibres scavenger
- Aniline oxidizing bacteria
- Micelle Enhanced Ultra Filtration

Video of Jar Tests

- https://www.youtube.com/shorts/-oTmY6LKdQQ
- https://www.youtube.com/watch?v=aOSAbv2NWbg

MF and UF

- **Microfiltration**

It is a membrane process which removes contaminants from thefluid using microporous membrane. This membrane is usually used to removesuspended solid particles. A typical microfiltration membrane is classified basedon its pore size range from of 0.1 to 10 micrometre (µm) (Cheryan 1998).

- **Ultrafiltration**

It is a membrane filtration system in which the hydrostatic pressureforces a liquid against a membrane. Ultrafiltration is employed for separation of macromolecules (103 –106 Da), especially starches, proteins and microbes such as viruses and bacteria. Ultrafiltration membrane prevents molecules in the range from1000 to 500,000 daltons in molecular weight (Cheryan 1998).

Nano- Filtration (NF)

- **Nanofiltration**

This membrane system prevents molecules ranging from 100 to 1000 daltons in molecular weight to pass. NF can prevents smaller (0.001µm) contaminants from passing through (Taylor and Jacobs 1996).

RO - Reverse Osmosis

- These membranes have a very small pore size compared to other membranes, and they can reject the smalles (0.0001µm) particles/molecules (Taylor and Jacobs 1996) in addition to salts.

  RO membranes are usually classified by efficiency in rejection of NaCl from solution, which ranges from 95 % to 99.4 %.

MEUF

- Micelle Enhanced Ultra Filtration, is Ultra Filtration enhanced by the use of surfactant formed micelles.
- In water, surfactants forms micelles in which their hydrophobic ends are turned inwards while their hydrophobic ends are faces the surrounding water.
- Certain pollutants such as Aniline, which is water insoluble, can be trapped inside the micelles thus enhancing their removal through UF.
- The Critical Michelle Concentration, CMC, is the minimum concentration of surfactant above which micelles form.

Anaerobic Digestion

- When organic chemicals are not biodegradable easily, then Anaerobic digestion is used to remove them from waste water.
- It is a slow process but it can remove COD from waste water and generate useful Methane.
- Many times the sludges from dyeing waste water as well as paper mills is treated by AD to recover energy.

Biofouling Control using Biological Methods

- Biological methods used to control biofouling of membrane bioreactors/other membranes are:

  A - Enzymatic,
  B - Nitric oxide,
  C – Using Bacteriophages and
  D- Quorum sensing inhibitors.

Biological Methods to Manage Biofouling

Biological method	Capabilities	Advantages	Limitations	Reference
Enzymatic				
Proteinase K	Disperse the established biofilm	Reduce biofilm and environment friendly	Limit its large-scale application	Chaignon et al. (2007)
Trypsin	Hydrolyzes lysine peptides and can also remove the mature *S. aureus* 383 biofilm	Reduced bacterial resistance	Require optimum conditions	Chaignon et al. (2007)
Protease	Control biofouling on UF membrane for wastewater treatment	High removal of foulants and high permeate recovery	Sensitive to elevated salt concentration	Leroy et al. (2008)
Antimycotic lysozyme	Candida biofilm formation control and attachment	Environment friendly and acts more specific than biocides	Limits widespread application	Caro et al. (2009)
Nitric Oxide *SNP*	Pretreatment of biofilm grown on the RO membrane led to a twofold increase in the biofilm removal efficiency	Attenuates the signalling mechanism rather than by toxic effects	Low solubility in water and not stable as it can be easily oxidized	Barraud et al. (2009)
Bacteriophage	UF membrane biofouling reduction of 40 % on average	Continuous infection and multiplication as long as the host is present	The phages detected in permeative solution	Goldman et al. (2009)

Other Methods

- Surface modification
- CIP cleaning
- Good pre-treatment
- Nutrient removal

Environmentally and Human Friendly Dyes

- What are OEKO-TEX dyes?

- The Oeko-Tex® Standard 100 sets out criteria for the human ecological profile of dyed and finished textiles. Textile quality is not just determined by the dyestuff applied, but also by the type and quality of the substrate, pre-treatments, finishing chemicals, auxiliaries and the dyeing methods used.

Standards

- EN 14362-1:2003 or EN 14362-2:2003

- This standard describes a procedure to detect the use of certain listed aromatic amines derived from azo colorants which are toxic.

References

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- https://www.sciencedirect.com/topics/materials-science/azo-dyes#:~:text=Molecular%20structure%20of%20azo%20dyes,color%20represents%20the%20auxochrome%20group.
- A History of the International Dyestuff Industry, Peter J.T. Morris and Anthony S. Travis, American Dyestuff Reporter, Vol. 81, No. 11, November 1992.