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A REVIEW OF WATER POLLUTION BY AZO DYES AND ITS IMPACT

Vijendra Batra[1] and Pravin Deshpande[2]
[1]Associate Professor, Department of chemistry ,
Sarvodaya Mahavidyalaya Sindewahi Dist-Chandrapur (M.S.) India.
[2]Department of Chemistry,Sevadal Mahila Mahavidyalaya Nagpur (M.S.) India.

ABSTRACT :
Dyes are integral part of colorfull world. Textile industries are one of the important industries using highest varieties of dyes, and generates large amount of effluents, variety of synthetic dyestuff released by Textile industries, creating severe threats to environment. More than 70% dyes used by textile industries are azo dyes. During the fixing and manufacturing of these dyes huge amount of waste water is discharged. This water contains toxic chemicals and material. The effect of this polluted water on environment and human life, its treatment to control damage, is the main theme of the paper.

KEYWORDS : *Dyes, toxicity, Textile industries, water pollution.*

INTRODUCTION

Dyes are those chemicals which makes human life more colorfull. Synthetic dyes are used by textile, packaging, leather, printing, cosmetics and food materials and metals industries. Only textile industry is using more than 10000 dyes, out of that more than70% dyes are azo dyes. Industries are using millions of tons of synthetic dyes, out of them textile industry is using highest amount of these synthetic dyes and pigment.

The dyes which are used in textile industries are many times found unsafe, In some cases it is found that after prolonged wearing of clothes side effects are observed, when dyes made by toxic chemicals are absorbed into the skin especially when body is warm and skin pores are opened to allow perspiration skin rashes, headaches, dizziness and fatique were reported. According to kirck-othmer major dyes are Acid dyes, Basic dyes, Direct dyes Reactive, vat dyes, sulphur dyes, Disperse dyes etc.

The main reason of pollution are effluent discharged by the industries, this effluent is the main cause of soil and water pollution. Due to water pollution flora and fauna changes dramatically. To assess the degree of impact, each class of dyes must be taken in account, In addition to the amount of color produced, degree of attachment to the fibres and consequent loss to waste water is shown Table No. 1.

Table 1: Dyes, target fibres, degree of fixation and percentage of dye lost to the effluent.

Type of Dye	Fibre	Degree of Fixation (%)	Loss to effluent (%)
Acid	Wool, Silk, Polyamide	80-95	5-20
Basic	Silk and Wool	95-100	0-5
Direct	Cotton (Cellulose)	70-95	5-30
Disperse	Polyester	90-100	0-10
Mordant	Wool and Cotton	90-98	2-10

Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Vat	Cellulose	80-95	5-40

Due to the high molar extinction coefficient, the colors are visible in water even at concentrations as low as 1 mg L^{-1}. So, to get an idea of the seriousness of the problem, it is important to stress that the textile industry generates waste water with concentration of dye that can varies between 5 and 1500 mg L^{-1} . By decreasing the transparency of the water and prevent the penetration of solar radiation, these compounds decrease the colored photosynthesis activity and cause distrubances in the solubility of gasses, causing damage to the gills of aquatic organism and disrupt their places of refuse and spawning. These compound can remain for decades in aquatic environments endangering the stability and lives of these ecosystems.

The degradation products of the dyes in these environments and in human may be more harmful than the dyes themselves. This due to breaking of azo connection that could origin aromatic amines potentially carcinogenic and /or mutagenic.Azo dyes are those having one or more –N= N – as chromophore group, azo dyes complex in nature. They have aromatic amins in there structures, Aniline and its derivatives are toxic in nature, in many azo dyes phenols are present, these are also toxic in nature. Many azo dyes have sulphonic group – SO_3H which is very strong acidic in nature.

Azo dyes are capable of changing physical and chemical properties of soil and water of the area. Many azo dyes are highly poisonous to the ecosystem because of their stability enabling them to remain unchanged for long period of time.

The waste water released from textile dyeing industry is a dangerous source for environmental contamination, since they produce about 100 liters per kilogram of dyed tissues. This shows high values of chemical oxygen demand (COD), total solids (TS), high pH, temperature fluctuating according to the industrial process involved, high amount of surfactants and intense color. These may also present high concentration of heavy metals such as chromium, copper, mercury, etc, which are used in dye formulation. Hence the discharge of textiles effluents into surrounding water bodies is a serious problem not only from the asthetic point of view but also due to its toxicity to aquatic environment.These also represents a potential mutagenic character to humans. Therefore an efficient treatment to textile waste water is essential for the betterment of flora and fauna.

Effect of toxic nature of dyes on human health and environment:

In textile industry, waste water is produced as a result of spinning of spinning of yarn and weaving of cloth. This waste water contain toxic chemicals hazardous compounds, phenols, aldehydes, ketones, amines, cyanides, toxic acids, starch, etc. The waste water from dyeing section, color depending upon the type of dye used (whether vat dye, sulphur dye, reactive dye or azo dye).

Organic dyes constitute one of the larger groups of pollutants in wastewater released from textile and other industries. The wastewater from the dye house is generally multi-colored. The dye effluent disposed into the land and river water reduces the depth of penetration of sunlight into the water environment, which in turn decreases photosynthetic activity and dissolved oxygen. The adverse effects can spell disaster for aquatic life and the soil. The discharge of highly colored wastewater into the ecosystem involves environmental problems like aesthetic pollution (even a small amount of dye is clearly apparent), and perturbation of aquatic life.Effect of some of these dyes on human are taken as an examples.

Among the most useful dyes, there is indigo carmine (3,3- dioxo-2,2-bis-indolyden-5,5-disulfonic acid disodium salt). Apart from its use as textile coloring agent and additive in pharmaceutical tablets and capsules as well as in confectionery items, indigo carmine is also used for medical diagnostic purposes. In conjunction with acetic acid, the dye facilitates diagnosis of Barrett's oesophagus. It can also help to target biopsies, since inhomogeneously stained or unstained areas seem to correlate with intraepithelial neoplasia. However, indigo carmine is not readily metabolized but is rather freely filterable by the kidneys. Giving intravenous injection of indigo carmine for intra-operative cystoscopy is a safe technique that can detect otherwise undetected intra-operative compromise of the urinary tract. It also contributes to intra-vital staining for contrasting and accentuating changed mucosal processes.

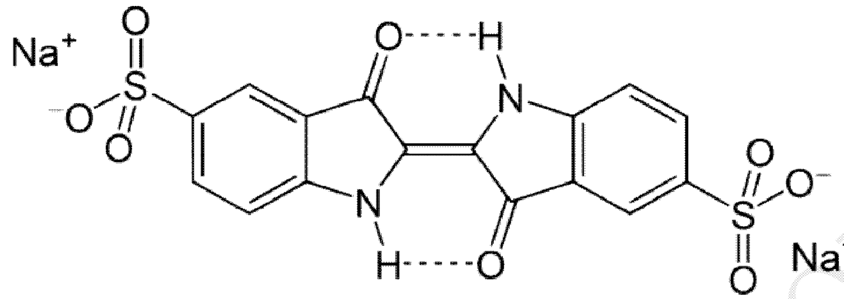

Fig. : Indigo Carmine (IC), Molecular weight: 466.36 g mol^{-1}

The indigo carmine is considered as highly toxic indigoid class of dye. Contact with it can cause skin and eye irritations. It can also cause permanent injury to cornea and conjunctiva. The consumption of the dye can also prove fatal, as it is carcinogenic and can lead to reproductive, developmental, neuron and acute toxicity. It has also been established that the dye leads to tumours at the site of application. When administered intravenously to determine potency of the urinary collecting system, it is also known to cause mild to severe hypertension, cardiovascular and respiratory effects in patients. It may also cause gastrointestinal irritations with nausea, vomiting and diarrhea. The toxicity tests of the dye revealed longterm toxicity in mice and short-term toxicity in the pig.

Congo Red (CR) dye (1-Naphthalenesulfonic acid, 3, 3'-(4, 4; biphenylenebis (azo) bis 4-amino) di sodium salt) is a benzidine-based anionic disazo dye. It has the tendency to metabolize into benzidine, a human carcinogen. Congo Red is toxic to many organisms and has also been recognized as carcinogen and mutagen. Exposure to the dye has been known to cause an allergic reaction (and possibly anaphylactic shock). Benzidine and Congo Red are, however, banned in many countries because of health concerns. But, it is still widely used in several countries. It also represents a significant effluent problem along with related dyes from textile, printing and dyeing, paper, rubber and plastic industries. Its structural stability makes it highly resistant to biodegradation and obviously its bright color and toxicity are entirely undesirable in the environment.

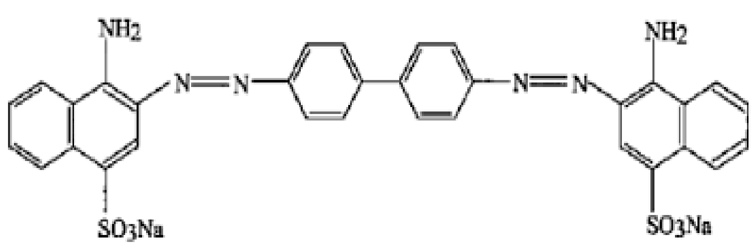

Fig. : Congo Red (CR), Molecular weight: 696.66 g mol^{-1}

Naphthol Blue Black (NBB) (4-Amino-5-hydroxy-3-[(4-nitrophenyl)azo]-6-(phenylazo)-2,7-Naphthalene disulfonic acid, disodium salt) is a diazo dye. Due to its high degree of fastness to light, the commercial grades of NBB are widely used in the textile industry for dyeing wool, nylon, silk and textile printing. Other industrial use includes coloring of soaps, anodized aluminum and casein, wood stains and writing ink preparation. It has a structure consisting of azo, phenolic, aniline, naphthalene and sulfonated groups.

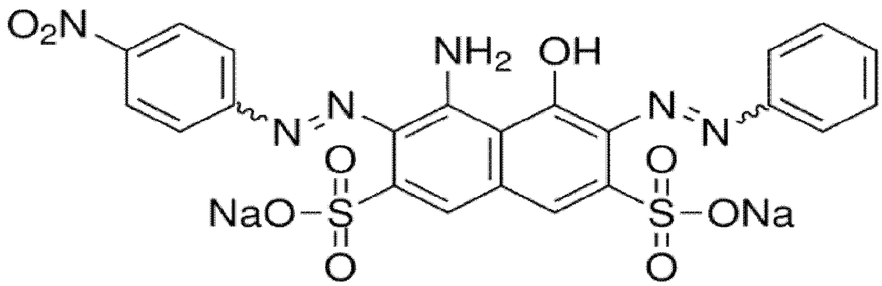

Fig. : Naphthol Blue Black (NBB), Molecular weight: 616.49g mol^{-1}

The azo and benzidine dyes, which are used extensively in textile and leather industry, could cause cancer. Using these chemicals is considered criminal offence in most of the European countries, specially in Germany. Indian textile exporters will have to switch to eco-friendly dyes because of Germany has ban on import of textiles using azo dyes. In India, the ministry of environment has banned 116 hazardous azo dyes as they could cancer to human. This prohibition covers manufacture, processing, treatment, package, storage, transportation, use, collection, destruction, conversion, offering for sale and transfer.

Azo dyes have also been found to release harmful amines which causes skin diseases. The damage that textile production causes to the environment has been recognized by environmentalist. Pollutants from textile production such as zinc, sulphides and copper-salts are non-biodegradable.

Textile Wastewater Treatment Processes:

The removal of dyes from waste water in the textile industry is one of the major environmental problems faced by textile sector. In general, the current practice in textile mills is to discharge the waste water directly into the local environment or into the municipal sewer system. In any cases, to accomplished with current local legislations (which are becoming more stringent), textile mills are sometimes forced to have their own treatment plant prior discharge. A varied range of methods have been developed for textile waste water treatment at laboratory, pilot or full scale.

The technologies most widely used are membranes filtration (inverse osmosis, microfiltration, and ultra filtrations), adsorption (activated carbon, inorganic adsorbates, ion exchange resins and natural and synthetic biosorbents), coagulation / flocculation, biological treatments (mainly conventional aerobic activated sludge treatments) and chemical oxidation (e.g. Electrochemical method). However, its efficiency is sometimes limited by several factors.

Coagulation, flocculation, adsorption, forth flotation and membrane filtration are common practices, but rest in phase transfer to pollutants, leading to another form of waste, such as spent carbon or sludge, that would require additional treatment or disposal (e.g. incineration). In view of that, destructive methods such as chemical or biological process are desirable.

Biological process are good are choice for waste treatment. The aerobic biological treatment of textile effluents most commonly used is the activated sludge. They are relative inexpensive, the running costs are low and the end products of complete degradation are not toxic [68]. However, due to the refractor nature of some constituents of the effluents, the biological treatment by activated sludge is sometimes quite difficult. The refractory character displayed by these effluents should be on the physical and chemical stability of textile dyes and their low content of biodegradable organic matter creator a high resistance to their degradation by micro-organisms. In particular, reactive dyes, acid and direct dyes are hardly biodegradable, in most cases, unchanged by the traditional methods of treatment because of their high solubility and low molecular weights. The anaerobic biological treatment has shown good results in the removal of color from textile effluents. However, these processes have the potential disadvantages of converting dyes into more toxic products than the original dyes. This increase in toxicity is due to the breaking of the links with the consequent rise of carcinogenic aromatic amines formation.

Membrane filtration can be applied to the separation of salts and large molecules such as dyes. These technologies are very attractive because they allow the reuse of water in industry. Its major limitations are the high cost and potential clogging of the membrane. This last limitation involves the frequent cleaning and replacements of filtration membranes with consequent increased costs.

The adsorption technological are limited to the amount of flow produced since high flow rates for these techniques are not feasible due to rapid saturation of the adsorbents, leading to its regeneration. This limitation, plus the fact, that both adsorption process and membrane filtration are non destructive. This technology is essentially limited to the contaminants phase transfer and does not allow the definitive elimination of the dyes.

The use of coagulation / flocculation processes for de-colorization of high flow rates of textile effluents is very expensive, mainly due to large quantities of reagent required for an effective treatment. Moreover, the high production of sludge is also a factor to take into account given the economic evaluation of this technology as the treatment/disposal of sludge produced is significant expensive. Thus, considering the obvious difficulty of treatment of effluents from textile industry, in particular the removal of color, there should be the study of one more alternative treatment processes that allow total removal of color of the final effluent, preferably without the generation of sludge, with obvious economical, aesthetic and environmental advantages.

An important class of technologies named Advanced Oxidation Processes (AOPs) has emerged as suitable for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water. Advanced oxidation processes were developed to generate hydroxyl free radicals using different oxidants under different combinations and these radicals were found to destroy components that are not destroyed under conventional oxidation processes.

AOP using ozone (O_3), ultra violet (UV), TiO_2, fenton, photo-fenton, hydrogen peroxides (H_2O_2) and ultrasonic (US) can be used to treat dyes. The main advantage of AOPs over the other treatment processes is its pronounced destructive nature which results in the mineralization of organic contaminants present in wastewater. Also, AOPs are considered as a low or non-waste generation technology, which destroys the complex structures using short lived chemical species with a high oxidation power. The hydroxyl radical (.OH) is the main oxidative power of AOPs. The .OH radicals can be generated by chemical, electrical, mechanical or radiation energy. Therefore, AOPs are classified under chemical, catalytic, photochemical, photocatalytic, mechanical and electrical processes.

CONCLUSION:

Dyes used by textile and other industries are adding color to human life but at the same they are becoming cause of concern.It was reported that the synthetic textile dyes exhibited detrimental impacts on the environment, as well as, some of them can cause hazards to humans. Therefore, more environmental friendly more better fixing method, greener route for synthesis control on effluent and proper treatment of waste water discharge by industries is a matter of more discussion.

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