Environmental Impact of Azo Dyes: A Review

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Abstract:
Through photosynthesis and other processes, green plants function as one of nature's factories, converting inorganic molecules into organic substances. One of nature's most useful tools, microbes decompose and mineralize organic things such as dead plants and animals, to inorganic forms. Microbes and green plants work together to keep the organic and inorganic worlds in balance, but contaminants like synthetic dyes can throw this equilibrium off. Azo dyes are organic compounds that contain one or more azo groups (−N=N−) as chromophores. They are widely used in dying industries. Natural dyes are safer and better for the environment than synthetic dyes, but they are also more expensive and more complex to use, making them unsuitable for most commercial purposes. These are the most widely used class of synthetic dyes because they are inexpensive, have great intensity, and are colour fast. When untreated azo dyes are dumped into the environment, their primary by-products, aromatic amines are produced by the breaking of central azo bonds pose a serious risk to both humans and the environment. These compounds have been identified as significant carcinogens. Degradation of synthetic azo dyes is a promising treatment option for azo dye waste water to counter this issue.

A summary of the studies on azo dyes' effects on the environment, including their effects on water ecosystems, plants, crops and biochemical and chemical oxygen demand, is given after the classification of azo dyes and colour mechanism.

Keywords: azo dyes, chromophores, aromatic amines, biochemical oxygen demand, chemical oxygen demand.

Introduction:
Industry is the biggest source of environmental pollution, which is the main factor contributing to climate change. The biggest source of water contamination in the textile sector is the dyeing process. With detrimental effects on the ecology and aesthetics, this pollution can impede sunlight's ability to reach water, which in turn affects photosynthetic organisms and the biochemical oxygen demand (BOD) [1].

Since 3500 BC, natural colours have been utilised. The use of dyes in cave paintings shows how significant colour was even back then. Colour is a medium of expression that can represent a visual communication style and is associated with leadership, hierarchy, and authority [2–3]. In the past, natural dyes have been made from minerals, Mediterranean plants like Rubia tinctorum and Paubrasilia echinata, both contain anthraquinone pigments and animal sources as the extracts from specific insect species, like Dactylopius coccus that contain naphthoquinones [4].

Natural dyes have been produced by combining a wide range of ingredients, such as organic elements like plant matter and animal fats with inorganic materials like water, clay, soil, minerals, metal salts and even semi-precious stones like malachite. Natural dyes can be less toxic and more ecologically friendly than synthetic dyes, but because they are sometimes more expensive to buy and more challenging to utilise, they are not practical for use in many industrial applications. More specifically, huge amounts of raw materials need to be treated because the necessary dyeing elements usually make up just 2% of the bulk of natural dye sources. Because of this, natural dyes may become too expensive to produce in large quantities. The first synthetic dye, Mauvein was inadvertently created in 1856 by William Henry Perkin [5]. Approximately 10,000 synthetic dyes had been created and produced by the end of the 19th century. India, China, South Korea, Taiwan, and Eastern Europe now use 600,000 tonnes of dye annually [6]. Approximately 15% of the overall production of synthetic dyes is disposed of in the environment. The depletion of oxygen in the water and the blocking of sunlight from reaching water bodies have a damaging impact on photosynthetic organisms, resulting in metabolic stress, floral necrosis, mortality and a reduction in faunal growth [7].
Dye colour mechanism:
Chromophores are molecules that are found in dyes. They are composed of atoms such as nitrogen (N), oxygen (O) and sulphur (S) and incorporated into groups called azo (−N=N−), carbonyl (−C=O), sulphide (C=S), nitrous (NO or N-OH) and nitro (−NO2 or NO-OH) \[8\]. Unsaturated chromophores are made up of heteroatoms or heteroatom groups with consecutive single- and double-bond arrangement. Since a chromophore absorbs light at a specific wavelength in the visible portion of the spectrum, it takes on colour. An intense colour that is correlated with a high molar extinction coefficient can be produced by a modest amount of dye in an aqueous solution. Colour can be measured via high-performance capillary electrophoresis, chromatography and visible-spectrum spectrophotometry. \[9\]

Because of their great structural diversity, synthetic dyes—like azo dyes—can have a wide range of chemical and physical characteristics \[10\]. Examples of primary chromophores used to categorise synthetic colours are shown in the following table:

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Chemical Structures</th>
<th>Examples</th>
<th>Characteristics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitro and Nitroso</td>
<td>HO-N=O</td>
<td>Naphthol yellow Disperse Yellow 26 Disperse Yellow 14</td>
<td>In nitro dyes, a nitro group conjugates to an electron donor group via an aromatic system. Nitro dyes always contain an -OH group as a donor.</td>
<td>[20]</td>
</tr>
<tr>
<td>Xanthene</td>
<td><img src="image.png" alt="Image" /></td>
<td>Rhodamine 60 Rhodamine 123 Fluorescein</td>
<td>These dyes are heat-resistant.</td>
<td>[22]</td>
</tr>
<tr>
<td>Acridine</td>
<td><img src="image.png" alt="Image" /></td>
<td>Acridine orange Basic yellow</td>
<td>These dyes are heat-resistant.</td>
<td>[23]</td>
</tr>
</tbody>
</table>

The majority of dyes have auxochrome groups, which intensify colour but are not the source of colour. These groups include sulfonates (HSO3), carboxyls (-COOH), amines (-NH3) and hydroxyls (-OH) \[10,11\]. These groups have the crucial characteristic of increasing the compound's affinity for the fabric's fibres. An essential component of the dye molecule is the chromogen, which is an aromatic structure often consisting of benzene, naphthalene, or anthracene. Because of their wide range of structural variations, synthetic dyes have a variety of distinct chemical and physical characteristics.

The category of dyes most frequently used in industries are azo dyes \[12\]. On industrial basis, azo, anthraquinone, indigo, xanthene and triarylmethane are the most often used dyes \[15\].

In the textile, tanning, pharmaceutical, cosmetic, paper, food and service industries, azo dyes are the most widely used synthetic dyes. As azo dyes can biodegrade by other viable means, it is crucial to comprehend the serious issues that arise from releasing them into the environment untreated.

**Azo Dyes:**
Diffusion, reactivity, cost, fixing properties and affinity and bond stability of the dye with the fibre all play a role in choosing the right dye. Azo dyes make up 60% of the market and are the most widely used class because to their simple accessibility, low cost and excellent dyeing performance. They also have the highest intensity, lowest cost and best colour fastness of all synthetic dyes.

Organic chemical compounds known as synthetic azo dyes are used in a variety of fields. They are a significant environmental problem because of their stability, chemical flexibility, high fixation and resistance to light and moisture, all of which have a direct bearing on how easily they can decay \[13,14\].
Chemical representation for the compounds of the synthetic azo group is \( R \cdot N=N \cdot R' \), where \( N=N \) is the chromophore group known as azo group. The International Union of Pure and Applied Chemistry's classification scheme states that azo dye compounds are diazine (HN-NH) derivatives in which the hydrogen (H) atoms have been replaced by groups such as azobenzene, hydrocarbyl, or diphenyl diazene. They might have one to three azo bonds between the phenyl and naphthyl rings; which may be substituted by hydroxyl, amino, nitro, or chloro groups. Azo dyes are known for their rich coloration and two-thirds of today's synthetic dyes are thought to be made from them. They are the category of commercial organic dyes with the widest application range and the greatest structural variety [15].

The principal by-products of untreated azo dyes are aromatic amines. These are produced when the primary azo bonds are broken, and they are primarily responsible for the environmental dangers connected with their disposal. These are considered major carcinogens and pose a serious risk to human health [16]. Even at low quantities, azo dyes have a harmful influence on ecosystems [17]. Specifically, the transmission of sunlight is limited when dyes are dumped into water bodies without first being treated.

High BOD and chemical oxygen demand (COD) as a result suppress photosynthesis and have an adverse effect on plant growth. Recalcitrant, poisonous, mutagenic, toxic, carcinogenic and bio accumulative are the characteristics of synthetic azo dyes [18].

**Impacts on Plant growth and agriculture:**
The various health and environmental concerns associated with azo dyes are a major cause for worry [19]. Each harmful component's contribution to overall toxicity varies depending on its concentration and distribution across the environment, which affects the diversity of the living environment [20].

Living organisms are exposed to genotoxic environmental agents at cellular and molecular levels. Research on genotoxic potential is continued for forecasting the effects of particular substances on flora and animals and on humans [21, 22]. According to Wang and Keturi, root: shoot ratios and % seed germination can be employed as quick, easy, repeatable and dependable methods for examining the damage that azo dyes and other harmful substances bring to contaminated wastewater reservoirs [23, 24].

A number of factors, such as the dye's concentration in water, the metals present in the soil, their solubility indices and the kind of plant, affect the processes of dye and mineral uptake and accumulation by crops and other plants [25]. The rate of absorption and accumulation of heavy metals is higher in leafy vegetables than other types of plants [26]. Savin and Butnaru discovered that reactive azo dyes are poisonous and this can kill soil microorganisms and lower agricultural output [27]. Therefore, when water is obtained straight from wastewater for the cultivation of crops and vegetables, industrial effluent pre-treatment and detoxification are needed.

**Impact on Water systems:**
Azo dye waste is one of the main causes of environmental issues and a significant source of water pollution. It has been demonstrated that when aquatic species consume azo-dye effluent, serious physiological diseases such as hypertension, intermittent fever and kidney damage result. Physiological characteristics, persistence in the food chain and water ecology, and other factors determine the build-up of organic and inorganic toxicants in aquatic environments. Because their gills—the main organs for breathing and acid-base balance—allow aquatic vertebrates, including fish and tadpoles, to live in close proximity to the aquatic ecosystem, they are particularly vulnerable to the toxins found in the water. High pollution levels can lead to physiological problems in these organs, which can lead to homeostatic abnormalities and poor overall life performance. Azo dyes in aquatic environments have an inhibiting effect on the aquatic biota and impact species found in the green biome with regard to photosynthesis. Synthetic azo dyes are not biodegradable in nature, although they do break down anaerobically in sediments, yielding hazardous amines [28].

Karthikeyan et al. investigated the effects of artificial azo effluents on the proteinous freshwater fish-Macrasembelus armatus, by observing the change in the ionic regulation of specific tissues (liver, kidney, and muscle) before and after following a 35-day treatment with sublethal concentrations of Acid Blue 92, a reactive dye [29]. It was found that the concentrations of K\(^+\) and Ca\(^{2+}\) ions increased greatly, while the concentrations of Mg\(^{2+}\) ions somewhat increased. Conversely, the concentrations of Na\(^+\) and Cl\(^-\) ions decreased. These findings demonstrate how textile effluents impact ionic regulation in fish.
Soni et al. compared the effects of treated and untreated textile-dye wastewater on the freshwater fish Gambusia affinis in toxicological research [30]. The results showed that the treatment significantly decreased the rates of death as well as the cytotoxic effects on red blood cells, which included a decrease in the frequency and degree of poikilocytosis—a condition in which abnormal growth of red blood cells occurs.

Using Winogradsky columns that held a microecosystem made up of soil (derived from a river bed), water, and essential nutrients, De Sousa et al. assessed the impact of simulated textile azo-dye effluent on phytoplankton [31]. It has been discovered that Remazol Red Brilliant dye inhibits photosynthesis and creates an ecological imbalance in the food chain. Therefore, phytoplankton and other microorganisms in aquatic ecosystems are adversely affected by water that contains large amounts of industrial azo dyes.

Environmental Impact of Synthetic Dyes:
Undoubtedly, one of the biggest issues facing humanity today is environmental pollution, and the textile sector is a major contributor to this problem because of the large volumes of effluent pollutants it releases into waterways. Excessive biological oxygen demand (BOD) and prolonged colour have been shown to be visually and environmentally undesirable.

It is the textile industry that produces the most coloured wastewater [32]. When synthetic dyes are used to dye textile fibres, about 20% of the dyes are not attached to the fibres and end up in wastewater streams [33]. This leads to significant pollution because the residual azo dyes, which are not linked to the fibres or fabrics, go reach wastewater streams.

Because of their synthetic nature and complicated structure, azo dyes are very difficult to biodegrade. Generally speaking, azo dyes are toxic; they are carcinogenic (able to cause cancer), cytotoxic (a substance's ability to produce poisoning or toxicity), and mutagenic (allowing mutations to occur). Still, genotoxicity—the ability of textile dyes to break DNA or chromosomes—may pose the most long-term threat to human health.

Untreated wastewater from textile processing plants can contain large amounts of azo dyes, which can pose a serious threat to the environment and have toxic effects on living organisms. As a result, many water bodies receive large amounts of this untreated wastewater. Furthermore, traditional wastewater treatment methods have difficulty eliminating colours, heavy metals, and electrolytes. Untreated textile wastewater discharge is an aesthetically unpleasant practise. More importantly, though, it leaves behind a trail of environmental problems: it decreases the ability of water bodies to reabsorb oxygen; it interferes with sunlight's ability to penetrate water, disrupting aquatic plants’ ability to photosynthesize; it increases the number of solid particles and oxygen-demanding substances in water bodies; and, finally under the right circumstances, it produces aromatic amines, which are thought to be carcinogenic agents. The environmental damage depends upon quantity of disposal dye and composition of the dye mixture with various common constituents having toxic properties [34]. The chemical composition and structure of synthetic azo dyes generally prevent them from biodegrading, and the majority of them are poisonous, carcinogenic and recalcitrant, all of which have long-lasting negative consequences on the environment [35]. In the environment, certain synthetic dyes have a lengthy half-life (50 years or longer) [10]. The reactivity of their molecules determines how long they last.

An increase in the persistence of azo-ionic dyes can occur when they are discharged into surface water or wastewater because they can attach to sediments or wastewater sludge and bind to floating organic matter through electrostatic interactions [36]. A variety of health issues, including hypertension, cramps, nausea, bleeding and ulcers of the skin or mucous membranes, can be brought on by ingesting tainted sludge and coloured water. These hazardous substances can then be passed down through the food chain to humans.

Methods of Removal of Azo Dyes:
Because azo dyes are harmful to aquatic life and can cause disease in humans, many treatment techniques, such as chemical, physical, biological and hybrid approaches, have been shown to be effective in getting rid of them. Unfortunately, the drawback of chemical and physical treatments is that they produce sludge that is costly to handle and needs big treatment facilities. White-rot fungi are the most efficient for breaking downs synthetic dyes because they produce the enzymes that catalyse dye removal and degradation reactions [37]. The efficacy of azo-dye removal is influenced by various factors such as pH, nutritional load, treatment duration, aeration, carbon (C:N) ratio, biomass morphology, inoculum concentration, co-substrate additions and salt presence [38].
Physico-chemical Treatment methods:
Although wastewater can be treated physico-chemically quite easily, there are a number of disadvantages to this method, including high costs, poor efficiency, restricted adaptability and even interference from other wastewater components. Physico-chemical techniques are multistage treatment processes with extended retention periods rather than single techniques. Higher energy consumption is required due to the large amount of sludge and by-products produced by the processes.

Physical procedures are successful in removing colour, but they do not completely break down the dyes; instead, they become concentrated and require additional disposal. Conversely, chemical treatments can remove the colours by flocculation and coagulation, but they produce concentrated sludge. Further environmental issues could also result from many chemicals interacting with one another, which is both feasible and possible.

Biological Treatment Methods:
The breakdown of dyes via biological processes is the basis of biological treatment techniques, which offer several benefits over physico-chemical ones. Their main methods involve the use of either living or dead microbial biomass for adsorption, or the application of enzymes for the biodegradation of dyes. They are less energy-intensive, produce less sludge, use fewer chemical combinations and are generally simple to use. Furthermore, the bioremediation process yields less harmful inorganic molecules as by-products. Converting undesirable organic dyes into non-toxic substances is the primary goal of biological treatment techniques.

Legislation on the use and disposal of Dyes:
The use of azo dyes in consumer goods, including food, toys, apparel and cosmetics is strictly regulated in the EU. The EU's "Registration, Evaluation, Authorization, and Restriction of Chemicals" (REACH) regulation prohibits the use of synthetic azo dyes that produce 30 mg kg⁻¹ or more of these amines in products that may come into direct or extended contact with human skin. It also lists 24 different types of aromatic amines that are thought to be hazardous and toxic to human life.

India was the first nation in Asia to regulate chemicals in 1997. The restrictions covered 112 synthetic colours, including azo dyes. The REACH Regulation sheet 1907/2006 contains the same list of aromatic amines that are forbidden. A number of other nations, including China, South Korea, Taiwan and Egypt have also released laws pertaining to the use of azo dyes and the permissible quantities of aromatic amines. When Japan classified azo dyes as dangerous compounds in 2014, it became the first country on this list. Other countries, such as Australia, Canada, France, Turkey, Brazil, Pakistan, Malaysia and Morocco have also regulated the impacts of industrial synthetic dyes [39].

Scientific committees from all over the world have examined the toxic nature and negative consequences of synthetic azo dyes and pigments. They have come to the conclusion that these effects are caused by certain mandrats that must be employed with the dyes in addition to the dyes' inherent toxicity. In 1993, the Indian government implemented restrictions on the handling of 42 dyes based on benzidine, and in 1997, the Ministry of Environment and Forests prohibited the use of more than 70 synthetic azo dyes, under the Environment Protection Act 1986 [40].

Conclusion:
Synthetic dyes have revolutionised the colour business and are now used in many industrial sectors due to their high intensity, low cost and colour fastness. However, even at low concentrations, azo dyes have a negative impact on the environment and significantly contribute to the phenomena of climate change. It is well known that adding azo dyes to water bodies reduces sunlight penetration and raises BOD and COD, which obstruct photosynthesis and stunt plant growth. When untreated azo dyes are dumped into the environment, their core azo bonds break, releasing aromatic amines that are poisonous, mutagenic, carcinogenic, and bio accumulative. Hybrid chemical, physical and biological treatment techniques should be used to decompose azo dyes and their metabolites. The laws and guidelines published by governments and international organisations, such as the European Commission in the EU, the Food and Drug Administration in the USA, the Ministry of Health, Labour, and Welfare in Japan and the Government of Canada state that hybrid chemical, physical and biological treatment approaches should be used to degrade azo dyes and their by-products.
References:


