The Environmental, Health and Economic Impacts of Textile Azo Dyes

There is mounting pressure for companies to be environmentally responsible in the way they produce and source materials. The previously overshadowed issue of water contamination by toxic chemicals from the dyeing industry, such as Azo dyes, is becoming more visible. This POSTnote examines the hazards associated with the use of Azo dyes in the textile industry, with a particular emphasis on wastewater contamination.

Overview

■ Azo dyes, a type of textile colourant, are integral to the textile industry and make up 70% of commercial dyes.
■ Research has shown that some Azo dyes pose very serious health risks to humans if they are used in particular textiles and if they get into certain water supplies.
■ Azo dyes have been shown to damage ecosystems when discharged into water systems by dyeing factories, predominantly in developing countries.
■ In 2002, the EU responded by banning Azo dyes that could break down to one of any of 24 possible carcinogenic products. There is little equivalent regulation for potentially more serious wastewater contamination.
■ When tackling the issue or investigating harmonisation of environmental policy, care needs to be taken for the needs of developing countries with a high reliance on their dyeing industries.
■ More research into new, cheap ways of removing Azo dyes and dangerous aromatic amines from wastewater is needed.

Background

Azo Dyes

'Azo colourants' are used to colour textile fibres, leather, plastics, papers, hair, mineral oils, waxes, foodstuffs and cosmetics. 'Azo dye' is the collective term used to describe a group of synthetic that rose to prominence in the 1880s and are now comprise 70% of all organic commercial dyes[1]. The word 'Azo' signifies the presence of a chemical azo group (-N=N-) in the dye. Today, they are produced for the most part in China and India, followed by Korea, Chinese Taipei and Argentina[2]. Azo dyes are popularly used, because they dye cloth at 60°C, while Azo-free dyes require 100°C. Also, Azo dyes offer an extensive range of colours, better colour fastness and four times the intensity of the closest alternatives, making them invaluable to the textile industry.

Box 1. EU legislation concerning Azo Dyes:
The European Commission has laid out its stance on Azo dyes in Section 43 (Azo dyes and Azocolourants) of Annex XVII of REACH. Azo dyes, which, by cleavage of their azo groups, produce one or more of the known carinogenic aromatic amines, listed in Box.2, in detectable concentrations, defined as 30ppm, may not be used in the following articles[3]:
■ clothing, bedding, towels, hairpieces, wigs, hats, nappies and other sanitary items, sleeping bags.
■ footwear, gloves, wristwatch straps, handbags.
■ purses/wallets, briefcases, chair covers, purses worn round the neck.
■ textile or leather toys and toys which include textile or leather garments.
■ yarn and fabrics intended for use by the final consumer.

The EU directive does not have any restriction on Azo pigments. The solubility of pigments, used in, for example, cosmetics, is low and so they are not thought to pose a risk to human health.

However, under certain (reductive) conditions the Azo group can cleave, producing potentially dangerous substances known as aromatic amines. These conditions are met in the digestive tracts and some organs of animals, including humans[1]. 24 aromatic amines have been confirmed as, or implicated to be, carcinogens in humans, and as many as 5% of Azo dyes can cleave to form these dangerous compounds[3]. They can present in dyed product and in the environment due to incomplete synthesis or degradation of Azo dyes.

Instigated by the German Azo ban, measures were taken in 2002 by The European Commission[3] and other regulatory bodies worldwide in order to prohibit the marketing of products containing certain restricted Azo dyes in articles that may come into contact with skin for a prolonged period of time. However, little equivalent regulation oversees the expulsion of hazardous dyes, restricted or not restricted, into the environment at the initial point of use, largely as waste from dyeing factories, despite mounting evidence that this continued practice is damaging local ecosystems, with potential detriment to human health and wellbeing.

Environmental Concerns

Ecological Impact of Azo Dyes

The textile industry is a heavy polluter of waste gas, solids, water and noise. Wastewater is the most environmentally damaging, and the effluent from textile plants is classified as the most polluting of all the industrial sectors[1], considering the volume generated as well as its composition.

The dyestuff lost through the processes of the textile industry poses a major problem for wastewater management. An estimated 200,000 tons of dyestuff is expelled into the global environment every year[1]. The concentration of Azo dye in textile effluent can reach 500 parts per million (ppm).

Through the dyeing process it has been calculated that colorant loss to the environment can be as high as 50%. Colour is the first wastewater contaminant to be recognized, since a very small amount of Azo dye in water (<1ppm) are highly visible[4]. This affects aesthetic merit, transparency and water-gas solubility. Decreasing light penetration through water decreases photosynthetic activity, generating oxygen deficiency and de-regulating the biological cycles of aquatic biota[5]. Many Azo dyes are also highly toxic to the ecosystem and mutagens, meaning they can have acute to chronic effects upon organisms, depending on exposure time and Azo dye concentration. For example, dye effluent has been conntected to growth reduction, neurosensory damage, metabolic stress and death in fish, and growth and productivity in plants. Contamination therefore limits downstream human water use such as recreation, drinking, fishing and irrigation[4].

Environmental Legislation

With respect to legislation, there is as yet no international consensus concerning discharging textile effluent, including Azo dyes, and there is no official document listing the different effluent limit values applied in different countries[1]. Many developed countries, such as the United States of America, Canada, Australia and the nations of the EU enforce environmental legislation, which establishes limits. Countries, such as Thailand, have copied the US system, whereas others, such as Turkey and Morocco, have copied the EU model. In other nations, including India, Pakistan and Malaysia, the effluent contamination limits are recommended, not mandatory. In the majority of cases, Azo dye limitations are not specified as separate from that of groupings such as 'total dissolved solid' concentration[6].

In nations such as China, with environmental management enhanced, pollution has been controlled to some degree. 90% of wastewater from state-owned Chinese dyeing enterprises is treated, 70% of which reaching national discharge standards, while 50% from private enterprises is treated, only a small proportion of it reaching national discharge standards because of inadequate management[7]. Moreover, with the growth of the global textile market, the volumes of water that need management have seen dramatic increases, most significantly by 87.74% between 1985 and 1995[2], and so the release of Azo dye into the environment in real terms cannot be said to be improving.

Health Concerns

Scientific study in 1992 initially ascertained that occupational exposure to some aromatic amines, particularly benzidine, 2-naphthylamine, and 4-aminobiphenyl, dramatically elevates bladder cancer risk[9,10,11]. In one German dye plant, 100% of workers (15) involved in distilling 2-naphthylamine developed bladder cancer[2]. Aromatic amines are also present in tobacco smoke, which may explain why smoking seems to elevate the risk of bladder cancer**.** EU restricted aromatic amines have also been linked to splenic sarcomas and hepatocarcinomas[9].

Box 2. EU Restricted Aromatic Amines

Scientific confirmation on the carcinogenicity of all 24 aromatic amines is still incomplete. The literature is most compelling for the first 4 below, which are considered Category 1 carcinogens. The ban on the others are evidenced, but initially made in the name of precaution:

- 4-aminodiphenyl/xenylamine/Biphenyl-4-ylamine (CAS no. 92-67-1)
- Benzidine (CAS no. 92-87-5)
- 4-chloro-o-toluidine (CAS no. 95-69-2)
- 2-naphthylamine (CAS no. 91-59-8)
- o-aminoazotoluene/4-o-tolylazo-o-toluidine/4-amino-2',3-dimethylazobenzene (CAS no. 97-56-3)
- 2-amino-4-nitrotoluol/5-nitro-o-toluidine (CAS no. 99-55-8)
- p-chloranilin/4-chloroaniline (CAS no. 106-47-8)
- 2,4-diaminoanisole/4-methoxy-m-phenylenediamine (CAS no. 615-05-4)
- 4,4'-diaminodiphenylmethane/4,4-methylenedianiline (CAS no. 101-77-9)
- 3,3'-dichlorobenzidine/3,3'dichlorobiphenyl-4,4'-ylenediamine (CAS no. 91-94-1)
- 3,3'-dimethoxybenzidine/o-dianisidine (CAS no. 119-90-4)
- 3,3'-dimethybenzidine/4,4'-bi-o-Toluidine (CAS no. 119-93-7)
- 3,3'-dimethyl-4,4'-diaminodiphenylmethane/4,4'-methylenedi-o-toluidine (CAS no. 838-88-0)
- p-cresidin/6-methoxy-m-toluidine (CAS no. 120-71-8)
- 4,4'-methylene-bis-(2-chloro-aniline)/2,2'-dichloro-4,4'methylenedianiline (CAS no. 101-14-4)
- 2,4-Xylidine (CAS no. 95-68-1)
- 2,6-Xylidine (CAS no. 87-62-7)
- 4,4'-oxydianiline (CAS no. 101-80-4)
- 4,4'-thiodianiline (CAS no. 139-65-1)

1,4-diamino benezene is an aromatic amine whose parent azo dyes can cause skin irritation, contact dermatitis, chemosis, lacrimation, exopthamlmose, permanent blindness, rhabdomyolysis, acute tubular necrosis supervene, vomiting gastritis, hypertension, vertigo and, upon ingestion, oedema of the face, neck, pharynx, tongue and larynx along with respiratory distress[11].

Aromatic amines can be mobilised by water or sweat, which aids their absorption through the skin and other exposed areas, such as the mouth. Absorption by ingestion is faster and so potentially more dangerous, as more dye can be absorbed in a smaller time frame[9]. Water soluble Azo dyes become dangerous when metabolised by liver enzymes.

Azo dye release in industrial effluent can also have an impact on human health in certain countries. In 2007, a study linked an Azo dyeing plant as one of the sources of mutagenic activity detected in the Cristais River in Brazil, a source of drinking water for 60,000 locals[12]. Though the drinking water was treated in a plant 6km downstream of the discharge site, testing confirmed the presence of carcinogenic aromatic amines. When laboratory rodents consumed industrial effluent at 1-10% concentration, an increase in pre-tumour lesions of the colon was observed[12].

Although Azo dye extractability from fabrics is generally low, as is the probability of health detriment from Azo dye poisoning, the severity of cancer has demanded the dramatic response of ETAD, the EU and other organizations. Taking poisoning in its worst case scenario, the total exposure of an adult over a lifetime use of a garment covering the whole body is calculated as 723 µg/kg, posing a very low cancer risk, though this risk has not been satisfactorily quantified[9]. Consumption through water can reach much higher levels of exposure with higher absorption rates, and is theoretically more dangerous. No epidemiological studies regarding possible carcinogenic effects of Azo dyes in humans are available[9].

Trade Issues and the Developing World

In 1992, in light of the occupational hazards that had come to be connected with certain Azo dyes, the Board of the Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) requested that all member companies cease manufacturing problematic benzedine dyes and salts. In anticipation, many EU and North American companies has ceased such production, but of those that continued, when faced with leaving ETAD or continuing their practice, chose to leave ETAD, demonstrating the significance of Azo dye to the industry[2].

The EU sanctions on certain Azo dyes were felt most severely in India, whose dye making capacity had grown to be integral to many of its regional economies. 25% of Indian export in 2000-2001 consisted of textiles and clothing of which the share attributed to the EU ranges from 25-70% depending on the article[2].

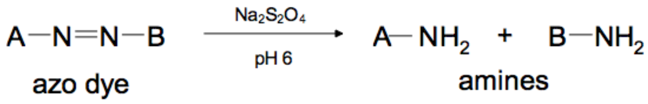
The EU ban on certain Azo dyes led to an unintended surge of second-hand clothing export, often being handed out free of charge, to African nations and other developing countries over concerns that they were no longer marketable in the EU.

Facing loosing a large chunk of their textile export market, India reacted by developing an eco-label to guarantee that its manufactured textiles contained less than 50ppm of any Azo dye, not just those known to decompose into carcinogenic aromatic amines, over fears that the list of banned substances may expand and due to limited testing capability in the country, ironically making India a more restricted dyeing market than the EU. Though these dyes are still used off-label, the ban will have seen a reduction in Azo dye wastewater content, though the benefit this may or may not have brought is difficult to estimate given a lack of focused pre-ban ecological data.

Despite compliance, the local economic fallout was significant for small dyeing businesses, given than 20% of India's dyeing industry comprised Azo dyes[8]. Indian manufacturers accused the EU of effecting hidden protectionism, since more expensive, patented, replacement dyes had been developed in its member states. Since small businesses do not have the facilities to qualify for the eco-label, many continue to use Azo dyes liberally, and since these businesses also lack effective water remediation methods, environmental problems continue.

Overall, in India's case, health conscientious policy making has lead to potential environmentally positive results, but

Box.3 Chemical Nature of Azo Dyes and Aromatic Amines
Azo dyes contain one or more nitrogen-nitrogen double bonds called azo groups in their chemical structure. Under reductive conditions, for example the presence sodium dithionite ($Na_2S_2O_4$) in diagnostic tests, these azo groups can be cleaved to form two amines, which has been schematically shown below:



as this process was economically motivated the environmental benefits have had to be weighed against damage to local Indian businesses and livelihoods, a problem often seen with broad bans as opposed to, in this case, innovation towards dye replacement and remediation. Insisting that countries employ effluent contamination limits as law may have a similar effect as the German Azo dye ban had in India, unless cheap, efficient remediation technology is made available.

The Ahmedabad Textile Industry Research Association (ATIRA) has estimated that the cost of azo-free substitutes is 2.5 times that of Azo dyes, making it preferable, especially for developing countries, to retain the ability to use Azo dyes that do not break down to banned aromatic amines, by effecting a system that manages the environmental damage most Azo dyes can cause. The direct health threat as regards hazardous Azo dyes in clothing appears mitigated, with tests at the eco-laboratories of the Textile Committee demonstrating compliance rate of over 96% for textiles produced for export to the EU[2].

Finding Solutions

Harmonisation of Environmental Standards

Harmonisation of environmental standards appeals as a way to help solve valid environmental objectives worldwide, because:

- Environmental issues often transgress national borders and are of concern to the people of even disparate and distant nations.
- Different importers' standards can elevate exporters' manufacturing expenses, as different methods are required of different standards.
- Prevents the use of environmental standards as a form of protectionism.

Harmonising effluent contamination limitations from dyeing factories could help mitigate the environmental issues associated with Azo dyes and other dyes. However, since the environments in each country is not standardised, harmonization can lead to inefficiency. As concerns dye discharge from dyeing factories:

- Every environment has a different absorptive capacity for water pollutants.
- The cost required to remove dye pollution differs between countries.
- Willingness to invest in a healthier environment at personal expense differs from country to country, for example, in relation to the degree of local poverty.

Hopefully scientific investigation and control will standardise and regulate this colourant matter on a worldwide level, but the application of innovative, cheap technologies to counter the problem may be the most viable solution.

Water Remediation

In many countries it is mandatory for textile dyeing factories to install effluent treatment plants (ETPs) to treat wastewater before it leaves the factory premises. Pressure for effective effluent treatment is also mounting and many international buyers are now showing more concern over whether or not textiles are produced with due ecological consideration. This shift in the textile trade's paradigm means that in the future it is likely that the operation of an ETP will be integral to sustain business in the competitive world market.

Because of their chemical stability and synthetic nature, reactive Azo dyes are not totally degraded and exhibit slow degradation by conventional wastewater treatment methods[11]. They are additionally difficult to remove, because they are designed to be stable in aerobic conditions but biotreatment in anaerobic conditions can result in the generation of dangerous aromatic amines[11]. Remediation does not currently capitalise on this fact.

Wastewater is usually treated with activated sludge, and the liquid effluent is released to nearby surface waters. Ekici et al. (2001) tested Azo dye stability in both activated sludge and water, concluding that they were relatively stable in the aquatic environs and cannot be effectively degraded in standard wastewater plants. Physico-chemical methods can be used to minimize toxicity levels, but neutralisation is not complete and a more concentrated sludge is created, effectively transferring the pollution problem between phases. The cost and processing time are also unsatisfactory.

New, cheap and efficient methods of remediation need to be sought. Examples of emerging technologies include, but are not restricted to:

- ■ Advanced oxidation processes (AOPs). (Legrini 1993)
- ■ Zero-valent iron degradation processes. (Braz 2006)
- ■ Better physico-chemical treatment methods (precipitation, coagulation, adsorption, flocculation, flotation, electrochemical destruction, mineralisation and decolorisation process). (Gogate and Pandit, 2004)
- ■ Fungal Degradation. (Bumpus, 2004)
- ■ Bacterial remediation. (Sudha 2014)
- ■ Waterless dyeing technology.
- ■ Synthetic biology. (UCL iGEM 2014)

UK Action and Concerns

The dye and pigment manufacturing and the dyeing industries are a very small component of the UK chemical sector, and so while any Azo dye contamination into UK water systems is not ideal, it does not pose a relatively large problem in regard to environmental and public health.

And yet, the UK has a responsibility on the global stage to ensure that its business partners and foreign associates uphold good environmental practice, such as attempting to mitigate the Azo dye wastewater concern. However, environmental and health focused legislation to prevent environmental contamination by Azo dyes may not be possible in the same way as the EU Directive led to India's Azo dye ban. The World Trade Organisation's (WTO's) legal framework comprises enduring General Agreements on Tariffs and Trade (GATT) statutes, including Article XX, allow countries to impose trade restrictions if their goals are considered more important that liberalised trade. Article XX implies that this includes the environmental, health and security interests of the importing country, but is not clear on whether the importer may exercise restrictions based on the same issues in the exporting country. This is best highlighted by the tuna-dilphin dispute between the USA and Mexico, who objected to Mexican fishing methods that harmed dolphins, but GATT dismissed the case since the dolphins were not killed in an area of responsibility for the USA. Further clarification by WTO on the application of Article XX is required.

It is also difficult to set restrictions and standards that apply to production methods, such has the dyeing process and location in relation to waterways, as such may be misconstrued as protectionism.

Therefore, it may be possible for the UK government to advise and incentivise importing companies to only trade with exporters that employ suitable ETPs and meet local effluent limitations. Development of and trading technologies to achieve this cheaply and efficiently in the UK could better the environments of the UK's trade partners.

Currently the UK imposes a £5,000 fine a six months sentence for breaking the EU directive on Azo dyes, which is considered a safety regulation under the 1987 Act.

Issues for consideration

Research has indicated gaps in our response and knowledge about the environmental impacts of Azo dyes. Issues to consider are:

- ■ UK companies and the general public should be made aware of how their textile imports affect the integrity of foreign environments.
- ■ The UK government could advise and incentivise UK companies to foster trade with bodies that do not use Azo dyes, or use them in an environmentally conscientious manner.
- ■ Research needs to be carried out into improving bioremediation processes to remove Azo dyes from wastewater, focusing on promising areas such as AOPs and biological processes, such as synthetic biology.
- ■ Epidemiological studies into the environmental and health effects of Azo dyes are required for further insight.

Endnotes

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