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Synthetic Dye Application in Textiles: A Review on the Efficacies and Toxicities Involved

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Review

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ABSTRACT

The application of dyes in textile colouration has existed for centuries. Dyes are obtained from both natural and synthetic sources. Synthetic dyes are manufactured from chemical compounds and have been placed on a high pedestal in the textile industry due to their improved colour fastness, varied range of pigments and easy application as compared to natural dyes. However, they have been identified to be harmful to the environment and human health by researchers. When effluent containing harmful chemicals like sodium sulphide is discharged into the environment improperly, they cause a lot of diseases and hinder smooth air flow. With current submissions made by researchers on synthetic dyes application as a backbone, this review throws more light on the dangers and benefits involved in the use of synthetic dyes in the textile industry. It also touches on waste management as far as textile dyes are concerned. The application of synthetic dyes, precisely vat, reactive and sulphur dyes are highlighted in the study. With the purpose of addressing appropriate means of curbing undesired hazards caused by textile wastes water, several technological approaches to effluent treatment such as Physical, Chemical and Biological are brought to light in the study. The study recommends the adaptation of waste management principles such as the 5R hierarchy to curb environmental harm caused by synthetic dye effluents.

KEYWORDS

textile dyeing, synthetic dyes, hazards, efficacies, effluent management

INTRODUCTION

Textile dyeing has existed since civilization. The various pieces of dyed textiles found around the globe during archaeological excavation serve as evidence to the long existence of textile dyeing [1,2]. Textile dyeing is a wet process which involves the fusion of dye molecules into textiles materials in the form of fibre, yarn and fabric either manually or the use of appropriate dyeing machines [3]. Dyes could be categorized broadly into natural and synthetic. Natural dyes are extracted from natural matters such as plants, animals and mineral resources. These dyes lacked colour and light fastness property with limited and dull range of colours until the introduction of additives (mordants) which raised their application to a certain degree. Synthetic dyes, as opposed to their counterpart natural dyes are obtained from organic and inorganic molecules and are

manufactured in the laboratory with chemicals [4]. They have been used extensively by textile practitioners in their profession to achieve significant results. However, with respect to production and application, natural dyes are preferred over synthetic dyes due to the harmful nature of the latter [5]. The first synthetic dye was accidentally discovered in 1856 by a chemist called William Henry Perkin in an attempt to obtain a cure for malaria in a scientific research. Several synthetic dyes with varied chemical classes have been developed after Perkin's invention. A statistical research on synthetic dye manufacturing shows that, about 1,200 synthetic dyes succeeded Perkin's mauveine [6]. The various dye classes and the years they were invented are presented in figure 1. From the figure, it could be observed that the azo class of dyes gained a great attention and rose to the top around 1895. Anthraquinone and sulphur dyes became popular between the years 1905-1915. Indigoids came to light around 1915 while triphenylmethane and xanthene is observed to have been generated in almost every year across the periods. The classes of dyes which don't fall under the aforementioned are tagged 'Other'.

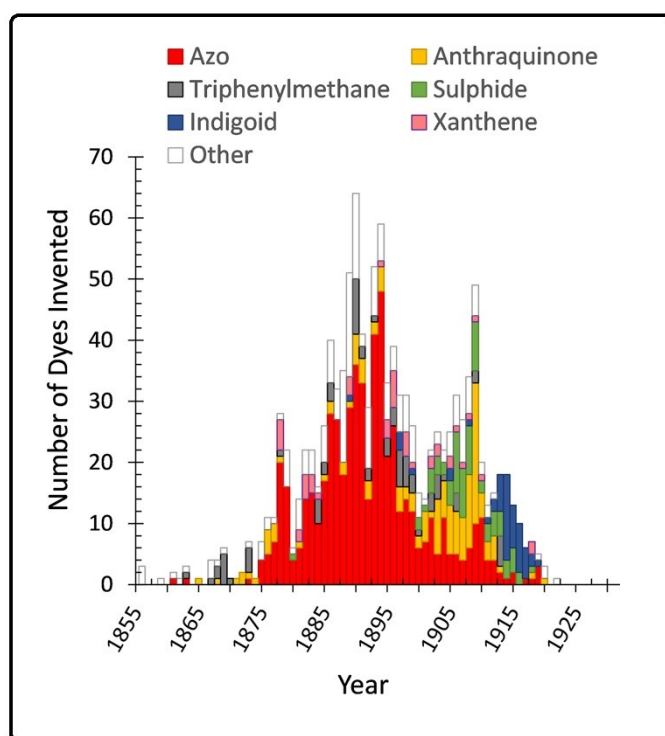


Figure 1. Synthetic dye classes and their years of invention [6]

Synthetic dyes are of significant use in numerous industries such as textiles, pharmaceutical, food, printing, leather etc. [7,8]. This is because they have a laudable colour fastness property and higher intensity than the natural fellow [9]. Due to their large spectrum of colour pigments and uniform colouring, they are currently dominating the textile market, producing approximately

8 × 10⁵ tons every year [10-12]. Buttrressing this, Rosu et al. [13] established that, 10,000 synthetic dyes are made commercially available annually for the textile colouration industries at different stages. Although, other chemical classes of synthetic dyes including oxazine, azine, triphenylmethane, nitro, xanthene, anthraquinone and indigoid have had a significant impact on the industry, the most abundant class of synthetic dyes is the azo [6]. They contain about 66% of all colorants which increases their versatility and preference over other classes [14]. Synthetic dyes do not require mordants as most natural dyes do. A mordant is a metallic compound which helps dye molecules to be fixed well into the pores of fibres during textile dyeing. Dyes classification is fibre-specific with a simple reason being that not all fibres could be died with all dyes. Technically, the degree of molecular structure compatibility among fibres and dyes in textile dyeing greatly influences the colour fastness property and vibrancy of the dyed article. Table 1 shows the classes of synthetic dyes based on the fibres they are capable of dyeing.

Table 1. Classification of synthetic dyes (fibre-specific) [15,16]

Dyestuff	Fibre
Acid	Modified acrylics, Nylon, Wool and silk
Azo	Silk, cotton, nylon
Basic	Polyester, wool, silk, mod-acrylic nylon
Disperse	Polyester, nylon, cellulose acetate and acrylic fibres
Direct	Cotton, nylon, rayon, linen,
Reactive	Cotton, linen, wool, nylon, rayon, silk.
Sulphur	Cotton, rayon, silk
Vat	Cotton, linen, rayon, wool.

In textile dyeing, several synthetic additives are employed in the process causing harm and biodegradable difficulties [17]. The processing and use of synthetic dyes, however, have been identified by researchers to be harmful to the health and causes several discomforts in the environment [7,17,18]. A study conducted by Salauddin et al. [19] shows that, after dyeing with synthetic dyes, the wastewater is carelessly dispensed into rivers and fields which eventually leads to skin diseases when such water is used, especially for bathing. The textile industry is among the largest industrial users of water, especially the dyeing section where synthetic dyes are used massively [5,12,20]. It employs up to 8000 chemicals which greatly cause pollution to both ground and surface water resources [10]. It is estimated that about 70% of dyestuffs are consumed by the textile industry. The textile industry has been ranked the most water polluting industry in Bangladesh partly because of synthetic dyes [21]. The need to address the harm caused by synthetic dyes to lives therefore arises as water plays a major role in the sustenance of living things.

Although several drawbacks of synthetic dyes have been identified, they have been placed on a recognized pedestal in the textile industry due to their unique qualities observed in textile colouration. Their efficacious property therefore makes them indispensable in the textiles industry irrespective of their environmental impacts. This review highlights the pros and cons involved in the use of synthetic dyes by textile practitioners. It is revealed in the study that improper discharge of effluent which is practiced by most textile industries is a great threat to the environment [19,21-23]. The study discovers appropriate means of discharging effluents into the environment and conventional methods of treating wastes to reduce toxicities and improve dyeing efficiency. It seeks to manufacture environmentally friendly and efficacious dyes through green technologies in future studies.

DYEING WITH SYNTHETIC DYES

Generally, three stages are involved in the transfer of dye molecules from the dye liquor into the innermost part of textile fibres [3,24]. Firstly, adsorption which involves the deposition of the dye molecules onto the surface of the fibres occurs. Secondly, diffusion of the dye molecules into the innermost part of the textile fibres. Lastly, fixation which involves a physical or chemical bond formation between the dye molecules and the fibre. The efficacy of the second stage is dependent upon the molecular size of the dye, the morphology of the fibre and temperature. Several synthetic dyes are available at the practitioners' disposal for exploration in textile dyeing. Among these dyes are sulphur, acid, direct, disperse, basic, reactive, vat etc. The choice of dyes determine the procedure to follow in achieving the desired colour of the textile material.

Vat dyes

Vat dyes together with reactive and direct dyes are requisite dyes for cellulosic dyeing [25]. The process of dyeing with vat dyes involves four stages according to Mahapatra [14]. They include; Reduction of dyes, Dye-uptake of leuco, Leuco oxidizing and Soaping treatment.

Reduction of dyes

Reducing agents are compounds which change the state of chemicals with hydrogen, oxygen or electrons. They either give out hydrogen, reduce oxygen or increase electrons of chemicals [26]. Vat dyes need reducing agents in order to change them from insoluble to soluble leuco. Strong reducing/solubilizing agents such as sodium hydroxide and sodium hydrosulphite are used for this purpose [27]. In this state, the dyes become soluble and could be dissolved in water.

Dye-uptake of leuco

The leuco is taken up by the fibre at this stage of the dyeing process. Diffusion of the dye molecules into the fibre is quickened by the use of soft water. This allows a smooth migration of the leuco into the innermost regions of the fibre. It therefore calls for the addition of water softener when hard water is used.

Leuco oxidizing

The leuco is transformed back to the original insoluble state and colour after being oxygenated at this stage [26]. The process of oxidation is practically the reverse of Reduction in vat dye application in textiles dyeing.

Soaping treatment

The final stage of vat dyeing process involves a careful treatment of the dyed textiles with boiling soap under a high temperature. Subjecting the dyed textiles to this activity allows its fastness to be improved. Figure 2 shows the reduction and oxidation reactions in vat dyeing process with C.I. Vat Red 23

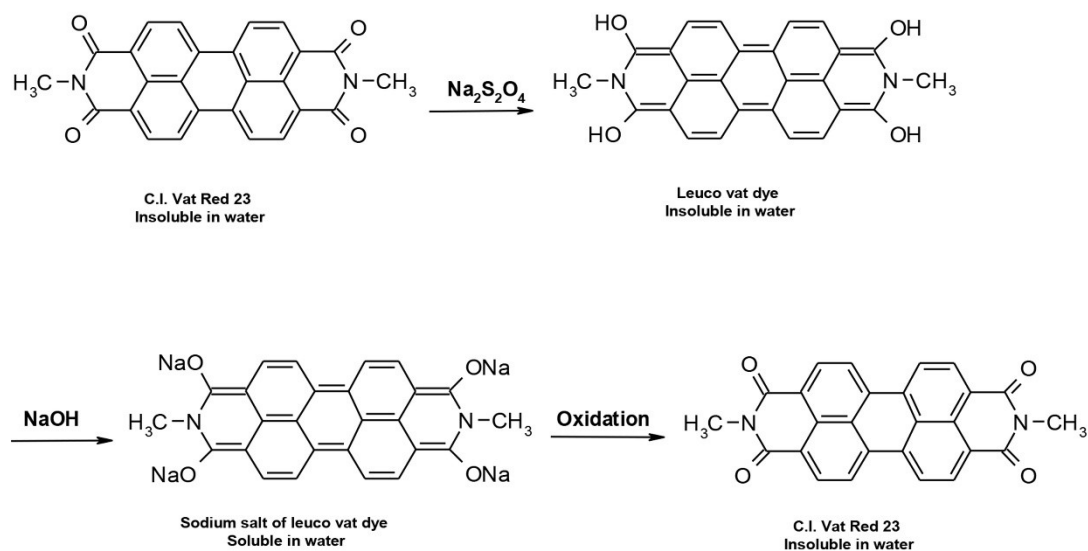


Figure 2. Reduction and oxidation reactions of vat dye [25]

Sulphur dyes

Sulphur dyes are water insoluble compounds and therefore required to be converted into water soluble or leuco form with reducing agents as happens in vat dyeing. Sulphur dyes contain 'S' and 'SH' groups. In the reduction process, the 'S' groups are metamorphosed into 'SH' groups with reducing agents such as Sodium sulphide (Na₂S) [28]. The dye molecules are converted back into the insoluble state after dyeing through oxidation. Oxidation could be done with atmospheric oxygen (air) or agents like Sodium dichromate (Na₂Cr₂O₇). Oxidation could also be done with acidic potassium dichromate at a temperature of 50-60°C with a varied duration of 15-20 minutes [29]. Figure 3 shows the reaction which takes place in Sulphur dye application.

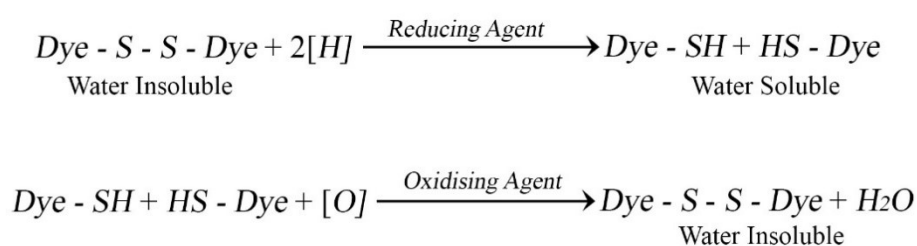


Figure 3. Sulphur dye reaction [29-31]

After oxidation has taken place, 'Aftertreatment' is given to the dyed textiles to improve upon some desirable properties such as wash and light fastness. A Recent study by Mohtashim, Asim & Farooq [32] focuses on the improvement of colour retention property of Sulphur black 1 dyed cotton fabric with a cationic fixative and synthetic tanning agent (syntan). The study made use of Tinofix ECO, Solophenyl & CIBA Geigy as fixatives and Nylofixan PSA, Clariant as synthetic tanning agents. Sulphur dyes have good affinity for cellulosic fibres and their blends. Their alkaline traits make them non-recommended for wool fibre/fabric.

Reactive dyes

Out of 10, 000 synthetic dyes used for textile colouration annually by the textile industries, 50% are reactive dyes [13]. This presupposes that, most textiles released into the textile market one way or the other have some traces of reactive dyes in the colour they exhibit. Reactive dyes offer diverse range of shades and are easy to be applied. They exhibit excellent fastness property on fibres such as silk, cotton, wool and regenerated cellulosic derivatives [33]. Siddiqua et al. [34] confirm that among all the classes of synthetic dyes available, reactive dye is singled out to be the only class that makes covalent bond and fuses with the fibre. This however, lends credence to its good response to wash and light fastness, making it a more desired class of dye in the textile industry.

The application of reactive dyes, especially on cotton require the addition of inorganic salts like sodium sulfate (Na_2SO_4) and Sodium chloride (NaCl) to speed up the rate of dye exhaustion [35]. For shades to build up perfectly in reactive dye application, the dye molecules in a solution must all exhaust at the same rate and react with the fibre [36]. Figures 4a and 4b show the chemical structure of reactive dyes Blue 204 and Red 195 respectively.

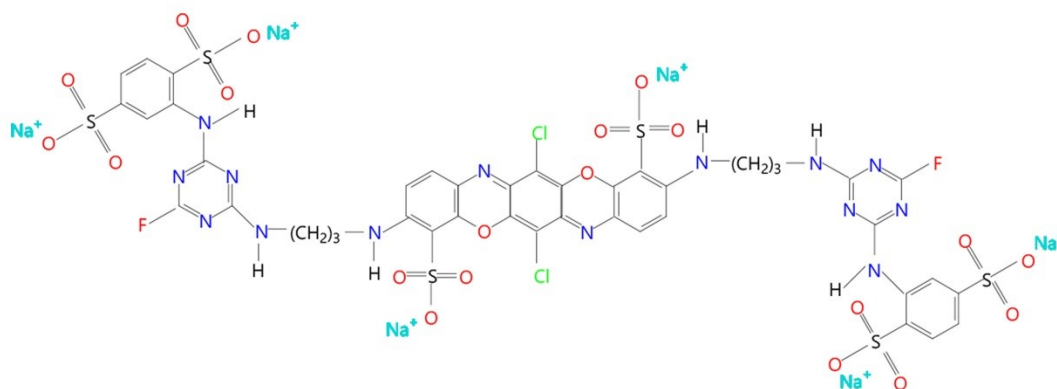


Fig. 4a

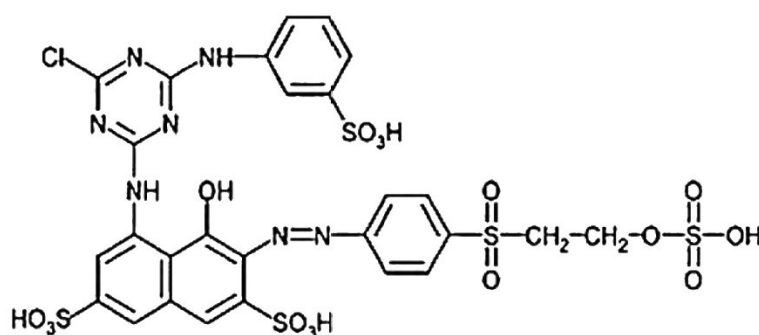


Fig. 4b

Figure 4. (a) Reactive Blue 204 [13]. (b) Reactive Red 195 [37].

Merits of Synthetic Dyes

The increasing demand for synthetic dyes despite its setbacks is centred on its fastness qualities and easy execution in textiles dyeing. It also exhibits varied colour shades. Natural dyes, unlike synthetic dyes, are obtained from natural matters. This has resulted in the overexploitation of natural resources which leads to deforestation and undue harm to several species. Industries would rather go for synthetic dyes which are manufactured with chemical compounds in order to conserve the forest as well as protect dye-producing species. It is less costly to manufacture synthetic dyes than natural dyes. Although almost all vegetables contain colouring matter, only a few of these are significant in natural

dye extraction for commercial purposes [38]. This makes natural dyeing extraction more tedious than synthetic dye manufacturing.

Drawbacks of Synthetic Dyes

Dyes have a significant impact on the photosynthetic activity of the aquatic environment because they block light from penetrating the water, reducing the growth of algae, which are not only necessary for oxygen production but also a key component of the food chain [39]. Again, they can induce allergic reactions such as irritation of the skin, eyes, and mucous membranes, dermatitis, and respiratory difficulties [39]. Synthetic dyes cause a lot of harm to the environment irrespective of their concentration level, either high or low [40]. They are uncooperative, bioaccumulative, poisonous, mutagenic, and carcinogenic substances [17,40]. Sulphur dyes for instance need Sodium sulphide (Na_2S) as a reducing agent in its application process. Apparently this effective agent has been identified by Chakraborty and Madhu et al. [28,41] as a very harmful chemical which greatly pollutes waste water. Also, the usage of electrolyte and alkaline in reactive dye application on cellulosic fibres makes the process a more costly one, and a major cause of waste generation in the textile industry [42]. This is however, a major initiator of environmental pollution.

The toxicity of synthetic dyes are based on the molecular structure of the dyes rather than the dyeing procedure. The harmful nature of synthetic dyes are therefore inherent and could be controlled during its production, although reduced traces of harmful molecules could be identified. Table 2 shows some conclusions drawn from researchers' submissions on the toxicities and efficacies in textile dyeing with synthetic dyes.

Table 2. Pros and cons of synthetic dyes

Author(s)	Efficacies of synthetic dyes (Pros)	Toxicities involved (Cons)
[12]	Synthetic dyes are generated from petrochemical compounds which are more cost effective than natural dye extraction. They display diverse colour pigments and consistent coloration in textile dyeing	Synthetic dyes have harmful effects on air, water, soil and plants when they are not properly discharged after their usage in the textile industry. This causes several dangerous diseases to humans.
[40]	The invention of synthetic dyes gave a new phase to the production and usage of dyes in the textiles industry. It resulted in industrial development, especially the textile sector.	Synthetic dyes cause a lot of changes to the environment due to their poor biodegradable property. They affect water bodies and cause harm to living organisms.
[43]	The economic viability of synthetic-dyed textiles is increased. This submission to the	The content of synthetic dyes include toxic chemicals such as naphthol, nitrates, acetic acid,

	fact that synthetic dyes provide effective colourfast and varied bright hues which is the major attraction of fabrics on the market.	sulphur etc. These chemicals, when released into the environment, have the ability to interfere with the smooth flow of oxygen.
[44]	Synthetic dyes invention solved the problem of limited dye availability for textile dyeing due to the scarcity of raw materials used in the production of natural dyes. Synthetic dyes also ensured easy replication of techniques in textile dyeing. Natural dye application sometimes could be controversial.	Synthetic dyes cause ecological issues due to their non-biodegradable nature. They are difficult to extract from wastewater produced by the textiles industry. They have also been approved of many health hazards.
[45]	Due to the high consumption of synthetic dyes globally, its production and export generates a lot of income to producing countries such as China and India	Environmental pollution is a major global challenge. Although most industries cause pollution with the chemicals used, the textile industry is the highest polluter of the environment as it releases more wastewater which contains highly toxic chemicals into the environment.

HANDLING OF DYE EFFLUENT IN THE TEXTILES INDUSTRY

Waste from the textiles industry undoubtedly contain unfriendly chemicals as far as dyeing is concerned; especially where synthetic dyes become the chief agent for textile colouration. The method adopted in waste discharge by the industry determines the degree of harm caused by the effluent. In a research on waste management, Leblanc [46] outlines six components of waste management system which could be explored by industries to reduce environmental pollution. These include '*Waste generation*' where unusable materials are identified to be discarded; '*onsite handling*' which makes waste collection easier by providing the necessary resources like bins at centres where wastes are generated; '*Waste collection*' where wastes are collected into transportable resources; '*Waste transport*' which involves the transfer of waste from local areas of waste generation to regional waste dumping spots; '*Waste processing and recovery*' which refers to the use of techniques and equipment to convert the waste back to reusable; and finally '*Disposal*' which involves discarding of waste in sites such as landfills.

Due to the dangers involved in improper discharge of waste, especially from the textile industry, several studies have been conducted to device proper ways of handling these effluent to curb the undesired pollution caused. Chemingui et al. [47] reports on the use of er-doped zinc oxide in the removal of colour from synthetic dye solution. The results confirm the requisite concentration of er-doped ZnO in colour removal to be 3 wt. %.A study conducted by Hoveidi et al. [48] using Rapid Impact

Assessment Matrix (RIAM) shows that, landfilling is the appropriate waste disposal method, and therefore highly recommended over Open damping, Gasification and Incineration.

Howard, Frimpong & Seidu [49] establish that most textile industries, especially the small-scale ones adopt the open damping/discharge of effluent. This unfortunately is frowned upon by Hoveidi et al. [48]. Although, Hoveidi et al. [48] places Landfilling over incineration, the latter and Liquid Segmentation are reported to be a more fitting liquid waste management method for small scale industries. Effective principles are therefore required in the handling of effluents from the textiles industries.

Adopted Technologies in Textile Effluent Treatment

Varied technologies have been mentioned by researchers as appropriate means of eliminating toxic pollutants from waste water. Adane et al., Al-Tohamy et al., Rápó & Tonk and Yaseen & Scholz [15,16,39,50] mention significant technological approaches to waste water treatment in the textile industry such as Physical (Adsorption, Ion exchange and membrane filtration), Chemical (Coagulation-flocculation, Oxidation and electrochemical) and Biological (Enzyme, bacteria, fungal, yeast and algae). Physical technology in waste water treatment removes impurities through air flotation or gravity settling. It makes use of a surface-based process called 'Adsorption' in which particles are deposited onto a solid surface through floatation. Physical technology again uses ion exchange and membrane filtration technologies in which a bond is created between a resin and the solution in the former technique whereas membranes with diverse pore sizes are used in the latter technique to decontaminate waste water through a sieving mechanism [51,52]. Chemical and biological waste water treatments are centred on aerobic and anaerobic process [53]. In biological technology, impurities are consumed as food by the active microbial growth when they are exposed to waste water. Chemical technology utilises chemical reagents to decontaminate water. In advanced oxidation process for instance, effluents are removed from waste water by reacting with hydroxyl radical (OH). A combination of the physical, chemical or biological technologies in the removal of effluents from water are referred to as a conventional waste water treatment method [54].

Institute for Sustainable Process Technology- (ISPT) [55] presents the EcoloRo technology which is an amalgamation of electrocoagulation, membrane filtration and reverse osmosis. The Technology is reported to be appropriate for the reduction of waste in the textiles industry and it's a more cost effective one. Figure 5 shows a flow diagram of the EcoloRo Technology.

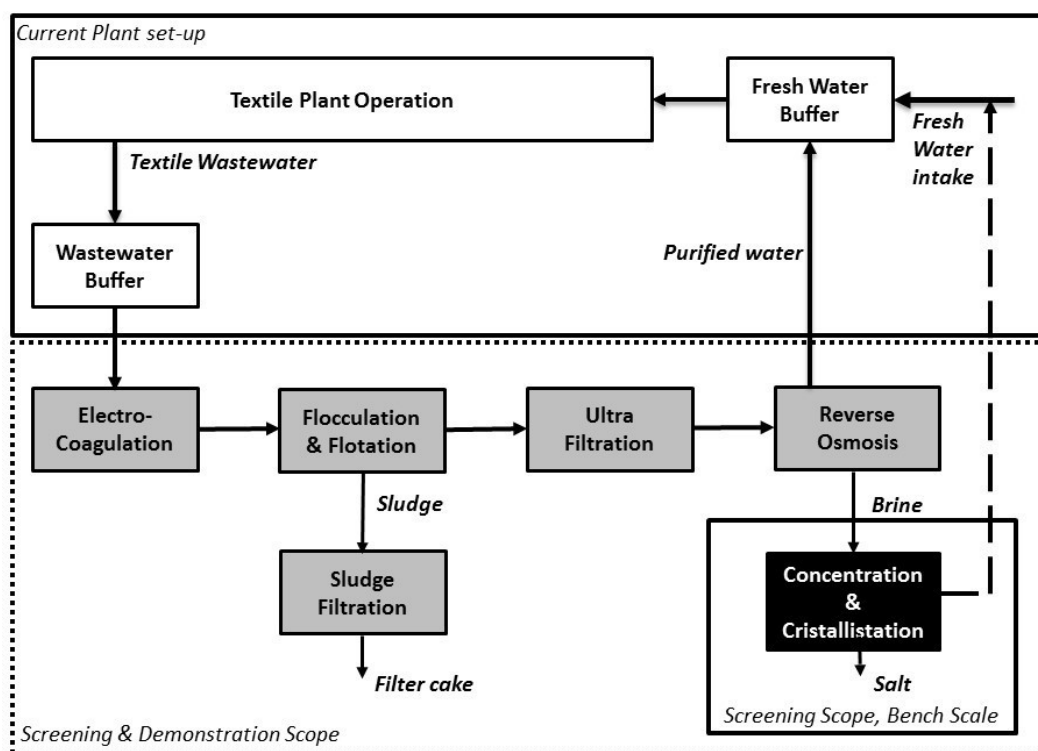


Figure 5. Flow diagram of the EcoloRo Technology [55]

Waste Management Principles

Due to the toxicity of synthetic dyes, strategies could be adopted to control effluents from the textiles industries. Strategic application of chemicals and dyeing agents which would remain efficacious when used in reduced quantities are highly desired. For instance, dye bath which could be used several times before being discharged from the industry. Again, colouring substances which has the ability to vanish from the dye liquor after several application to allow toxic-free waste water whose treatment would be less costly and easier. This would help reduce pollution and the toxicities thereof.

On the other hand, Fehr et al. [56] in a study recommend waste management principles in quest to save the environment from harm through the 'Zero waste' concept. A typical example of this principle is presented in figure 6. This theory is summarized in a hierarchical order of five stages and is popularly known as the 5Rs. The 5Rs allow waste to be Refused, Reduced, Reused, Repurposed and Recycled.

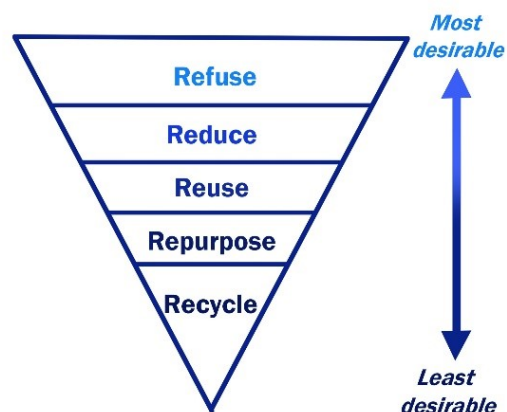


Figure 6. The 5R principle of waste management

The first level of the hierarchy which is regarded as the most desired, urges the refusal of materials which may not be more useful in the industry. These materials could be replaced with a more beneficial ones as far as waste management is concerned. In Sulphur dye application for instance, this stage of the theory could be explored significantly by replacing more harmful chemicals with environmental friendly chemicals. Sodium sulphide which is more harmful and a great water pollutant could be refused as reducing agents; thus, Glucose and hydroxyacetone which are more eco-friendly could be accepted as alternative reducing agents [28]. This assertion to the fact that, glucose is confirmed to be an effective reducing agent as it offers a similar result as sodium sulphide, although high temperatures are required [41]. The second level of the hierarchy admonishes industries to minimize harmful chemicals application in their operations. Again, Jaruhar & Chakraborty [29] recommends the use of alkaline protease as a substitute to sodium sulphide in sulphur dye application on cellulosic fibres due to the harmful nature of the latter.

By reuse, industries are encouraged to use a given material severally in their operations. In resist dyeing for instance, wax could be used as a resist agent on several occasions due to its reusable property. Such materials need not to be discarded after their first use in order to save money and reduce waste. Although recycling is an appropriate waste management method, reuse is more preferred [57]. In an experimental study, Buscio et al. [58] explored Hydracore10 and Hydracore50 as Nanofiltration membranes with electrochemical processes for the treatment of waste water containing reactive dyes. The 5R principle encourages the adaptation of such methods in the industries to make effluents reusable.

Repurposing, also known as upcycling means finding another use for items rather than discarding them into the environment to cause pollution. These items may seem irrelevant for their intended purpose, however they could be explored in other areas significantly. The final and the least desired

level of the principle is 'Recycle'. It is expected of individuals/industries to recycle items which are no longer needed. This level of the hierarchy becomes necessary when all the other levels are said to have been explored. Recent studies [57,59-61] encourage the recycling principle in the textile industry. Composting, regeneration, non-woven technology, technical textiles and paper making are suggested as appropriate textiles waste management options. Composting option campaigns for natural products which have the tendency to undergo self-degradation when discarded into the environment. In regeneration, decontaminated water could be obtained from effluents through effective treatment process such as the biological process which adapts microorganism to degrade or purify waste water [12,15]. Non-woven technology calls for the use of environmental friendly textiles products which features minimal or no synthetics, whereas technical textiles mostly emerge out of a waste management process (recycling). Paper making as an alternative to waste management encourages the exploration of textiles waste into paper making to reduce textiles waste generation. The aforementioned principles could be implemented in all spheres of the textile industry operations in order to combat against the harm caused to the environment by effluents from the industry.

CONCLUSIONS

Textile dyeing efficiency is improved with synthetic dyes, although natural dyes are preferred because of their eco-friendly nature. This review has spelt out the benefits of working with synthetic dyes, their side effects, technologies in decontaminating waste water from the textile industry and the various principles of handling waste. It has also dealt with the classification of synthetic dyes based on the fibre type and the procedures involved in synthetic dye application; thus vat, sulphur and reactive dyes.

Although synthetic dyes have been identified to be harmful, this review has disclosed several benefits of synthetic dyes which have contributed immensely to the nourishment of the textile industry since the 19th century. It could be said that, the side effects of synthetic dyes are largely manifested when effluents from the textile industry are not properly discharged. The study however, suggests the adaptation of waste management theories such as the 5R principle in the textile industries to help reduce the volume of harmful waste generated. This principle creates opportunity for industries to 'Reuse' textile effluents with several means including the use of nanofiltration membranes and electrochemical processes as confirmed by research to be an effective approach to waste water treatment.

Small scale textile dyeing industries whose effluents are mainly liquid can adopt the segmentation method which is a more environmentally friendly means of discharging effluents. This method could be adopted as an option when the 5R principle has practically been exhausted. Synthetic dyes are toxic-inherent. Care is therefore needed to handle them and the waste products generated by textile industries where synthetic dyes are unavoidable in order to minimize the harm caused by such dyes.

Conflicts of Interest

The author declare no conflict of interest.

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