Diversity and Classification of Textile Dye

Sakshi Yadav[1], Dr. Nandlal Vyas[2]
[1] Research Scholar in Jodhpur National University, Jodhpur, Rajasthan
[2]Dean, Professor, Department of Microbiology, Jodhpur National, University, Jodhpur, Rajasthan

Abstract

Natural dyes have been utilized for a variety of applications since antiquity, most notably in the field of textile dying. The invention of synthetic dyes from petrochemical compounds was prompted by rising demand and high prices of natural dye extraction. Due to their large spectrum of colour pigments and uniform colouring, they now dominate the textile business, producing approximately 8× 105 tonnes every year. Textile businesses use a lot of water in their dyeing processes, making it difficult to clean the massive amounts of harmful effluent. Using silica-supported boron tri-fluoride (BF3.SiO_2) as a catalyst to promote diazotization and combination of heterocyclic amines with various heterocyclic couplers at room temperature, a simple one-step synthesis has been developed to generate heterocyclic azo colours. Different approaches were used to prove the structure of the produced substances. Utilizing these synthetic dyes and ultrasonication for 10 minutes, nano inks were created using the microencapsulation approach.

Keywords: *Synthesis, Chemistry, Dyes, Classification, Textile Industries.*

1. INTRODUCTION

Dyes are coloured organic compounds that are used to colour a variety of substrates such as paper, leather, fur, and hair, as well as pharmaceuticals, cosmetics, waxes, greases, plastics, and textile materials. A Dye is a coloured substance that may be fixed to a fabric and is generally employed in solution. Textile finishing dyes and pigments used in the dyeing and printing of natural, synthetic, man-made, and mixed textile materials such as wool, silk, nylon, polyester, acrylic, polyacetate, and polyurethane are numerous, with around 700,000 tonnes of global yearly output.

Due to the inefficiency of the dyeing process, up to 200,000 tonnes of these colours are lost to effluents every year in the textile sector during dyeing and finishing activities. Unfortunately, because of their high resilience to light, temperature, water, detergents, chemicals, soap, and other characteristics such as bleach and perspiration, most of these dyes escape standard wastewater treatment techniques and persist in the environment.

Water is utilized extensively in the textile industry's manufacturing processes, primarily in the dyeing and finishing activities of the plants. Textile plant wastewater is the most polluting of all industrial sectors, both in terms of volume and effluent composition. Furthermore, rising demand for textile items and corresponding increases in manufacturing, as well as the usage of synthetic dyes, has combined to make dye wastewater one of the major sources of serious pollution concerns in modern times.

2. LITERATURE REVIEW

H. Es-sahbany et. al. (2018) In this study, we used natural clay from the El Oulja-Sale region of Morocco as an inorganic adsorbent to lower the number of cobalt ions Co2+ in wastewater. The effects of several experimental factors on adsorption kinetics were investigated, including the different masses of adsorbent, initial cobalt ion concentrations, contact time, stirring rate, and pH of produced solutions. The following values were recorded for the examined parameters in the removal of cobalt ions: 3 g per mass of adsorbent, 200 mg/l of cobalt ion concentration, 400 tr/min of speed agitation, 2 fortunes for contact time, and pH equal to 6. The maximum quantity adsorbed of the examined ions metals has been validated by the linear models of Langmuir and Freundlich isotherms, according to the adsorption kinetics research and according to the adsorption equations of Langmuir and Freundlich whose linear forms.

Karuna Singh et. al. (2017) The textile business produces a large volume of dye-containing waste water, which pollutes water and land and has negative consequences for human health, animals, and plants. Due to dyeing process flaws, roughly 10-15% of synthetic dyes are released into industrial waste, posing major environmental risks to the flora and fauna of aquatic and terrestrial ecosystems. It pollutes surface water and causes hazardous and carcinogenic substances to accumulate in the water. Physico-chemical or biological procedures must be used to remove dyes from dye-containing waste water. Fungi, algae, actinomycetes, and bacteria are used in biological procedures, which outnumber physico-chemical approaches. The biological process is thought to be more efficient in terms of long-term advantages and no negative environmental impact. Integration of physical, chemical, and biological approaches is required for comprehensive treatment of textile waste water. The biological process is thought to be more efficient in terms of long-term advantages and no negative environmental impact. An important idea and guideline is to choose microbial strains with care.

Said Benkhaya (2017) A survey of the literature on the chemical structure of the textile dyes. This study covers aspects related with the manufacturing and usage of textile dyes across the globe. In addition, the data presented primarily concerns the in terms of their chemical structure and use of these colors in the textile business. Keywords: Chemical structure of the textile dye and usage of textile dyes.

Shashi Prabha (2016) Biodiversity is a major concern for developing countries because of rapid urbanization and industrialization for economic growth. Microscopic life plays a crucial role in decontaminating polluted sites and reducing textile effluent pollution load As part of the current research, microbial diversity around Noyaal River in Tirupur was identified. After testing river water samples from both industrial and non-industrial locations, as well as effluent samples taken before and after the treatment process, it was discovered that the microbial diversity was greater in the river water at the industrial site (Kasipalayam) than at the non-industrial site (Perur). The microbial populations were also found to be higher in the untreated effluent than in the treated effluent. As with the MBR treatment systems, similar patterns were found. Some bacteria and fungi isolated from the industrial site, such as Pseudomonas sp., Achromobacter sp. and Aspergillus fumigates, have been observed to have decolorization capability for dye effluent, and may thus be utilized for treatment. Microbes' breakdown dyes, decrease toxicity of wastewaters, etc. There is little doubt about it: the microbial community helps keep pollutants under control and limit their effects. In order to understand the systematic fluctuation in microbial diversity as a result of pollution load buildup, monitoring is required.

3. CLASSIFICATION OF DYES

Textile mills create fibres that are spun into yarn and then sewn into fabric. On textile fabric, they utilize dyes in a variety of ways. Dyeing, for example, is the process of uniformly covering the textile fibre with colours. Printing is the process of applying dyes to a specified area of a fabric. Bleaching (decolorization) is the process of removing dye colour from textile fibres, whereas finishing includes crosslinking, softening, and waterproofing. Dyes are divided into two categories based on where they come from. Natural colours, which have been used since ancient times, are primarily derived from plants, whereas synthetic dyes are created artificially from chemical compounds. Synthetic dyes are split into three categories based on the created fiber's nature. Cellulose - based dyes, protein fibre dyes, and synthetic fibre dyes are the three types.

- **Cellulose Fiber Dyes**

Plants such as linen, cotton, ramie, rayon, lyocell, and hemp produce cellulose fibre. With reactive dyes, direct dyes, indigo dyes, and sulphur dyes, these fabrics produce flawless results.

Reactive Dyes

Reactive dyes are the most common type of cellulose fibre dye and are compatible with some protein fibres. They're noted for their high pigmentation, long-lasting impact, ease of manipulation across a wide temperature range, and adaptability, thanks to a variety of reactive groups that can create covalent connections with a variety of fibres.

Direct Dyes

The term "direct dye" refers to the fact that these dyes do not need to be "fixed." They are virtually always azo dyes, which resemble acid dyes in some aspects. They have sulphonated activity as well, but mainly to promote solubility because the negative charges on dye and fibre oppose each other. Because of their flat shape and length, they can lie next to cellulose fibres and maximize Van-der-Waals, dipole, and hydrogen bonding. To improve their fabric binding qualities, they are coupled with inorganic electrolytes and anionic salts in the form of sodium sulphate (Na_2SO_4) or sodium chloride (NaCl). As a result, it's best to wash them on a cold cycle with similar-colored items.

Indigo Dyes

The colour indigo, or dark blue, is classified as a vat dye, which was formerly insoluble in water but became so after an alkaline reduction. To achieve a complete bonding of the dye to the fabric, the textile dyeing process begins with the water-soluble or leuco form of indigo, which then oxidises under air exposure and returns to its original insoluble or keto form. Indigo dyes are primarily utilised in blue denim dyeing, which explains why they are produced in such large quantities all over the world.

Sulfur Dyes

Because of their outstanding dyeing qualities, ease of application, and low cost, sulphur dyes are a small but important class. They have a disulfide (S–S) bridge in their structure. They are classified as vat dyes, and as a result, they are reduced from the keto to the leuco form using sodium sulphide. To fulfil the colouring objective, Leuco sulphur becomes soluble in water.

- **Protein Fiber Dyes**

Silk, cashmere, angora, mohair, and wool are all protein fibres derived from animals. Because they are sensitive to high pH levels, they are dyed with a water-soluble acid dyestuff to obtain an insoluble dye molecule on the fibre. Acid dyes include azo dyes, which are the most common, as well as anthraquinone, triarylmethane, and phtalocyanine colours.

Azo Dyes

Because of their variety, cost-effectiveness, ease of use, high stability, and colour intensity, azo dyes account for the largest category (60–70%) of the entire synthetic dyes business. This dye contains a pronounced chromophore (-N = N-) structure, which ensures the dyes' solubility in water and fibre attachment. Azo dyes are divided into three categories based on the number of azo groups in their structure (mono, di, and poly). On one side, these groups are connected to an aromatic or heterocyclic molecule, while on the other side, they are attached to an unsaturated heterocycle, carboxyl, sulphonyl, or aliphatic group.

Anthraquinone Dyes

Anthraquinone dyestuffs are widely employed in the textile dyeing industry; red dyestuff in particular has been used for a long time. These dyes are noted for their water solubility, vibrant colours, and outstanding fastness. Junctions with azo dyes could be formed using the antharaquinone structure.

Triarylmethane Dyes

When made composed of two groups of sulfonic acid, triphenylmethane dyes are commonly used in the textile industry for colouring wool and silk protein fibres (SO_3H). If they only have one sulfonic acid (SO_3H) auxochrome in their chemical structure, they can be employed as indicators. The solubility of these dyestuffs in water, as well as their wide and strong colour spectrum, make them popular.

Phtalocyanine Dyes

Green and blue hues are produced through a reaction between the 1,4- Dicyanobenzene molecule and a metallic atom (Nickel, Cobalt, Copper, etc.) in the phtalocyanine family of dyes. They have a variety of intrinsic qualities, including good colorfastness to light, oxidation resistance, water solubility, and chemical stability.

- **Synthetic Fiber Dyes**

Fabrics made of synthetic fibres include spandex, polyester, acrylic, polyamide, polyoacetate, polypropylene, ingeo, and acetate. Because of their extensive application range, they are used in 60 percent of global fibre manufacturing. Direct dyes, basic dyes, and disperse dyes are used to colour these fibres.

Disperse Dyes

The smallest molecules in all dyes are disperse dyes. These dyes are insoluble in water yet remain stable when exposed to high temperatures. The dyestuff powder and the dispersion agent are mixed together to make the high-temperature dyeing solution.

Basic Dyes

Because they change into colourful cationic ions that dye anionic fibre textiles, basic dyes are also known as cationic dyes. Because these dyes are light-sensitive, they are only used to dye paper nylon and modified polyesters. Cyanine, triarylmethane, anthraquinone, diarylmethane, diazahemicyanine, oxazine, hemicyanine, thiazine, and hemicyanine are their main structures.

4. CHEMISTRY OF AZO DYE

Dyes are coloured substances that are commonly used in aqueous solutions due to their high affinity for water. The dye's hue is primarily determined by the presence of a chromophore group in its chemical structure, and it is utilised in the textile, paper, leather, and food industries. Petroleum by-products and earth minerals are commonly used to make synthetic colours. Reactive dyes, azo dyes, and other synthetic dyes are utilised in the textile business. Azo dyes are the most common synthetic aromatic dyes used in the textile industry for dyeing and are extremely water soluble. It is made up of one or more azo (N=N) and sulfonic (SO_3) groups and has a lot of commercial potential. Azole dyes often comprise one, two, three, or more azo linkages, which connect phenyl and naphthyl rings with functional groups such as triazine amine, chloro, hydroxyl, methyl, nitro, and sulfonate. Monoazo dyes have only one nitrogennitrogen bond (N=N); diazo dyes have two N=N bonds, triazo dyes have three N=N bonds, and polyazo dyes have more than three.

azo dyes are divided into two varieties based on their hydrophobicity: I hydrophobic azo dyes that are taken up by bacteria and reduced inside the cell, and (ii) hydrophilic azo dyes that are reduced outside the cell. Various azo dyes are also readily available for commercial application. Because azo dyes are nonfluorescent, fluorescent probes are employed to trace their route, which is connected to the azo dye by an alkyl bond. Synthetic dye, reactive dye, acid dye, sulphur dye, basic dye, oxidation dye, anthraquinone dye, acridine dye, and a variety of additional colourants are used in textile azo dyes. The diverse utilisation goals of cellulosic fibre, protein fibre, and synthetic fibre are the main reasons why different types of azo dyes are utilised in the dying process. Because not all dyes are bonded to the fibre at the moment of dying, some unfixed dyes are discharged into the effluent, causing pollution.

5. MATERIALS AND METHODS

Materials and reagents

Fabrics: Misr El- Mahalla Co., Egypt, provided nonwoven Egyptian cotton and polyamide fabrics.

Chemicals: Heterocyclic coupler (benzothiazole-2-amine and 5-phenylthiazole-2-amine, 5-methylthiazole-2-amine), silica-supported boron trifluoride (BF3.SiO2), 2,2'- oxydiethanol, propane-1,2,3-triol, urea, sodium hydroxide of polyvinyl alcohol (PVA), and deionized distilled water Sigma-Aldrich Company provides all chemicals, which are laboratory quality.

Synthesis of dyes

The novel colours were synthesised using the free grinding diazotization technique, according to Filimonov and colleagues. A heterocyclic amine (0.01 mol), silica-supported boron tri-fluoride (BF3.SiO2; 0.15 mol), and sodium nitrite (0.01 mol) were milled at ambient temperature for three minutes. After that, 1 mL deionized water was added and stirred for 2 minutes. To make the dyes, a heterocyclic coupler (0.01 mol) was added to the mixture and stirred for 2 minutes. To isolate the catalyst, the produced dyes are dissolved in 20 mL chloroform and filtered. From 20 to 50 mL ethanol, the products were recrystallized. IR spectra were used to confirm that diazotization was complete. Elemental analysis, 1H-NMR, 13C-NMR, and mass spectra were used to characterise the final product.

Preparation of inks

The dyes are converted to inks using the microencapsulation process. Six inks were made with a dye-to-polymer ratio of 2:1. The ink was prepared by this formulation: Dye dispersion 8 %, 2,2'-Oxydiethanol 10 %, Propane-1,2,3-triol 10 %, Urea 5 %, Polyvinyl alcohol (PVA) 4 % and deionized distilled water 63 %.

The dye particle is surrounded by a polymer with a COOH group (shell-core). The dispersion is dominated by the attraction force between the dye molecule and the polymer; particle stability is obtained through the repulsion force between the particles in water and the polymer-polymer entropic interaction.

The ink components were combined at 100 rpm for 30 minutes with an ultrasonic (Sonics and Materials INC model VCX 750 volts 230 vac) until a homogenous solution was formed. The pH of the ink was then adjusted with sodium hydroxide (10% by weight) to a range of 7–9. The inks were then filtered through an 8-micron pore size filtering sieve. To limit moisture absorption from the air, the inks were stored in capped glass jars and placed in a desiccator once they were created. The inks were then loaded into the inkjet printer's inking unit (hong Jet-8420).

6. RESULTS AND DISCUSSION

Synthesis of azo dyes

Diazotization occurs at temperatures below 0°C, and diazonium salts are generated with reduced thermal stability when it occurs at 0-10°C. In this study, nano $BF_3.SiO_2$ was used to make heteroaryl diazonium salts. In the dry grinding procedure, it was found to be stable enough to be maintained at a normal temperature. In the presence of $NaNO_2$ and BF_3, amines (benzo[d]thiazole-2-amine, 5-methylthiazole-2-amine, and 5-phenylthiazole-2-amine) were rapidly reacted with heterocyclic couplers to form azo colours SiO_2 (Table 1).

Table 1. Average molecular size of origin synthesized dyes and nano – inks

Ink no.	The average molecular size of originsynthesized dyes (nanoscale)	The average molecular size of microencapsulated inks (nanoscale)
a	305.87	18.33
b	205.79	20.35
c	218.01	14.55
d	102.61	46.12
e	355	60.75
f	500	45.66

Transmission electron microscopy (TEM) images of produced dyes and nano-inks morphologies are shown in Figures 1 and 2. The average particle diameter of the produced dyes is higher than 100 nm, as evidenced by pictures. Nano ink, on the other hand, has an average particle diameter of 14 to 60 nanometers.

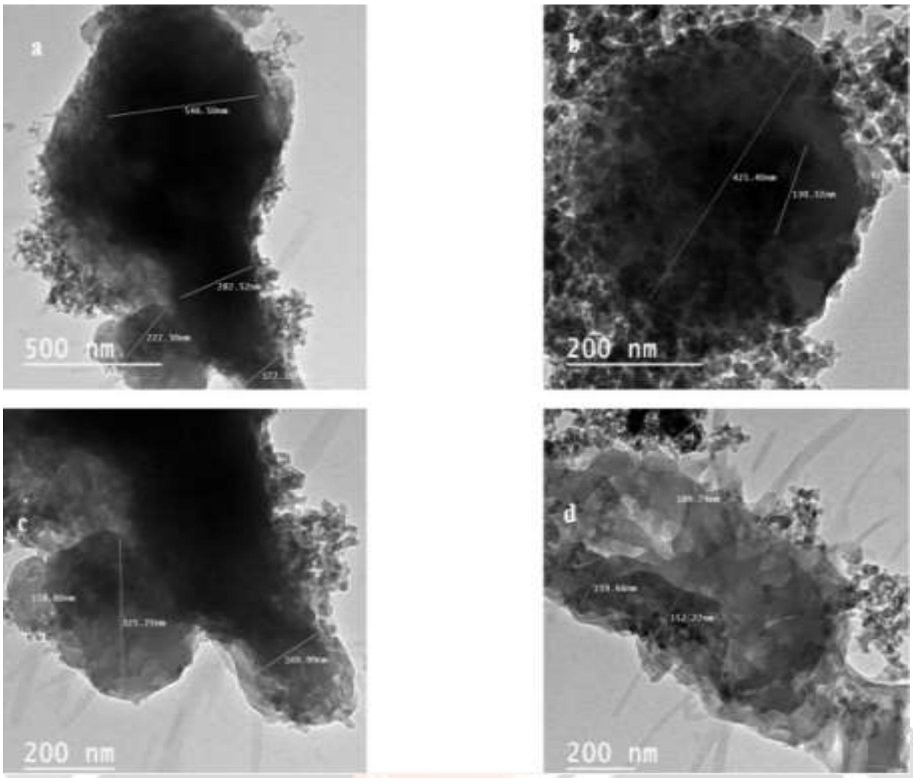

Figure 1. TEM image of synthesized dyes (a-d) respectively

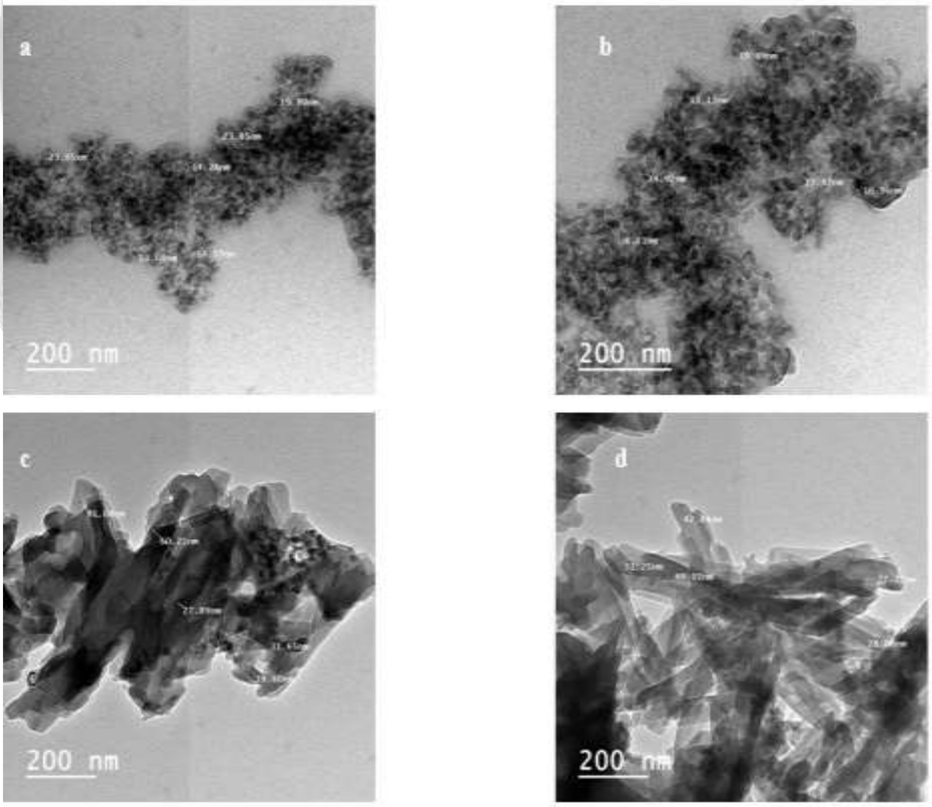

Figure 2. TEM images of microencapsulation inks (a-d), respectively

Table 2. Colour assessment for inkjet-printed samples

Ink No.	λmax (nm)	K/S (cotton)	K/S (polyamide)	L*	a*	b*
a	445	19.2	19.2	77.23	5.82	32.34
b	477	18.34	20.24	78.2	6.77	43.21
c	483	16.1	18.1	67.72	6.42	42.51
d	512	25.2	27.2	81.23	6.56	32.78
e	495	24.2	26.2	79.3	4.21	45.23
f	475	23.4	24.2	69.45	5.13	39.21

Table 2 shows the colour assessments of produced inks that exhibited positive values for a* "red-green axis" on cotton and polyamide fabrics pointing in the reddish direction, as well as positive values for b* "yellow-blue axis" on cotton and polyamide fabrics pointing in the yellow direction.

The chemical structure of the two inks comprising phenyl groups (electron-donating) bound to the first thiazole ring and the methyl group (electron-withdrawing) on the other thiazole ring, which result in the bathochromic shift, can also be observed.

The fastness qualities of inkjet-printed samples utilising the newly synthesised inks are shown in Tables 3 and 4. The data reveal that inks with lower particle sizes have outstanding fastness. Digital pictures for digital and brush printed cotton and polyamide fabrics utilising nano ink are shown in Figure 3.

Figure 3. Digital photographs for digital and brush printed cotton fabrics using nano inks

Table 3. Fastness Properties of Inkjet Printing cotton Fabric Using the Newly Synthesized inks (a - d)

Ink No.	Rubbing		Washing		Perspiration				Light-fastness
					Alkali		Acid		
	Dry	Wet	Alt.	St.	Alt	St.	Alt.	St.	
a	4-5	4	4-5	4	4-5	4	4	4	5
b	5	4-5	5	5	5	5	5	5	5

c	4-5	4-5	5	5	5	5	5	5	5-6
d	4-5	4	5	5	5	5	5	5	5-6

Table 4. Fastness properties of inkjet printing polyamide fabric using the newly synthesized inks (a - d)

Ink No.	**Rubbing**		**Washing**		**Perspiration**				**Light-fastness**
	Dry	Wet	Alt.	St.	Alkali		Acid		
					Alt	St.	Alt.	St.	
a	4-5	4	4-5	4	5	5	5	5	5
b	4-5	4-5	5	4-5	5	5	5	5	5-6
c	5	4-5	5	5	5	5	5	5	5-6
d	5	4-5	5	5	5	5	5	5	5-6

Figures 4 and 5 illustrate the effect of a fixing period of 1 to 5 minutes at 150°C on brush-printed cotton and polyamide using synthetic inks. At a 5 minute fixation time, the greatest colour strength values are obtained.

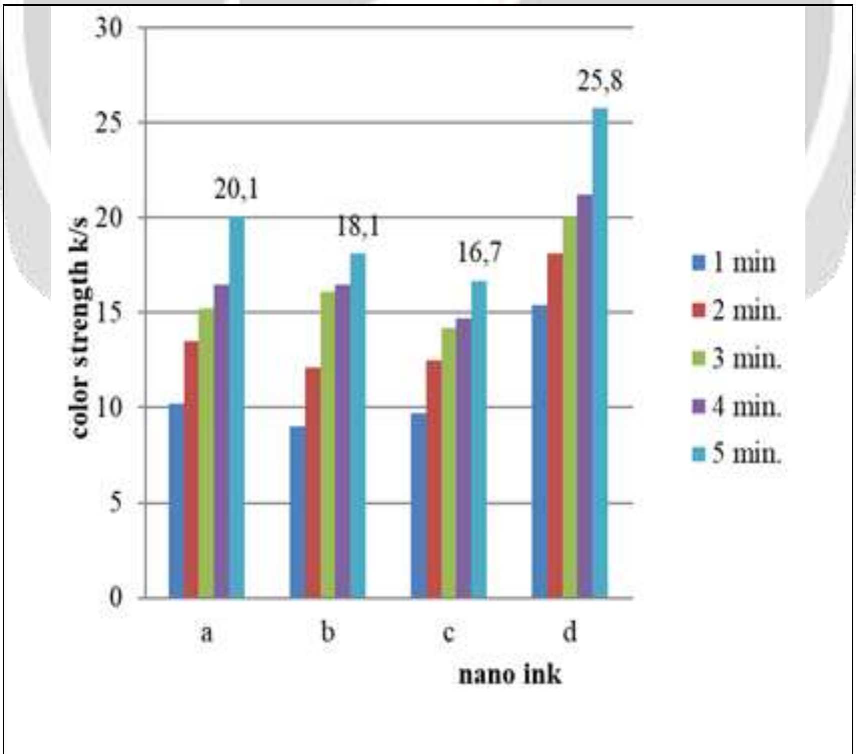

Figure 4. **Fixation time effect on the K/S of digitally printed cotton**

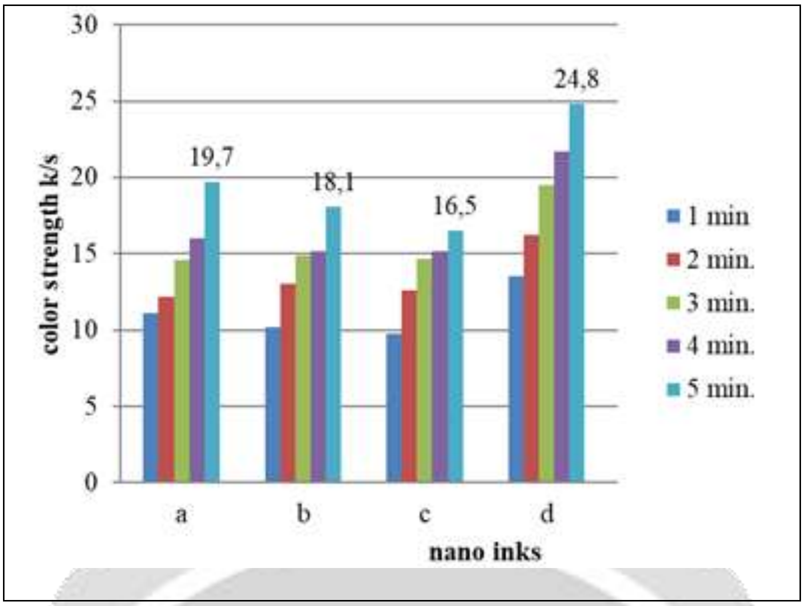

Figure 5. Fixation time effect on the K/S of digitally printed polyamide

7. CONCLUSION

In the first section, the study delineated the harmful effects of synthetic dyes and other pollutants found in textile effluents when discharged in untreated or partially treated forms, and in the second section, it introduced physical, chemical, and biological treatments, as well as their efficacy when used alone or in combination to produce clean and reusable water. Textile dyeing industries are expected to expand in the future, with producers looking for new applications. The creation of nanoparticle-enzyme conjugates, which make the microbial enzyme more substrate selective, has resulted in a paradigm change in azo dye degradation. Some chemically stabilised nanoparticles are also employed to effectively breakdown the azo dye. At room temperature, BF3.SiO2 is utilised as an acid catalyst to enhance diazotization and coupling of heterocyclic compounds. Because the reaction takes place at ambient temperature and without the use of solvents, this approach saves time, energy, and money. The compounds created are employed as inks in the printing of cotton and polyamide fabrics, and the prints have excellent fastness qualities.

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