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A Review on Applications of Metal Complexes in Textiles

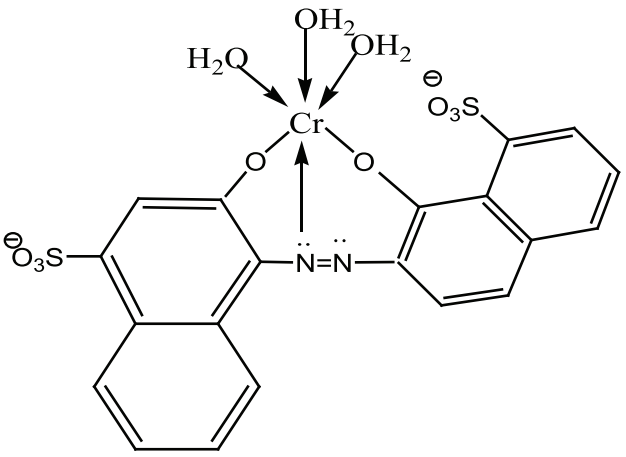
Shuchismita Dey*[≠]
Department of Textile Engineering, Southeast University, Dhaka, Bangladesh.
**Corresponding author: E-mail: shuchismta.dey@seu.edu.bd*
[≠]Currently pursuing PhD studies at University of Dhaka with study leave.

Abstract
Metal complexes are coordination compounds which are formed by the interaction of metals with ligands containing donor atoms like O, S and N. Several researchers have found various applications of metal complexes in textiles. This article covers the findings related to the applications of metal complexes in textile processing. Researchers have synthesized metal complexes in 1:1 and 2:1 ratios and then characterized the complexes by elemental analysis and spectral techniques like UV, IR, NMR etc. In some cases, the structures of synthesized complexes were confirmed by thermal analysis and conductivity measurement. Metal complexes are used as dyeing and finishing agent in textile processing. Metal complex dye is the best choice for the dyeing of protein and polyamide fiber because of the improved light and wash fastness properties relative to the non-metallized dye. Metal complexes also found a huge application in the production of smart textiles such as military textile, sportswear, medical & health care textile, providing flame retardant finish and antimicrobial effect. So, Further synthesis of more new eco-friendly metal complexes with versatile textile applications is necessary.

Keywords : Metal Complexes, Ligand, Textile, Dye, Finishing Agent.

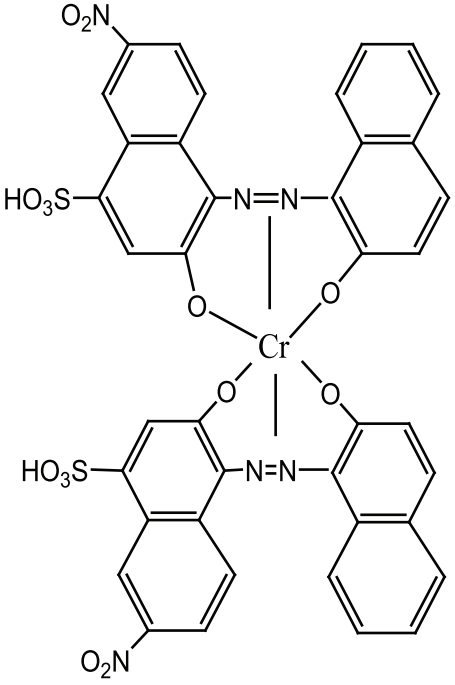
1. Introduction
Several metals such as Cu, Ni, Co, Ag, Cr can make various complexes with different ligands which are widely used in textiles [1]. The products which are formed due to Lewis acid-base interaction between metal ions and ligands are called metal complexes [2]. The central positively charged metal ions behave as Lewis acid and the ligands containing donor atoms with one or two lone pair electrons like N, S, O behave as the Lewis base. In a complex, the ligands are all same or may be different. Depending on the number of atoms involved in attachment to the metal ion, ligands can be monodentate, bidentate and polydentate types. A polydentate ligand is joined to the central metal atom through two or more different ligand atoms and results in a cyclic complex which is known as chelate [3]. The d-block elements, f-block elements, even the main group elements can form metal complex through the electron transfer mechanism [4].

Generally metal complexes are synthesized in the ratio of 1:1 or 2:1 while maintaining proper condition. In 1:1 metal complex one metal ion is complexed with one ligand molecule. On the other hand, two ligand molecules are complexed with one metal atom in 2:1 metal complex. The synthesized metal complexes are then characterized by elemental analysis, FT-IR, ^{1}H NMR, ^{13}C NMR, TGA, DSC and single-crystal X-ray diffraction analysis [5-6].



Acid Blue 158 (C.I.14880)

Figure 1. An example of 1:1 metal complex.



Acid Black 194 (AB194)

Figure 2. An example of 2:1 metal complex.

Transition metals having partially filled the d sub - shell can form colored complex due to the electronic transition by absorption of light and these complexes play an important role in dyeing and finishing process of textile [7]. Apart from textile, metal complexes, also known as coordination complexes or chelates have versatile use in pharmaceuticals [8] and polymer industries [9]. Several interesting properties of metal complexes like color, optical properties, magnetism, biological activity, catalytic behavior, structure etc. are responsible for various applications of coordination complexes in many aspects of human life. In recent years, some reports have been published on the application of metal complexes in textile as eco-friendly dyes [10], antibacterial agents [11], antimicrobial agents [12], flame retardant finishes and photo stabilization finishes [13] in textile processing. So, the development of new metal complexes with more promising biological properties is an urgent necessity to meet our demand. In this regard, a comprehensive literature survey has been done on the application of metal complexes in textiles and is discussed in this review article.

2. Discussion

2.1 Use of metal complex in textile: A critical analysis

It has been mentioned that metal complexes can be used as dyeing and finishing agent in textile industry. For the dyeing of protein and polyamide fiber, metal complex dye holds an ubiquitous position because of their better light and wash fastness properties relative to the dyeing with non-metallized acid dyes [14]. An overview on metal complex dye, a class of dye that contains metal is coordinated to organic ligand was reported in literature [7]. They are not necessarily the derivatives of acid dyes. Reactive-, direct- and metal-complexed vat dyes are also well developed. Typically, metal complex dyes are obtained by coordination of metals of different types (Cu, Cr, Co, Ni) with selective acid dyes. These dyes are mainly used for dyeing protein fiber such as wool and silk or polyamides. Based on the synthetic procedure, the dyes are of pre-metalized (1:1 or 1:2) and mordant type. The author focused on benefits of metal complex dyes of pre-metalized type like light fastness, wash fastness and waste

water load. It was mentioned that 1:2 chromium pre-metalized dyes are commercially important because of good fastness towards exposure to light as well as improved wet fastness properties. In another report [15], the author stated that, 1:2 metal-complex dye is essential for dyeing silk with improved light and wash fastness properties, due to its strong dye-fiber interaction.

Azo dyes have vivid colors which cover the whole visible region. P. Gregory [16] gave a brief description on metal complex azo dye and its applications. The author mentioned that 1:1 Cu complex azo dye (Reactive violet 1) is used for dyeing cotton, cellulosic fibre and 2:1 Cr complex azo dye (acid violet 121) is used for dyeing wool and nylon. It was also reported that boron complex azo dye such as red dye is used for polyester dyeing and plastic coloration. Kocaokutgen et al. [17] studied on 1:2 chromium or cobalt complexes based on 5-methyl substituted groups of o-o′ dihydroxy azo dye and found excellent exhaustion on nylon, a synthetic polyamide fiber along with outstanding fastness properties. Moreover the azo compounds possessed biological activity and can be used for biocidal treatment of textile material. Ayaz et al. [18] reported an the investigation on synthesis of a new acid azo dye and its Cu, Ni, Co, Fe and Cr complexes. After characterization with spectral and thermal techniques, the complexes were screened for biological activity and good inhibition effect against Candida albicans were found, thus used in textile industry. Wakiel et al. [19] reported the synthetic procedure and characterization techniques to synthesize several metal (Cu, Ni, Mn, Co) complexes of an azo dye. Spectral data suggest the formation of 1:1 Mn(II) complex and 2:1 formation of other metals. Measuring color and wet fastness properties they concluded that ligand as well as its complexes have a good to moderate affinity to polyester fibres. Van et al. [20] demonstrated the synthesis of metal complexes of a heterocyclic bispyrazole azo dye and their color properties for polyamide fibers.

At present, researchers have been trying to overcome the environmental threats caused by textile dyeing industry. It is well known that Cr and Co - complex azo dyes have very good wet fastness (rating 4-5 in ISO five member "grey scale") and also light fastness (rating 6-7 in ISO eight member "blue scale") [21], which are frequently used for dyeing protein fibers. But the processes involved in the treatment of protein and polyamide fiber by Cr and Co - complex dyes create environmental pollution [22]. Considering the environmental issues caused by Cr and Co- complex dyes, researchers showed greater interest in developing eco-friendly dyes. It is also known that some iron (II, III) and Al complex dyes [23, 24] have comparable fastness and cause little or no pollution. In a study, Maria et al. [10] proposed Cu, Al, Zn, Ni and Mn complexes as an alternative of ecologically problematic Cr and Co-complex acid azo dyes. The researchers have synthesized and characterized novel metal (Cu, Al, Zn, Ni and Mn) complex dyes and also introduced an improved technology named “Ultrafiltration” to remove free metals present in the dyes as well as solvents in the liquid dye formulation results in metal complex dyes with improved purity, strength and solubility, thus gives a solution to resolve environmental effects. After dyeing of wool and nylon fabric with ultra-filtrated and non-ultra-filtrated dye, dyeing performance (color measurements and fastness properties) of the fabric were studied and finally the results were compared with Cr -complex dyeing. Improved wash fastness properties were observed for the synthesized metal complex dyes compared to Cr-complex dye and metallized dye showed better wash and light fastness properties than non-metallized dye. Based on the environmental factors, the authors proposed Cu, Al, Zn, Ni and Mn complexes as alternatives for the Cr and Co-complex azo dyes with reduced environmental impacts. Considering the environmental issues, Hamadaoui et al. [25] developed a dyeing method without using chemical auxiliaries to dye cellulosic fiber (cotton). For this, the cellulosic fiber has to be precationized before dyeing. Generally, 1:2 metal complex dye shows an affinity for protein and

polyamide fiber, but no affinity for cellulosic fiber (cotton). This chemical modification (cationized) helps the exterior dyeing of cotton fiber using anionic dyes as 1:2 metal complex dyes (direct and reactive), introducing an eco-friendly dyeing method. Except textile dyeing, metal complex dyes are also used for the dyeing of leather, hair, paper and plastic materials.

In case of outdoor use cloths are generally and externally exposed. As a result a microbial attack is feasible from an ambient environment. Cotton, a natural cellulosic fiber provides a good environment to grow microorganisms, because of its moisture retaining property and large surface area. Microbial infection through textiles can cause several health issues. So it is essential to use antimicrobial finishing agents in many textile products such as general cloths and value added items like sports-wear, fancy cloths, medical items. The antimicrobial properties of textile materials can be achieved by incorporating the functional agent physically or chemically on to the fibers or fabrics. Metal complexes, metal salt and metal nanoparticles also serve as functional agent [11-12].

Wang et al. [26] synthesized and characterized bivalent metal (Cu, Zn and Fe) complexes of chitosan. Biological studies of the complexes showed a wide range of antibacterial and antifungal activity. Greater biological activities were observed in metal complexes than in the case of free chitosan or metal salts. So, they proposed chitosan metal complexes as novel antimicrobial agents for textile processing. In another study, chitosan metal complexes were applied on jute, a lignocellulosic natural fiber to impart antimicrobial activity. An improved performance here was also observed in case of metal complex treated jute fabric than free chitosan or metal salts treated jute fabric individually. Yildiz et al. [27] have reported the synthesis, characterization and antibacterial study of new Ag-metal complex of abietic acid. The complex was found to have no hazardous effect on environment and antibacterial activities of the complex were performed after being applied to cotton fabric. Based on the findings, the authors proposed the synthesized Ag-complex could be used as new antibacterial agent in textile.

K. Nurcan [28] prepared Ni(II), Cu(II) and Co(II) complexes of an azomethine dye and characterized by elemental analysis, UV, FT-IR and molar conductance measurement. Antimicrobial properties of free ligand as well as metal complexes of that ligand were studied. Enhanced antimicrobial activities of metal complexes were observed relatively to ligand itself. So, these dye-metal complexes can fulfill the requirement of health care textile.

Medical textile, also known as healthcare textile, has an urgent need to prevent infection and control. Actually it provides cost-effective ways to protect human being especially hospital staff and their patients from virus, bacteria and other micro-organism. Metal complexes can play an important role in medical textiles, providing an antimicrobial effect.

Metal complex can also be used as flame retardant and photo stabilizer in textile. Flame retardant fabrics can be obtained by using metal complexes like Zirconium (K_2ZrF_6), titanium (K_2TiF_6) and other metal complexes during the finishing of fabric. In a study, Chang et al. [29] studied on wool fabric. They have performed dyeing as well as flame retardant finishing by using acid metal complex dye and an eco-friendly agent phytic acid.

Silk is a historically important fiber. But it has some limitations. One of the biggest limitation of protein fiber especially for silk is photochemical tendering which is caused by UV light when it is exposed to sunlight. Stabilizer such as Ni-Chelates were used to overcome the limitation [13].

3. Gap Analysis and Recommendations

As per the literature survey, there exists some limitations which are as follows:

Enough research papers were not found in literature in this area. Some articles have been published based on metal complexation with dyes. More metal complexes with other textile chemicals and auxiliaries need to be studied. In textile processing various chemicals and auxiliaries are used. So verification of usefulness of metal complexes with various chemicals may be significant in this sector.

Based on the critical review and gap analysis, several recommendations are as follows:
(a) More metal complexes should be synthesized and characterized properly.
(b) Some toxic dyes become eco-friendly by reducing toxicity when those are incorporated with metals as metal complexes. Eco-friendlier new metal complexes should be synthesized considering textile applications.
(c) Newly synthesized metal complex could be converted to nano-materials for remarkable textile applications.
(d) Metal complexes are used in dyeing and finishing techniques in textiles. More applications are needed to be discovered such as in yarn and fabric storage and wastewater treatment.
(e) Some metal complexes are used as antibacterial agent in textiles. More metal complexes should be discovered which will be applicable in multipurpose textile applications.

4. Conclusion

In this review, an overview of the metal complexes and applications in textiles have been presented. Metal complexes with different organic ligands can function as dyeing and finishing agents in textiles. Enormous opportunities exist there to develop eco-friendly dyestuff, antimicrobial and cost effective textile finishing agents. It is clear that upon complexation, new and more promising properties can be developed that cannot be found in pure organic ligands. So, the complexes are of great interest over the last few years, because of the versatile application of metal complexes in different areas of textile sector. Metal complexes can hold an ubiquitous position in the production of smart textiles such as military textile, sports-wear, medical and health care textile. In this regard, synthesis, proper characterization and investigation of biological activities of more new metal complexes are essential considering textile applications.

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