Chapter

Application of Smart and Functional Dyes in Textiles

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Abstract

Our future will be based on functional and AI based smart products, where every industry wants to develop these kinds of products. Textile industry also cannot remain untouched with this technological innovation. Dyes have been utilising for coloration of textiles since ancient time. But at present with various advancement in technology as well as requirements of consumers, the need for functional and smart dyes arises. Various current researches are based on application of smart and functional dyes on textile to develop smart and functional textiles. The dyes which add the functional and smart properties to the textiles can be called as functional and smart dyes. Functional and smart dyes are available in both synthetic and natural form. But with the environment concern, the researchers are going on to find out natural source of these dyes. Functional dyes such as UV protective dye, antimicrobial dye, moth repellent dye offer specific function after application on textiles. Smart dyes like photochromic, thermochromic, electrochromic and solvatochromic etc. are playing very imp role to develop a smart textile which can offer reversible colour change which leads to impart various properties such as thermoregulation, camophlage properties into the textiles. Functional dyes generally limited to the textiles sector but smart dyes are not just restricted to it. Application of smart dyes is extended to various fields such as automobiles, robotics, aircrafts, medicine and surgery etc. This chapter will mainly deal with the types, application methods and application area of functional and smart dyes especially in connection with textiles.

Keywords: functional dyes, smart dyes, photochromic dyes, thermochromic dyes, electrochromic dyes, solvatochromic dyes, UV protective dyes, antimicrobial dyes, smart textiles, functional textiles

1. Introduction

Smart and functional textiles is the need of the future. There are various methods to develop smart and functional textile which start right form the fibre stage and end in the dyeing and finishing stage. Among these methods, application of smart and functional dyes is considered the most affordable method to develop smart and functional textiles. Traditionally, Dyes has been utilising in textiles generally for coloration purpose. Earlier, consumer wants to buy the textiles mainly due to its aesthetic aspect. Presently, consumer has smart choices. A textile product only having aesthetic property could not allure them. In near future, the product should be smart and functional one to attract the consumer. Smart textiles refer, a textile which can act according to their nearby environment while functional textiles refer, a textile which provides a particular function specially protection from nearby environment. Smart and functional textiles are considered as the part technical textiles. Since last few decade the researchers have been searching the functional as well as smart aspect of dyes. The dyes which can offer smart and functional textiles can be considered as smart and functional dyes. Earlier dyes were categorised as natural dyes and synthetic dyes. Natural dyes were categorised as based on origin (vegetable, mineral and animal), colour (yellow, red, blue), chemical constitution, (indigoid, anthraquinone, alphanapthaquinone, dihydropyrans, anthocynidins, cretonoids), application method (direct, basic, acid, vat, disperse, reactive, mordant) while synthetic dyes were classified as water soluble (direct, basic, acid, reactive), water in soluble (vat, disperse, sulphur) and in situ colour formation (azoic dyes) [1, 2]. But Presently and in near future, the dyes can as be categorised as smart dyes and functional dyes on the basis of providing AI based smartness as well as functionality to the textiles. The types of smart and functional dyes are being described in this chapter.

Smart dyes can sense the nearby environment and make changes accordingly [3]. Smart dyes can change the colour due to various external stimuli such as pH, pressure, temperature, solvents, moisture and electricity. These changes can be permanent or temporary on the basis of need [4]. This phenomenon is known as chromism [5]. There are different types of chromism such as photochromism (induced by sunlight or UV rays), thermochromism (induced by changes in temperature), solvato chromism (induced by polarity of the solvent), hygrochromism (induced by moisture), ionochromism (induced by ions), halochromism (induced by pH value), acido chromism (induced by acids), chemochromism (induced by specific chemical agents like dangerous gases, warfare agents, etc.), electrochromism (induced by electricity), piezochromism (induced by pressure), mechanochromism (induced by deformation of substances) [6]. In the field of textiles mainly photochromism, thermochromism, electrochromism and solvatochromism types of chromism is reported [7–10]. Smart dyes are based on these different kinds of chromism. Several natural and synthetic smart dyes have been discovered. On the basis of external stimuli smart dyes are classified as photochromic dye, thermochromic dye, solvato chromic dye, hygro chromic dye, iono chromic dye, halo chromic dye, acido chromic dye, chemo chromic dye, electrochromic dye, piezo chromic dye, mechnao chromic dye which changes colour respectively due to UV rays, temperature, polarity of solvents, moisture, ions, pH value, acids, specific chemical agent, electricity, pressure, deformation of substance [11]. Despite of having a large group of these dye only a few one makes a way towards textile. Several factors such as bonding with textiles, end uses and comfort of the wearer etc. are considered while application of smart dyes on textiles. Smart dyes like photochromic dyes and thermochromic dyes, are mainly used in textiles sector. Earlier in 90's, the thermochromism and photochromism were widely used particularly in fashion designing field [12, 13]. Thermochromic dyes have better stability in comparison to photochromic dyes hence these are mostly used dyes in textiles in comparison to other smart dyes [14]. Very few researches related to the use of electrochromic dyes, solvatochromic dyes and mechanochromic dyes on fabric are available. Researches related to the use of electrochromic dyes on textiles are still going on [15]. Different parameter of dye such as maximum absorption, no. of wash cycle, different fastness describes the properties of smart dyes [16]. Application of smart dyes are generally extended to fashion, sport and defence and medical related sector. After application of smart dyes, a simple textile can act as a smart textile which can perform the various function such as Camouflage, thermoregulation etc. [17–19].

Functional dyes can add a specific function to the textile such as protection from UV radiation, microbes as well as insects and moth [20–22]. On the basis of these mentioned function, functional dyes can be categorised into UV protective dyes, antimicrobial dyes and insect and moth repellent dyes. Synthetic and natural dyes can provide these functions but presently more attention is being given to natural dyes due to several environmental concerns. Presently due to climate change issue researches on UV protective dyes and antimicrobial dyes have been increased.

Despite of being constant researches on smart and functional dyes, commercial application is very limited. To widen the application area of smart and functional dyes, it is necessary to use a proper application method to impart these dyes onto textile surface. The knowledge of proper bonding mechanism is important in this regard. The relation between fabric properties and application method should be well known to the researcher. It is also important to work on the light stability and washing stability aspect of these dyes. Researches related to preparation and application of these smart and functional dyes on textiles should be carried out in a significant number. Functional group can be added to a traditionally used dye to enhance its functionality. These kinds of researches would be help in the current scenario and also helpful to increases its commercial application.

2. Types of smart dyes

As discussed in introduction part, only few smart dyes such as photochromic, thermochromic, electrochromic, solvatochromic paved a way for its application in textiles industry. Although researches are still going on to utilise more no. of smart dyes in textile sector. Types of smart dyes that are being used in textiles sector are as follows:

2.1 Electrochromic dyes

Electrochromic dyes are based on electrochromism in which reversible changes of colour occurs due to electricity (gain and loss of electron) [23]. This process occurs generally with some transition metal oxides which conduct both electrically and ions [24]. It is reported that strong electric field can alter the colour of certain dyes [25]. Phthalocyanine dye is a good example of electrochromism [26]. Common electrochromic materials are Polyaniline. In a study, conducting polymer polyaniline layer was formed electrochemically on conducting woven textile substrate which exhibited reversible colour change [27]. During application of electrochromic dyes on textile, performance parameters such as electrochromic contrast, coloration efficiency, write-erase efficiency, switching speed, stability, cycle life, and optical memory are considered. Polyethylene terephthalate (PEPES) membranes were coated with poly-3,4-ethylenedioxythiophene polystyrene sulfonate (PEDOT:PSS) to develop electrochromic textile system [28]. Application of Electrochromic dyes can also be extended to develop smart window curtain which filter sun light accordingly [29]. Other smart application such as display of information or for camouflaging purposes of electrochromic dyes have also been reported [30].

2.2 Thermochromic dyes

Thermochromic dyes causes reversible changes in colour within the absorption spectrum of a thermochromic molecule, usually in the visible light range. These changes are induced by heat. Thermochromic material can be organic, inorganic polymers and sol-gels in nature [31]. Presently, only two type of thermochromic system are used in textiles i.e. liquid crystal type and molecular rearrangement type. Organic leuco dyes also create thermochromic system [32]. Organic thermochromic systems perhaps occur due to equilibrium between molecular species like acid–base, keto-enol, lactim-lactam, stereoisomers or between different crystal structures [33]. Among inorganic thermochromic substances, few examples of metal oxides are known such as indium oxide, zinc oxide, chromium hemitrioxide-alum earth [34]. Application of thermochromic dye on textile can be done using 3 methods which can be used exhaust, continuous method, microencapsulation and printing. In exhaust method thermochromic pigment are applied on to textile with a cationic agent, non-ionic dispersing agent and binder using Material to liquor ratio 1:30 at 70 ° C temperature for half hour [35]. In continuous method thermochromic dye, cationic and non-ionic dispersing levelling agent are applied with acrylic soft binder solution. This solution is applied on textiles through pad dry cure machine. Drying of samples is generally done at 80°C for 3 min while curing is done at 140°C for 2 to 3 minutes [36]. In microencapsulation method, microcapsules were created using colourless dye, precursor and colour developer [37]. These materials melt and solidifies with respective to the application of heat and cold. On melting these material changes its colour, while on solidification come back to its original colour.

Various novel colour effects as well as camouflage designs can be produced using combination of thermochromic, non-thermochromic and mixture of both on the conductive cotton [38]. These thermochromic dyes can take heat from there nearby environment such as sun rays and cause a reversible change in the colour of textiles. These dyes are also establishing their presence in the field of Protective clothing for military [39]. Protective clothing using thermochromic colourant can mimic the colour of its surrounding environment with the change in temperature. Even sometimes colour can change with body temperature. Thermochromic dyes on textiles also used to protect a brand from fake imitation [40]. Microparticles (made of thermochromic and photophoresent dyes) and binder are used to make the brand logo. These logos can be temporary and permanent based on the binder used. The logo made up of thermochromic dye change colour with body temperature [41]. Thermoregulation is also a very imp application of thermochromic dye which is based on heat absorbance (in case of dark colours) and reflectance (in case of light colours). A suitable example of this phenomenon is coating of thermochromic dyes on firemen's uniform on high temperature. The Colour of uniform will be converted to white colour which reflect the heat. Thermochromic dyes can also do thermoregulation via expanding or shrinking the textiles fibre. This Shrinking and expanding of fibres in a fabric causes opening or closing of pores which help regulate the passage of air to the body according to external environment [42].

2.3 Photochromic dyes

Photochromic dyes change its chemical structure due to UV rays. Photochromic effect was first time seen on the tetracene and after that it was observed in potassium salt of dinitomethane [43]. In 1960 first photochromic spiropyrans was developed using printing technique by Ksnebo ltd, Japan. In 1998, photochromic dyes were first time used in textiles to produce camouflage effect. Photochromic dyes also decolorise. This decolourisation is called negative photochromism [44]. Various metal oxides, alkaline earth metal sulphides come under the category of Photochromic dyes. Photochromic dyes are water insoluble hence cannot be applied on wool and cotton [45]. Presently Researches are also going on Water-soluble photochromic dyes. These dyes are relatively cheaper option for textiles and leather. Spirooxazine-based Water-soluble photochromic dyes having sulphonate group have been developed. Sulphonate gp impart water solubility. These water-soluble photochromic dyes are mainly for proteins fibres [46]. The wash fastness and photostability of these dyes are moderate [47].

Application of photochromic dyes can be done on the window curtains and facades. This would be helpful to control sunlight [48]. Heat sensitive photochromic dyes also used as temperature indicator [49, 50]. Dupont company are also working on the camouflaging property of these photochromic dyes to develop camouflaging clothing for armies [51, 52]. Flexible UV sensors based on Photochromic dyes also change its colour due to UV rays which makes a UV detective fabric which help to tell the intensity of UV rays to get protection accordingly [53].

Different application methods have been reported to apply Photochromic dyes and pigments. In a study exhaust method (direct Coloration), photochromic colourants were used with auxiliaries such as dispersing agent and ceramic balls (250 g) and aqueous acetic acid. The dyeing was started at 40° C temperature and temperature raised to 60 ° C and then to 90 ° C [54].

Photochromic colourants as disperse dyes has also been used to dye polyester using exhaust dyeing technique. Photochromic colourants are insoluble in water therefore organic solvents such as Acetone is used to dissolve the photochromic colourant. After dissolution of colourant, dispersing agent is added. Acetic acid is also used to maintain the weak acidity (4.5) of solution. This weak acidity helps to minimise the degradation of colourant. The material to liquor ratio of solution was kept to 1:50. The fabric is dyed at 120 ° C for 45 min. Further, rinsing in cold water was done to reduce the temperature to 70 ° C. This 70 ° C temperature was maintained for 20 minutes with in the solution of sodium hydroxide, sodium dithionite and a non-ionic surfactant. Material to liquor ratio was maintained to 1:30.

Photochromic colourants can also be applied through pad dry cure method. In this method the fabric is dried at 80 ° C for 2 minutes in hot air, followed by 140°C of curing temperature for 3 minutes. Microencapsulation was also used for application of photochromic colourants [55–57].

2.4 Chemo chromic dyes

Chemo chromic dyes change its colour due to differences in pH. Phthalides, fluoranes, triarymethines, and simple azo dyes are the examples of pH sensitive dyes [58].

Conventional exhaust dyeing, solgel method as well as prior addition to electrospinning solution has been reported as methods of application for chemo chromic dyes. Chemo chromic dyes can be used in identify the proteins (of certain microbes) with change of colour. This identification with changing colour indicates the presence of microbes in textiles [59]. Therefore, Application area of Chemo chromic dyes can be widened to medical textiles bandages [60].

2.5 Solvatochromic dyes

Solvatochromic dyes work on the principle of Solvatochromism which corresponds to reversible changes of colour due to solvent polarity. The change in colour is occurred due to shifting in maximum absorption of different solvents [61]. There are two types of solvato chromism i.e. positive solvatochromism and negative solvatochromism. Positive solvatochromism corresponds to a hypsochromic shift induced by a decrease of solvent polarity“ and “negative solvatochromism corresponds to a hypsochromic shift induced by an increase of solvent polarity” [62]. Common example Solvatochromic dyes are pyridinium, merocyanine, and stilbazolium dyes. Solvatochormic dyes can be applied in the textiles using microencapsulation technique. Assembly of microsphere on fabric causes colour change on drying and wetting of the fabric. Application of Solvatochromic dyes in textiles is very limited. These dyes can be used to identify the stale or toxic food due to colour change of packaging [63].

S. No	Smart Dyes	External Stimuli responsible for colour change	Suitable methods of application for textiles	Application in textiles	References
1.	Electrochromic dye	Electricity (gain and loss of electron)	Coating	For displaying information or for camouflaging purposes	[23–30]
2.	Thermochromic dye	Heat (absorption spectrum of a thermochromic molecule)	Exhaust, Continuous method, micro encapsulation	Thermoregulation, Brand forgery detection	[31–42]
3.	Photochromic dye	Light	Exhaust and pad dry cure method	Camophlaging textiles, window curtains, UV detective fabric	[43–57]
4.	Chemo chromic dyes	pH	Conventional exhaust dyeing, solgel method, prior addition to electrospinning solution.	Medical textiles	[58–60]
5.	Solvatochromic dye	UV rays	Micro encapsulation	Packaging	[61–63]
6.	Mechanochromic dye	Deformation (elongation and compression) of polymer on which applied	Melt processing technique, physically dispersed in form of supramolecular aggregates in a matrix in a polymer, Covalent insertion of chromophoric units	Footwear and shaped garment industry	[64–66]

Table 1.
Types of smart dyes used in textile industry.

2.6 Mechanochromic dyes

Mechanachromism is a phenomenon in which a polymer changes it colour due to deformation such as elongation and compression. Elongation and compression occur due to the change in pH, temperature. Mechanachromic dyes are the organic dyes which is applied on polymer and causes changes in colour due to certain mechanical pressure. Mechanochormic dye cannot act alone it require a polymer (material) because only polymer can deform (elongate or compress). In a study 1,4-bis (R-cyano-4- methoxystyryl)-2,5-dimethoxybenzene9 (C1-RG, F) has been incorporated in polyethylene using melt processing technique [64]. In another research mechanochromic polymers have been developed by incorporating a dye filled microcapsules [65]. In a study Polydiacetylenes (PDA) was synthesised by thermal polymerisation of diphenyl sulphide containing bisdiacetylene. It is reported in that study that PDA changes its colour from blue to red due to elongation and compression. In the cool (non-extended state) form, the material has a particular colour, this particular colour changes due to mechanical abrasion which causes heating of surface. Mechanochromic colourants can be physically dispersed in form of supramolecular aggregates in a matrix in a polymer. Covalent insertion of chromophoric units into the macromolecule backbone or side chains has also been used to apply mechanochromic colourants [66]. Application area of mechanochromic dyes can be done in footwear and shaped garment industry in which product can change colour due to deformation (**Table 1**).

3. Types of functional dyes

Functional groups like -OH, -NH2, – COOH of dyes offer various functional properties when applied onto the textile [67]. Both natural and synthetic dyes can perform various functions after application on textiles. Now days more emphasise is being given to the green and sustainable functional dyes which directly comes from nature. Types functional dyes are as follows:

3.1 Antimicrobial/antibacterial dye

Microbes and bacteria cause several kinds of dermal infection, body odour and several other severe health issue [68]. Antimicrobial dyes provide the protection from variety of micro-organisms like gram-positive bacteria such as *Staphylococcus aureus, Streptococcus epidermidis and Bacillus cereus* and gram-negative bacteria such as *Escherichia coli, Klebsiella pneumonia, Shigella flexneri and Proteus vulgaris* and other microbes [69]. A large no. of antimicrobial dyes possesses antimicrobial activity against human pathogen but very few have been reported for textiles. Number of researches have been conducting to find out the antimicrobial properties in various synthetic and natural dyes. Various studies reported that synthetic dyes such as direct, cationic, reactive and disperse dyes provides antimicrobial property to the fabric after dyeing. In a study it was found that Direct Blue 168 dye and copper sulphate as mordanting agent incorporate antimicrobial properties in the acrylic fabric [70]. Similarly, antimicrobial dyes based on azo heterocyclic and/or homocyclic Systems also have biocidal behaviour [71]. Multifunctional antimicrobial dyes have also been developed by adding a functional gp (quaternary ammonium salt group) to a traditional aminoanthraquinoid dye [72]. Most research has been focused on polycationic systems that are more supple for modification. Reactive dyes form homopolar bonds with textile substrates. The synthesised thiazolidinone derivatives exhibiting antimicrobial properties. Synthesised monoazo disperse dyes showed better results against gram positive as well as gram negative bacteria [73]. Application of natural dyes on textiles also offer antimicrobial textiles. Phenolic compounds such as anthraquinones, flavonoids, tannins, naphthoquinones and others in natural dyes are responsible for the antimicrobial activity. When these phenolic compounds reacted with textiles, formation of complex form. This complex hinders (bacteriostatic) or kill (bactericidal) the enzyme production in microbes. At present more emphasis is being given to antimicrobial activity of natural dye due to various environmental concern. From various studies it was found that natural dyes extracted from Pomegranate (*Punica granatum)* peels, Henna (*Lawsonia inermis*) leaves, *M. composita* leaves, Madder (*Rubia tinctorium*) root, safflower, *Rumex maritimus (*Golden dock*)*, *Indigo (Quercus infectoria) leaves,* Berberine provides antimicrobial properties to the fabric. Application of Natural dyes such as peony, clove, *Coptis chinensis* (Chinese goldthread) and gallnut on fabric also provides protection against *Staphylococcus aureus* due to presence of phenolic compounds [74–78].

Perspiration cause formation of bacterial colonies on textiles, which led to bad odour [79]. Various natural dyes can act as a barrier to form these colonies. Natural dyes such as pomegranate, coffe arabica, *Cassia tora*, gardenia Indigo, Peony, clove and pomegranate (*Punica granatum*) reported as a good deodorising agent when applied on textiles [80–82]. Natural dyes extracted from gallnut also act as a deodoriser for textile due to the presence of gallotannin [83].

There is no. of methods to impart antimicrobial dyes on textiles. For proper bonding of textile and dye, the textile surface can be modified through various treatments such as treatment with chemicals, chitosan, enzymes, UV radiation, ultrasound [84]. Application methods can be altered with regard to type of fibre dye and the end use. Therefore, researchers should consider the structure of dye and fibre. The researchers should also have knowledge how this bonding of fibre and dye affect the fabric properties. The products of Health, hygiene as well as medical textiles comes under the application area of antimicrobial dyes.

3.2 UV protective dyes

Presently UV ryas are causing various harmful effects. UV protective dyes enhance the UPF (Ultraviolet Protection Factor) of the textiles. UPF means how much a fabric can protect the wearer from harmful UV rays. In general, all dyes act as a UV absorber because spectral region falls into UV region. Various kind of synthetic dyes are commercially available to enhances the UPF of the fabric. Direct, vat and reactive dyes increases the UPF of fabric [85–87]. Various researches reported that natural dyes can also enhances the UPF of the fabric. Absorption characteristics of natural dyes generally determines the UPF of the fabric [88]. Phenolic compounds in natural dyes work as UV protective agent as these molecules absorb the UV radiation. For instance, *R. maritimus, M. philippinensis, K. lacca, A. catechu and A. nilotica* have tannin content (phenolic compond) thus provide good UPF to the fabric. It is also reported in various studies that, Natural dyes from eucalyptus leaf extract, *Xylocarpus granatum* (*Cedar Mangrove*) bark extract, blossoms of broom (*Cytisus scoparius*) and dandelion (*Taraxacum officinale*), Weld, woad, logwood lipstick tree, madder, brasil wood, and cochineal, gromwell roots, *Acacia*, henna dye extract, chitosan and turmeric dye gallnuts, areca nuts, and pomegranate peels banana peel *babool, ratanjot*, annatto and *manjistha* enhances the UPF of textiles [89–95]. Mordants are used with natural dyes to enhances the fastness properties of the dyes. Several studies reported the positive impact of mordant on the UPF of the fabric. But very few studies also reported the negative impact of mordant on the UPF of the fabric. It means type of the mordant, mordanting method also affect the UPF of the fabric [96, 97]. In case of both synthetic as well as natural dyes, several parameters such as concentration of dye, exhaustion time and extraction and exhaustion temperature affect the UPF of fabric [98, 99]. For instance, it is reported that with the increase of concentration of dye, the UPF of dyed fabric also increases. While exhaustion time and temperature are not causing significant change in the UPF of the fabric. Various studies also report the correlation between the dyeing parameters and UPF.

In a study exhaust method was used for the application of herbal plant extract to enhance the UV protection of the fabric. Madder and cutch dye was applied on nettle fabric using exhaust dyeing method [100]. Pad dry cure method were also used for application of UV protective dye [101].

Application of UV protective dyes can be extended mainly to the clothing of outdoor activities such as fishing, farming, horticulture, gardening, building construction, road construction, postcard distribution, oil production field, military defence services, skiing, police work, professional cycling, surfing [102].

S. No	Functional Dyes	Source	Suitable methods of application for textiles	References
1.	Antimicrobial dyes	**Natural source:** Pomegranate (*Punica granatum*) peels, Henna (*Lawsonia inermis*) leaves, *M. composita* leaves, Madder (*Rubia tinctorium*) root, safflower, *Rumex maritimus* (Golden dock), *Indigo (Quercus infectoria) leaves,* Berberine, peony, clove, *Coptis chinensis* (Chinese goldthread) and gallnut *Synthesised source:* direct, cationic, reactive and disperse dyes, Direct Blue 168 dye and copper sulphate, dyes based on azo heterocyclic and/or homocyclic Systems, developed by adding a functional gp (quaternary ammonium salt group) to a traditional aminoanthraquinoid dye, polycationic systems, Synthesised thiazolidinone derivatives, Synthesised monoazo disperse dyes	Treatment of textiles surface with chemicals, chitosan, enzymes, UV radiation, ultrasound	[70–84]
2.	UV protective dyes	*Natural source: R. maritimus, M. philippinensis, K. lacca, A. catechu and A. nilotica* eucalyptus leaf extract, *Xylocarpus granatum* (*Cedar Mangrove*) bark extract, blossoms of broom (*Cytisus scoparius*) and dandelion (*Taraxacum officinale*), Weld, woad, logwood lipstick tree, madder, brasil wood, and cochineal, gromwell roots, *Acacia*, henna dye extract, chitosan and turmeric dye gallnuts, areca nuts, and pomegranate peels, banana peel, *babool, ratanjot*, annatto and *manjistha* *Synthesised source:* Direct, vat and reactive dyes	Exhaust, pad dry cure and microencapsulation	[85–104]
3.	Moth repellent dyes	Saffron flower waste, onion skin, henna, myrobalan, silver oak leaf, madder, wall nut, dholkanali and yellow roots	Simultaneous dyeing	[105–110]
4.	Mosquito repellent dyes	**Natural source:** Pomegranate peel with polyvinyl alcohol **Synthesised source:** *4-Amino-N, N-diethyl–3-methyl benzamide* (MD).	Exhaust, microencapsulation	

Table 2.
Types of functional dyes used in textile industry.

UV protective dye can also be applied to the clothing of Indoor workers who are potentially exposed to UV radiation for example in hospitals where UV radiation is required for some kind of treatments in some laboratory works, plasma torch operating, printing, lithographing, painting, wood curing, plastic working, in some cases food industry also [103]. Army personnel who have been working in extreme climate conditions also experiences intense solar radiation with terrible heat stress also requires protection from UV rays [104].

3.3 Moth proof and mosquito repellent dyes

Moth proof and mosquito repellent dyes provides protection against moths and mosquitos after application on textiles. Synthetic moth proof or mosquito repellent are generally available in colourless form. Therefore, moth proof and mosquito repellent dyes available in natural form. Various natural dyes contain tannin which can also act as a moth proofing agent. It has been reported in a research that the natural dyes having more than about 40% tannin is effective as an anti-moth agent. In various studies, it was reported that natural dye extracted from Saffron flower waste, onion skin, henna, myrobalan, silver oak leaf, madder, wall nut, dholkanali and yellow roots provides anti-moth properties after application on textiles [105]. Application of dye extracted form pomegranate peel with polyvinyl alcohol can act as mosquito repellent [106]. The mosquito repellent property of synthesised *4-Amino-N, N-diethyl–3-methyl benzamide* (MD) coupled with three different naphthol were assessed. Cotton fabric dyed with MD and naphthol showed very good and durable mosquito repellence. *N, N-diethyl-m-toluamide* (DEET) is used to synthesise the MD [107]. Pomegranate peels Extract can also act as mosquito repellent dye after its application on textiles.

Moth proof dyes were applied using exhaust method in which condition such as (Concentration of colourant-5%, temperature. 90°C degree, M:L- 1;:40, and pH 5–6, were maintained. Simultaneous dyeing with mothproofing agent on wool fabric were also reported. Result of this study showed that undyed and only mordanted fabric provides lesser protection from *D. maculatus* in comparison to madder dyed wool fabric. Mosquito repellent dyes are applied on fabric using either using exhaust method, pad dry cure and microencapsulation methods. [108, 109].

Mothproof and insect repellent dyes is textile museum and library to protect the textiles and books. Mosquito repellent dyes can also be applied to the children's clothing, pram and curtains [110] (**Table 2**).

4. Conclusion

This high technological era is not only based on beautiful products but it is based on "beauty with artificial intelligence". Various researches are being conducted to develop a smart and functional textile which is not only appealing due to its looks but also have an artificial intelligence to give signal according to the change in nearby environment. Dyes can play important role to develop smart and functional textiles. Besides the functionality, sustainable and green aspect of dyeing are also being considered during synthesis and application smart and functional dyes. In comparison to the conventional dyes smart dyes can add a special intelligence to textile fabric such as thermoregulation, camouflaging. Similarly, functional dyes application on textile provides protection form UV rays, unhygienic conditions and insects. Despite of having such an intelligence of to perform according to nearby environment, various smart dyes have lost their ability to develop colour after several molecular transformation. This phenomenon is known as fatigue resistance.

Similarly, functional dyes also have limitation with regards to durability and comfort properties of the fabric. For instance, UV protective dyes have less stability in light and laundry. The fabric dyed with antimicrobial dyes as well as moth and Mosquito repellent also do not have very good wash fastness. These stability-related issue of smart and functional dyes can be enhanced to utilise proper application methods. Different application methods like surface modification (plasma treatment and UV irradiation, etc.) and microencapsulation to enhance the stability of these functional as well as smart dyes. Application method should be such type that could make a balance between comfort properties and stability.

Abbreviations

AI	Artificial Intelligence
UPF	Ultraviolet Protection Factor
UV	Ultraviolet Radiation
PDA	Polydiacetylenes
M:L	Material to liquor ratio

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Chapter

Applications of Metal Complexes Dyes in Analytical Chemistry

Mariame Coulibaly

Abstract

Trace elements, especially heavy metals, are considered to be one of the main sources of pollution in the environment since they have a significant effect on ecological quality. Commonly, the analytical methods for the determination of trace metals are the spectrometry techniques. While, the electroanalytical methods are recognized as a powerful technique for trace metals owing to its remarkable sensitivity, relatively inexpensive instrumentation, ability for multi-element determination at trace and ultra trace level. New alternative electrode materials are highly desired to develop sensitive stripping sensors for meeting the growing demands for on-site environmental monitoring. Dyes aromatic heterocyclic compound, used in food, textile and cosmetic industries has been used for spectrophotometric determination of metals. In electrochemitry, methods for metals determination based on their complexation with dyes were proposed. In this chapter, a brief summary of spectrometry methods and electrochemical sensors for heavy metals detection based on the formation of metals dyes complexes is presented.

Keywords: heavy metals, dyes, dye/complexation, electrochemical analysis, metal complex dye, spectrometry

1. Introduction

Dyes are known to be used in the textile industry, printing, food industry, as well as cosmetic industry. Since the invention of synthetic dyes in 1856, chemistry has been enriched by these large group of chemical compounds. More than 800,000 tons are manufactured by year [1–4]. Dyes are organic substances with chromophore and auxochromic groups (**Figure 1**) classified into several groups (indigoid dyes, xanthene dyes, etc.) of various structures for different applications.

These applications depend on dyes chemical structure, their hue and their entire light absorbing system. The chromophores are the groups of atoms responsible for the dye colour and auxochromes are an electron withdrawing or donating substituents that cause or intensify the colour of the chromophores [6] in shifting the adsorption towards longer wavelength along with an increase in the intensity of absorption. Some commonly known chromophores groups are: azo (–N=N–), carbonyl (–C=O), methine (–CH=, nitro (–NO2) and quinoid groups. The auxochromes are acids or bases; the most important are amine (–NH3), carboxyl (–COOH), sulfonate (–SO3H) and hydroxyl (–OH).

The use of dyes in analytical chemistry is well known. Dyes applications in analytical chemistry are feasible because of the presence of chromophores and auxochromes [7]. Most of dyes form complexes with pollutans in aqueous media [8].

Figure 1.
Structure of the azo reactive dye [5].

They are used as titrations indicator in analytical chemistry, and their complexes with the metal ions in aqueous media are used in spectrophotometric analysis. The complexation between dyes and some essential metals including Cu(II), Hg(II) allows the detection of them by the spectrophotometric method or cromatography [9–11].

As in spectrophotometry, titration, colorimetry or chromatogarphy, dyes are also used in electrochemistry specially in metal ions detection. Electrochemical analysis is recognized to be a method for industrial process control, environmental monitoring, and different applications in medicine [12–16]. The electrochemical technique, especially stripping voltammetry for the trace analysis of metal ions, obtained considerable interest because of its low cost, easy operation, good sensitivity, high selectivity and accuracy [17]. The usual working electrode for stripping voltammetry was a mercury electrode [18] and bare electrodes. However mercury is toxic and causes harm to the environment and human bodies. Concerning bare electrodes, they have numerous limitations such as poisoning, low sensibility, poor stability. Therefore, many groups tried to develop mercury free-electrodes and modified electrode to determine metal ions by voltammetric analysis [19–22]. These chemically modified electrodes (CME) have received an increasing attention in recent years in the fields of electroanalysis due to well recognized advantages in comparison with conventional electrodes [23]. Several reagents and techniques are used to modify the electrodes surfaces [24–28]. The complexation reactions with organic or inorganic reagents on electrodes surfaces, incorporate in electrode paste or in solution for electrochemical anaysis have been reported [29–32]. Among them, the dyes which are important complexing agents for metals. Electrochemical methods for metal ions determination based on their reaction with dyes, their complexation with dye film on electrode surface or inside of electrode paste have been studied [33–35].

2. Metal-complex dyes in spectrophotometric analysis

2.1 Overview

Many studies have been based on the spectrophotometric determination of metal ions after their reactions with complexing reagents including dyes [36–38]. The dyes are organic substances with chromophore and auxochrome groups which can be classified in different type. Among these different type of dyes, azo dyes represent the largest production volume. They make up about 70% of all synthesized dyes annually [39]. The importance of these may increase in the future and also their use in a variety of applications such as complexing agent in spectrophotometric analysis. However, their stability causes environmental pollution once the dyes are discharged with liquid effluents without adequate treatment before release into the natural environment.

The formation of dye complex depends of the number of ligands in the dye structure, and the coordination number of the metal. The electron donating ligand or ion combines with the metal ion to form the complex. For instance, for copper ion which is a bivalent ion with coordination number four, it can complexed with two bidentate ligands in an acid dye or a trivalent or a tetravalent one [40]. Metal-complex dyes formed may be broadly divided into two classes: 1:1 metal complexes and 1:2 metal complexes [41]. These complexes have versatile application in various fields include the dyeing of nylon and protein fibers, paint, toners for photocopiers, laser and ink-jet printers, photoconductors for laser printers, nonlinear optics, singlet oxygen generators, dark oxidation catalysts, and high-density memory storage devices [42]. Their colors span the entire spectrum allowing their use in spectrometry.

By UV–Vis Spectrophotometry, the absorption spectra of solutions allows the determination of metals concentration. The absorption spectra of dye soltution and metal ions solutions are measured first Then, after the mix of the dye and the metal ion, the formation of coloured complex between the both compound give a new color peaking and a new absorption spectra.

2.2 Spectrophotometric determination of trace metal by formation of complexes with dye

It well know that dyes can form a stable complexes with metal ions. Dyes applications in spectrophotometric analysis are possible because of the presence of chromophores and auxochromes (**Figure 2**) [7]. Dyes especially the azo dyes are used as spectrophotometric chemosensor. These compounds interact easily with metal ions through the heteroatoms S, N, and O and can chelate with a large number of metal ions to form a metal-dye complex (**Figure 3**). Numerous works have been dedicated to the synthesis and spectral characterization of new azo dyes and their metal complexes [44, 45]. These studies allow to establish the optimal conditions of formation of the complexes (ratio metal: dye, pH, temperature, the maximum light absorption, the influence of foreign ions …) and the determination of the constants of complexes.

The complex formation equilibrium and formation constant of the complex can be represented by Eqs. (1) and (2) [46].

$$M + nL \rightarrow ML_n \tag{1}$$

$$K = \frac{[ML_n]}{[M][L]^n} \tag{2}$$

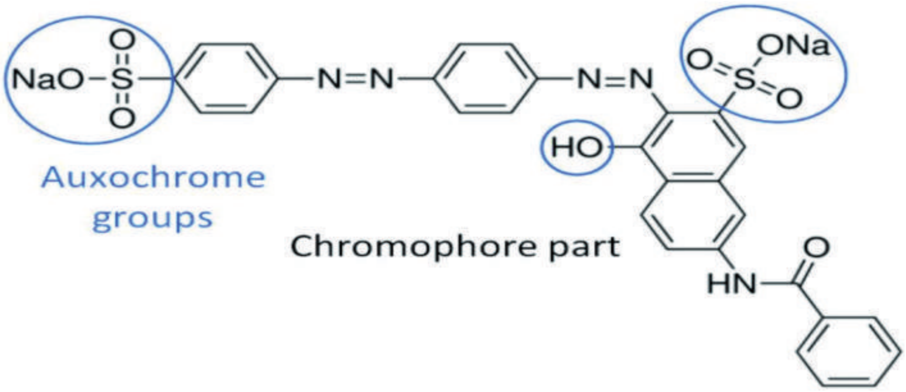


Figure 2.
The light absorption system of dyes [43].

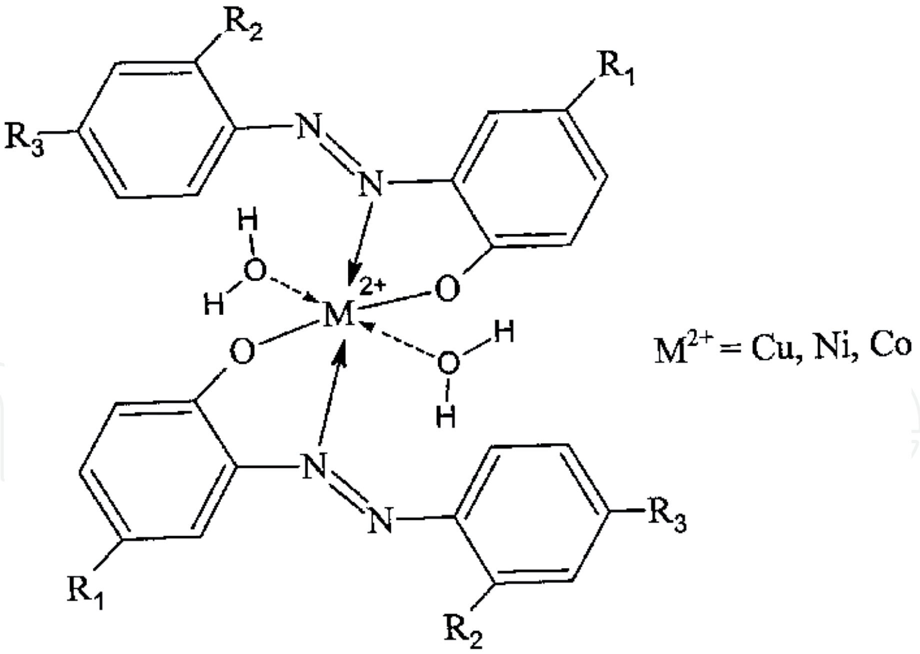


Figure 3.
Chemical structure of the azo-metal chelates [44].

[M], [L] and [MLn] represent the molar equilibrium concentrations of the metal ion, ligand dye and the complex, respectively.

Thus, several new spectrophotometric methods for determination of metal ions based on their complexation with dyes have been developed and tested in real samples [47–49]. Bonishko et al. [48] have developed, a simple spectrophotometric method for the determination of osmium (IV) ions, based on the formation of a complex of this metal with Congo Red. While, the orange G has been used as a complexing reagent in spectrophotometric determination of osmium(IV) by Rydchuk et al. [49]. They showed that the optimum conditions for the formation of coloured complex compound between Os(IV) and acidic monoazo dye Orange G (OG) were: the stoichiometric ration in the complex was 2:1 at pH = 5.80. Moreover, their study showed that at the room temperature Os(IV) practically did not interact with OG. Os(IV)-OG compound was almost fully obtained after 30 min of heating on a boiling water bath (~98°C).

In general, the formation of complexes lead a significant decreases in the absorption band of the dyes and the emergence concomitantly of a new absorption band with different absorbance. Thus, the formation of complex species between mercury and indigo carmine((Hg)IC and (Hg)2IC) allowed a optical determination of mercury [36]. The interaction between Cu(II) ions and indigo carmine forms Cu2(IC) complex characterized by the stoichiometric ratio between indigo carmine and copper 2:1, the molar absorptivity 1.17 x 10^4 mol L^{-1} cm^{-1} at 715 nm and the stability constant of the complex log K = 5.75, at pH 10, obtained by spectrophotometric data. This complex has been successfully tested for determination of copper in pharmaceutical compounds [37].

3. Electrochemical method for the determination of trace metal by formation of complexes with dye

3.1 Electrochemical behaviour of dye

The electrochemical behaviour of dyes depends of their characteristics, the working electrodes and the pH of supporting electrolyte. According nature of electrodes, the voltammograms of dyes exhibited irreversible oxidation peaks [50] or can be involved in a two or more steps redox reaction [51]. The voltammetric response of indigo carmine shows two well separated peak pairs on graphite electrode (**Figure 4**) at pH 7, while the first pair of peak disapear at ph more basic.

As indicated previously, azo dyes are an important class of organic dyes which consist of at least a conjugated chromophore azo (–N=N–) group. This is the largest and most versatile class of dyes. These dyes are characterised by the presence in their molecules of one or more azo groups —N=N— which form links with organic groups, of which at least one is usually an aromatic nucleus (**Figure 2**). Taking account their potential toxicity, electrochemical methods was developed for the analyzing of azo dye. The mechanism based on the reduction of the azo group with a classical dropping mercury electrode or static mercury drop electrode has been described in detail [52]. Recently, several modified electrodes have been used to study the electrochemical characteristics of azo dyes and their electrochemical determination [54–57]. On a glassy carbon modified, the voltammograms exhibited a irreversible oxidation peaks and a well-resolved oxidation wave was observed at approximately 0.74 V for the azo dye sudan I, sudan II, sudan III, and sudan IV [50] and similar irreversible oxidation peaks was obtained with the congo red on graphene oxide modified electrode [56]. However, the release potential of anodic peak depends of dye and electrode.

These studies show that some of azo dyes are electrochemically reactive. They can reduced or oxidized on different bare or modified electrode (**Table 1**). These electrochemical behaviour allows the detection of dye by voltammetric technique but also the detection of trace metals based on the decrease of dyes oxidation/reduction peak after their complexation.

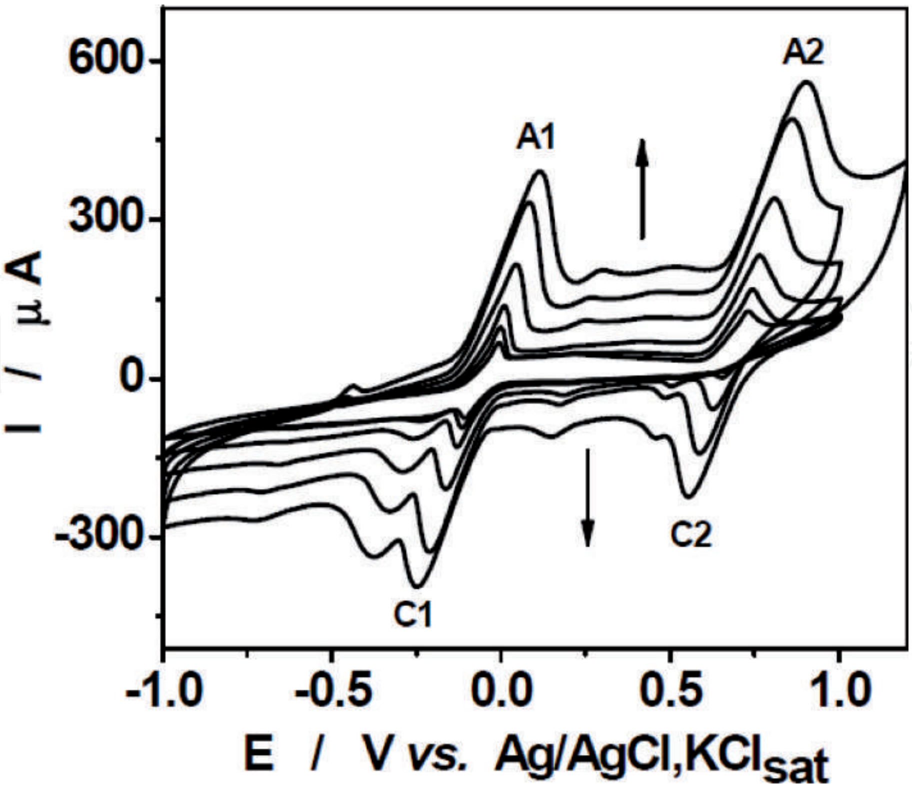
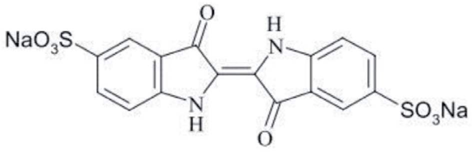
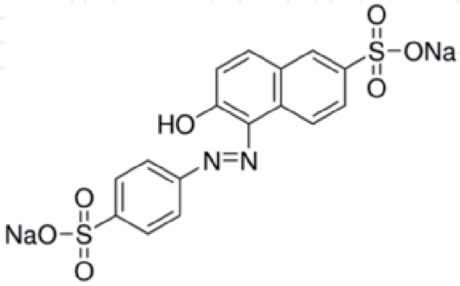
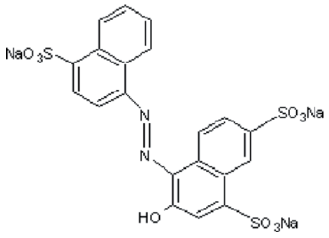
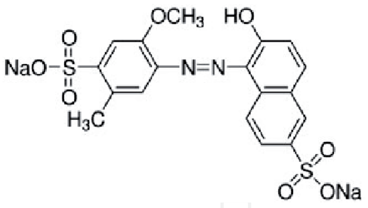
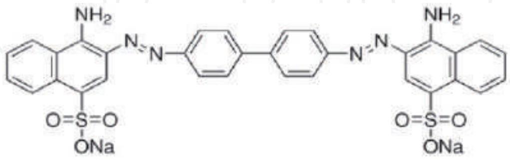
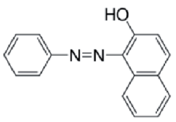
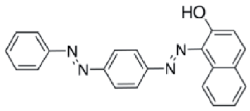
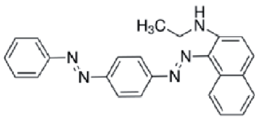


Figure 4.
Cyclic voltammograms recorded at graphite electrode for 10–3 M IC. Experimental conditions: supporting electrolyte 0.1 M phosphate buffer (pH 7); start potential, −1.0 V vs. Ag/AgCl,KClsat; scan rates: 25, 50, 100, 250, 500 and 750 mV/s. [51].

Electrode	Dye/structure	Electrochemical behaviour	Reference
Graphite	Indigo carmine 	Two pairs reversible oxidation and reduction	[51]
Nanoclay modified carbon electrode	Sunset yellow 	Irreversible oxidation	[58]
Amalgam electrodes	Amaranth 	Irreversible reduction	[52]
Amalgam electrodes	Allura Red AC 	Irreversible reduction	[52]
Graphene oxide casted glassy carbon electrode	Congo red 	Irreversible oxidation	[56]
Carbon nanotube ionic liquid gel modified glassy carbon	Sudan I, II, III and IV  Sudan I  Sudan III  Sudan IV	Irreversible oxidation	[55]

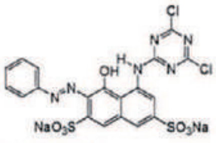
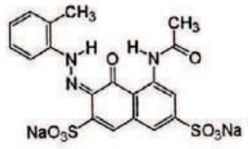
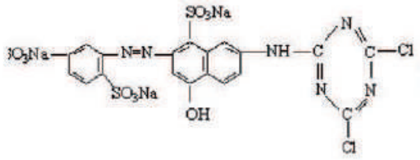
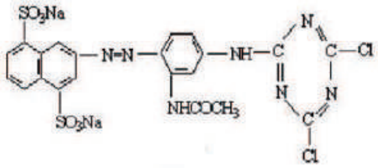
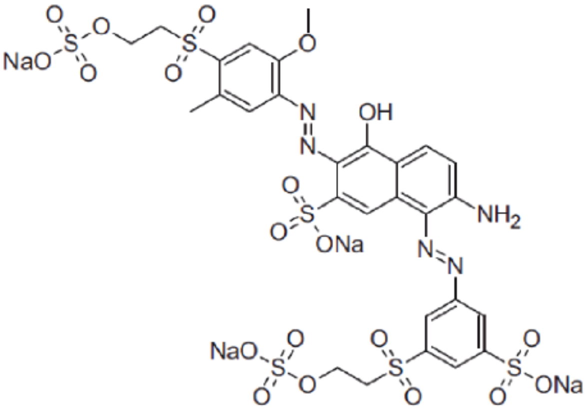
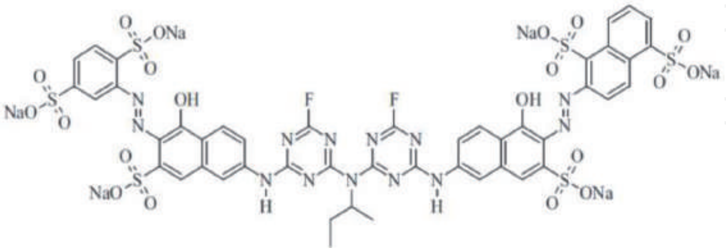
Electrode	Dye/structure	Electrochemical behaviour	Reference
Glassy carbon electrode.	Reactive Brilliant Red x (RBR x-3b); Acid Red 6b (AR 6b); Reactive Yellow x-rg (RY x-rg); Reactive Orange x-gn (RO x-gn)  RBR x- 3b  AR 6b RO x- gn  RY x- rg 	Irreversible oxidation	[59]
Graphite carbon electrodes.	Novacron Deep Red C-D;  Novacron Orange C-RN 	Reversible oxidation reduction	[60]

Table 1.
Electrochemical behaviour of some dyes investigated in electrochemistry.

3.2 Detection of metals using their reaction with dyes

The coordination complexes of metals with azo-ligands are used in several applications due to the interesting material properties synthetized. The metal complexation by dyes modify the photophysical and coloristic properties of dyes. The formation of complexes are influenced by several by parameters such as dye concentration, dye structure, pH, temperature, solvents and ionic strengths [61]. This reaction is due to the interactions by Van der Waals forces, hydrogen bonds and hydrophobic interactions [62]. In electrochemistry, the metals complexation with dyes has been investigated for the selective determination of metals trace by voltammetric techniques. For this, the oxidation/reduction current of dye is measured in the presence and the absence of metal ions. The decrease of the redox peaks caused by the formation of electro inactive complexes is function of the metals concentration and allows their determination. Thus, an electrochemical method for Cu(II) determination based on its reaction with indigo carmine (IC) in alkaline medium and differential pulse voltammetry performed at graphite electrode, was elaborated [51]. When Cu(II) ions are added to an alkaline solution of IC, the Cu2IC complex is formed [51]. This complex electro-inactive at the working potential trains the decrease of the oxidation peak current, which is depending on Cu(II) concentration. The detection limit was 4.74 μM [51]. The complexation studies between the indigo carmine food dye and mercury were carried out [63] and used for the determination of Hg (II) by electrochemical method. These studies show the suitability of voltammetric detection of metals trace using a decrease of oxidation/reduction current of dyes due to the formation of electro inactive metal -dye-complexes. However, there is very little work in literature concerning this approach. In general, these are electrodes modified by dyes which are used for the detection of metals in electrochemistry.

3.3 Dye modified electrodes for the determination of metal

The chemically modified electrodes have received an increasing attention in recent years in the fields of electroanalysis due to well recognized advantages in comparison with conventional electrodes [23]. The methods for modified electrode preparation are varied. The construction of dyes modified electrodes can be done by electrodeposition [64], by sol–gel method, by incorporation of dye into the carbon paste [65], by composite dye film or by the polymerization of dye on electrode surface. Thus, electrodes modified by chitosan -dye-enzyme composite film or copper complex dye (C.I. Direct Blue 200) film have been reported [64]. Studies have also been carried out on the polymerisation of dyes as modified agent. The poly-congo red (PCR) has been used to modified electrodes by electro-deposition [66, 67] or by polycondensation [5]. However, in voltammetric measurement, the polymerizations of congo red reported are generally carried out with the incorporation of poly congo into other components. These components can be polymers such as aniline [58] or nanoparticles [66]. We will notably encounter the synthesis of poly pyrole on glassy carbon in the presence of Congo red in view of the detection of dopamine [67], but also the use of poly Congo red in composition with nanoparticles such as CdS for the quantification of α-1-fetoprotein [66], several studies also relate to the use of Congo red in the presence of nanotube [59]. However, the use of dye as modifying reagent in electrochemical analysis is limited. Very little works about this topic have been reported in literature.

4. Conclusion

Dyes are widely used for industrial, printing, food, cosmetic and clinical purposes as well as in analytical chemistry. They play an important role in spectrophometry and electrochemistry analysis as complexing reagent for the detection of metal ions but they potential is still underestimated in electroanalysis.

It is well known that thousands tons of synthesis dyes are annually produced worldwide. Despite considerable work in recent years on the synthesis of new dyes which can be used reagent for the determination of trace amounts metals, the use of dye as modifying agents is still limited in electroanalysis. Further investigations are required to synthesis dyes in function of metal and use them to modified electrodes for electrochemical determination of metal ions.

5. Future outlook

The ill effects of metals on health and the environment are well documented, yet there is a lack of reliable, robust, cheap, and accurate sensors for monitoring toxics metals level in environment. Although much progress has been achieved in the last few decades in the field of chemically modified electrodes, techniques developed so far in electroanalysis have used very little the properties of dyes. This signifying that more research and development of new electrodes or new metal complexes for spectrophotometric analysis are required. The inconvenients of current sensors concern largely on their reproductibilty, sensitivity and their selectivity toward target metal. The cost associated with portable nature and speciation analysis are also a limiting factor.

Thus there is an urgent need to synthesis new dyes in function of target metal for the application to the electroanalysis of metal cation and in spectrophotometric analysis. Several investigations can therefore be carried out: synthesis of new dye as ligand for metal complexation; study of physicochemical characteristics of new synthesis ligands; study of their electrochemical behavior and complexation; characterization of metal dyes complexes for the electro and spectro analysis; polymerization of dye; thermodynamic study of the complexation of metal cations in poly-dye/poly film dye; study of chemically modified electrodes (ECM) by dye and their application to the detection of metal ions, etc.

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Chapter

Structure and Properties of Dyes and Pigments

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Abstract

Colour is one of the elements of nature that makes human life more aesthetic and fascinating in the world. Plants, animals, and minerals have been used as primary sources for colourants, dyes or pigments since ancient times. In our daily life, we know about many substances which have specific colours. These are the substances which are used as colourants i.e.; colour imparting species. Both dyes and pigments are coloured as they absorb only some wavelength of visible light. Their structures have Aryl rings that have delocalized electron systems. These structures are said to be responsible for the absorption of electromagnetic radiation that has varying wavelengths, based upon the energy of the electron clouds. Dyes are coloured organic compounds that are used to impart colour to various substrates, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials. A Dye is a coloured compound due to the presence of chromophore and its fixed property to the acid or basic groups such as OH, SO_3H, NH_2, NR_2, etc. The polar auxochrome makes the dye water-soluble and binds the dye to the fabric by interaction with the oppositely charged groups of the fabric structure. Pigments are organic and inorganic compounds which are practically insoluble in medium in which they are incorporated. Dyes and pigments are the most important colourants used to add colour or to change the colour of something. They are widely used in the textile, pharmaceutical, food, cosmetics, plastics, paint, ink, photographic and paper industries. This chapter is devoted to the structure and properties of dyes and pigments.

Keywords: Structure, Colourants, Chromophore, Auxochrome

1. Introduction

Colour provides a significant glimpse of our world. Everyday materials we tend to use different kinds of materials like - textiles, paints, plastics, paper, and foodstuffs. Colours make them most appealing. In summer there is a wild burst of colourful flowers and new leaves of various shades of green on trees [1]. However, in contrast, autumn makes the beautiful impression with green leaves turn to brilliant shades of yellow, orange, and red. Colour derives from the spectrum of light interacting in the eye with the spectral sensitivities the light receptors [1, 2].

A dye is nothing but a coloured substance that has an affinity to the substrate to which it is being applied. The dye is applied in an aqueous solution and needs a mordant to boost the fastness of the dye on the textile fibre. The pigment may be a material that modifies the colour of mirrored or transmitted light as the result of wavelength-selective absorption. Pigments are used for colouring paint, ink, plastic, fabric, cosmetics, food and other materials.

Both dyes and pigments appear to be coloured as a result of absorption of some wavelengths of light more than others. However, there are some basic differences between the dyes and pigments

- The major difference between the dyes and the pigments is that particle size of pigments is much higher as compared to dyes. Due to this small particle size dyes are not UV stable whereas pigments are UV stable.
- Dyes after dissolving in liquid are absorbed on the material while pigments make a suspension with a liquid that bonds with the material surface.
- Dyes are generally soluble in water while pigments are almost insoluble in water.
- Most of the dyes are organic while most of the pigments are inorganic
- Dyes are available in large number in the market while the number of pigments is very less.
- Dyes impart colour by selective adsorption while pigments adsorb colour either by selective adsorption or by scattering of light.
- Dyes are combustible while pigments are non-combustible.
- Dyes have a short lifetime in comparison to pigments.

Over the years, man has used colouring matters, which are known as dyes and pigments, for their aesthetic qualities and used them to embellish various articles and the world in which he lived. Indigo, the oldest known dye, was discovered in India; Tyrian purple (or Royal Purple) was discovered in the ancient city of Tyre; Alizarin was discovered among the Turks; and Cochineal was discovered among European and Mexican dyers [3]. Indigenous dye-yielding plants have been discovered in almost every area of the world. The first synthetic dyes were found in the early twentieth century. Parenteral administration was not formulated until the 1930s: methylene blues and methyl violet, for example, were used to treat leprosy and filariasis, respectively [4]. Following World War II, the use of intravenous dyes for medicinal purposes decreased rapidly. Just a few dyes, such as patent blue V or fluorescein, are still used as diagnostic drugs today [5].

The textile industry now uses more synthetic dyes. Coal tar and petroleum-based intermediates are the two main sources of these chemicals. Powders, granules, pastes, and liquid dispersions are all available [6, 7]. Active ingredient concentrations usually vary from 20 to 80 percent. The textile dye segment is distinguished by the introduction of new dyes. These new dyes are produced on a regular basis to meet the demands of new technologies, new types of fabrics, detergents, and developments in dyeing machinery, as well as to address the significant environmental issues posed by some existing dyes [8–10]. With the rapid shift in the textile industry's product profile, from high-cost cotton textiles to durable and flexible synthetic fibres, the pattern of dye use is also shifting rapidly. Polyesters now account for the majority of dye use. Disperse dyes, which are used in Polyesters, are expected to expand at a faster pace as a result. Textile dyestuffs may be grouped into the following groups for better comprehension if general dye chemistry is used as one of the classification criteria as acid dyes, direct dyes, azoic dyes, disperse dyes, sulphur dyes, reactive dyes, basic dyes, oxidation dyes, mordant dyes (chrome dyes) and vat dyes [11–15].

2. Historical background of dyes and pigments

In the ancient age usually used all the dyes were natural. Some of the natural dyes used in ancient age were alizarin and indigo. Indigo is probably the oldest known dye obtained from the leaves of dyers woad herb *Isatis tinctoria*, and the indigo plant *Indigofera tinctoria* [16]. Early dyes were obtained from animal, vegetable or mineral sources, with no to very little processing. The first synthetic dye, mauve, was discovered serendipitously by William Henry Perkin in 1856. The discovery of mauveine started a surge in synthetic dyes and inorganic chemistry in general.

Artists invented the first pigments—a combination of soil, animal fat, burnt charcoal, and chalk—as early as 40,000 years ago, creating a basic palette of five colours: red, yellow, brown, black, and white. In the early age man used earth pigments on cave walls such as yellow earth (ochre), red earth (ochre) and white chalk. Ochres are probably the oldest known pigments, which are coloured clays found as soft deposits within the earth [17–21].

2.1 Reason for the colour of a dye

Many theories have been given to correlate the colour of dyes with their molecular structure. In 1876, Otto Witt, a German Chemist observed that the colour of a dye is due the certain groups containing multiple bonds known as chromophores. Some examples of the chromophores are nitro group(-NO_2), nitroso group(-NO), carbonyl group(-CO-), ethylenic bond(-C=C), acetylenic bond etc. As the number of chromophores increases for a dye, the colour of the dye also deepens [17–21].

He also observed that not only the chromophores are responsible for the deepening of colour but also there are certain groups which itself does not act as the chromophore but the presence of which deepens the colour of the dye. These groups are known as Auxochromes. Some examples of the auxochromes are -OH, -NH_2, -NHR, -NR_2, X (Cl, Br or I), COOH. 1,3-Dinitronapthalene (**Figure 1**) is pale yellow but the dye Martius Yellow (2,4-Dinitro-1-naphthol) is orange-red (**Figure 2**) [17–21]. Here group -OH is acting as the autochrome as the presence of it has deepened the colour of 1,3-Dinitronapthalene.

To explain the origin of colour, Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT) are proposed in modern time. The vital difference between the VBT and MOT is that in VBT electrons are treated in pairs while in MOT electrons are treated singly [17–22].

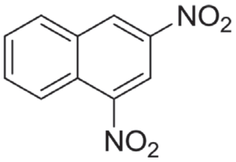


Figure 1.
1, 3-Dinitronaphthalene.

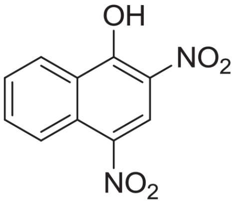


Figure 2.
2,4-Dinitro-1 naphthol.

I. **Valence bond theory (VBT):** According to VBT, in the ground state the electron pairs of a molecule are in a state of oscillation and absorb a photon of appropriate energy and get excited when placed in the path of a beam of light. The wavelength of a photon of light adsorbed depends upon the energy difference between the ground state and the excited state.

II. **Molecular orbital theory (MOT):** According to MOT, whenever a molecule absorbs a photon of light, one electron is transferred from bonding (non-bonding) orbital to an anti-bonding orbital. Based on different type of electron present in a molecule, different types of electronic transitions are possible.

3. Nomenclature

The chemical names of dyes are very complicated hence trade names are more popular instead of their chemical names. From the ancient time humans have tried to extract the dyes from plants and other natural sources to colour their clothes and other belongings, such dyes are known as Natural Dyes. Indigo and Alizarin are two examples of natural dyes. As the natural dyes have very few colours and shades so now a day's most of the used dyes are synthetic dyes having several colours and shades. Almost all synthetic dyes are aromatic and obtained from coal-tar [22]. Hence synthetic dyes are also called coal-tar dyes. Dyes can be classified by the following ways;

I. **Based on their constitution:** In this classification dyes are classified based on the functional group to which the dyes owe their colour. Some examples are *azo dyes, nitro dyes, nitroso dyes, triphenylmethane dyes, indigoid dyes, phthalein dyes, acridine dyes etc.*

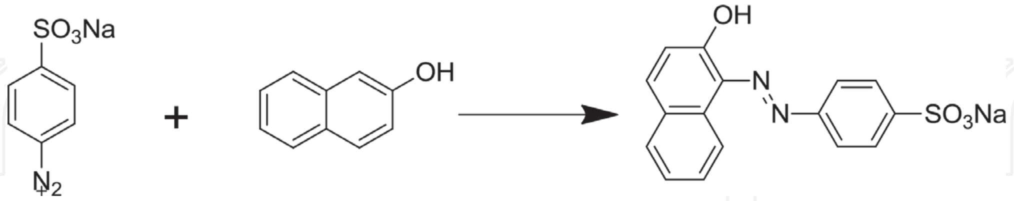
II. **Based on their application:** The colouring of dye on a particular fibre depends on the nature of both the dye and the fibre. A dye molecule can be attached to fibre by following methods;

- Covalent Bonds
- Hydrogen Bonds
- Ionic Bonds
- Van Der Waals Forces

Based on application dyes can be categorised as follows;

I. **Acid dyes:** The sodium salt of azo dyes containing sulphonic acid ($-SO_3H$) and carboxylic acid(-COOH) groups are called acid dyes. To colour the fabric from these dyes the acidic solution of these dyes is used. These can be used to colour wool, silk, nylon and polyurethane fibres. The affinity of acid dyes for nylon is very high due to the higher protonation of the free amino group present in polycaprolactam fibres. Orange-I (**Figure 3**), orange-II, methyl orange and congo red are some examples of it [22, 23].

The dye orange I and orange II can be obtained by coupling diazotised sulphonic acid with α and β- Naphthol respectively.



Diazotisedsulphonic β-Naphthol Orange-I acid sodium salt

II. **Basic dyes:** Those dyes which are salts of coloured bases containing amino or dialkylamino group as autochrome is known as Basic dyes. These include triphenylmethane and azo dyes. Modified nylons and polyesters can be dyed with the help of these dyes [22, 23]. Some examples of basic dyes are aniline yellow (**Figure 4**), butter yellow (**Figure 5**) and chrysodine G (**Figure 6**).

III. **Direct or substantive dyes:** These are water-soluble dyes hence they can be applied to the fabric directly [22, 23]. Congo red and Martius yellow (**Figure 7**) are two examples of these dyes.

IV. **Disperse dyes:** These are water-insoluble dyes and applied to the fabric in the form of a dispersion in presence of some stabilising agent such as phenol, cresol or benzoic acid. The two examples of disperse dyes are Celliton fast pink B and Celliton fast blue B [22, 23].

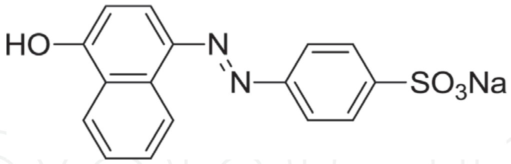


Figure 3.
Orange-I.

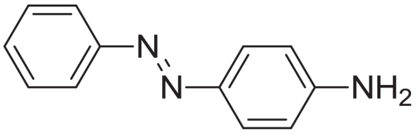


Figure 4.
Aniline yellow.

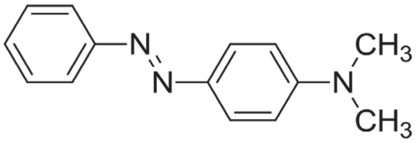


Figure 5.
Butter yellow.

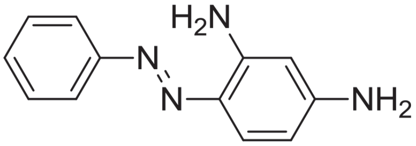


Figure 6.
Chrysodine G.

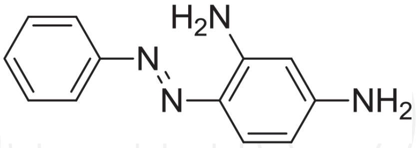


Figure 7.
Martius yellow.

V. **Fibre reactive dyes:** These dyes contain a reactive group which combines directly with the hydroxyl or amino group of the fibre. As a permanent bond formed between the fibre and dye in this case so the colour of the dyed fabric is very fast and has a long life [22, 23].

VI. **Ingrain dyes or insoluble azo dyes:** These constitute about 60% of total dyes used. These dyes are obtained by the coupling of phenols, naphthols, arylamines, aminophenols. These dyes are adsorbed only on the surface of the fabric, colouring by this dye is not so fast. These can be used to dye cellulose, silk, nylon and leather [22, 23]. Para red (**Figure 8**) is an example of such a class of dye. Para red (**Figure 8**) dye can be prepared as follow:

These dyes are also used in foodstuffs, cosmetics, drugs and as an indicator in chemical analysis.

VII. **Vat dyes:** Vat dyes are insoluble in water so they cannot be used directly for dyeing. They are first reduced to soluble colourless form (leuco form) with a reducing agent such as an alkaline solution of sodium hydrosulphite. Under these conditions, the leucoform develops an affinity for cellulose fibres [22, 23]. Hence these dyes are mainly used to dye cotton fibre. The example of vat dyes is indigo (**Figure 9**).

VIII. **Mordant dyes:** Those dyes which do not bind directly but require a mordant to dye the fabric directly come under this category. The mordant act as the binding agent between the fibre and the dye.

Metal ions are used as mordants for the acid dyes while tannic acid is used as the mordant for basic dyes. The desired fabric is first soaked in the suitable metal salt and then this soaked fibre is dipped in the solution of dye when insoluble coloured complexes formed on the fabric. These insoluble coloured complexes are called

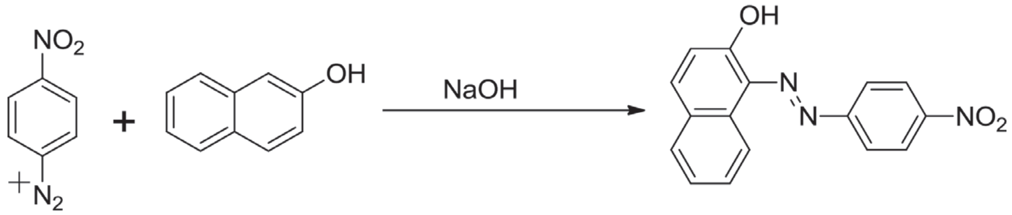


Figure 8.
Para red.

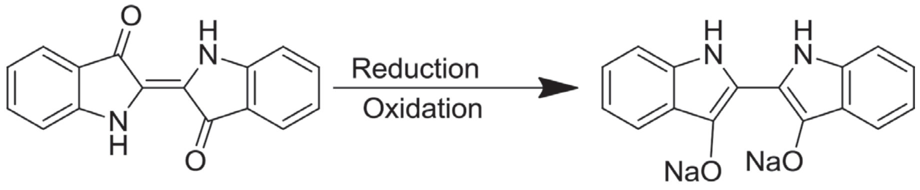


Figure 9.
Indigo or Indigotin (Leuco form).

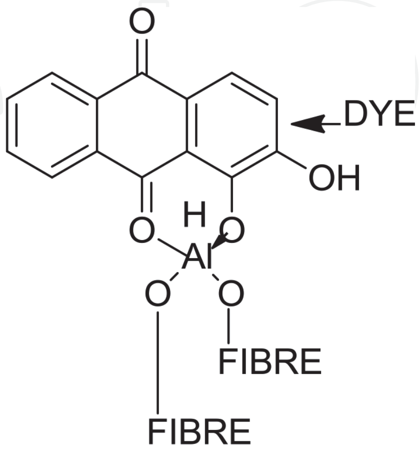


Figure 10.
Alizarin-aluminium fibre complex (rose red lake).

lakes [22, 23]. So, the metal ions first get attached to the fabric and then the dye molecules are linked to the metal ion through covalent and or coordinate bond (**Figure 10**).

4. Classification of dyes based on their constitution

4.1 Azo dyes

These dyes constitute the largest part of the synthetic dyes. The chromophore of the azo dyes is aromatic system joined to the azo group and auxochromes are NH_2, NR_2, OH.

Azo dyes are classified as the number of azo group in the molecule such as monoazo, diazo and triazole etc. The characteristic of two important azo dyes methyl orange (**Figure 11)** and congo red can be described as follows:

4.1.1 Methyl orange

It is obtained by coupling of N, N-dimethylaniline with diazotised sulphanilic acid.

Properties: Methyl orange is a colouring dye for the wool and silk but its colour fades on the exposure to the light and washing. Usually, it is not used as a dye but

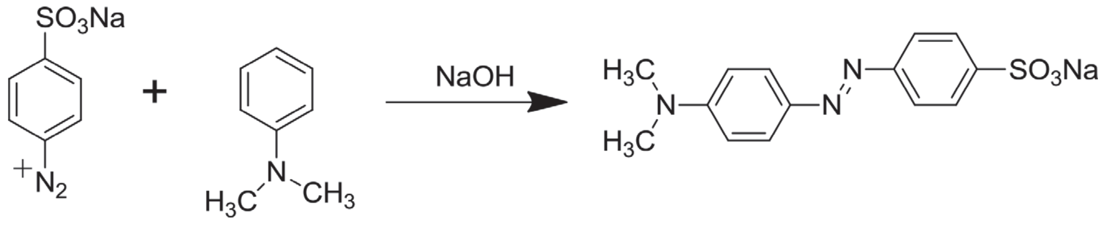


Figure 11.
Methyl Orange.

used as an indicator in the acid–base titrations. The pH range of methyl orange is 3.1–4.4. It is yellow in basic solutions (above pH 4.4) while red in acidic solutions (below pH 3.1) [24–26]. The colour change takes place because of the change in the structure of ions in acidic and basic medium. In acidic medium, the ion contains p-quinonoid chromophore while in basic medium ion contains azo chromophore (**Figure 12**).

4.1.2 Congo red

Congo red (**Figure 13**) is the example of diazo dye as it contains two azo groups. It is obtained by the coupling of tetrazotised benzidine with two molecules of napthionic acid (4-aminonapthalene-1-sulphonic acid).

Properties: it is a direct dye and sodium salt of this dye gives red colour on the applied cotton. As on addition of acid, its colour changes so it is also not used as a dye generally. Mostly it is used as an indicator. It is blue in acidic solution (below pH 3) and red in solutions (above pH 3). The change in colour from red to blue in the acidic solution is due to the resonance among charged canonical structures.

4.2 Triphenylmethane dyes

These are the derivatives of -NH_2, -NR_2, and -OH groups in the rings. The compound obtained by this method are generally colourless and called leuco bases. On oxidation, these are converted to the corresponding colourless tertiary alcohols called carbinol bases. These carbinol bases readily change from the colourless benzenoid form to the coloured quinonoid forms in the presence of acids due to salt formation, which is known to be dye [26–30]. The structure and properties of two important triphenylmethane dyes can be discussed as follows;

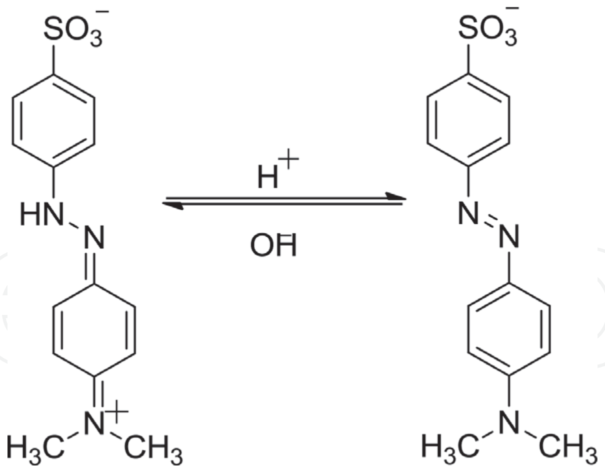


Figure 12.
Red (acidic medium) yellow (basic medium).

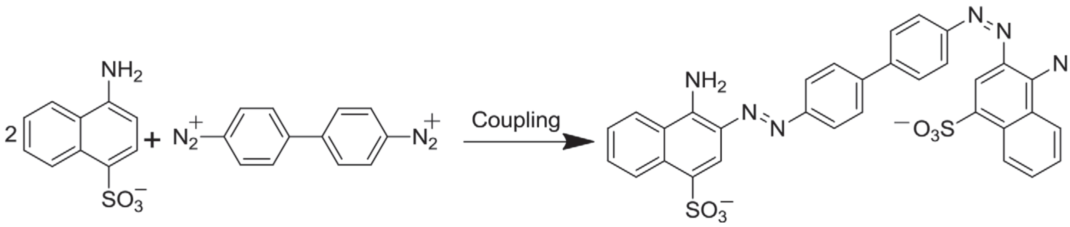


Figure 13.
Congo red.

4.2.1 Malachite green

It is used for dying wool and silk directly and cotton mordanted with tannin. The colour of it fades slowly on the addition of acid and base (**Figure 14**).

4.2.2 Crystal violet

A weakly acidic solution of it is purple, a strongly acidic solution is green and still more acidic solution is yellow (**Figure 15**).

4.3 Phthalein dyes

4.3.1 Phenolphthalein

It is insoluble in water but dissolves in alkalies to form a deep red solution. When an excess of strong alkali is added, the solution of phenolphthalein becomes colourless again. Because of the colour change, it is used as an indicator in acid–base titrations. It is also a powerful laxative (**Figure 16**).

4.3.2 Fluorescein

It is a xanthan derivative. In properties, it more closely resembles phthalein dyes. It is a red powder insoluble in water. It dissolves in alkalies to give a reddish-brown solution which, on dilution, gives a strong yellowish-green fluorescence (**Figure 17**).

4.3.3 Alizarin

It is one of the most important anthraquinone dye. It occurs in madder root in form of its glucoside called, ruberthyric acid.

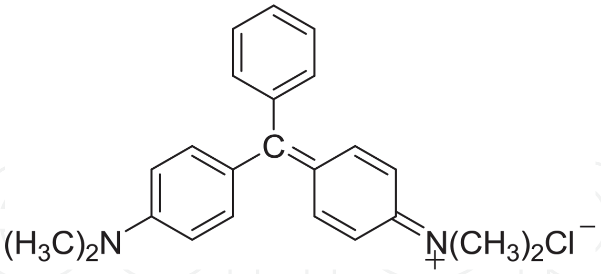


Figure 14.
Malachite green.

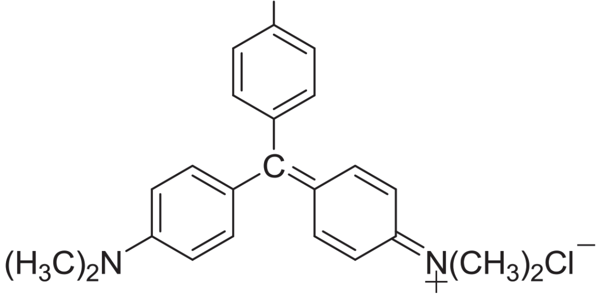


Figure 15.
Crystal violet.

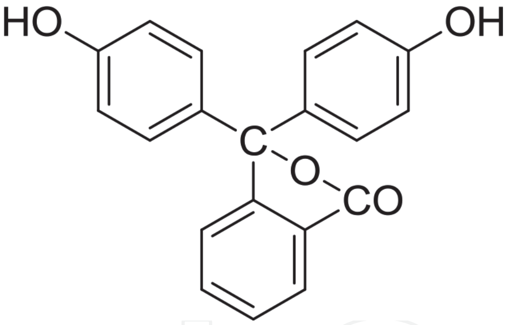


Figure 16.
Phenolphthalein.

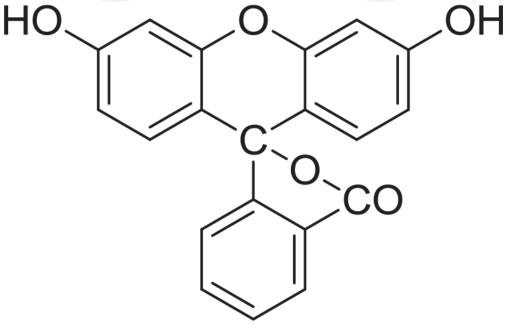


Figure 17.
Fluorescein.

On reduction with zinc dust, it gives anthracene. This implies that alizarin is a derivative of anthracene. It forms ruby red crystals, insoluble in water and alcohol but dissolves in alkalies to form purple solution, sublimes on heating.

It is a mordant dye, and the colour of the lake depends on the metal used. Aluminium gives a red lake, ferric salts give violet-black while chromium salts form a brown-violet lake. It is also used as a purgative (**Figure 18**).

4.3.4 Indigo

It is the oldest vat dye known. India is the birthplace of Indigo (**Figure 19**). A fusion of indigo at a low temperature produces anthranilic acid.

It is a dark blue powder, with coppered lustre, m.p. 663 K. It is insoluble in water and most organic solvents. It is widely used for dyeing cotton. The quality of colour is excellent and is stable to light, washing etc. It is also used in printing inks [26–30].

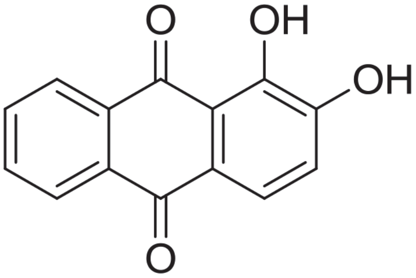


Figure 18.
Alizarin.

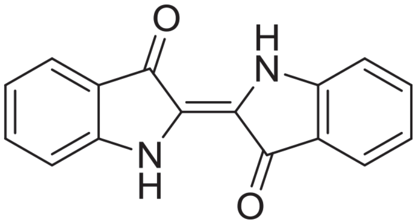


Figure 19.
Indigo.

5. Pigments

Those organic and inorganic substances which are widely used as surface coatings, employed in ink, plastic, rubber etc. to impart colour. A large number of pigments are used for commercial manufacture of paints.

5.1 History of pigments

Pigments are believed to be 3.5 lakh to 4 lakh years old. They have been reported in a cave at Twin Rivers, near Lusaka, Zambia. Blue pigment was derived from lapis lazuli. Pigments based on minerals and clays often bear the name of the city or region where they were originally mined. Synthetic pigments are believed to be introduced in early second millennium BCE. White lead $2PbCO_3$. $Pb(OH)_2$ and blue frit (Egyptian Blue) also known as calcium copper sulphate $CaCuSi_4O_{10}$ are the two examples of early synthetic pigments [17–30].

5.2 Classification of pigments

Pigments are mainly classified into two types:

1. White pigments

2. Coloured pigments

However, they may differentiate broadly into two category organic & inorganic pigments (**Table 1**) [23–26].

S.No.	Organic pigments	Inorganic pigments
1.	Pthalocyanines, Quinacidrones, Dioxazenes, Napthols, and other pigments made in the lab are examples	Examples include phthalocyanines, quinacridones, dioxazenes, napthols, and other lab-made pigments
2.	Plants and plant products are the primary source of organic pigments	Topical cosmetics, as well as dirt, are used to make inorganic pigments
3.	Carbon chains or carbon rings are still found in Organic Pigment molecules.	Metal cations are present in an array shape with nonmetallic anions in the molecules of Inorganic Pigments. This arrangement prevents the pigments from dissolving in the solvent or the plastic.
4.	Organic pigments have a high index of refraction	Inorganic pigments have significantly lower values
5.	Organic pigments are transparent	Most inorganic pigments are opaque

Table 1.
Difference between Organic & Inorganic Pigments.

5.2.1 White pigments

They are of various types. The composition, properties and applications of some white pigments can be summarised as follows;

5.2.1.1 White lead {$2PbCO_3.Pb\ (OH)_2$}

The composition of the Lead Carbonate is 68.9% and Lead Hydroxide is 31.1%. It is used in the manufacture of paints.

Properties:

- Easily applied
- High covering power
- Toxic in nature
- Yellows badly on exposure to the atmosphere
- Soluble in alkali and paints

5.2.1.2 Sublimed white lead (basic sulphate)

The composition of Lead Sulphate is 75%, Lead Oxide 20% and zinc oxide 5%. It is used in the manufacture of paints.

Properties:

- High specific gravity and refractive index
- Slow chalking out of the film producing a rough surface

5.2.1.3 Zinc oxide (ZnO)

The composition of Zinc Oxide is 100%. It is opaque to UV light and thus protects us from UV, prevents chalking.

Properties:

- Brilliantly white having excellent texture
- Causes no discolouration even in contact with CO_2 gas
- More durable in combination with white lead

5.2.1.4 Lithopone

The composition of lithopone is 28.30% zinc oxide and 72.70% barium sulphate. It is widely used for the cold water paints, traffic plants, floor covering and oilcloth industry.

Properties:

- Extremely fine and cheap pigment
- Good hiding power

- Not as durable as white lead and zinc oxide

5.2.1.5 Titanium dioxide

It consist of $TiFeO_3$, TiO_2 (iliminite+rutile). It is widely used in paints, in paper and textiles.

Properties:

- High capacity and hiding power
- High oil-absorbing capacity
- Spreading power is almost double as that of white lead
- No tendency of chalking

5.2.2 Blue pigments

Ultramarine Blue and Cobalt Blues are the most widely used blue pigments. The composition, properties and applications of these can be summarised as follows:

5.2.2.1 Ultramarine blue

There are three varieties of ultramarine namely blue, white and green. It is used as bluing in laundering to neutralise the yellowish tone in cotton and linen fabrics. White Ultramarine Blue: $Na_5Al_3Si_3SO_{12}$, Green Ultramarine Blue: $Na_5Al_3Si_2S_2O_{12}$, Blue Ultramarine Blue: $Na_5Al_3Si_2S_3O_{12}$.

Properties:

- Silicate skeleton have a potential influence on the colour
- Colour is because S present is in the form of polysulphide.

5.2.2.2 Cobalt blues

The composition of cobalt blues is 30–35% Co_3O_4 and 65–70% Al_2O_3. It is used in the manufacture of blue paints, inks, carbon paper and carbon ribbons.

Properties:

- Very expensive and are not used in paints for ordinary purposes.

5.2.3 Red pigments

These are one of the oldest-pigments. They are mainly used for inhibiting rusting of iron and steel structures. The composition, properties and applications of these can be summarised as follows:

5.2.3.1 Red lead

It consists of Pb_3O_4 and PbO, used for a primary coat on structural steel and in imparting red colour to the glass for making bangles.

Properties:

- Bright-red powder with a high specific gravity
- Excellent covering power
- Inhibits corrosion

5.2.3.2 Synthetic iron (Fe_3O_4)

It is widely used in domestic paints, enamels, floors and paints.

Properties:

- Has a dark brilliant colour
- High covering power and tinting strength

5.2.4 Green pigments

There are two types of commonly used green pigments. The composition, properties and applications of these can be summarised as follows:

5.2.4.1 Chrome green (Cr_2O_3)

It is generally used as green pigments.

Properties:

- High power of oil absorption.
- It has disadvantages such as lack of brilliancy and opacity

5.2.5 Chromium oxide or guignet's green [$Cr_2O(OH)_4$]

It is used as paint for metal surface and as non-fading green for washable distempers.

Properties:

- Have high covering power
- High corrosion inhibition capacity

5.2.6 Black pigments

They have good tinting strength and as well as high hiding power. The composition, properties and applications of these can be summarised as follows:

5.2.6.1 Natural black oxide

The composition of Fe_2O_3 is 94–95%. It is used in making paints for priming metal.

Properties:

- Oil absorption power is 10–15 kg of linseed oil per 100 kg of Pigment

5.2.6.2 Precipitated black iron oxide

It is used in cement emulsions and water paints. It has a high hiding power.

5.2.6.3 Carbon black/furnace black

It is used in making waterproof paints.
Properties:

- Increases the life of paints
- Good tinting strength
- Not affected by light, acids and alkalies

5.2.6.4 Lamp black

It is used in making black pigments.
Properties:

- Good tinting strength
- Resistant to high temperature

5.2.7 Yellow pigments

The composition, properties and applications of these can be summarised as follows:

5.2.7.1 Ochre

It consists of naturally occurring yellow Fe_2O_3. It is used in the paint industry.
Properties:

- Fast to light
- Inert to chemical action

5.2.8 Chrome yellow

It is used in making yellow paints.
Properties:

- Great opacity
- High brilliance
- High hiding power
- High tinting strength

5.2.9 Toners

Insoluble organic dyes are known as tonners. These can be used as pigments, quite durable and have high colouring power. Various dyes such as para red, Hansa Yellow G (lemon yellow), Hansa Yellow 10G (primrose yellow) etc. have been used as toners in the pigment industry.

5.2.10 Metallic powders as pigments

The powdered form of some metals, as well as some alloys, are used as pigments. Finely powdered aluminium and bronze have been used as pigments in lacquers. Pigments containing finely powdered zinc have been used for protective coatings on iron and steel to protect them from atmospheric corrosion [17–30].

6. Conclusions

This comprehensive chapter on structure and properties of dyes and pigments including some specific applications has been discussed. Moreover, recently the consumers have become very much conscious about the environment, renaissance of eco-friendly products and process like dyeing textiles with natural dyes, which has thus become also important now. Thus, revival of natural dye application on textiles and summary of earlier researches on standardisation of its method of extraction, mordanting, dyeing process variables and even natural finishing, etc. have been elaborated in this chapter. Thus this part has become a unique comprehensive chapter for information on structure and properties of dyes and pigments.

Conflict of interest

There is no conflict of interest.

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Chapter

A Brief Comparative Study on Removal of Toxic Dyes by Different Types of Clay

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Abstract

Increasing amount of organic dyes in the ecosystem particularly in wastewater has propelled the search for more efficient low-cost bio adsorbents. Different techniques have been used for the treatment of wastewater containing toxic dyes such as: biological degradation, oxidation, adsorption, reverse osmosis, and membrane filtration. Among all these processes mentioned, adsorption with low cost adsorbents has been recognized as one of the cost effective and efficient techniques for treatment of industrial wastewater from organic and inorganic pollutants. Clays as material adsorbents for the removal of various toxic dyes from aqueous solutions as potential alternatives to activated carbons has recently received widespread attention because of the environmental-friendly nature of clay materials. This chapter presents a comprehensive account of the techniques used for the removal of industrial cationic and anionic dyes from water during the last 10 years with special reference to the adsorption by using low cost materials in decontamination processes. Effects of different adsorption parameters on the performance of clays as adsorbents have been also discussed. Various challenges encountered in using clay materials are highlighted and a number of future prospects for the adsorbents are proposed.

Keywords: adsorption, toxic dyes, Clays, wastewater treatment

1. Introduction

The treatment of industrial wastewater particularly loaded with dangerous dyes is considered among the global environmental issues and the concerns of researchers [1]. According to recent reports, over one million dyes are available commercially with an annual output of over $7x10^5$ tons [2]. The textile industry around the world consumes approximately 10^4 tons of dyes annually and discharges about 100 tons of dyes into wastewater every year [3]. These dyes are highly toxic, carcinogenic, and cause dire consequences for human health and the marine system. The removal of these toxic dyes from polluted water and wastewater is highly desirable in order to meet regulatory obligations for wastewater recycling or discharging into natural environments [4]. Currently, there is several physico-chemical and biological technologies in the use for the treatment of these polluted effluents namely, ion exchange, membrane separation, biological treatment and adsorption [5–10]. Physico-chemical processes such as ion exchange, electro dialysis and reverse osmosis are expensive, difficult to operate and require significant technologies. While in recent years, adsorption has continued to attract the attention of the researchers worldwide [11, 12] and appears to be an alternative, which has some advantages such as simple design, and ease of operation. Whereas, the biological treatment which is based on the microbial digestive metabolism, has the major drawback of the risk of microbiological contamination and a significant production of sludge, which poses problems of storage and handling [13, 14]. In the present work a comparative study between the capacities of raw, synthetic and modified clays for the removal of toxic dyes from aqueous solution has been given, with particular review of the main factors influencing the adsorption of dyes by clays such as pH of the solution, temperature and initial dye concentration on the adsorption capacities of the these clays.

2. Removal methods for toxic dyes

Currently, a number of different technologies and methods such as membrane separation, ion exchange, adsorption and biological methods are widely used for the removal of toxic anionic and cationic dyes from polluted water and wastewaters.

2.1 Membrane filtration

Membrane separation is a pressure driven process. Pressure-focused processes are generally divided into four overlapping classes of increased selectivity: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and hyperfiltration or reverse osmosis (RO). Microfiltration can be used to remove bacteria and suspended solids with pore sizes from 0.1 to microns. Whereas, Ultrafiltration eliminates colloids, viruses, and some proteins by pores from 0.0003 to 0.1 microns. Nanofiltration is based on physical rejection based on molecular size and charge. The pore sizes are between 0.001 and 0.003 microns [15]. Reverse osmosis has a pore size approximately 0.0005 microns and can be used for desalination. High pressures are needed to makepass water through the membrane from a concentrated solution to dilute. Shih [16] has studied the elimination of dyes on membrane and explored the parameters that could influence the efficiency of toxic dyes removal by membrane technologies such as parameters source, membrane type and membrane process.

2.2 Ion exchange

Ion exchange has been widely used to remove dyes due to its many advantages, such as high processing capacity, speed and increasing the efficiency of dye retention [17]. Ion exchange resin, either natural or resin solid synthetic, has the specific ability to exchange its cations with dyes in wastewater. Among materials most used in the ion exchange process, synthetic resins: are commonly preferred because they are effective in virtually removing dyes in solution [18].

2.3 Adsorption

Adsorption is a process in which solids are used for removing organic and inorganic substances from either gaseous or liquid solutions. The phenomena

Removal process		**Advantages**	**Disadvantages**
Chemical methods			
	Photo-catalyst	Low cost operational and economically feasible	Some photo catalyst degrades into toxic by-products.
	Ozonation	No sludge generation	Operational cost is very high, half life is short (20 min)
Biological methods			
	Anaerobic degradation	By-products can be used as energy	Resources under aerobic conditions require more treatment and yield of methane and hydrogen sulphide
	Aerobic degradation	Operational cost is low and effective in removal of azo dyes	Provide suitable environment for growth of microorganisms and very slow process
Physico-chemical methods			
	Adsorption	High adsorption capacity for all dyes.	Low surface area and high cost of some adsorbents.
	Ion exchange	No loss of sorbents	For disperse dyes not effective
	Membrane filtration	Effective for dyes with high quality effluents	Production of sludge and suitable for treating low volume

Table 1.
Separation techniques and their advantages and disadvantages [21, 22].

driven adsorption are operative in most natural physical, biological, and chemical systems. The solid adsorbents widely used in the industries for the removal of these pollutants from industrial wastewater are diverse such as activated carbon, metal hydrides and synthetic resins.

The adsorption process involves the separation of a substance from one phase by retaining it on the surface of another. The physical adsorption is mainly due to weak interactions such as van der Waals bonds and the electrostatic forces created between the adsorbate and the atoms which make up the surface of the adsorbent. The capacity of this process depends some parameters namely, adsorbent properties, adsorbate chemical properties, temperature, and pH of the medium. It should be noted that even if the adsorbents are available, they are still expensive and few of them are selective. Therefore, over the last decades the research has been redirected towards the search for other improved materials which will meet certain requirements such as regenerative capacity, easy availability, and cost effectiveness. Consequently, clays adsorbents have drawn attention to many researchers and characteristics as well as application of many such adsorbents are reported [19, 20]. However, clays adsorbents are discussed herein after. A summary of advantages and disadvantages of some separation methods are presented in **Table 1**.

3. Clay materials used as adsorbents for dye treatment

3.1 Layered double hydroxides (LDHs)

Layered double hydroxides (LDHs) are intensively studied because of their high anionic exchange capacity [23], reuse, larger surface area, porosity, and fundamental properties [24]. They have advantages over commercially available adsorbents in terms of low cost, high adsorption properties, and non-toxicity. The use of LDH

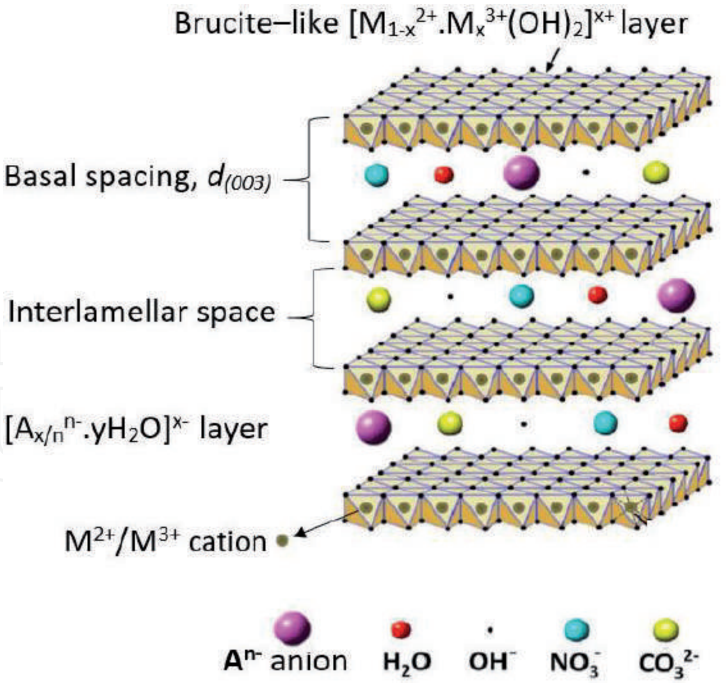

Figure 1.
A schematic representation of the LDH structure [28, 29].

could bring significant economic and environmental benefits to the wastewater treatment industries. Previous works [25] have proven their usefulness as adsorbents for the removal of some organic and inorganic pollutants from polluted water and wastewater. Among the different types of LDH material, a species similar to hydrotalcite, a compound consisting of a double compound of MgAl-LDH hydroxides with carbonate as interlayer anions, is commonly used for various applications [26, 27]. A schematic representation of the general structure of the LDH structure is given in **Figure 1**.

The effectiveness of these compounds in the treatment of polluted water and in particular organic pollutants such as textile dyes has already been demonstrated by various research teams [30–33]. Studies that have been done by Elmoubarki *et al*. [34] demonstrate the effectiveness of Layered double hydroxides based on Mg and Fe for the removal of methyl orange. Shan et al. [35] has studied the trapping of Congo red on carbonated HDL Mg (II) /Al (III), this study showed that the materials are more efficient, and have a very high yield of Congo red elimination. **Table 2** shows some adsorbents of the lamellaires types, used for the removal of some toxic dyes from aqueous solutions.

3.2 Kaolinite

The kaolinite group is comprised of trioctahedral minerals such as, chrysotile, antigorite, cronstedite, and chamosite, dioctahedral minerals such as kaolinite, halloysite, dickite and nacrite. It is white and soft clay, composed primarily of the mineral kaolinite, a hydrated aluminum silicate. Commonly, the kaolinite structure group is known to be composed of silicate sheets (Si_2O_5) linked to aluminum oxide/hydroxide layers ($Al_2(OH)_4$) called gibbsitelayers [51]. Additionally, the primary structural unit of this group is a layer composed of one octahedral sheet condensed with one tetrahedral sheet. About the dioctahedral minerals, the octahedral sites are occupied by aluminum, while those of trioctahedral minerals are occupied by magnesium and iron. Kaolinite and halloysite are single layer structures. Furthermore, kaolinite, nacrite and dickite occur as plates; halloysite, which can have a single

Adsorbent	Dye	Reference
NiFe-LDH	Methyl orange	[36]
ZnMgAl–CO_3	Methyl orange	[37]
MgNiAl	Methyl orange	[38]
MgAl- LDH	Methyl orange	[39]
rGO/Ni/MMO	Methyl orange	[40]
ZnO/CuO/γ-Al_2O_3	Methyl orange	[41]
Fe_3O_4/ZnCr-LDH	Methyl orange	[42]
NiAl-LDH	Congo red	[43]
Mg–Al–LDH	Congo red	[44]
CaAl-NO_3	Congo red	[45]
Ni/Fe-CO_3	Congo red	[46]
Mg/FeCO_3	Congo red	[47]
Mg - Al - Cl	Congo red	[48]
Zn-Fe–LDH	Methylene blue	[49]
Mn-Fe–LDH	Methylene blue	[49]
Mg-Fe–LDH	Methylene blue	[49]
GOaerogels/MgAl	Methylene blue	[49]
Zn- Fe -CO_3	Indigo Carmine	[50]
Zn-Cr -CO_3	Indigo Carmine	[50]
Zn-Mn -CO_3	Indigo Carmine	[50]
Zn-Al -CO_3	Indigo Carmine	[50]

Table 2.
Adsorbents used for the removal of dyes.

layer of water between its sheets, occurs in a tubular form. It consists of feldspar and muscovite formed by the alteration of [51, 52], and is a layered silicate mineral composed of a tetrahedral sheet, bonded through oxygen atoms to an octahedral sheet of alumina, which are layered silicate minerals composed of one tetrahedral sheet, linked through the oxygen atoms to one octahedral sheet of alumina octahedra. Nacrite, kaolinite and dickite exist as plates, halloysite occurs in a tubular form, have a single layer of water between its sheets. Rocks having large amount of kaolinite are referred to as kaolin or china clay [53]. Kaolinite contains heterogeneous surface charge is a well-known fact. It is believed that its basal surface has a constant structural charge which is attributed to isomorphs substitutions of Si^{4+} by Al^{3+}. The charge on the edges is due to protonation or deprotonation of surface hydroxyl groups and so it depends on pH of solution. Adsorption can occur on flat exposed planes of silica and alumina sheets. It is least reactive clay. Kaolin has no side effects, no health problems till the fine dust particle is controlled, thus it is safe environmentally [54, 55].

3.3 Bentonite

The most common group of clay used in water treatment is bentonite. It is a low-cost, effective and eco-friendly adsorbent, and it is commonly impure clay consisting mostly of montmorillonite, although some may consist of the rare clay minerals such as, nontronite saponite, and beidellite. Montmorillonite structure is a layer of gypsum site sandwiched between two sheets of silica to form the structural unit [56, 57]. The substitutes are found mainly in the octahedral layer (Mg^{2+}, Fe^{2+}) and to a lesser extent in the silicate layer. The clay mineral group is mainly composed of a hydroxyl-aluminosilicate framework. As well as, the crystal structures of the clay minerals are composed of a combination of silica tetrahedral sheets and alumino octahedral. Apart of the trivalent Al^{3+} is substituted by Mg^{2+} or Fe^{2+} ions in some cases. In such cases, substitution is accompanied by the addition of alkaline metals like Na^+ and K^+ or alkaline earth metals like Mg^{2+} and Ca^{2+} to provide charge balance [57]. Stockmeyer et al. (1991) [58] have investigated the adsorption of some organic compounds from aqueous solutions by using organophilic bentonites. Phenol, diethyl ketone, nitroethane, aniline ethoxy acetic acid, maleic acid and hexadecyl pyridinium bromide were investigated as test organic compounds. The used organophilic bentonites vary in the degree of their total cation exchange capacity exchanged by organic counter ions [58].

4. Parameters influencing the adsorption of dyes by clays

4.1 Effect of pH

The pH value of the solution is an important factor for the adsorption, which influences the structure of the adsorbates and the surface properties of adsorbents [59]. Commonly, at low pH of solution, the adsorption capacity and percentage removal of anionic dyes from aqueous solution increases due to electrostatic forces between the anionic dye molecule and positive surface charge of adsorbent. There is an electrostatic attraction between the positively charged dye molecule and negatively charged adsorbent. Besides, at high pH, the removal efficiency of anionic dyes decreases with increase in pH [60–62]. Whereas, the percentage removal and the amount adsorbed of cationic dyes at high pH increases because positive charges on the dye molecules ensured that they are attracted by anionic adsorbent, so there are electrostatic attractions between the negative surface of adsorbent and positive charges of dye molecules [63–66].

The previously reported literature indicates that optimized pH depends upon nature of dye and type of clay. Zaghloul et al. [67] studies the effect of pH on the removal of methyl orange (anionic dye) from aqueous solutions using synthetic clay type MgAl-LDH. It was observed in the range of pH from 2 to pH = 10, the percentage removal is very important (98%), due to the electrostatic forces between the anionic dye and the positively charged H^+ surface of the synthetic clay as an adsorbent. At higher pH adsorption capacity and percentage removal of dyes decreased and this decrease has been explained by the fact that at pH = 10, number of hydroxyl ions is more and hence the competition between OH^- ions and anionic molecules for active adsorption sites. A similar investigation of the textile dye removal by another adsorbents has been reported by other researchers in the literature [59, 68].

4.2 Effect of temperature

Temperature is a crucial parameter in adsorption reactions. In general, the influence of temperature on the adsorption kinetics is very variable. Adsorption may increase, decrease, or remain constant with increasing temperature. Some studies have shown that a decrease in toxic dyes retention by clay materials is often accentuated by an increase in temperature [69]. Other works have shown that the adsorption of industrial dyes on different adsorbents increases with increasing temperature [70, 71]. Elmoubarki et al. [72] studied the adsorption of methylene blue and methyl orange on synthetic clays of Ni-LDH, Mg-LDH types, in a temperature range (30 to 50 °C). They have observed that the quantities of MB and MO adsorbed as a function of temperature increase with the increase in temperature. On the other hand, the research carried out by Zaghloul et al. [67] on the adsorption of methyl orange by MgAl-LDH (2:1) have shown that the temperature increase from 30 to 35 °C disadvantages the adsorption of methyl orange onto LDH.

4.3 Effect of initial dye concentration

The initial concentration of adsorbate and adsorbent has a great importance in batch and fixed bed column adsorption experiments, because it depends on the nature of the system used. Sureshkumar et al. [73] showed that an increase in the retention of dyes by clays is promoted by an increase in the initial concentration of these dyes. Likewise, the others work [74] shows that the retained concentration of dyes (methyl orange, crystal violet, blue acid) increases with the initial concentration of these dyes. In our previous reports [67], we have studied the effect of initial concentration of methyl orange by MgAl-LDH (2:1), it was observed that the amount of methyl orange adsorbed as a function of temperature increases with increase in concentration. The same remark was recorded by Krika and Benlahbib [75] during the retention of methyl orange by cork powder. They have demonstrated that adsorption process is an effective method because of its efficiency, capacity, and applicability on large scale dye-removal, as well as the potential for regeneration, recovery, and recycling of adsorbents.

5. Equilibrium studies

Equilibrium studies explore the relationship between adsorbent and adsorbate which is described by adsorption isotherms [76]. The adsorption isotherm studies are important both a theoretical and a practical point of view. Further, isotherm data must precisely fit different isotherm models to find an appropriate model that can be used for the design process [77, 78]. The obtained parameters from the different models provide important information on the adsorption mechanisms, the surface properties and affinities of the adsorbent. Several models have been published in the literature to describe experimental equilibrium data of adsorption isotherms. The most famous adsorption models for single-solute systems are Freundlich, Langmuir, Redlich–Peterson, Radke–Prausnitz, Koble–Corrigan, Temkin, Dubinin–Radushkevich (D–R), BET (Brunauner, Emmett, Teller), Sips and Generalized isotherms.

Langmuir adsorption isotherm assumes that the solid surface has a finite number of identical sites which shows homogeneous surfaces. Langmuir equation may be represented as [79]:

$$q_e = q_L \frac{K_L C_e}{1 + K_L C_e} \tag{1}$$

where q_e (mg/g) is the amount of the dye adsorbed per unit weight of clay at equilibrium, C_e (g/L) is the equilibrium concentration of dye in the solution, q_L (mg/g) is Langmuir maximum adsorption capacity and K_L (L/g) is Langmuir constant related to a free energy of adsorption.

The Freundlich isotherm is an empirical equation that assumes that the adsorption surface becomes heterogeneous during the adsorption process. The Freundlich isotherm is expressed by the following Equation [80].

$$q_e = K_F C_e^{1/n} \tag{2}$$

where, q_e (mg/g) is the amount of the dye adsorbed per unit weight of clay; C_e (g/L) is the equilibrium concentration of the dye in the bulk solution; K_f is Freundlich constant, which is a comparative measure of the adsorption capacity for the clay, and n_f is an empirical constant related to the heterogeneity of the material surface.

Zaghloul et al. [67] use a synthetic clay type MgAl-HDL for the removal of methyl orange. The Langmuir and Freundlich models were applied to the experimental data. The results indicated that the Langmuir isotherm fully describes the nature and sorption mechanism of methyl orange (MO) on the synthetic clay used. The adsorption capacity of MgAl-LDH calculated from the Langmuir model was found to be 1250 mg. g^{-1}. The value of 1/n at 298 K was 0.34 (i.e. $(1 < n < 10)$ indicating that the adsorption system solid–liquid studied was favorable. Bentahar et al. [81] have used clay minerals like bentonite, kaolin and zeolite for removal of Congo red dye from aqueous solutions. The results of both Freundlich and Langmuir models indicates that zeolite and bentonite were best described by the Freundlich model, however Langmuir model provided a better fit on the experimental data of kaolin with high R^2 value ($R^2 = 0.98$).

6. Kinetic studies

Kinetic studies are very important in regards of adsorption studies because they can describe the adsorption rate and provide valuable data for understanding the mechanism of adsorption reactions [82]. In order to understand the behavior of the adsorbent and to investigate the controlling mechanism of the adsorption procedure, the pseudo first-order, pseudo second order and intraparticle diffusion models are useful to check the kinetic information [83]. To explore the mechanism of adsorption regarding the adsorptive removal of methylene bleu (MB) by using amino-functionalized attapulgite clay nanoparticle Zhou et al. [84] fitted the experimental data to pseudo-first-order and pseudo-second-order kinetic models. The correlation coefficients of the pseudo second-order kinetic model were relatively greater than those of the pseudo first order kinetic model, implying that the MB adsorption can be described more appropriately by the pseudo-second-order model. Therefore, it can be concluded that a large number of vacant surface sites were available for adsorption during initial stage.

The reviewed research articles regarding kinetic studies show that pseudo-second order kinetic model is more suited to the experimental data compared to other models, however; depending upon the reaction other kinetic models also show correlation to the data.

7. Thermodynamic studies

Thermodynamic investigations are another important parameter of adsorption studies. The determination of thermodynamic parameters is an essential means of describing the energetic mechanism which operates in an adsorbent / adsorbate system during the adsorption process. For thermodynamic studies, the adsorption experiment should carry out at different temperature conditions and calculated parameters included standard enthalpy (ΔH°), standard entropy (ΔS°), and standard Gibbs free energy (ΔG°) [59].

$$K_d = \frac{q_e}{C_e} \tag{3}$$

$$\Delta G^\circ = -RTLnK_d \tag{4}$$

$$LnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{5}$$

Fan et al. [85] have studied the effect of temperature on the removal of methylene bleu by adsorption onto Mt-SB12. The thermodynamic study provides good information about the energetic changes related to adsorption process. The standard Gibbs free energy (ΔG°) values at different temperatures were found negative and standard enthalpy (ΔH°) were positive. These results indicates a spontaneous and endothermic nature of the adsorption process. Furthermore, the positive values of ΔS° reflected an increase in randomness at the solid/solution interface during the adsorption of methylene bleu onto Mt-SB12 [86]. In the same context, Zaghloul et al. [67] studied the effect of temperature on the removal of methyl orange using synthetic clay (MgAl-LDH) at different temperatures 25, 30 and 35 °C. ΔG° values at all temperatures were found to be negative implied that the adsorption of MO on MgAl-LDH was thermodynamically feasible and spontaneous [87]. The negative values of ΔH indicated that the adsorption process was exothermic in nature, and the negative values of ΔS designated a greater order of reaction during adsorption of MO dye by MgAl-LDH, which may be attributed to the adherence of dye molecule with MgAl-LDH adsorbent resulting a decrease in the degree of freedom of the system solid/ liquid [72]. Summary of the thermodynamic studies shows that the sorption process may be exothermic or endothermic for dyes adsorption onto clays.

8. Comparison of adsorption capacities

In order to justify the validity of low cost adsorbent for removal of toxic dyes, its adsorption potential must be compared with other materials used for this purpose. The values of maximum adsorption capacities in term of percentage removal of textile dyes onto different adsorbents reported in the literature are given in **Table 3**. The direct comparison of adsorption capacities of the adsorbents reported in the literature is difficult due to the varying experimental conditions employed in those studies. The adsorption capacity differences of toxic dyes uptake are ascribed to the properties of each adsorbent such as adsorbent structure, functional groups and surface areas.

9. Conclusion

For many decades, the raw, synthetic and modified clays have been considered low-cost and effective adsorbents, which have been successfully used for the adsorption of cationic and anionic dyes from polluted water and wastewater in the laboratory scale, although these several experiments but up to day few of researchers have focused on the use of these clays as adsorbent for the removal of industrial dyes from real effluents. The performance of different types of clays, whether raw,

Adsorbent	Adsorbate	% removal	Reference
NiFe-CO_3	Methyl orange	88	[59]
Mg/Fe-CO_3	Methyl orange	33	[88]
Montmorillonite	Methyl orange	90	[89]
Bentonite modified	Methyl orange	98	[90]
Ni/Al-CO_3	Congo Red	92	[91]
Mg/Al-CO_3	Congo Red	90	[92]
Natural kaolinitic clay	Congo Red	84	[93]
Ca-bentonite	Congo Red	95	[94]
Ghassoul	Methylene Blue	90	[95]
Algerian bentonite	Methylene Blue	91	[96]
Alginate/PVA–kaolin	Methylene Blue	99	[97]
Zeolite	Methylene Blue	88	[98]
Mg/Fe-CO_3	Malachite Green	86	[90]
Raw Moroccan clay	Malachite Green	—	[89]
Bentonite	Malachite Green	90	[98]
Moroccan clay	Basic Red 46	95	[98]
Raw clay (smectite)	Reactive Red 120	88	[99]
Raw clay (kaolinite)	Reactive Red 120	94	[99]

Table 3.
Adsorption capacities of some clay adsorbents for the removal of toxic dyes from water and wastewater.

synthetic or modified, was compared with regard to removing dyes based on some experimental parameters including pH, temperature and initial dye concentration. It was found that synthetic and modified clays provide a greater efficiency relating the removal of these organic pollutants.

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Chapter

Preparation of Functionalized Hydroxyapatite with Biopolymers as Efficient Adsorbents of Methylene Blue

Hassen Agougui, Youssef Guesmi and Mahjoub Jabli

Abstract

In this study, we reported the synthesis of hydroxyapatite modified with biopolymers as λ-carrageenan and sodium alginate, which could be used as effective adsorbents of cationic dyes. Evidence of chemical modification was proved through chemical analysis, Fourier Trans-form Infrared spectroscopy, powder X-ray diffraction, scanning electron microscopy, and specific surface area. The adsorption process was studied using methylene blue as representative cationic dye. The adsorbed quantity reached, at equilibrium, 142.85 mg/g and 98.23 mg/g using hydroxyapatite-sodium alginate and hydroxyapatite-(λ-carrageenan), respectively. However, it does not exceed 58.8 mg/g in the case of the unmodified hydroxyapatite. The adsorption of methylene blue using hybrid materials complied well with the pseudo-second-order suggesting a chemi-sorption. Freundlich and Langmuir isotherm described well the adsorption mechanism of the hydroxyapatite-(λ-carrageenan) and hydroxyapatite-sodium alginate, respectively. The high capacities of MB removal obtained in this study suggest the potential use of these materials in the treatment from wastewaters.

Keywords: hydroxyapatite, biopolymer alginate, dye, kinetic

1. Introduction

Contaminated waters can be successfully treated using inexpensive adsorbents. In this sense, many biopolymers were proposed including cellulose [1–3], chitosan [4, 5], chitin [6, 7], etc. Hybrid materials have attracted a particular attention. The interaction between calcium hydroxyapatite and biopolymers has been the subject of many studies such as carboxymethyl cellulose [8], polygalacturonic acid [9], collagen [10], Agar-Agar [11], polycaprolactone [12], banana peel [13], chitosan [14], and gelatin [15]. Currently, the application of hydroxyapatite modified by biopolymers for immobilization of various pollutants has been considered as a promising pollution control technology [16–20]. For example, Huijuan and colleagues [21] have, recently, reported interesting results about the preparation of hydroxyapatite-Chitosan composite and its efficiency for the removal of Congo red dye from aqueous solution.

The results indicate that the kinetic and isotherm studies showed that pseudo-second-order model and Langmuir model could well describe the adsorption behavior, while thermodynamic investigation of Congo red adsorption by hydroxyapatite-Chitosan composite confirmed a spontaneous adsorption. It has been demonstrated that this composite is an effective and low-cost adsorbent for the dye-polluted water purification [21].

In the same framework, the present work describes the synthesis of hybrid compounds CaHAp-Alginate and CaHAp-(Carrageenan) as an adsorbent using a facile method by varying the content of the bio-polymer. Evidence of interaction between hydroxyapatite and Alg or (λ-Carr) was confirmed using various techniques including FT-IR, SSA, DRX and SEM. The factors that influence the dye uptake by the prepared adsorbents were also investigated and discussed.

2. Experimental

2.1 Synthesis of hydroxyapatite (CaHAp1 and CaHAp2)

Hydroxyapatite was synthesized via co-precipitation method [22, 23]. As starting reagents, analytical grade $CaCl_2$, Na_2HPO_4, $Ca(NO_3)_2.4H_2O$, $(NH_4)_2HPO_4$ and NH_4OH were used. The chemicals equations that describes the reactions is given as follow:

CaHAp1

$$\begin{aligned}&10Ca(NO_3)_2.4H_2O+6(NH_4)_2HPO_4+8(NH_4OH)\rightarrow\\&Ca_{10}(PO_4)_6(OH)_2+20(NH_4^+)+20(NO_3^-)+46H_2O\end{aligned}\tag{1}$$

CaHAp2

$$10CaCl_2+6Na_2HPO_4+2H_2O\rightarrow Ca_{10}(PO_4)_6(OH)_2+12(Na+,Cl-)+8(H+,Cl^-)\tag{2}$$

An aqueous solution of 250 mL of $Ca(NO_3)_2.4H_2O$ or $CaCl_2$ (0.2 M) was added drop-wise to 150 mL of $(NH_4)_2HPO_4$ or Na_2HPO_4 (0.2 M) solution under N_2 bubbling with a stoichiometric ratio of $Ca/P = 1.67$.

The pH was adjusted to 10 by adding NH_4OH solution gradually. After the complete addition, the suspension was matured for 72 h at room temperature under magnetic stirring, the resultant precipitate was filtered, washed with distilled water, and dried overnight at 80°C.

2.2 Synthesis of hydroxyapatite modified by sodium alginate CaHAp1-Alg

A similar procedure of CaHAp1 was adopted to synthesize the modified hydroxyapatite by sodium alginate CaHAp1-(Alg), except for the fact that the $(NH_4)_2HPO_4$was prepared with x mass of sodium alginate (5%, 10% or 20% of the total mass of $Ca(NO_3)_2.4H_2O$ in the starting solution).

2.3 Synthesis of hydroxyapatite modified by sodium alginate CaHAp1-(λ-Carr)

CaHAp2-(Carr) was synthesized, following a similar procedure of CaHAp2, except for the calcium containing solutions that were prepared by mixing 0.05 moles of $CaCl_2$ with x mol (x = 0.0025, 0.005 and 0.01) of (λ Carr).

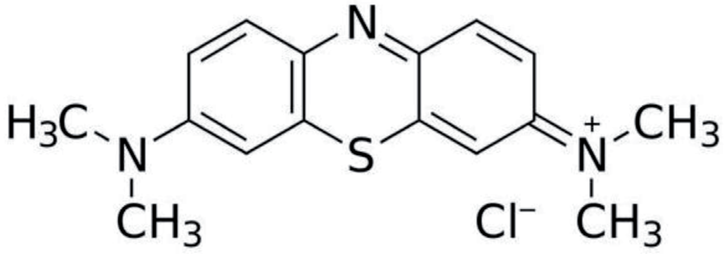

Figure 1.
Structure of methylene blue.

In the text, Hydroxyapatite modified with (λ-Carr) is abbreviated as (CaHAp-(Carr) n), where n represents the mass ratio $\frac{m(Carr)}{m(calcium)}\times 100$.

2.4 Adsorption experiments

MB (its structure is given in **Figure 1**) solution was prepared by dissolving the calculated powder dye in distilled water with different required concentrations. NaOH and acetic acid solutions were used for adjusting the p*H* of the dye solution. For the adsorption experiments, MB solution was mixed with modified hydroxyapatite. MB concentrations were measured before and after experiments using a double beam UV–vis spectrophotometer (UV-1601 Shimadzu, Japan) at 664 nm. The adsorbed amount of dye onto modified hydroxyapatite (q mg/g) was calculated using the following equation [24]:

$$q_e = (C_O - C_e)\,x\,\frac{V}{m} \tag{3}$$

Where C_o and C_e are the initial and equilibrium dye concentration (mg/L), V is the solution volume (mL) and m is the weight of used modified hydroxyapatite sample (g) for the adsorption.

3. Characterization techniques

The FT-IR spectra were recorded on a Perkin Elmer model 597 using KBr pellet method in the 4000–400 cm^{-1} region. X-ray powder diffractograms were obtained at room temperature on a PANalytical X'Pert PRO MPD equipped with copper anticathode tube. The morphological observation of the synthesized samples was undertaken using a JEOL JSM-5400 scanning electron microscope. Specific surface area (SSA) measurements were performed by BET-method (adsorptive gas N_2, carrier gas He, heating temperature 100°C) using an Quantachrome Instruments, model: ASIM. LP2. The pH of the zero point charge (pH_{ZPC}) was determined by putting 0.15 g of adsorbent in a closed Erlenmeyer flask containing 50 mL of NaCl solutions (0.1 M). The initial pH of these solutions was adjusted by either adding NaOH (0.1 M) or HCl (0.1 M) and were then agitated for 48 h at 150 rpm at room temperature to reach equilibrium. The final pH of supernatant was, further, measured and the $\Delta pH = pH\ (final) - pH\ (initial)$ was plotted against the initial pH. The pH at which ΔpH was zero was taken as a pH_{ZPC}.

4. Results and discussion

4.1 Characterization of adsorbents

4.1.1 X-ray diffraction

X-ray diffractograms of hydroxyapatite-Alg and hydroxyapatite-(λ-Carr) are presented in **Figures 2** and **3**. For all compounds, the hydroxyapatite phase is conserved according to 00-024-0033 reference from the ICDD-PDF2 2003 database. However, in the case of CaHAp1-(Alg)20% new peaks appear at $2\theta = 26.60°$ and 30.14°. These peaks are characteristic of monetite phase ($CaHPO_4$) according to 01-077-0128 reference from the ICDD-PDF22003 database. The increase of the amount of biopolymer induced the broadening of peaks, which proves their incorporation on the apatitic surface.

4.1.2 FT-IR spectroscopy

Figures 4 and **5** shows the FT-IR spectra of CaHAp, CaHAp-Alg and CaHAp-(Carr). In all IR spectra, the vibration bands of PO_4^{3-} groups of the apatite structure are observed at (ν_s) 965 cm^{-1}, (δ_s) 482 cm^{-1}, (ν_{as}) 1041-1094 cm^{-1} and (δ_{as})$_,$ 567-605 cm^{-1} [25]. Moreover, for characteristic bands of hydroxyl ions were observed towards (ν_s) 3572 cm^{-1} and (ν_L) 634 cm^{-1} [26].

The two broad bands located at 1403-1462 and 1640 cm^{-1} were assigned, respectively, to the carbonate ions and water adsorbed on the surface. Besides, the band located at 877 cm^{-1} was assigned to the (HPO_4^{2-}) group [27].

After grafting, the intensity of the hydroxyls bands (υ_s and ν_L) decrease progressively with increasing Alg or (λ-Carr) amount. This can be explained by the low degree of crystallinity [28].

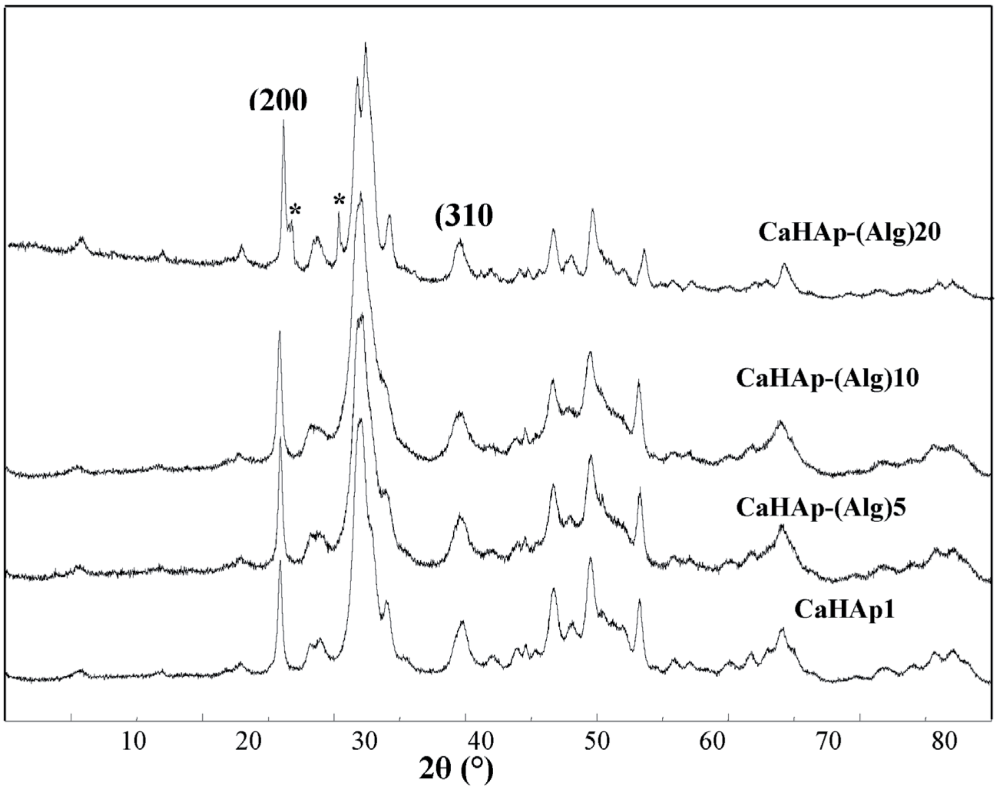

Figure 2.
Powder x-ray diffraction patterns of modified hydroxyapatites by sodium alginate.

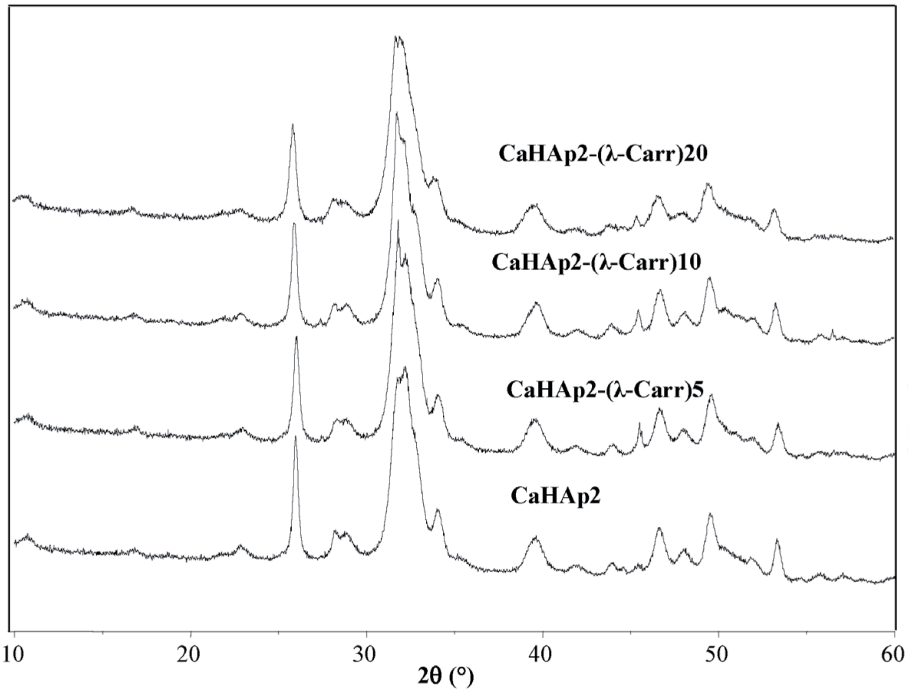

Figure 3.
Powder x-ray diffraction patterns of modified hydroxyapatites by lambda carrageenan.

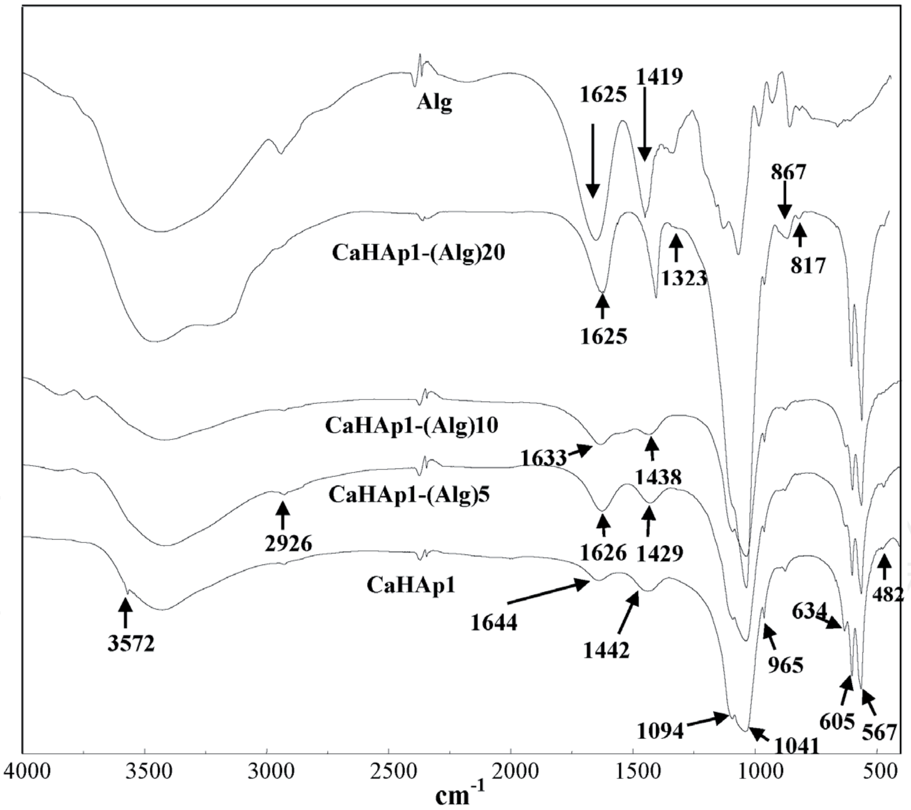

Figure 4.
FTIR spectra of modified hydroxyapatites by sodium alginate.

The presence of biopolymers (Alg or carr) on the apatitic surface is confirmed by the appears of new vibrations bands at 1231 cm^{-1} and (1626, 1323 and 1428 cm^{-1}) which are assigned respectively, to S-O groups of (λ-Carr) and COO^{-} groups of (Alg) [29, 30].

On the other hand, the conservation in the band intensity of P-OH group at 870 cm^{-1} indicates that fixing process of (λ-Carr) or Alg is done only by the interaction

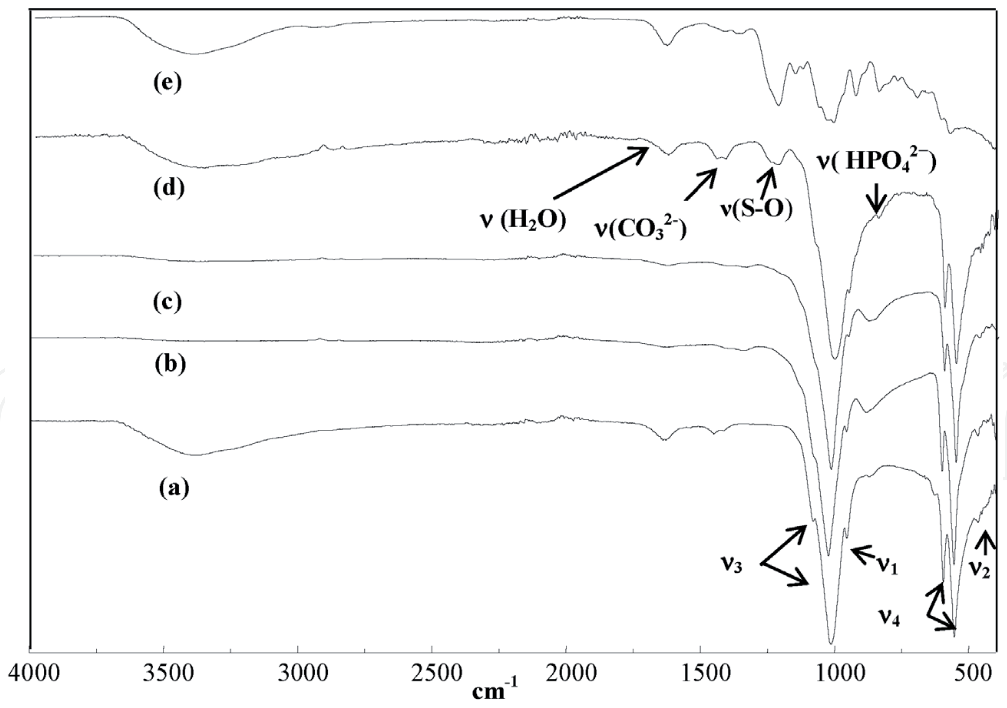

Figure 5.
FTIR spectra of modified hydroxyapatites by lambda carrageenan.

between ≡Ca-OH groups of apatitic surface and functional groups of each biopolymer.

The possible modes of interaction of (Alg) or (λ-Carr) with the CaHAp1 or CaHap2 surface have been gathered in **Figures 6** and 7.

4.1.3 Scanning electron microscope (SEM)

Figure 8 shows the morphological variations of CaHAp1 or CaHAp1 before and after reaction with Alg or (λ-Carr). The CaHAp1 or caHap2 is composed of irregular particles with a strong tendency to aggregate (**Figure 8a, b**), whereas the modified hydroxyapatites showed that their shapes become relatively agglomerates

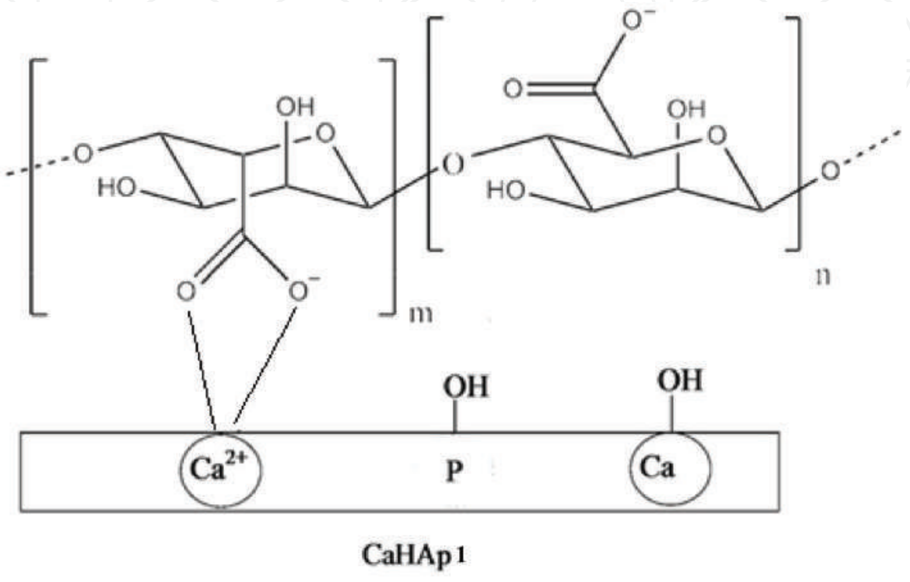

Figure 6.
Proposed mechanism of the interaction between Alg and CaHAp1 surface.

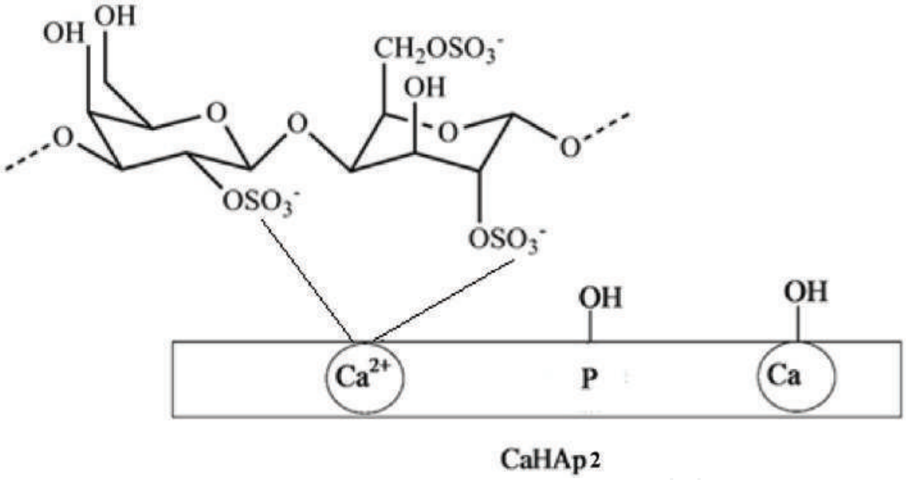

Figure 7.
Proposed mechanism of the interaction between (λ-Carr) and CaHAp2 surface.

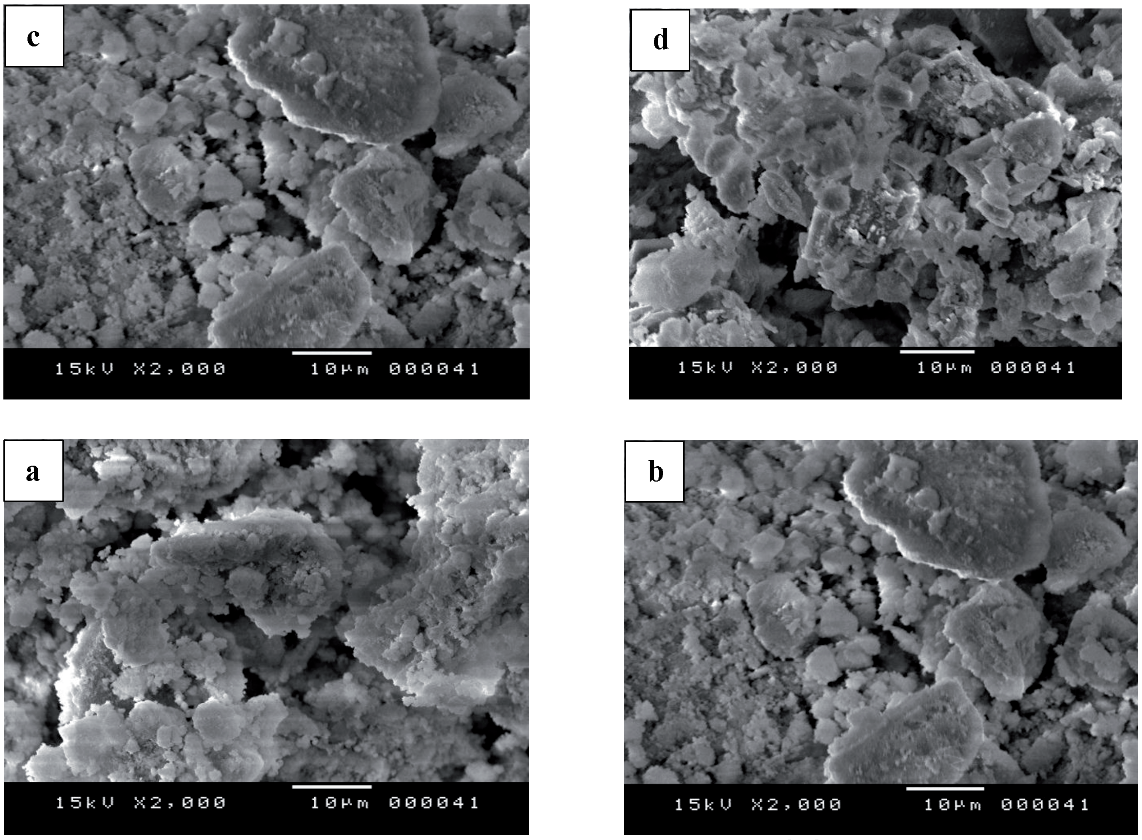

Figure 8.
SEM photomicrograph of modified hydroxyapatites: (a) CaHAp1, (b) CaHAp2, (c) CaHAp1-(Alg)10 and (d) CaHAp2-(Carr)10.

of different sizes and poorly defined shape (**Figure 8**(**c**, **d**)). This change is due to the formation of new hybrid compounds CaHAp2–(λ-Carr) and CaHAp1-(Alg).

4.1.4 Textural properties

The surface characteristics of the Hydroxyapatite samples obtained by the BET method, both before and after modification, are shown in **Table 1**. The treatment of hydroxyapatite with Alg biopolymer leads to the decreasing of specific surface area compared to that of ungrafted CaHAp1, covering the range from 20.52 to 3.39 m^2/g. According to BET results, The fact that the surface area of CaHAp1-(Alg)5 and

Samples	Surface area (m^2/g)
CaHAp1	21.64
CaHAp2	93.00
CaHAp1-(Alg)5	12.84
CaHAp1-(Alg)10	3.39
CaHAp2-(λ-Carr)5	168.00
CaHAp2-(λ-Carr)10	253.00
CaHAp2-(λ-Carr)20	260.00

Table 1.
Measurement of surface area of grafted hydroxyapatites.

CaHAp1-(Alg)10 materials is lower than those in CaHAp1 can be explained with the filling of pores on the surface of hydroxyapatite by sodium alginate biopolymer. On the other hand, the specific surface of modified hydroxyapatite by lambda carrageenan increases with the increasing of grafting rate. The maximum value is obtained for CaHAp2-(λ-Carr) 20 (SSA = 260 m^2/g).

4.2 Evaluation of the performance of the prepared compounds for the adsorption of MB

4.2.1 Effect of pH

Figures 9 and **10** represent the variation of the adsorption capacity of MB on the surface of CaHAp1, CaHAp2, CaHAp1-(Alg) and CaHAp2-(λ-Carr) at different pH values. According to these figures, the MB removal increases gradually up to a pH very close to 5, and after kept nearly constant with further pH increase. The effect

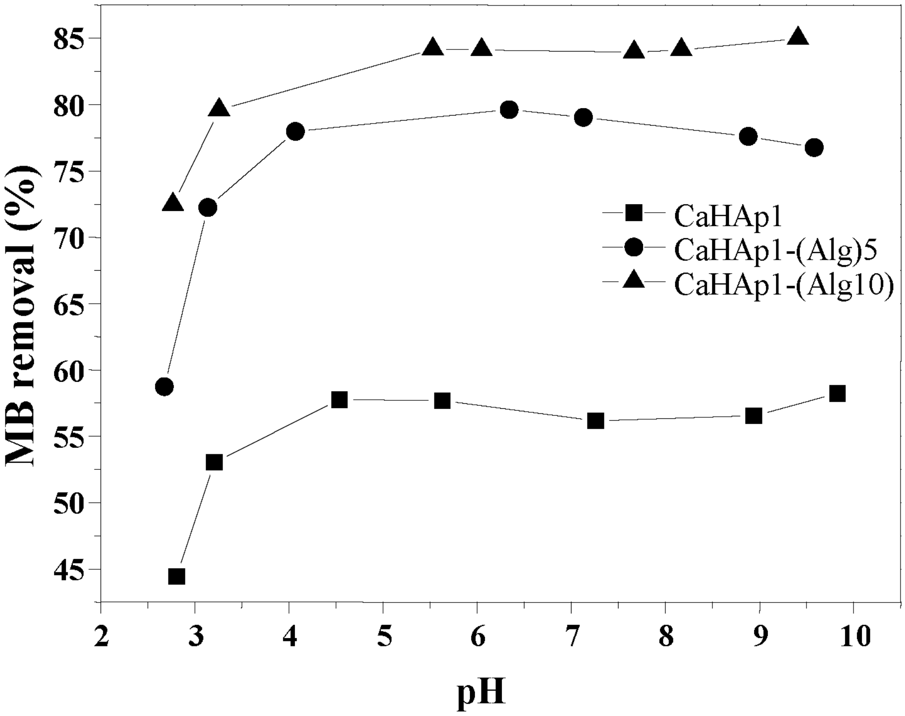

Figure 9.
Effect of initial pH on the adsorption of MB (Adsorbent dosage = 1 g/L, initial MB concentration = 50 mg/L, solution volume = 50 mL, temperature = 25°C, contact time = 3h).

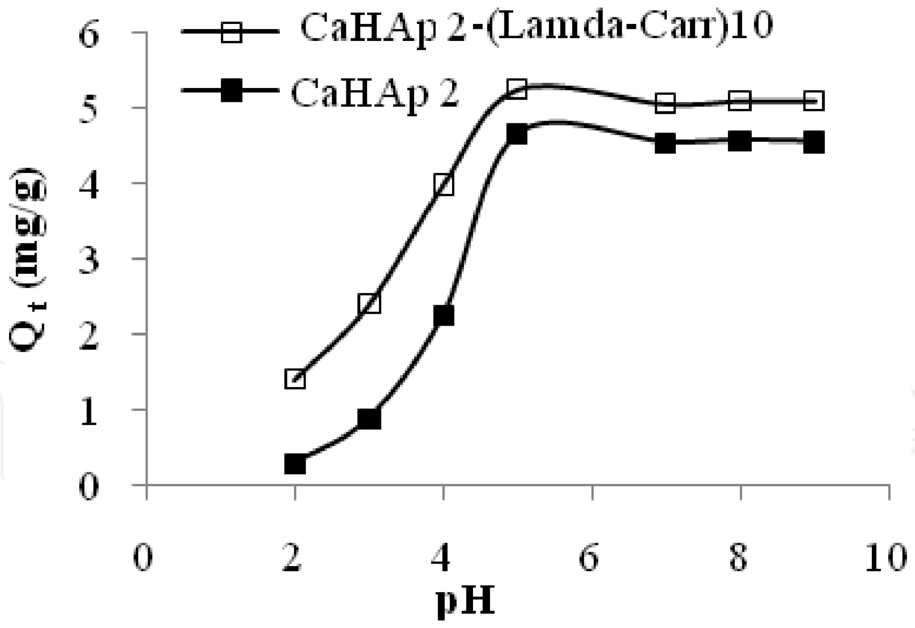

Figure 10.
Effect of initial pH on the adsorption of MB (Adsorbent dosage = 1 g/L, initial MB concentration = 10 mg/L, solution volume =25 mL, temperature = 25°C, contact time = 3h).

of pH on adsorption depends on the point zero charge (pH pzc) of adsorbent. The value of pHpzc was found to be 6.2, 6.7 and 7.3 by CaHAp1, CaHAp2-(Carr)10 and CaHAp1-(Alg)10, respectively, in good agreement with literature data [31]. Indeed, for pH< pH pzc, the surface of hydroxyapatite is positively charged which causes the repulsion of cationic groups of the MB molecule ($=N^+$), and hence low adsorption of dye. In the case of modified hydroxyapatite, the amount of dye adsorbed is higher than unmodified because (Alg) or (λ-Carr) contains carboxylate ($-COO^-$) and sulphonate (OSO_3^-) groups, respectively, that increase the interaction with dye molecules.

4.2.2 Effect of contact time and adsorbent dose

The adsorptions of MB onto modified hydroxyapatites were studied with different biopolymer doses and at different periods of time. As shown in **Figures 11** and **12**, the adsorption amounts of MB on the modified hydroxyapatites increased rapidly with an increase in time and then became slower until the equilibrium was reached. Equilibrium is reached for all compounds prepared at low durations between 20 and 30 min. This may be due to the rapid saturation of the pores of ours prepared adsorbents. The maximum adsorption is obtained for hydroxyapatite synthetized in the presence of biopolymer with 10% content. Therefore, the increase of MB removal with the increasing of adsorbent dose is mainly due to the increasing of interaction forces between the carboxylate groups (COO^-) of (Alg) or sulphonate goups (OSO_3^-) of (λ-Carr) and MB molecules via N^+ groups. The possible modes of interaction between MB and either CaHAp1-(Alg) or or CaHAp2-(λ-Carr) surface are given in **Figures 13** and **14**.

4.2.3 Effect of temperature and initial dye concentration on the adsorption process

Figures 15 and **16** shows the effect of temperature on the adsorption of MB on the surface of the prepared supports CaHAp1, CaHAp2, CaHAp1-(Alg) and CaHAp2-(λ-Carr). As it is observed, the removal of MB by CaHAp2 increases with increasing the temperature of the solution from 25 to 60°C, indicating that

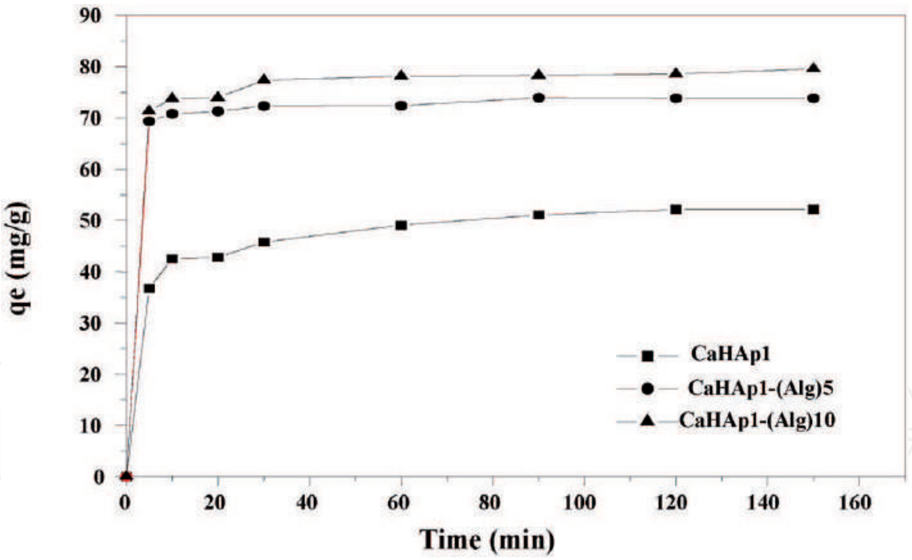

Figure 11.
Effect of contact time on MB adsorption by CaHAp1 and CaHAp1–Alg (adsorption conditions: 0.05 g of adsorbent, initial MB concentration = 50 mg/L, solution volume = 50 mL, 6 < pH< 7, rpn =110 tr/min and temperature = 25 °C).

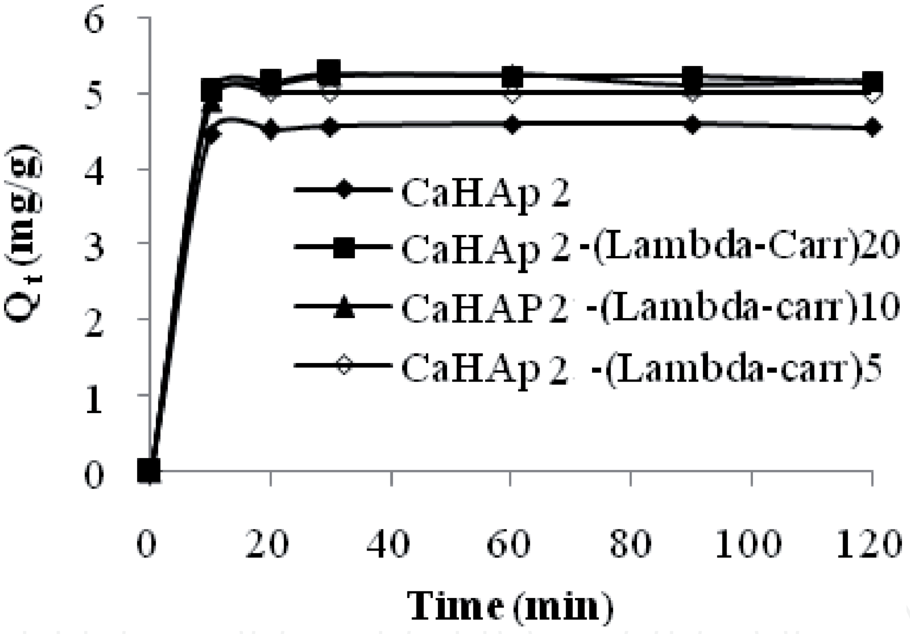

Figure 12.
Effect of contact time on MB adsorption by CaHAp1 and CaHAp2–(λ-Carr) (adsorption conditions: 0.05 g of adsorbent, initial MB concentration = 50 mg/L, solution volume = 50 mL, 6 < pH< 7, rpn =110 tr/min and temperature = 25 °C).

the process is endothermic. In the case for other absorbents, the decrease of the adsorption of MB with the increase of temperature indicates that the adsorption is exothermic in nature.

This phenomenon could be explained by the decrease of the interaction between the MB ions and active sites in hydroxyapatite surface and the weakening of adsorptive forces between the carboxylate (COO^-) groups of (Alg) or sulphate (OSO_3^-) groups of (λ-Carr) and cationic dye molecules. As also depicted from **Figures 15** and **16**, the adsorbed amounts increase with the initial dye concentration to a threshold concentration corresponding to the saturation of the adsorption sites.

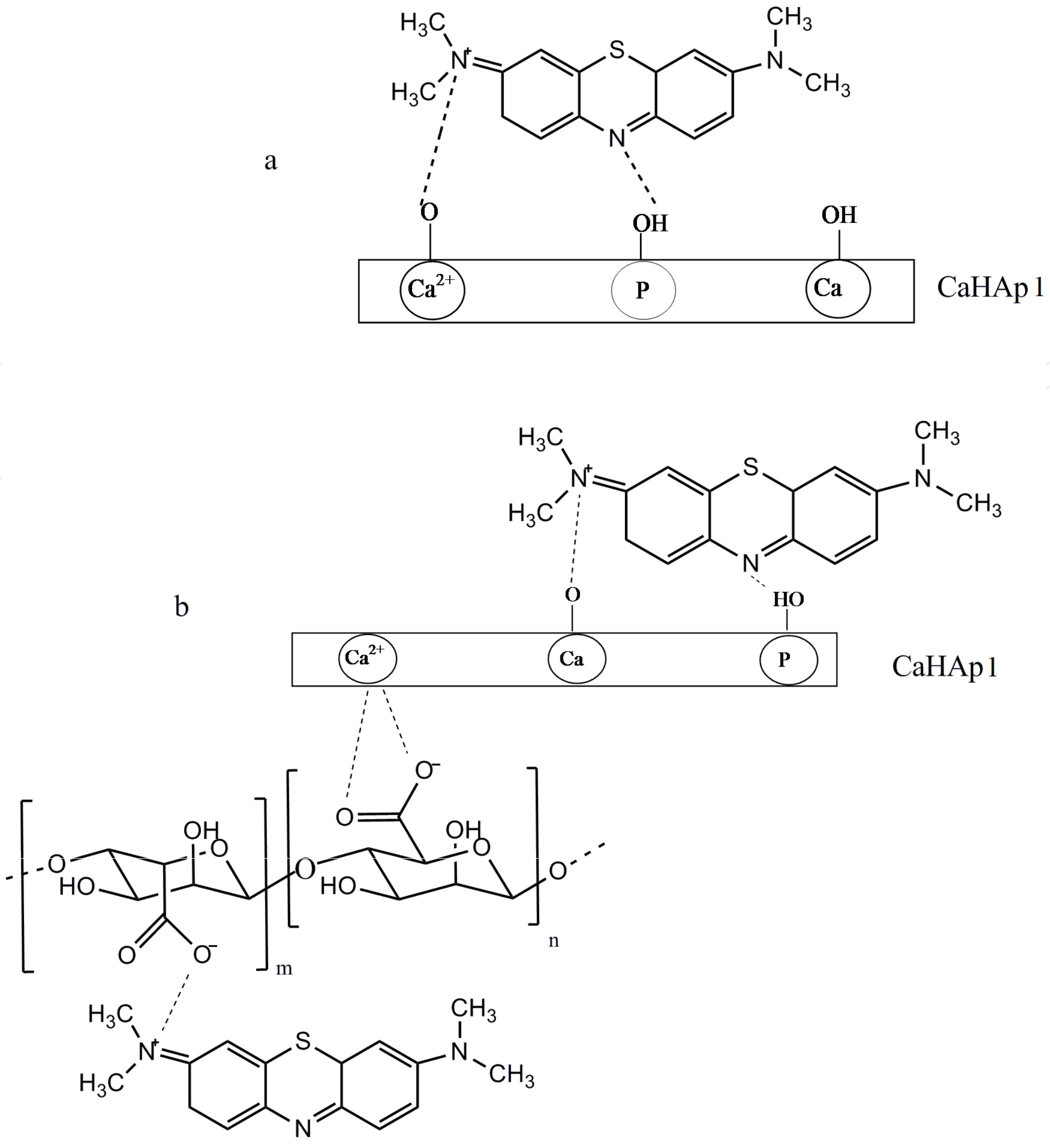

Figure 13.
The possible modes of interaction between MB and either (a) CaHAp1 or (b) CaHAp1-(Alg).

According to these figures, the maximum adsorption capacity of CaHap1-(ALg)10 is more important than those of CaHAp2-(λ-Carr)10, CaHAp1 and CaHAp2. The adsorbed quantities are respectively 128.4, 98.23, 68.5 and 58.8 mg/g. Compared to other adsorbents gathered from the literature (**Table 2**), this registered amount of dye removal is so very interesting and thus our developed product could be seen as a good adsorbent.

In fact, this value is more important com-pared to garlic peel used as adsorbent (82.64 mg/g), Raw date pits (80.3 mg/g) and wood (84 mg/g). It is nearly twice higher compared to Wood ash (50 mg/g). It is five times more important than the Cotton waste (24 mg/g) and. It is six times important than modified pumice stone (15.87 mg/g) and Pure kaolin (15.55 mg/g). It is hundred times important than Fly ash (1.3 mg/g). Consequently, the above results confirmed that CaHAp-(Alg)10 was a favorable adsorbent for MB dye removal.

4.2.4 Modeling and determination of kinetic parameters

In order to evaluate the kinetics involved in the process of the adsorption of MB dye onto CaHAp1, CaHAp2, CaHAp2-(Carr)10 and CaHAp1-(Alg)10 surface,

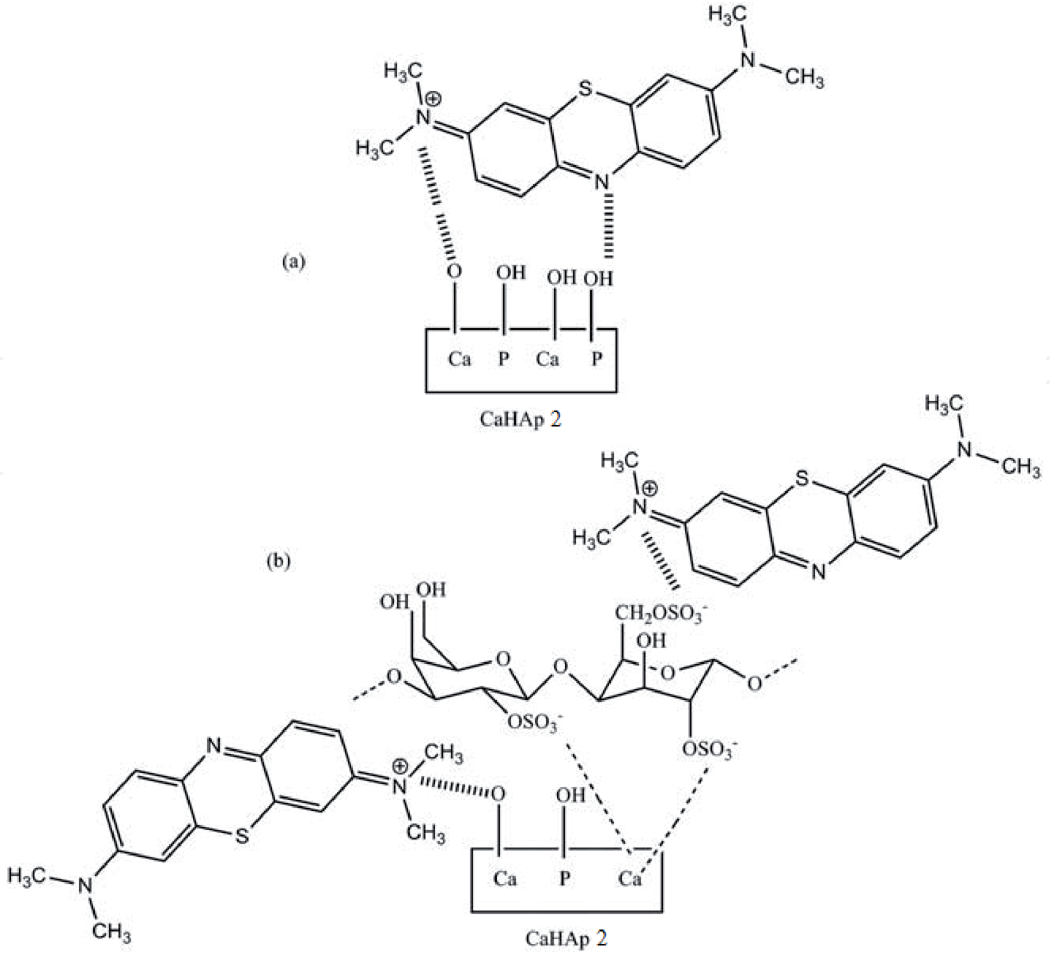

Figure 14.
The possible modes of interaction between MB and either (a) CaHAp2 or (b) CaHAp2-(λ-Carr).

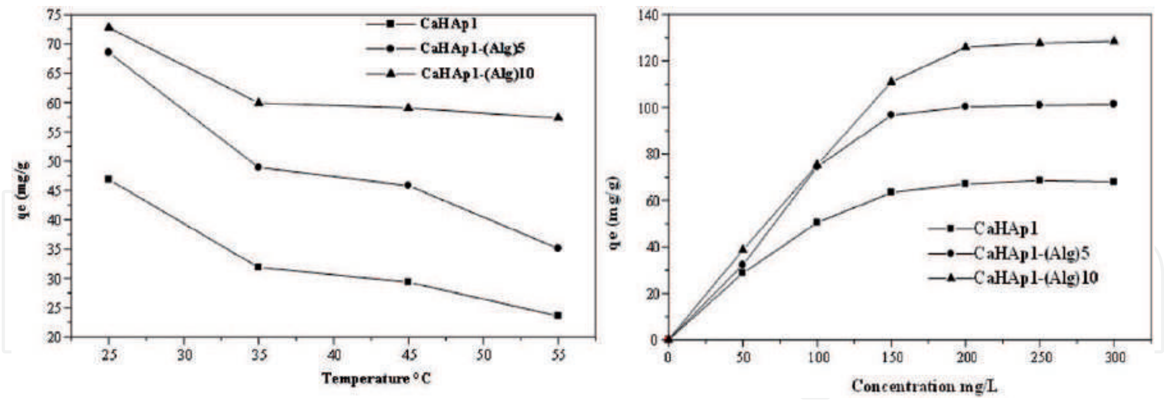

Figure 15.
Effect of temperature (a) and initial concentration (b) on the removal of MB using CaHAp1 and CaHAp1-(Alg).

pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion models were applied and results were discussed [42].

The results of the kinetic study, for hydroxyapatite synthesized in the presence of different amounts of Alg or (λ-Carr) are summarized in **Tables 3** and **4**. The best fit model was selected based on the linear regression correlation coefficient, R^2 values. According to the regression coefficients ($R^2 > 0.99$), the pseudo-second-order equation appears more suitable to describe the retention of MB on all prepared supports.

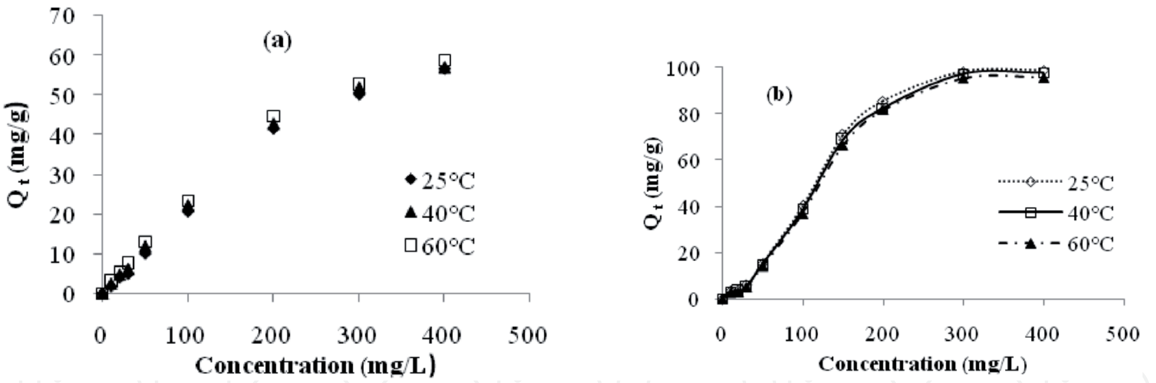

Figure 16.
Effect of temperature on the removal of MB using: (a) CaHAp2 and (b) CaHAp2-(λ-Carr)10.

Samples	q_m (mg/g)	References
CaHAp1-(Alg)10	128.40	In this work
Garlic peel	82.64	[32]
Wood ashes	50	[33]
Cotton waste	24	[34]
Modified pumice stone	15.87	[35]
Natural phosphate	7.23	[36]
natural zeolite	16.370	[37]
Raw date pits	80.30	[38]
Pure kaolin	15.55	[39]
Fly ash	1.3	[40]
Wood	84	[41]

Table 2.
Comparison of the maximum BM adsorption capacity of the adsorbents in this study with other adsorbents.

Consequently, it can be confirmed that the adsorption is chemical and assumes that the surface of our adsorbent is heterogeneous.

4.2.5 Adsorption isotherm

In this study, Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich (D-R) isotherm models were used to describe the adsorption of MB onto ungrafted and grafted hydroxyapatites [43].

The obtained parameters of each model are given in **Tables 5** and **6**. According to the analysis of regression coefficients (R^2), Langmuir model has the highest value than those of the other models for modified hydroxyapatite by sodium alginate. This indicates that the Langmuir model appears appropriate for modeling the adsorption isotherms of MB on CaHAp1 or CaHAp1-(Alg) surface. As seen in **Table 5**, the R_L values [44] are situated within the range of 0< RL< 1, which means that prepared CaHAp or CaHAp-(Alg) is favorable for the adsorption of MB dye under the experimental conditions conducted in this study.

For modified hydroxyapatite by lambda carrageenan, the analysis of regression coefficients shows better applicability of Freundlich model. Moreover, in all compounds, the values of calculated n are less than 1, indicating that the adsorption of MB is favorable.

	Pseudo-first-order			**Pseudo-second-order**			**Elovich**			**Intra-particular diffusion**	
	K_1	**q_e**	**R^2**	**K_2**	**q_e**	**R^2**	**α**	**β**	**R^2**	**K_i**	**R^2**
0%	0.0234	16.764	0.8305	0.00648	52.910	0.9991	12.946	12.210	0.8131	3.0578	0.6086
5%	0.149	4.769	0.3244	0.02641	74.074	0.9999	28.701	11.128	0.5838	3.505	0.3675
10%	0.0181	7.197	0.4388	0.01556	79.365	0.9999	28.931	8.903	0.6240	3.9032	0.4046

Table 3.
Kinetic constants for the adsorption of studied dyes on hydroxyapatite-Alginate (T = 25°C, C_0 *= 100 mg/L, 6 < pH < 7).*

	Pseudo-first-order			**Pseudo-second-order**			**Elovich**			**Intra-particular diffusion**	
	K_1	**q_e**	**R^2**	**K_2**	**q_e**	**R^2**	**α**	**β**	**R^2**	**K_i**	**R^2**
0%	0.0088	0.41	0.346	2.7	4.58	0.999	$7.49^{E}18$	10.41	0.670	0.317	0.488
5%	0.0085	0.29	0.271	5.51	5.02	1	$1.33^{E}57$	27.24	0.457	0.344	0.476
10%	0.0075	0.53	0.247	−20.86	5.162	0.999	$1.31^{E}10$	5.17	0.378	0.361	0.498
20%	0.0079	0.34	0.2	−1.18	5.184	0.999	$3.67^{E}15$	7.62	0.349	0.361	0.489

Table 4.
Kinetic constants for the adsorption of studied dyes on hydroxyapatite-Carrageenan (T = 25°C, C_0 = 10 mg/L, pH = 5).

Isotherm model	**Adsorption constant**	**Adsorbent**		
		CaHAp1	**CaHAp1-(Alg)5**	**CaHAp1-(Alg)10**
Langmuir	q max (mg/g)	77.51	117.64	142.85
	K_L (l/mg)	0.038	0.041	0.062
	R_L	0.34-0.08	0.33-0.07	0.25-0.04
	R^2	0.994	0.974	0.992
Freundlich	n	2.876	0.468	0.541
	K_F (l/mg)	11.762	0.0028	0.0209
	R^2	0.864	0.827	0.685
Tempkin	B_1	18.462	0.032	0.028
	K_T	0.286	$3.8 * 10^{19}$	$4.6 * 10^{13}$
	R^2	0.946	0.777	0.886
D-R	q max (mg/g)	66.62	105.50	120.50
	$K_{D\text{-}R}$ (mol^2/J^2)	$6*10^{-5}$	$5*10^{-5}$	$2*10^{-5}$
	E (KJ/mol)	91.28	100	158.11
	R^2	0.97	0.95	0.94

Table 5.
Isotherm constants and correlation coefficients (R^2) for MB adsorption on the surface of CaHAp1 and CaHAp1-(Alg) at different temperatures.

The values of E calculated from Dubinin-Redushkevich equation are greater than 40 KJ mol^{-1} for all samples, which confirms that the adsorption is chemical [42].

4.2.6 Determination of the thermodynamic parameters

The standard Gibbs free energy change (ΔG°) has been determined from the following equation [21].

$$\Delta G° = -RT\, LnK_L \tag{4}$$

Where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K) and K_L value is the Langmuir equilibrium constant. The enthalpy change ΔH°

	Langmuir constants			**Freundlich constants**			**Temkin constants**			**Dubinin-redushkevich constants**			**Thermodynamic parameters**		
								CaHAp2							
T (°C)	**K_L**	**$q_{m.L}$**	**R^2**	**K_F**	**n_F**	**R^2**	**B_T**	**A_T**	**R^2**	**$Q_{m.DR}$**	**E**	**R^2**	**ΔH°**	**ΔS°**	**ΔG°**
25	0.017	285.7	0.407	0.51	1.03	0.990	36.85	0.29	0.916	3.84	70.71	0.596	42.3	0.25	−32.2
40	0.025	156.2	0.851	0.62	1.12	0.991	37.1	0.30	0.925	3.98	70.71	0.588			−26.95
60	0.026	125	0.944	0.73	1.21	0.993	37.52	0.31	0.928	4.1	79.05	0.572			−40.95
								CaHAp2-(λ-Carr)10							
25	0.005	588.2	0.161	0.894	0.951	71.75	0.289	0.909	4.9	70.71	0.483	0.328	−3.1	−29.2	8.69
40	0.005	526.3	0.189	0.89	0.953	70.52	0.288	0.909	4.85	70.71	0.481	0.323			9.13
60	0.004	500	0.181	0.87	0.955	69.32	0.286	0.905	4.77	70.71	0.486	0.314			9.7

Table 6.
Isotherm constants and thermodynamic parameters for dye adsorption on the surface of CaHAp2 and CaHAp2-(Carr)10 at different temperatures.

	ΔH° (KJ/mol)	**ΔS° (KJ/mol)**	**ΔG° (KJ/mol)**			
			298°K	**308°K**	**318°K**	**328°K**
CaHAp1	−27.96	−0.094	0.218	1.163	2.109	3.055
CaHAp1-Alg(10)	−20.432	−0.059	−2.789	−2.197	−1.605	−1.013

Table 7.
Values of thermodynamic parameters for MB dye removal with CaHAp1 and CaHAp1-Alg.

and entropy change ΔS° of the adsorption were estimated from the following equation:

$$\mathrm{LnK_L} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{5}$$

The values of ΔH° and ΔS° were determined from the slopes and intercept of the linear plot of Ln K_L versus (1/T). The calculated thermodynamic parameters are summarized in **Tables 6** and 7.

The values of the enthalpy ΔH° indicates that the adsorption process is endothermic for CaHAp2 (ΔH° > 0), and exothermic for (CaHAp1, CaHap2-(λ-Carr)10, CaHAp1-(Alg)10) (ΔH° < 0). The ΔG° values were negative for (CaHap2, CaHAp1-(Alg)10) and positive for (CaHAp1, CaHAp2-(λ-Carr)10).

The positive ΔG° values indicates that the instability activation complex of the adsorption reaction increases with increasing temperature, The negative values of ΔG° means that the process is feasible and adsorption is spontaneous thermodynamically [45].

The negative value of entropy ΔS° confirms the decreased randomness at the solid–solution interface during adsorption.

5. Conclusion

In this study, the results of characterization techniques IR, XRD, SSA and SEM analysis showed that the sodium alginate or lambda carrageenan were successfully grafted on the hydroxyapatite surface. The modified hydroxyapatite could be potentially applied for the removal of methylene blue dye from aqueous solution. The determination of the amount of dye adsorbed on the various apatitic phase CaHAp1, CaHAp2, CaHAp1-(Alg) and CaHAp2-(λ-Carr) allowed us to build the adsorption isotherms which give information on the adsorption mechanism. The Modeling of the isotherms proved that the adsorption of MB on modified hydroxyapatite is described by the Freundlich equation for CaHAp2-(λ-Carr) and Langmuir for CaHAp1-(Alg). The calculated adsorption capacities of CaHAp1, CaHAp2, CaHAp1-Alg10 and CaHAp2-(λ-Carr)10 for MB, at 25°C, were 68.5, 58.8 128.40, and 98.23 mg/g, respectively. The results gave a clear indication that the modified hydroxyapatite has a great capacity than pure hydroxyapatite for dye removal.

Thermodynamic studies indicated that the physic-sorption is the dominating mechanism for the dye adsorption process onto CaHAp1-(Alg)10 or CaHAp2-(λ-Carr)10, spontaneous and exothermic in nature. The results indicate that the modified hydroxyapatite CaHAp2-(λ Carr) or CaHAp1-(Alg) possessed good adsorption ability towards MB dye and can be used as a low cost adsorbent for other environmental applications as retention of heavy metal and pesticides from wastewater. Further works will be extended for the functionalization of hydroxyapatite materials with surfactants and cationic reagents for the removal of organic pollutants from contaminated waters.

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Chapter

Treatment of Textile Dyeing Waste Water Using TiO_2/Zn Electrode by Spray Pyrolysis in Electrocoagulation Process

Parameswari Kalivel

Abstract

An alternative form of treatment for the remediation of textile waste water, electrocoagulation (EC) methods are used. This work deals mainly with the treatment of waste water for textile dyeing preceded by the use of wastewater. The goal of the proposed study is to evaluate the efficiency of the electrocoagulation process using TiO_2/Zn electrodes using $TiCl_3$ via spray pyrolysis. The surface morphology of the electrode was studied by SEM, XRD and EDS analysis. The efficiency of electrocoagulation treatment process to treat synthetic waste water containing Coralene Navy RDRLSR, Coralene Red 3G, Rubru RD GLFI dye was studied. The effect of parameters such as current density, influence of effluent pH, supporting electrolyte NaCl concentration, and EC time on dye removal efficiency were investigated. The result indicates that this process is very efficient and was able to achieve color removal (99.5%) at pH 8.5 and 0.15 A in 10 minutes.

Keywords: electrocoagulation, textile dye effluent, TiO_2/Zn electrode, EC time

1. Introduction

1.1 Water crisis

Water is the source of life and regarded as the most essential resource of natural resources. In recent days, demand for water has increased due to tremendous growth in technology and industries. The ever increasing world population and rapidly advancing industrialization is causing more demand than ever for the dwindling supply of water, which makes it precious [1]. Many water pollutants are yet to be addressed, due to rapid industrialization there are new pollutants which are being discovered. New chemical compounds are continuously being developed and brought to the market and sooner or later they will be utilized in the aquatic systems. There may be adverse effects on human health and marine environments from emerging contaminants found in water. For human health, safe water that is free of harmful chemicals and pathogens is essential [2]. Water shortages will contribute to social and political unrest, water wars and diseases in the coming decades, and it will take a dramatic turn in the opposite direction unless new methods of providing clean water are found. Increased public awareness has led governments and organizations worldwide to issue strict water pollution regulations. These days there is an increasing worldwide concern for the development of wastewater treatment technology [3]. The conversion of waste water into reusable water can be done by using scientific methods and that decreases the challenge towards the rising demand of water quality [4]. Comparing all industries, textile industries show a higher rate of consumption of water.

1.2 Status of pollution due to textile industries

Dyes can be characterized as substances that when applied to a substrate, provide color through a process that alters the crystal structure of the colored substances, at least temporarily. In the textile, pharmaceutical, food, cosmetics, plastics, photographic and paper industries, such substances with substantial coloring capability are commonly used. Dyes are categorized by application and chemical structure and consist of a group of atoms known as chromophores that are responsible for the color of the dye. The numerous functional groups, such as azo, anthraquinone, methine, nitro, carbonyl and others are used as chromophore-containing centers in dyes, in addition, electrons removing or donating substituents are called auxochromes in order to produce or enhance the color of the chromophores are also present in dyes. Over 10,000 different dyes and pigments are expected to be used industrially and over 7×10^5 tons of synthetic dyes are manufactured globally annually [5–7]. Using batch, continuous or semi-continuous processes, textile products can be dyed. The type of method used depends on many features, including the type of material such as fibre, yarn, fabric, construction of garments and clothes, as well as the generic type of fibre, the size of dye batches and the quality specifications of the dyed fabric. The batch process is the most common method of dyeing textile materials among these methods. In the textile industry, due to the inefficiency of the dyeing process, up to 200,000 tons of these dyes are lost to effluent every year during the dyeing and finishing operations. Unfortunately, as a result of their high stability to light, temperature, water, detergents, chemicals, soap and other parameters such as bleach and transpiration, most of these dyes avoid traditional wastewater treatment systems and remain in the setting. Furthermore, in the manufacture of textiles, anti-microbial agents resistant to biological degradation are frequently used, especially for natural fibres such as cotton. They are more recalcitrant to biodegradation by the synthetic origin and complex aromatic structure of these agents. A significant volume of water used mainly in the dyeing and finishing operations of the plants is used in the textile industry in its production methods. Both dry and wet processing include a textile unit. In an extended process series that produces a large amount of waste, the textile manufacturing process is distinguished by the high use of resources such as water, fuel and a broad variety of chemicals. A huge amount of solid and liquid waste is produced by textile processing units, some of which may be hazardous [8]. Considering the volume produced as well as the composition of the effluent, waste water from textile plants is listed as the most polluting of all industrial sectors. Moreover the increased demand for textile goods and the proportional increase in their production, along with the use of synthetic dyes, have led to make dye wastewater one of the key sources of serious pollution problems at the present time.

The nature of the waste produced depends on the range of fibres and chemical substances involved in the textile process, the processing methods and technologies that are being adopted. Usually the most important ecological problems associated with textile production are those associated with the degradation of the body of water caused by the discharge of raw waste [9]. Dyeing and finishing units are a key part of the produced waste water as they use a high volume of water in their operation, from fibre washing to bleaching, dyeing and washing of refined products [10]. On average, there is a sample mixture of compounds in around 200 L of water that could cause harm if strict precautions are not taken until they are released into the atmosphere. Wet process manufacturing utilizes color caustic soda, sulphuric acid, sodium peroxide, hydrochloric acid, dyes and chemicals. Moreover, other metals, which are carcinogenic in nature are reserved in the finished hosiery supplies and let out as wastewater [11].

Dyes used by the textile industry are now mainly synthetic. They are predominantly extracted from two sources, coal tar and intermediates based on petroleum. Powders, pellets, gels or colloidal dispersions are the state of these dyes in the market. Usually the active ingredient concentrations in the dyes vary from 20 to 80 percent. These new dyes are regularly produced for meeting the demands of new technologies, new kinds of fabrics, detergents, developments in dyeing machineries, along with addressing the significant environmental problems faced by some existing dyes.

With the rapid shift in the textile industry's product profile, from high-cost cotton textiles to durable and flexible synthetic fibres, the pattern of consumption of these dyes is also shifting rapidly. Polyesters now account for a large portion of dye use. Dispersed dyes used in polyesters are therefore also expected to expand at a faster rate.

To make it easier to understand, textile dyestuffs can be grouped into the following groups if we take general dye chemistry as one of the basis for grouping as azoic, acid sulfur, disperse, simple, reactive, mordant, oxidation vat solvent and fluorescent dyes.

Green and Saunders developed one form of coloured azo compound in 1922, in which an amino group is attached to a solubilizing group e.g. methyl sulphate, -CH2-SO3H. In dye bath, they are slowly hydrolyzed and contain azo compound and formaldehyde bi sulphate. This free azo compound was able to color the fibres of cellulose acetate. The name of that dye was "ionamine." This ion amine, however, did not give satisfactory dyeing results. Baddiley and Ellis later developed sulpho ricinoleic acid (SRA) for the dyeing of acetate fibres in 1924. This SRA has been used as an agent for dispersion. SRA was later shown to be capable of dyeing nylon, polyester, acrylic, etc. This dye was called 'Disperse Dye' in 1953. As per the chemical structure disperse dyes are classified as nitro, amino ketone dyes, anthraquinonoid dyes, aono azo dyes, di- azo dyes. In this study we had used azo type of disperse dyes with the commercial names as Coralene Navy RDRLSR, Coralene Red 3G, Rubru RD GLFI dye.

1.3 Background and motivation of the present study

India is the second largest exporter of dyestuffs, after China. It is estimated that approximately 2% of the dyes produced are discharged directly in aqueous effluent, and 10% is subsequently lost during the coloration process [12]. The size of India's market is expected to touch $250 billion in the next two years from $150 billion. Although textile industries play an important role in Indian economy, the waste water management is concerned predominant.

Tiruppur, a textile hub, in Tamil Nadu, has emerged as the leading industrial cluster of cotton knitwear in South India for both the overseas and domestic markets primarily because of climate conditions which facilitate fast processing of yarn. Moreover the availability of raw materials and cheap labour has ensured that the activities of the textile industry here, have experienced rapid growth over the last two decades. Almost 80 percent of India's exports of cotton knitwear are from Tirupur today. There are 6,250 units involved here in different textile industry operations. It consists of 4900 knitting and sewing units, approximately 736 dyeing and bleaching units, 300 printing units, 100 embroidery units and 200 compacting, raising and calendar catering units. Buyers come regularly to visit Tirupur from about 35 countries. In addition to an income matching or exceeding the above amount to cater to the domestic market, this small town contributes around INR.11000 crores (Rs. 110 billion) in foreign exchange earnings annually to the government. In short, Tirupur's economic success depends heavily on this industry and most local people are active in the knitwear sector in one way or another. With a rough estimation of 7×10^5–1×10^6 tons of fabrics produced per year, there are more than 100,000 commercial dyes. Though accurate statistics on the number of dyes released into the surroundings is not known, data shows that 10–15% of the used dyes are released into the environment as they are discharged as wastewater from textile industries causing severe pollution [13].

In Tirupur, the textile industry's water needs have been fulfilled by both surface water and ground water. About 28.8 billion litres of ground water are consumed annually by the units in Tirupur alone. This water is transported in tankers from the surrounding villages such as Avinashi, Palladam, Annur, Kangeyam, and from many parts of the nearby Erode district. Needless to mention, Tirupur faces extreme water shortages. Tankers supply about 80 percent of the total water requirement [14]. The textile units purchase water per tanker at a cost of Rs 250–450. The farmers sell the same thing at Rs 40–80 per tanker. Even at this rate, it is more profitable for farmers to sell water instead of carrying out agricultural activities.

1.4 Major challenges in the treatment of textile effluent

Knowledge of environmental issues has increased dramatically over the past few decades and has become an important concern in textile trade due to different environmental and health regulations, and environmental policy is also increasingly dictated by market forces. Many chemicals used in the textile industry are causing problems with the ecosystem and health [15].

Textile processing is a water intensive process. The waste water generated by the industry is high in BOD, COD, pH, temperature, color, turbidity and toxic chemicals. These polluted effluents ought to be treated chemically to remove the hazardous material and chemicals so that the waste water will comply with the prescribed limits and can be discharged into the public sewer or into aquatic bodies [16]. The major challenges existing in the treatment of textile industrial effluents are recycling and reuse of wastewater, removal of color and reduction of Total Dissolved Solids (TDS) in the treated effluent, generation of huge amount of sludge, large units have invested in Individual Effluent Treatment Units (IETPs) and medium scale units have invested in Common ETPs. However, no techno-economically viable option is available for treating the effluent in small units.

1.5 Existing conventional treatment methods and their limitations

Removal of dye is possible by different or a combination of physical, chemical and biological methods. Adsorption, absorption, membrane filtration, and ultrasonic waves are physical methods; ion exchange, electrolysis, coagulation, traditional and advanced oxidation are chemical methods; and biological methods can be described using algae, fungi, and bacteria [17].

In chemical coagulation, electrostatic gravity between the dye solution and polymeric molecules with opposite loads generates coagulation. The disadvantages of this method are high sludge production and high dissolved solids in treated wastewaters and polymeric molecules with opposite loads generate coagulation. Chemical coagulation is efficient for sulfurous and disperse dyes. Acidic, direct, vat and reactive dyes coagulate with this method too, but do not settle, while cationic dyes do not even coagulate [18]. The conventional treatment methods such as activated sludge, coagulation and flocculation process, reverse osmosis and evaporation consume a lot of chemicals, high energy and are not sufficient to break down azo double bonds of reactive dyes. Also the secondary products or sludge produced becomes more difficult to be disposed. Huge amount of rejects from Reverse Osmosis is another major problem [19].

A large number of well-established traditional decolourisation techniques involving physicochemical, chemical and biological processes, as well as some modern emerging techniques such as sonochemical or advanced oxidation processes, are shown in the available literature. In order to solve this problem, there is no single economically and technically feasible approach and typically two or three methods need to be combined to achieve an acceptable degree of colour removal [20, 21].

The main drawbacks of these physiochemical and biological treatment processes is that they generally lack the broad scope of treatment efficiency required to treat all diverse pollutants present in the textile waste water. The electrochemical technology that was developed can remove chemical components in an effective and economical way.

1.6 Electro chemical methods and their limitations

The electrochemical method is a safer, highly effective treatment method for the treatment of textile liquid waste containing a high concentration of dye. This technique has advantages for decolorization over others, such as the need for simple equipment, better accuracy, and shorter retention time to remove pollutants, less need for chemicals and simpler operation, and [22]. This challenge towards rising demand for quality water can be resolved by the application of certain sophisticated scientific techniques for the conversion of waste water into reusable water. The electrochemical methods for treatment of textile waste water include electro dialysis, electrical ion exchange, electro osmosis, electro oxidation etc. Though these methods have proven to be efficient it is not practically applicable because of its high cost and maintainability [23].

There exists a wide range of methods which can be employed to treat wastewater. With the recent technological development in electrochemical field, a new technique has been introduced in the industry, named as electro-coagulation. EC has been successfully used for decades in order to treat the wastewater of textile, food and protein, phosphate, tannery wastewater, restaurant wastewater and defluoridation. Electro-coagulation among them is cost effective and requires less maintenance. Hence electro-coagulation was applied in this study for the removal of dye from textile wastewater [24, 25].

1.7 Scope of the present study

This study focuses on the treatment of synthetic dyeing wastewater (obtained from Devi Threads, Pachapalayam) using EC method which addresses the need for techno-economically feasible option in treating the effluent from small scale clusters thereby solving the other above mentioned issues of dye removal, high sludge production and reuse of the effluent.

1.8 Objectives of the study

- To prepare TiO_2/Zn from $TiCl_3$ by Spray pyrolysis method and surface characterization of the electrode. (SEM, XRD, EDS)

- To investigate the influence of operational parameters in the removal of dye in textile waste water using TiO_2/Zn in EC process.

- To identify the strategy for improvement of the color removal efficiency (CRE) with reduction in electrolysis time and applied current.

- Sludge characterization.

2. Materials/methods

The detailed methodology of the present study, which was carried out in two phases to address the issues mentioned in the objectives.

- Preparation of TiO_2/Zn Electrode by spray pyrolysis method using the precursor $TiCl_3$

- Removal of disperse dye (Coralene Navy RDRLSR, Coralene Red 3G, Rubru RD GLFI) from synthetic wastewater using TiO_2/Zn Electrode in electrocoagulation process.

2.1 Preparation of TiO_2/Zn electrode by spray pyrolysis

In general the experimental procedure recommended by Beck and Co-workers was adopted for the preparation of TiO_2/Zn electrode by spray pyrolysis of $TiCl_3$ by the following procedure [26]. The TiO_2 coating was done on zinc substrate which was cleaned well and sand blasted to make the surface adherent for the coating. Etching was done for the same purpose using etchants (5% Oxalic acid in water) at 60° C for 1 hour. The surface was then washed properly with water, rinsed using triple distilled water.

Then it was coated with the precursor solution $TiCl_3$ (0.05 N) 4 ml, 1:1 HNO_3 water (2.5 ml). The precursor solution was cooled to 5°C to which isopropyl alcohol (15 ml) was added maintaining the temperature 5 to 10°C.

2.2 Deposition of TiO_2 coating on zinc by spray pyrolysis

Spray pyrolysis technique used in this work is a tubular reactor type as it is given in **Figure 1**. The precursor solution is pumped through a 100 kHz ultrasonic atomizer (Lechler Inc.) to the heated substrate held within a tubular quartz reactor (5 cm in i.d. and 30 cm in length). On the graphite sample holder, the zinc metal substrate was placed and heated by quartz heating bulbs located on top and below the tube. The temperature of the substrate was controlled by a thermocouple type K connected to the temperature controller display. The solution was pumped into the atomizer once the temperature controller indicated the desired temperature, and the atomized droplets of the precursor were dispersed and transported using nitrogen (N_2) and oxygen (O_2) as the carrier gases towards the substrate to the reaction chamber. The aerosol droplets were decomposed and transformed to very tiny

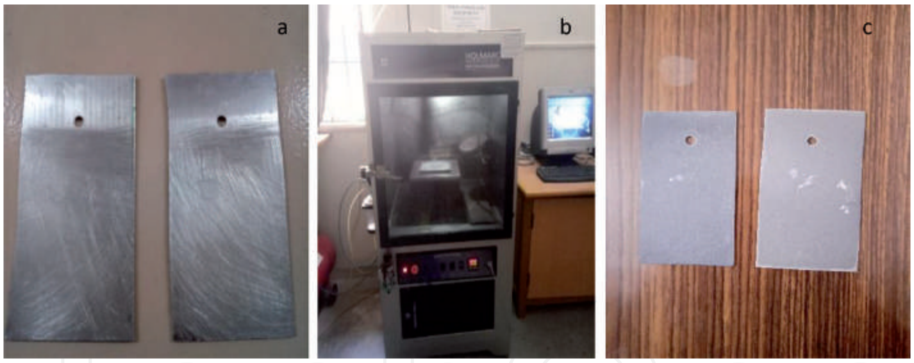

Figure 1.
(a) Photograph of the pretreated zinc plate, (b) Coating on zinc in spray pyrolysis, (c) TiO_2/Zn.

particles of oxide compounds upon meeting the hot surface of the zinc substrate. The usual spray time for one time deposition of a 50 ml solution batch was around 30–45 min depending on the spray conditions. The sample was then cooled down by 5–10°C/min from the deposition temperature slowly to room temperature. The electrodes were prepared with dimensions of 9 cm × 3.2 cm × .5 cm. **Figure 1** shows the photograph of the pretreated zinc plate, coating on zinc in spray pyrolysis and the TiO_2/Zn plate.

2.3 Electrocoagulation process

Disperse dye was obtained from one of the textile industry in Coimbatore, Tamil Nadu. (Commercial name; Coralene Navy RDRLSR, Coralene Red 3G, Rubru RD GLFI) The simulated wastewater was prepared by dissolving a 150 ppm of disperse dyes in distilled water. The experimental device is schematically shown in **Figure 2**. The EC unit consists of an electrochemical reactor which is a glass beaker with magnetic stirring, a D.C power supply and two sets of EC process were run with TiO_2/Zn – TiO_2/Zn and Zn – Zn. (Hereafter these electrodes will be represented as 'A' (TiO_2/Zn – TiO_2/Zn) and 'B' (Zn – Zn)).

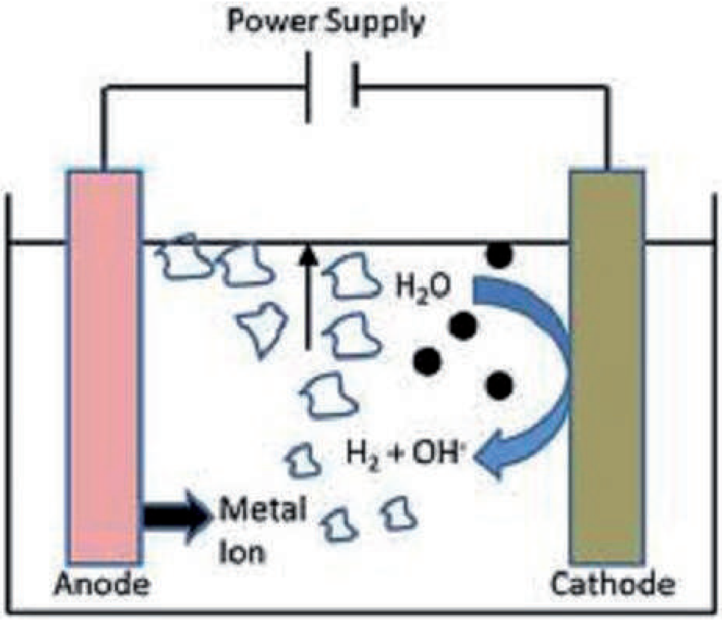

Figure 2.
Schematic representation of EC process (Source: http://pubs.sciepub.com).

The electrodes were used with dimensions of 9 cm × 3.2 cm × .5 cm. The total effective electrode area was 28.16 cm^2 and the spacing between electrodes was 1 cm. The electrodes were connected to a digital dc power supply (var tech) providing a current ranging from 0.05 to 0.3A. 500 ml electro coagulation cell that contained the 250 ml test solution and a magnetic stirrer was used to stir the solution, thereby enhancing the efficiency. The applied current was adjusted to a desired value and the coagulation was started. In each run, 250 ml of dye solution was placed into the electrolytic cell. Before each run, electrodes were washed with water and dipped in 15% hydrochloric acid in order to remove dust from the electrode plates and thus weigh the electrodes after drying. The electrode plates are washed with water at the end of each run, dried and weighed at last. Whattman filter paper was used to filter the subsequent treated sample and filtrate was used for the analysis. The individual effects of electrolysis time and applied current on colour removal efficiency were quantified in this analysis (CRE). The pH was adjusted by adding 0.5 M HCl or 0.5 M NaOH. The conductivity of solutions was raised and adjusted to different values by the addition of NaCl. All experiments were carried out at constant temperature of 25°C. Two sets of EC process were carried out with 'A' and 'B' electrodes with operating parameters like pH, EC time, dye concentration, addition of electrolyte NaCl and applied current for optimization to achieve higher Color Removal Efficiency (CRE%). On the basis of the initial experiments, other parameter rates were considered constant. The experimental set up in EC process, after the experiment, the coagulated dye solution getting separated as sludge settling and floating are given in **Figure 3**.

2.4 Colour removal efficiency

The ultraviolet–visible spectrophotometer (Jasco V-670 spectrophotometer) was used to measure the wavelength (542 nm) of dye. The calculation of color removal efficiencies (CRE %) after electrocoagulation treatment was performed using the formula, as it is given in Eq. (1).

$$\text{Colour removal efficiency}\,(\text{CRE}\%) = 100 * (A_i - A_f) / A_i \qquad (1)$$

Where A_i and A_f were the absorbance of the dye in solution afore electrocoagulation and at the time *t*, respectively. Using a conductivity metre (Elico CM180) and a pH metre (Eutech), the electrical conductivity and pH of different dye concentrations were measured.

2.5 Sludge characterization

EC method is said to generate less sludge compared to chemical coagulation, eventhen it is important to take appropriate measures for the reuse or safe disposal

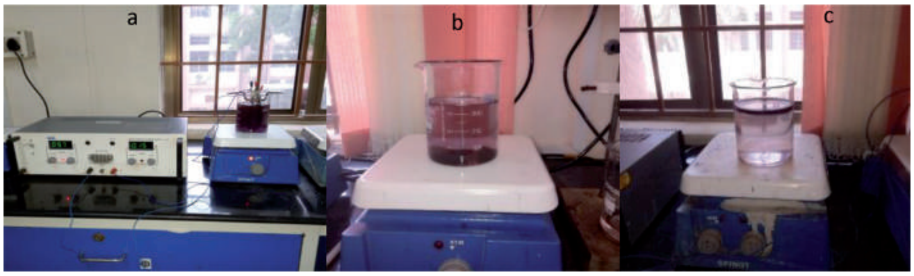

Figure 3.
Photograph of the (a) dye solution, (b) after EC sludge settling, (c) sludge floating.

of sludge in order to determine the quantification and characterization of the sludge generated and characterization of the sludge plays a major role in deciding healthy discarding or reclamation. Therefore by filtration technique, the sludge formed during the process was separated and placed in the drying oven for about 24 hours at 100°C and dried, which was then weighed [27].

3. Characterization techniques

3.1 Adhesion test

The adhesion strength between the coating and the substrate was tested by applying the Scotch tape test on the deposited films before any characterization. In general, if the film adheres to the substrate and it does not peel off the substrate, adhesion strength is considered to be good and it was found good for TiO_2/Zn.

3.2 Microstructural and phase characterization

The morphological, and structural analysis of TiO_2/Zn electrodes were carried out by X-Ray diffractometer and Scanning Electron Microscope (SEM).

Non-destructive tool X-ray diffraction (XRD) is used for the identification and determination of structural properties such as train, grain size, expitaxy, phase composition, and crystalline phases and orientation of the deposited film. The research was conducted to study the micro structure of the particles present in the electrode and sludge using the JEOL-JDX 8030 Model 6000 diffractometer with Cu-K a radiation (λ = 0,15406 nm).

Surface morphology studies were performed by JEOL, JSM 35 CF, Japan, using a Scanning Electron Microscope (SEM). Energy Dispersive X-Ray Spectroscopy Energy Dispersive X-Ray Spectroscopy (EDS) was used for the elemental analysis.

4. Results and discussion

4.1 Characterization of TiO_2/Zn

The surface morphology, composition of elements present and the microscopic structure in the electrode were analyzed using SEM, EDS and XRD.

Zinc substrate and TiO_2 coated zinc by spray pyrolysis were studied for their surface morphology and elemental analysis using Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Spectroscopy. The SEM micro-graph and EDS spectrum of zinc and TiO_2/Zn are given in **Figure 4**.

The TiO_2 SEM micrograph showed dense particles and their shape was in regular pattern. Obviously, the Ti and O peaks can be seen in both EDS spectra with peaks with chlorine on the coated surface. Morphology of SEM monographs show that the surface are porous. Furthermore the cracks in the surface layer are evident beyond the pores, which may imply too fast volume growth of the TiO_2 layer on the zinc substrate.

The elemental constituents of TiO_2 nanoparticles were analysed using EDS, **Figure 4** shows the EDS spectra for TiO_2 particles on the zinc substrate, peaks around 0.2, 0.3 and 4.3 keV are attributed to the binding energies of titanium and oxygen of TiO_2. This finding confirms the existence of elemental compounds with an impurity peak corresponding to chlorine from the precursor $TiCl_3$ on the zinc substrate. The peaks of 0.25, 8.5, 9.8 keV are linked to the oxygen-binding energies of zinc.

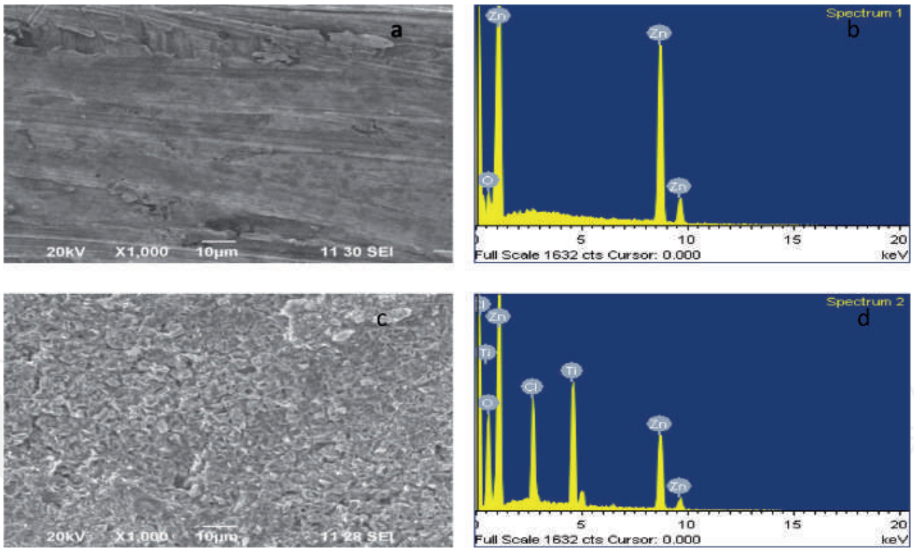

Figure 4.
(a, b) SEM, EDS image of Zinc, (c, d) TiO_2/Zn.

The X-ray diffractograms of TiO_2/Zn and zinc are shown in **Figure 5**. The diffraction peaks of TiO_2 phase, and the substrate zinc are present in the investigated electrode.

The particle size of TiO_2 is related to the diffraction peak broadening, so X-ray diffraction spectra of coated TiO_2 nanoparticles were taken and particle size and phase composition were determined. The lattice parameter observed a = b = 3.780, c = 9.513. The average particle size calculated by using Scherer Eq. indicated high surface area [28].

The particle size of nanomaterial is related to the diffraction peak broadening, so X-ray diffraction spectra of synthesized TiO_2 nanoparticles were taken and peak size and composition were determined. Sharp peaks obtained corresponding to the planes (104), (018), (110), (024), (024) and (300) confirmed the nanocrystalline anatase structure. It shows the primitive hexagonal structure of nanoparticles of TiO2. TiO2 deposition is consistent with 2 theta values (30,32,35,47,56,63,68) and Zn deposition with 2 theta values (36,43,54,70,78) from the XRD results. The data was compared with JCPDS card no:71-1059 for TiO_2 and 65-3358 for Zn. In the XRD pattern, no other impurity peak was observed.

4.2 Optimization of operational parameters

Optimization of operational parameters in electrocoagulation process such as (applied current, pH, reaction time, NaCl (electrolyte) concentration) were investigated. Optimization of the above mentioned operational parameters is necessary to improve the performance of EC process and the economic viability. Since the influence of these parameters depend on the type of waste water and its concentration, optimal value of the operational parameters were identified for the textile dyeing waste water synthesized using disperse dye powder. The CRE at varied current supplied for the process, pH, reaction time, and the concentration of the electrolyte used is discussed here with. Two sets of EC with TiO2/Zn-TiO2/Zn (electrode 'A') and Zn-Zn (electrode 'B') were conducted for optimization and the results were compared.

4.3 Effect of pH

The pH is one of the most important parameters in the performances of EC process in order to achieve a compromise between best coagulation and best

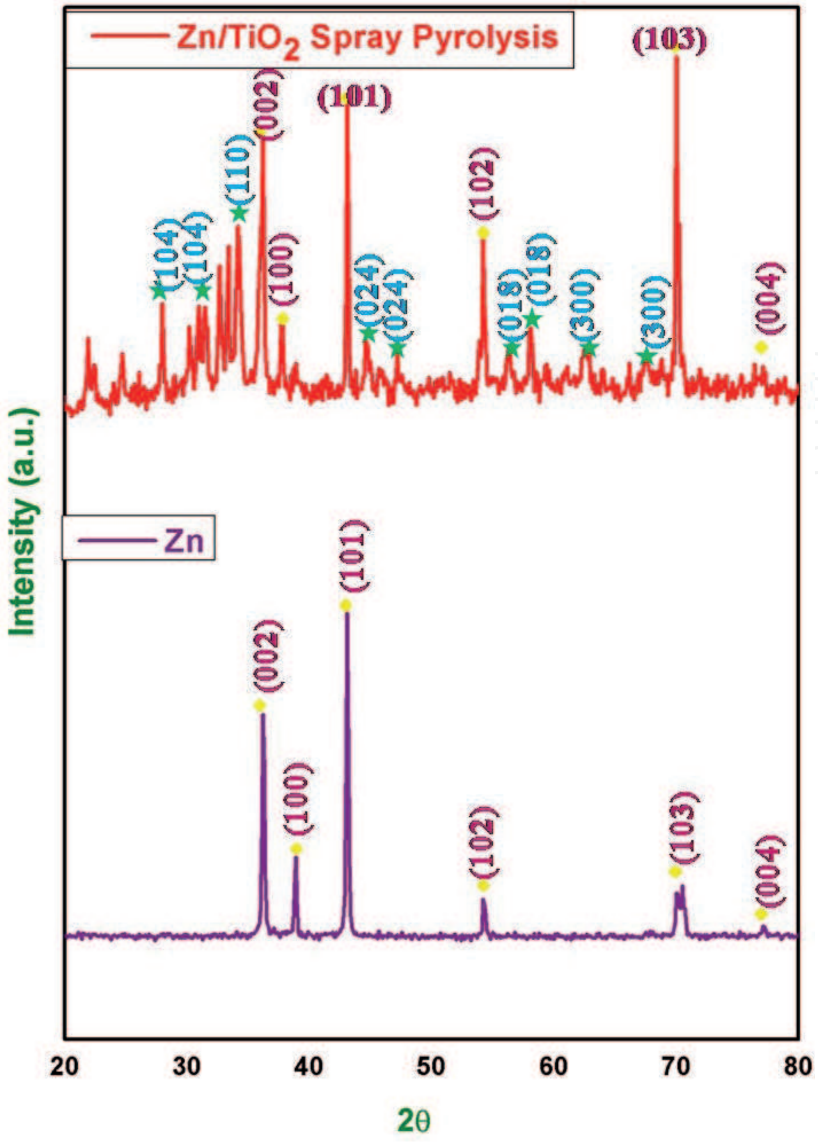

Figure 5.
XRD Pattern for Zn and TiO_2/Zn.

flotation. The optimum range may however vary as a function of electrode material and dye structure. And the fact is that pH determinates the metallic ions speciation, the chemical state of other species in the solution, and solubility. Hence the optimum pH is necessary to minimize environmental remediation costs and make the process more efficient. To investigate this effect in this work, a series of experiments were performed using synthetic disperse dye solution. Experiments were carried out at various values of pH (4.5, 5.5, 6.6, 7.5, 8.5 and 9.5) under which the applied current was kept at 0.05A for electrode 'A' and 0.15A for electrode 'B'. The pH was adjusted to a desirable value using NaOH, or H_2SO_4 and varied in the range 4.5 to 9.5. The treated sample is collected and filtered and the % of CRE estimated. The obtained results are shown in **Figure 6(a)**.

It can be noticed that decolorization was most effective in a pH range between 4.5 to 8.5 for coated and 4.5 for zinc electrodes and removal of CRE% reached values between 91.7 to 98.1 for the coated and 80.4 for Zn electrodes. This refers to the area where $Ti(OH)^{2+}$ and $Ti_2(OH)^{2+}$ would have been formed, and $Ti(OH)_3$ as insoluble species prevailed. On the other hand, above pH 8.5, % of CRE fell when soluble $Ti(OH)_4^-$ anions become predominant at high pH. At an initial pH of 4.5, dye process was completed within 5 minutes with high efficiency. And also at pH 4.5, the dye separated well from solution and the sludge floated with good

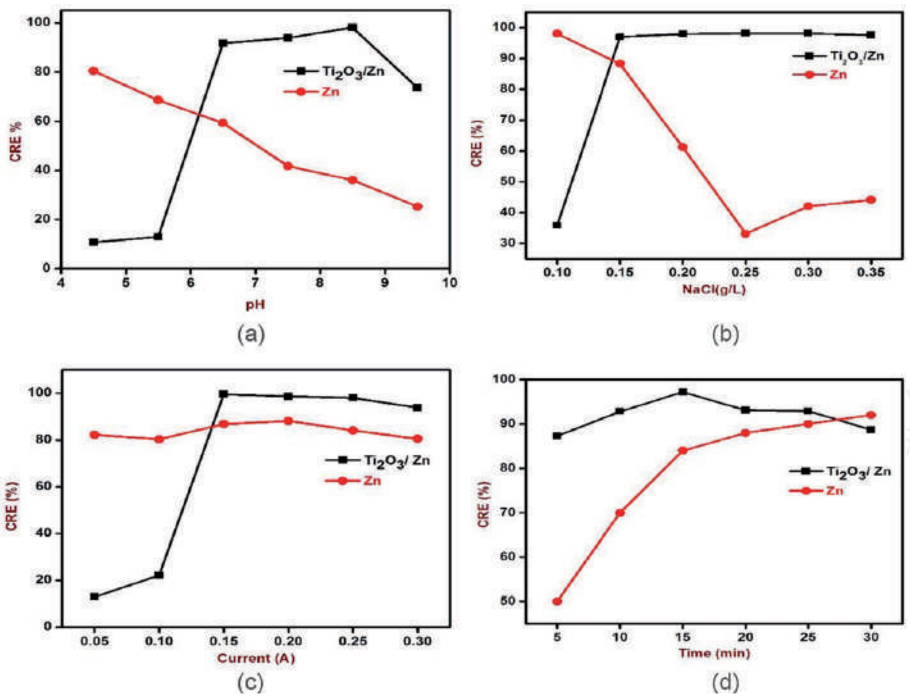

Figure 6.
Effect of varying (a) pH on CRE (%), (b) concentration of NaCl on CRE (%), (c) applied current on CRE (%), (d) Time on CRE (%).

percent of CRE removal in the case of electrode 'A', and the separation was clear and high % of CRE removal as the pH was increased from 4.5 to 7.5 may be due to the formation of more monomeric and polymeric insoluble Ti species.

The percentage of CRE was 80.49 in the case of zinc electrodes at pH 4.5, as the pH increased from 4.5 to 9.5 there was a gradual and sudden decrease in percent of CRE, this could be attributable to the development of more soluble Zn(OH)2 than insoluble zinc ion and prevented coagulation.

4.4 Effect of electrolyte

NaCl is typically used by electrocoagulation treatment to improve the solution conductivity, so that current consumption could be reduced. In addition, increasing water conductivity using NaCl has other advantages; for example, chloride anions can significantly reduce the adverse effects of other anions, such as bicarbonate and sulphate ions. Conversely, an excessive amount of NaCl induces an overconsumption of the TiO_2/Zn electrodes due to 'corrosion pitting'; zinc dissolution may become irregular. This is the reason why NaCl addition should be limited and optimized. It also allows the passivity of the electrodes to be decreased by removing the surface passivation of the oxide film produced because of its catalytic action on the electrode surface. The adverse effects of other anions (due to their oxidation) and the availability of metal hydroxide in the solution could greatly reduce chloride ions. This parameter could, therefore have a substantial effect on the efficiency of pollutant removal. The ability to remove pollutants under certain conditions depends on the amount of coagulant produced that is related to the media's conductivity. In order to improve the conductivity of the waste water to be treated, NaCl is applied in this process and the increase in salt concentration increases the concentration of ions in the solution, thus reducing the electrical resistance of the solution, thus reducing the resistance between electrodes. Greater the electrical conductivity means higher electrical conductivity of the solution, and for creating a fixed current conductivity, a higher voltage is needed. Therefore, for creating a fixed current conductivity, less NaCl is needed compared with other electrolytes like Na_2SO_4, or Na_2SO_3, Moreover NaCl has a higher ionization speed and mobility due to the lower radiuses of Na and Cl as a result, and more current passes through wastewater and by increasing passing current, the speed of anode dissolution increases. On the other hand, producing acidic species such as HCl and ClO^- enhances the desirability of revival conditions. Therefore, using NaCl as electrolyte has advantage for lower price. Also, textile and dying industries use plenty of NaCl and wastewaters of these industries comprise ions of NaCl, because it is cheap and the solution containing this salt has high conductivity thus it need low voltage for electro-coagulation and so it is economical in industrial scale.

To study the effect of wastewater conductivity on dye removal, various experiments were performed using NaCl as the electrolyte in the range of 0.1–0.35 g/L and the CRE removal efficiencies observed during EC process are given in **Figure 6(b)**.

It is believed that the main pollutant removal mechanism observed during electro-coagulation is adsorption and entrapment onto the amorphous titanium and $Zn(OH)_2$ precipitate formed due to the anodic reaction at maximum rate at pH 8.5 and 4.5 for 'A' and 'B' electrodes and the anodization of Ti, Zn are given in Eqs (2)and (3)

$$Ti(s) \rightarrow Ti^{3+}(aq) + 3e^- \tag{2}$$

$$Zn \rightarrow Zn^{2+}(aq) + 2e^- \tag{3}$$

As is evident in **Figure 6(b)** increasing the electrolyte concentration from 0.1 to 0.35 g/L the high % of CRE reducing rates (98.2 for electrode 'A' and for 'B' 98.1), Due to the improved conductivity of the aqueous medium and the addition of NaCl up to 0.35 g/L, the improvement in the removal efficiency of CRE can be related to a shift in ionic strength resulting in a moderate but substantial decrease in treatment efficiencies in terms of CRE removal in the electrode 'A.' But there was a sudden decrease in the CRE in the case of Zn electrodes as the electrolyte concentration increased from 0.1 g/L (from 98 percent sudden decrease in percentage of CRE) a further increase in electrolyte concentration did not improve, these findings can be clarified by the fact that when the NaCl concentration increased, the electrolyte conductivity correspondingly increased. This was possibly because the chloride ions could destroy the passivation layer and increase the metal's anodic dissolution rate, either by integrating chloride ion into the oxide film or by involving the same in the electrochemical reaction. A further increase in NaCl concentration in both electrodes showed negative degradation and salt film formation on the electrode surface, which would obstruct the interaction between the electrode and the waste water. The chance of successful interaction between the organic contaminants and the hydroxyl radicals was therefore reduced.

4.5 Effect of applied current

It is clear that the applied current is strongly influenced in EC. Increased current results in increased anodic dissolution of metal ions, resulting in the formation of high quantities of precipitate for pollutant removal. In batch electro-coagulation, operating current density is important as it is the only operational parameter which can be directly regulated. The quantity of oxidised metal ions increased when the current increased, and the quantity of metal hydroxide compounds for pollutant precipitation and adsorption also increased. In addition, as the applied current grows, the rate of development of hydrogen bubbles increases and their sizes decrease. For successful dye removal, all these effects are significant. Other side reactions in the vicinity of the anode, such as the direct oxidation of one of the components of the contaminant or the formation of oxygen that restricts the efficacy of electro-coagulation, can be caused by high-current activity. In comparison, a high current causes the passivity of the cathode to decrease, resulting in high energy consumption. The best conditions correspond to a low applied current and substantial electrolysis time especially in terms of energy consumption and electrode consumption. It is essentially critical to avoid operating at too high current to address the excessive generation of Ti, Zn poly hydroxides in wastewater. The efficiency of the reduction of contaminants depends on the production of Ti (IV or III) and Zn (II) by the anode, so that a high period of electrolysis will lead to a higher production of titanium hydroxide or zinc hydroxide, which is responsible for the coagulation process. To optimise the applied current in the EC method, experiments were performed under other optimised parameters at different applied current from 0.05 to 0.30A and the results are given in **Figure 6(c)**.

As the applied current increased from 0.05 to 0.30A, the anodisation accompanied by floc formation with the Ti^{n+} ions increased, the CRE percentage was 99.5 at 0.15A and consequently the removal efficiency decreased marginally in the case of electrode 'A' and in Zn-Zn electrodes as the applied current increased, the CRE removal increased gradually, the maximum CRE was 86 percent at 0.15A. The increase using the electrode 'A' was due to the dissolution of both Ti^{3+} and Zn^{2+}, whereby at lower applied current highest CRE removal was obtained, moreover it could be observed that increasing the applied current above the optimum value decreases the CRE is due to undesirable side reaction such as electrolysis of water and oxygen evolution from OH free radicals. However energy consumption leads to be higher for increased applied current and indicates that increase in current density led to less efficient sprocess.

4.6 Effect of time

The percentage color removal efficiency depends directly on the concentration of ions produced by the electrodes. This can be achieved by parameter like EC time. Because the formation of metal ions and concentration of the metal hydroxides play an important role on pollutant removal, this depends on operation time. To study its effect, the EC time was varied for different time intervals i.e., 5, 10, 15, 20, 25, 30 min and the other optimized parameters were kept constant. The results obtained are illustrated in **Figure 6(d)**. The H_2 and O_2 release and flocs formation increased over time and the foam became thicker.

A plot is drawn between time verses % CRE for two different electrodes as shown in graph, it was clearly known that as the time increases the percentage of CRE increased in the case of electrode 'A' at 15 mins was 97.2 and then there was slight reduction in CRE. Whereas in the case of electrodes 'B' there was a gradual increase of CRE from 50 to 92% and high % of CRE was achieved at 30 minutes which will be with more of energy as well electrode consumption compared to the electrodes 'A'.

In the EC process, the anode produces metal ions during electrochemical reaction. Metal ions are destabilization agent. If the charge loading were low, the metal ion released from the anode would not be sufficient to destabilize all the colloidal and suspended particles, so dye removal was not efficient in the case of zinc electrodes at applied current 5A. When EC time changed from 5 to 30 minutes the energy consumption increased from 0.0004966 to 0.00174 kWh/m^3in the case of electrode 'A' and 0.000843 to 0.005227 kWh/m^3 forZn electrodes. From these results it is shown that % CRE removal is high with less energy consumption in the case TiO_2/Zn than zinc electrodes. Treatment time is related with energy

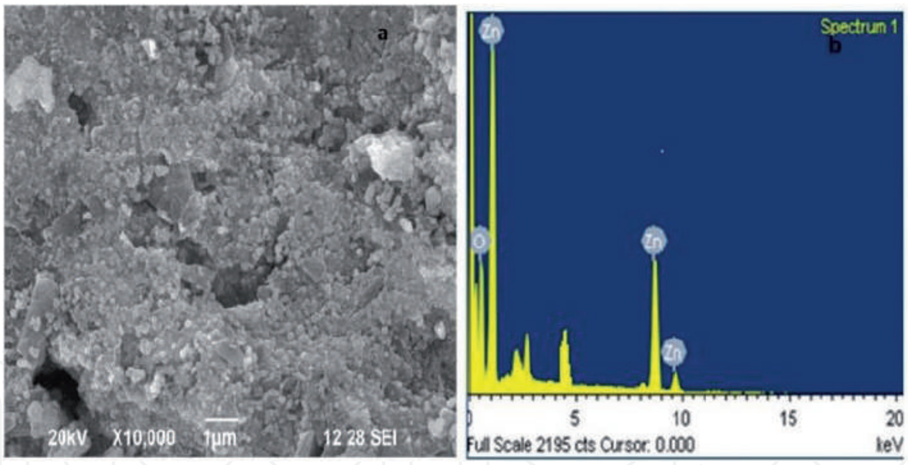

Figure 7.
a) SEM, b) EDS of Sludge after electrocoagulation.

consumption and wastewater treatment performance. It is well known that the removal efficiency did not improve much after 25 min electrolysis, but the prolonged time would increase the electrochemical treatment cost. The results indicate that the optimum electrolysis time for best removal efficiencies is 10 min for TiO_2/Zn and 30 min for Zn electrodes.

4.7 Sludge charaterization

The SEM images that display the sludge's morphology characteristics are shown in **Figure** 7. It can be visualised that the flaky structure of the particulates produced from electrocoagulation is confirmed by the adsorbed dye molecules (grey or black portion) on the surface and the presence of a peak at 4.8 keV in the EDS spectra confirms the titanium ion floc. It is assumed from SEM, EDS sludge study, that the first titanium flocs which were involved in electrocoagulation, once after the depletion of the same, then the dye molecules have been removed by zinc flocs.

5. Conclusion

The results obtained in this study shows that the color can be eliminated with high percentages using the newly prepared TiO_2/Zn electrodes from $TiCl_3$ by spray pyrolysis method compared with using Zn in EC process.

The effect of applied current on CRE% can clearly be understood. As the applied current increased the removal of organic matter also increased. In all the experimental parameters, dye removal efficiencies (CRE%) was observed in short period of operational time in using TiO_2/Zn. The increase in applied current is also considered to mean an increase in energy usage. Thus, due to local discharge limits, energy and electrode usage, local energy unit prices and some other limiting factors, an acceptable current density has to be considered.

Furthermore this research showed that the initial pH of the waste water at which high CRE% was obtained as the optimized pH 8.5 in the case of TiO_2/Zn but 4.5 for Zn electrode. Overall, high color removal efficiency of disperse dye was obtained using newly modified TiO_2/Zn.

The EC process has the potential to treat the textile dyeing wastewater and thus to reduce the contamination of the environment by the dye molecules as the real time textile dyeing waste water can be treated with this newly developed TiO_2/Zn. Further work can be done as given.

- Preparation of TiO_2/M electrode.
    - Attempt can be made in the preparation of TiO_2/M (M for metal) with different metals as electrode materials,
    - different precursor
    - preparation parameters like flow rate, number of coating etc. can be adopted in spary pyrolysis.
- Opretaional parameters in EC process
    - In EC process the other operational parameters like varying the distance between the electrodes, height of electrodes immersed in the waste water etc. can be optimized.
    - Investigation other than CRE%, like COD, BOD etc. can be calculated.
- Economic parameters and opretional cost can be designed for the other opretaional parameters like
    - Applied current,
    - dye concentration,
    - electrolyte concentration
    - and pH,
- The electrode can be applied to dyes other than disperse dyes and the real time waste water in dyeing units.

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