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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
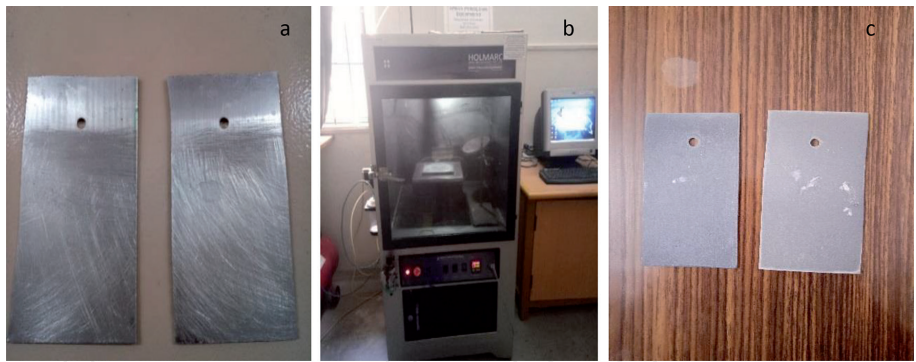
Figure 1.
(a) Photograph of the pretreated zinc plate, (b) Coating on zinc in spray pyrolysis, (c) TiO₂/Zn.

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 TiO₂/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 TiO₂/Zn – TiO₂/Zn and Zn – Zn. (Hereafter these electrodes will be represented as 'A' (TiO₂/Zn – TiO₂/Zn) and 'B' (Zn – Zn)).
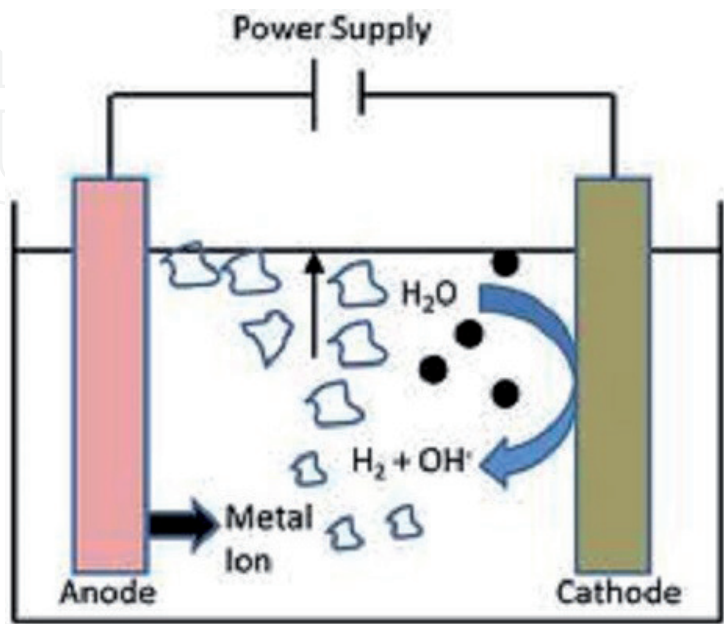

Figure 2.
Schematic representation of EC process (Source: http://pubs.sciepub.com).

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
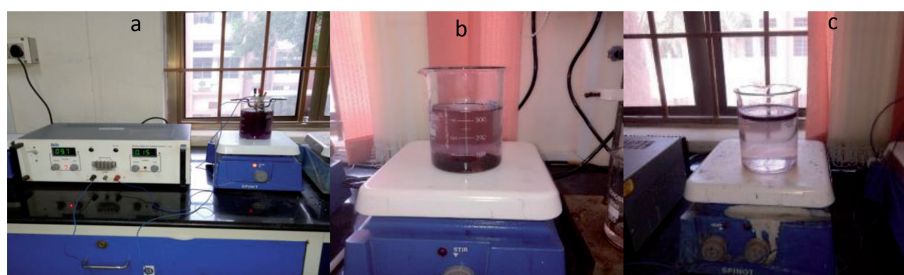

Figure 3.
Photograph of the (a) dye solution, (b) after EC sludge settling, (c) sludge floating.

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.
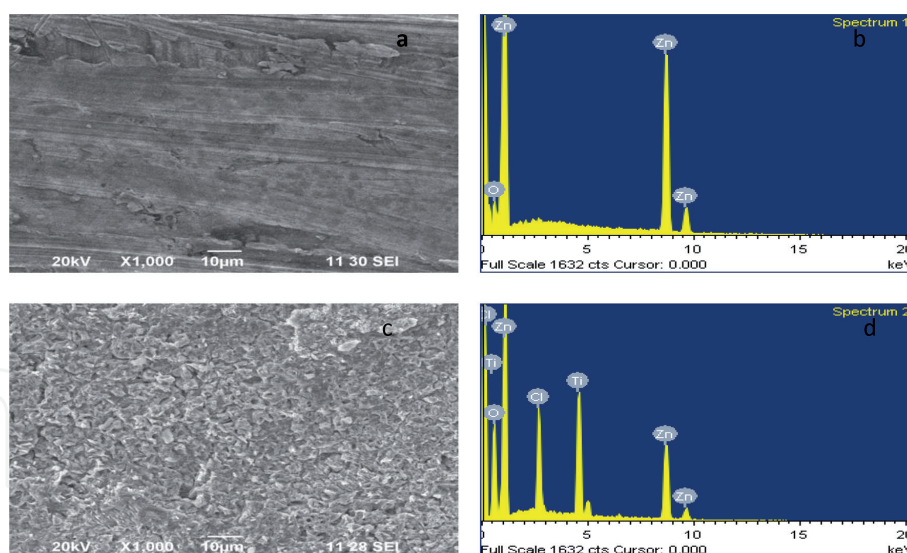
Figure 4.
(a, b) SEM, EDS image of Zinc, (c, d) TiO$_2$/Zn.

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
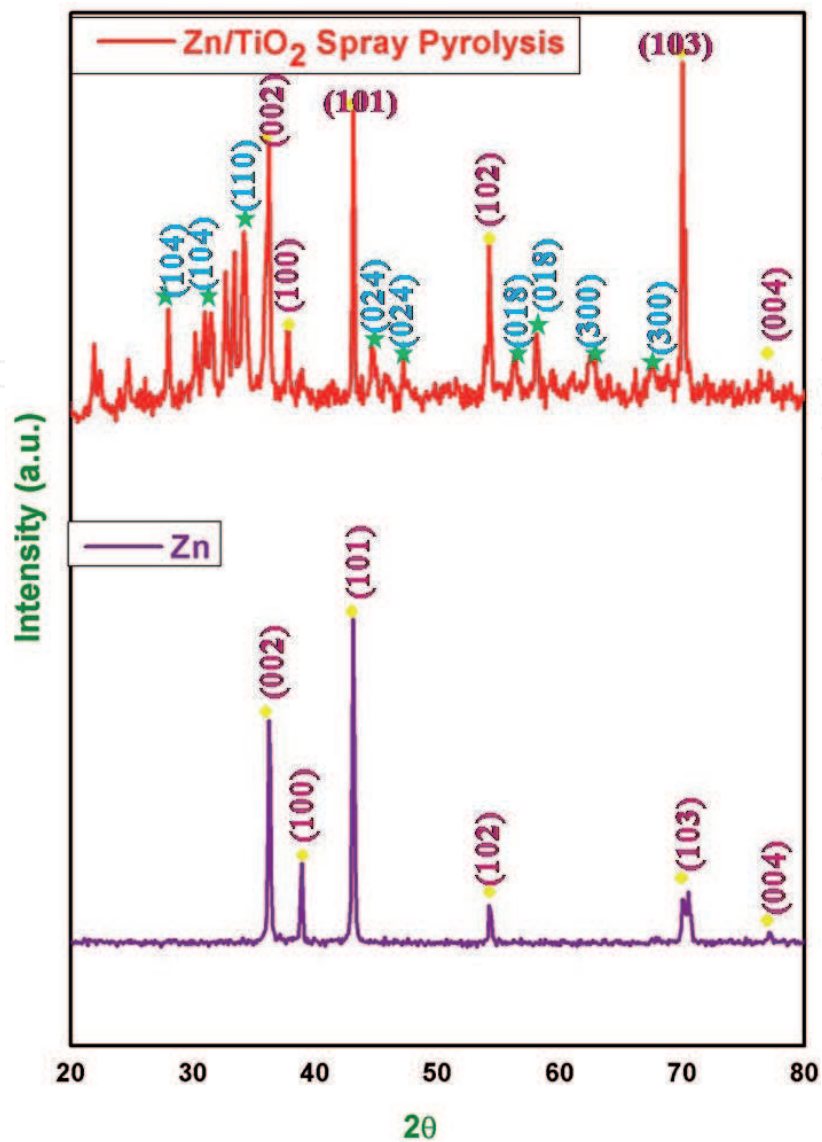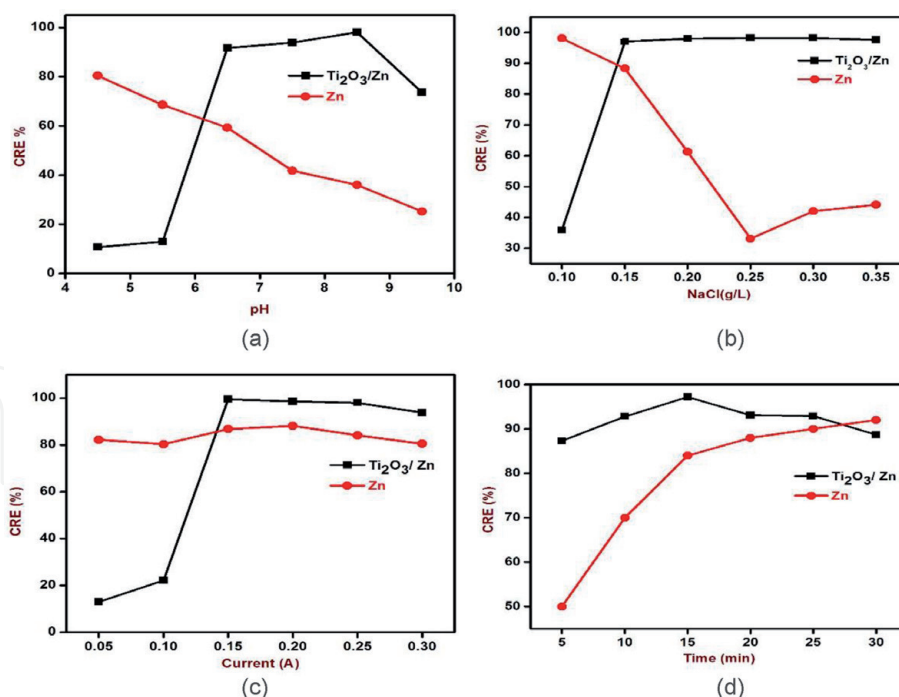
Figure 5.
XRD Pattern for Zn and TiO₂/Zn.

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 specia- tion, 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 experi- ments 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)

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

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

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/m³ in the case of electrode 'A' and 0.000843 to 0.005227 kWh/m³ for Zn 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
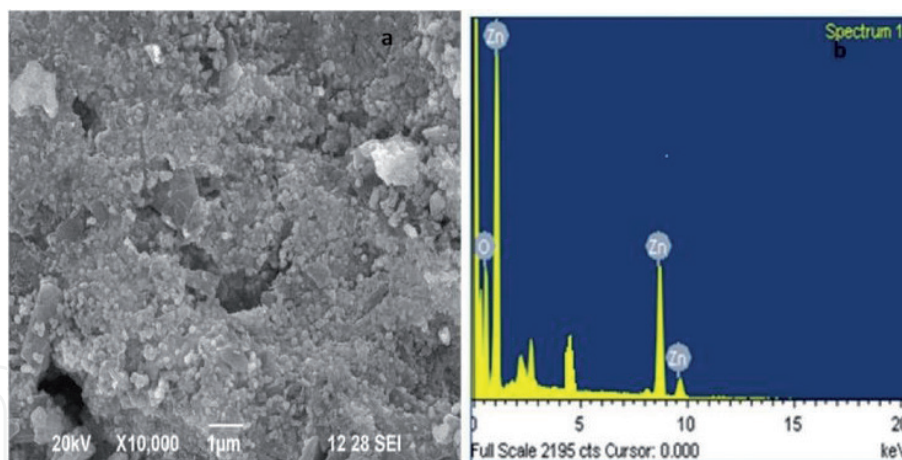
Figure 7.
a) SEM, b) EDS of Sludge after electrocoagulation.

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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