

Potential of Ti_2O_3/Zn Electrodes versus Zn by Electrocoagulation Process for Disperse Dye Removal

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Electrocoagulation methods are being used for the alternative treatment process for the remediation of textile waste water. This work primarily deals with the treatment of textile dyeing waste water followed by the utilization of waste material. The purpose of the proposed study is to evaluate the potential of electrocoagulation process using Ti_2O_3/Zn electrode prepared by spray pyrolysis using $TiCl_3$ and compared the performance with Zn electrodes. The surface morphology, structural analysis and percentage composition of the elements of the Ti_2O_3/Zn electrode was studied by SEM, XRD and EDS analysis. The efficiency of electrocoagulation treatment process to treat synthetic waste water containing Coralene Navy RDLSR, Coralene Red 3G, Rubru RD GLFI dye was studied for the effect of operational parameters. The result indicates that this process was able to achieve colour removal (97.2 %) at pH 8.5, with 34.42 % less energy consumption with Ti_2O_3/Zn compared with zinc electrodes.

Keywords: Electrocoagulation, Disperse dye, Ti_2O_3/Zn , Reaction time, Energy.

INTRODUCTION

Textile industries consumes large quantity of water compared to other industries [1]. When wastewaters are liquidated into the surroundings without action, they can distress marine bionetworks in different ways [2]. 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 [3]. Textile dyeing wastewater are treated for its colour removal through diverse physical, chemical, electrochemical and natural approaches or a grouping of such methods [4-6]. Electrocoagulation method is vulnerable to produce particles of increased magnitude and mass, which promotes colour abatement by settling in an aqueous solution. This process has merits over other type of treatment methods for colour removal, such as the need for simple equipment, efficiency, reduced retaining time to remove pollutants and simple operation [7]. Electrocoagulation process has been applied for the treatment of wastewater like cutting oil emulsion wastewater [8] and textile wastewater [9]. Also this process being found useful to treat wastewater containing heavy metals from wastewater [10-15].

The main errand that this technology encounters is that of high amount of electricity consumption and affects the operating costs, more research into the ways and means of reducing the power consumption would help in the endorsement of this process. As electrical energy requirement is proportional to the treatment time, this process with conventional electrodes like aluminium resulted in two-fold electrical energy consumption as compared with energy consumption using stainless steel electrodes [16]. Although conventional electrode materials (Al and Fe) can, good efficiency in colour removal and are likely to undergo dissolution. Accounts on innovative electrode resources in electrocoagulation process remain inadequate in the literature. So need for novel cost effective electrode material/hybrid electrocoagulation reactor which consumes less current and time. Secondly no previous studies have attempted to broadly investigate electrocoagulation using modified electrodes other than the conventional ones used [17]. Modified electrodes like TiO_2/Al is successfully used in batch process [18]. In electrocoagulation process if titanium and aluminium are not recovered from the sludge, it might cause pollution to water and soil. Aluminium chemistry is quite complex. Al^{3+} forms during precipitation in electrocoagulation

process [19]. Soluble aluminium can inhibit the plant growth in acid soils [20,21], greatly limiting crop productivity and hence we address the issue of Al alone in this study and instead of aluminium, zinc substrate is used. Zinc is known to be a favourable element, essential and beneficial for the man [22]. It is an essential element in human metabolism. A zinc deficiency may have serious consequences on man health [23].

Centered on these points, the scope of this study is to prepare Ti₂O₃ coated on zinc by spray pyrolysis using the precursor solution TiCl₃ and examine the efficiency of electrocoagulation process in which electrocoagulation performance were evaluated for the removal of disperse dye using Ti₂O₃/Zn-Ti₂O₃/Zn and compared with Zn-Zn. The two methodological criteria carried out in this work are colour removal and electrode efficiencies. This experiment was investigated for the optimization of operational parameters such as applied current, pH, time and of electrolyte. The main focus was to optimize the operating conditions, to apply the same for the treatment of real time wastewater.

EXPERIMENTAL

Preparation of Ti₂O₃/Zn electrode by spray pyrolysis:

In general the experimental procedure recommended by Beck and Gabriel [24] and Parameswari and Kennady [25] was adopted for the preparation of Ti₂O₃/Zn electrode by spray pyrolysis of TiCl₃ by the following procedure. The Ti₂O₃ coating was done on zinc substrate which was cleaned well and sand blasted to make the surface adherent for the coating. The surface was then washed properly with water, rinsed using triple distilled water. Then it was coated with the precursor solution TiCl₃ (0.05 N) 4 mL, 1:1 HNO₃. The precursor solution was cooled to 5 °C to which diluted isopropyl alcohol with water was added maintaining the temperature 5 to 10 °C.

The type of spray pyrolysis method used in this work is a spray pyrolysis in a tubular reactor. The precursor solution prepared as given above is pumped (Stroke pump) to a 100 kHz ultrasonic atomizer (Lechler Inc.) toward the heated substrate held inside a tubular quartz reactor (5 cm in i.d. and 30 cm in length). The zinc substrate was placed on the sample holder and heated by quartz heating bulbs located on top and below the tube. The substrate temperature was monitored by a type K thermocouple connected to the temperature controller monitor. At 200 °C, the precursor were sprayed on the substrate and under the carrier gas like nitrogen and oxygen with the nozzle to substrate distance was 20 cm. The solution flow rate was 3 mL/10 min with typical spray time for one time deposition of a 50 mL solution batch was around 30-45 min. 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 × 0.5 cm.

Electrocoagulation process

Synthetic dye solution: Disperse dye used in this work was obtained from one of the small textile dyeing industry in Coimbatore, Tamil Nadu. (Commercial name; Coralene Navy RDRLSR, Coralene Red 3G, Rubre RD GLF I) Synthetic wastewater was prepared in distilled water at dye concentrations of 0.03 %,

Electrocoagulation unit is set up with glass beaker along with magnetic stirrer and DC power supply as an electrochemical reactor. Two sets of electrocoagulation process were run with Ti₂O₃/Zn-Ti₂O₃/Zn and Zn-Zn. (Hereafter these electrodes will be represented as 'A' (Ti₂O₃/Zn-Ti₂O₃/Zn) and 'B' (Zn-Zn)).

9 cm × 3.2 cm × 0.5 cm magnitude of the electrodes were used with the total effective electrode area was 28.16 cm² and the distance between both the electrodes was 3 cm. 250 mL test solution was taken in 500 mL capacity beaker and a magnetic stirrer was used to stir the solution. Before each experiment, electrodes were splashed with water and placed in 15 % hydrochloric acid in order to remove dust from the electrode plates and thus weigh the electrodes after drying. After each experiment the electrodes are cleaned with water, dried and finally weighed. The subsequent treated sample was filtered using Whatman filter paper and filtrate was used for the characterization. In this study, individual effects of electrolysis time and applied current were quantified on colour removal efficiency (CRE). The pH of the test solution was adjusted with 0.5 N HCl or NaOH. All experiments were conducted at 25 °C. Two sets of electrocoagulation process were carried out with 'A' and 'B' electrodes with operating parameters like pH, electrocoagulation time, addition of electrolyte NaCl and applied current for optimization to achieve higher colour removal efficiency (CRE %). For each optimization of operational parameters, based on the initial experiments, other parameter rates were kept constant.

Colour removal efficiency (CRE): Jasco V-670 spectrophotometer was used to measure the wavelength (542 nm) of dye solution. The following equation was used to calculate colour removal efficiencies (CRE %) after electrocoagulation treatment

$$\text{Colour removal efficiency (\%)} = \frac{A_b - A_t}{A_b} \times 100 \quad (1)$$

where A_b and A_t were the absorbance of the dye in solution before electrocoagulation and at the time t, respectively. Conductivity meter (Elico CM180) was used to measure electrical conductivity and pH meter (Eutech) to measure pH of dye solution.

Electrode consumption: Since the dissociation of metal ions occurs at anode due to electron driven mechanism through applied current, the durability of the electrode material is of great concern. The theoretical amount of metal ions dissociated into the medium to assist coagulation process was calculated in g/m³.

$$\text{Theoretical electrode dissociation} = \frac{M \times I \times t}{n \times F} \quad (2)$$

where, M is the molecular weight of the metal used in g/mol, I is the current applied in amperes, t is the electrolysis time in minutes, n is the number of moles of electrons and F is the Faradays constant (F = 96497 C/mol). After washing with acid, cleaning with scrub and drying in an oven, the actual weight of metal dissociated [actual electrode dissociation (AED)] in grams per cubic meter was obtained by observing the weight loss during the treatment process.

Energy consumption: Energy consumption (due to the application of electricity) also known as electrical energy consumption in kWh/m^3 is a significant parameter which decides the economic viability of the method. Commonly used relation for the estimation of EEC is given below.

$$\text{EEC} = V \times I \times t \quad (3)$$

where, V and I are the voltage (V) and current applied (A) and t being the reaction time for the reaction.

Sludge measurement and characterization: Although the electrocoagulation process is said to generate less sludge compared to chemical coagulation, sludge characterization also plays a major role that decides safe discarding or reclaim. Hence, the sludge produced during the process was separated using filtration technique and kept in hot air oven for about 24 h at 100°C and dried which was then weighed and analyzed by SEM and EDS studies.

Characterization techniques

Morphology and structural analysis $\text{Ti}_2\text{O}_3/\text{Zn}$ electrodes: The morphological and structural analysis of $\text{Ti}_2\text{O}_3/\text{Zn}$ electrodes were analyzed by scanning electron microscope (SEM) by JEOL, JSM 35 CF, Japan. Energy dispersive X-ray spectroscopy (EDS) was used for the elemental analysis and chemical characterization and X-ray diffractometer using JEOL-JDX 8030 Model 6000 diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) to study the micro structure of the particles present in the electrode and sludge.

RESULTS AND DISCUSSION

Characterization of $\text{Ti}_2\text{O}_3/\text{Zn}$

SEM and EDS analysis: The SEM micrograph and EDS spectrum zinc substrate and $\text{Ti}_2\text{O}_3/\text{Zn}$ by spray pyrolysis is given in Fig. 1a,b. The SEM micrograph of Ti_2O_3 showed there is compressed units and was regular in form. The peaks corresponding to Ti and O peaks are found in both EDS spectra with peak like Cl specifies that the coated surface is found with chlorine. SEM pictures show that the obtained surfaces are permeable. Additionally, the crashes in the surface layer are visible beyond the pores, which may be symptomatic of speedy development in size of the layer of Ti_2O_3 on the zinc substrate.

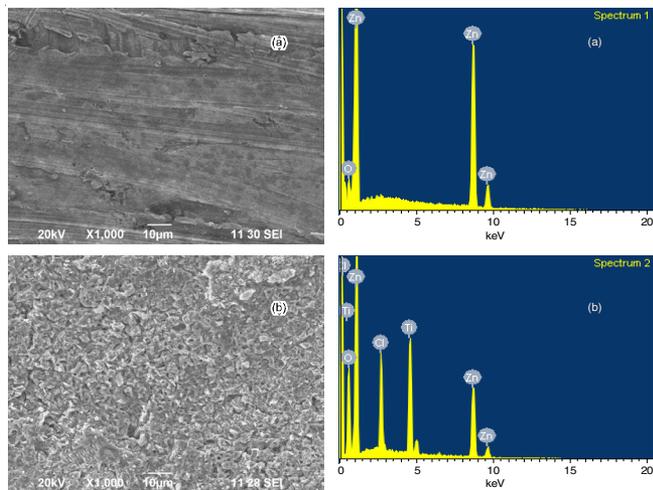


Fig. 1. SEM and EDS image of (a) zinc substrate, (b) $\text{Ti}_2\text{O}_3/\text{Zn}$

Fig. 1b shows the EDS spectra for the Ti_2O_3 particles on the zinc substrate, the peaks around 0.2, 0.3 and 4.3 keV are connected to the requisite energies of titanium and oxygen corresponds to the Ti_2O_3 particles and it approves the presence of elemental compounds in the coated zinc substrate, but with impurity peak corresponding to chlorine from the precursor TiCl_3 . The peaks around 0.25, 8.5, 9.8 keV are correlated to the required energies of zinc with oxygen.

XRD of $\text{Ti}_2\text{O}_3/\text{Zn}$ electrode: The X-ray diffractogram of $\text{Ti}_2\text{O}_3/\text{Zn}$ and zinc are shown in Fig. 2. The diffraction peaks of Ti_2O_3 phase and the zinc substrate are present in the investigated electrode. The particle size calculated from Debye-Scherrer equation indicated good surface area [26]. The nano crystalline structure was established by sharp peaks attained matching to the planes (104), (018), (110), (024), (300). It indicates the hexagonal primitive structure of Ti_2O_3 nanoparticles. From the XRD results, deposition of Ti_2O_3 is confirmed with 2θ values (30, 32, 35, 47, 56, 63, 68) and deposition of Zn with 2θ values (36, 43, 54, 70, 78). The data was compared with the JCPDS card no: 71-1059 for Ti_2O_3 and 65-3358 for Zn. The crystalline size calculated using Scherrer equation was ranging from 20.2-53.7 nm.

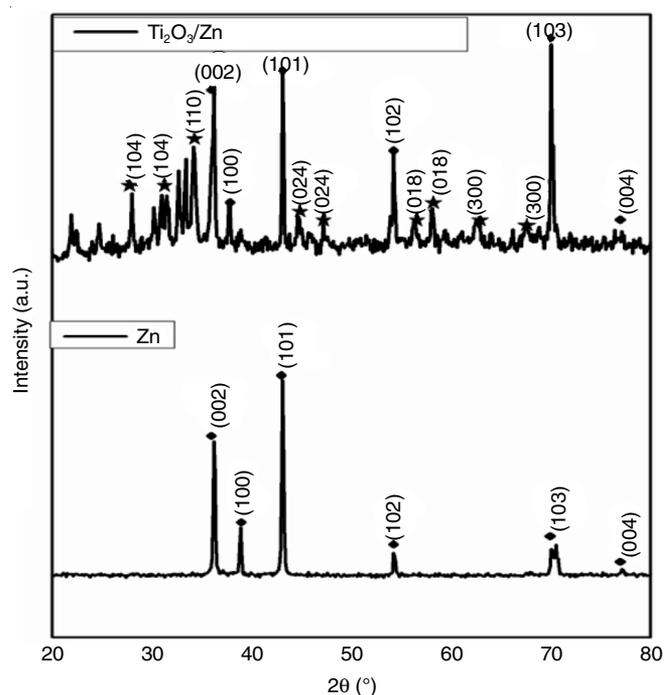


Fig. 2. XRD pattern for Zn substrate and $\text{Ti}_2\text{O}_3/\text{Zn}$

Optimization of operational parameters: Optimization of operational parameters in electrocoagulation procedure such as (pH, electrolyte concentration, reaction time and applied current) were examined. From the preliminary experiments, other parameter proportions were kept perpetual for the optimization of each operative parameters for both sets of electrocoagulation process with $\text{Ti}_2\text{O}_3/\text{Zn}$ - $\text{Ti}_2\text{O}_3/\text{Zn}$ (electrode 'A') and Zn-Zn (electrode 'B').

Effect of pH: Performance of electrocoagulation process is greatly affected by pH in bringing out the effective coagulation followed by flotation or sedimentation. The optimal pH range depends on the nature of electrode material and the

structure of dye used. The pH of the solution determines the formation of metallic ions, the chemical state of other ions in the solution and also have the control over the solubility of the formed products. Henceforth the optimum pH is necessary to reduce the environmental remediation prices and make this method more significant. To study the outcome, a series of experiments were carried out using synthetic disperse dye solution at varied pH (4.5, 5.5, 6.6, 7.5, 8.5 and 9.5) under the above mentioned condition. With NaOH or H₂SO₄ the pH of the experimental dye solution was adjusted to a desirable value which 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 Fig. 3a.

The pH of raw wastewater can influence in a positively or a negatively way on the competence of the process, as it affects the steadiness of different type of hydroxides which are formed [27]. The colour removal efficacy showed with no significant effect in the range of pH 4.5 to 6.5. It was observed that decolorization was most efficient at pH after 6.5 to 8.5 for the electrode 'A'. Possibly at this pH, most of the metal hydroxides such as Ti(OH)²⁺ and Ti₂(OH)²⁺ and unsolvable Ti(OH)₃ could be present. The insoluble metal hydroxide formed promote coagulation with dye pollutants by precipitation. Above pH 8.5, % of CRE decrease may be due to the formation

titanium tetra hydroxyl anion which is soluble Ti(OH)₄⁻ there by reducing the coagulation. At an initial pH of 4.5, CRE % is very less, the separation was not clear and as pH was increased from 4.5 to 8.5, the separation was clear and high % of CRE removal may be due to the formation of further monomeric and polymeric insoluble titanium hydroxides. For electrode 'A' at pH 8.5 Ti(OH)₃ are produced more thereby effective abatement of dye with quick settling [28,29].

In case zinc electrodes at pH 4.5 the % of CRE was 80.49, as the pH increased from 4.5 to 9.5 there was a gradual and sudden abatement in % of CRE, this may be due to the formation of more soluble Zn(OH)₂ than insoluble species of zinc ion due to which less favour towards coagulation and thereby precipitation.

Effect of electrolyte: The supporting electrolyte in electrolysis, reduces the current utilization there by reducing energy consumption. Electrolyte increase the solution conductivity in any electrochemical method, it also helps in increasing water conductivity. But over addition of the same in this case NaCl might induce the dissolution of the coated one in Ti₂O₃/Zn electrodes due to corrosion followed by zinc. Hence, the addition of NaCl addition need to be optimized [30]. Chloride ions from the added electrolyte may decrease the adverse effects of other anions and thereby upsurges the availability of metal

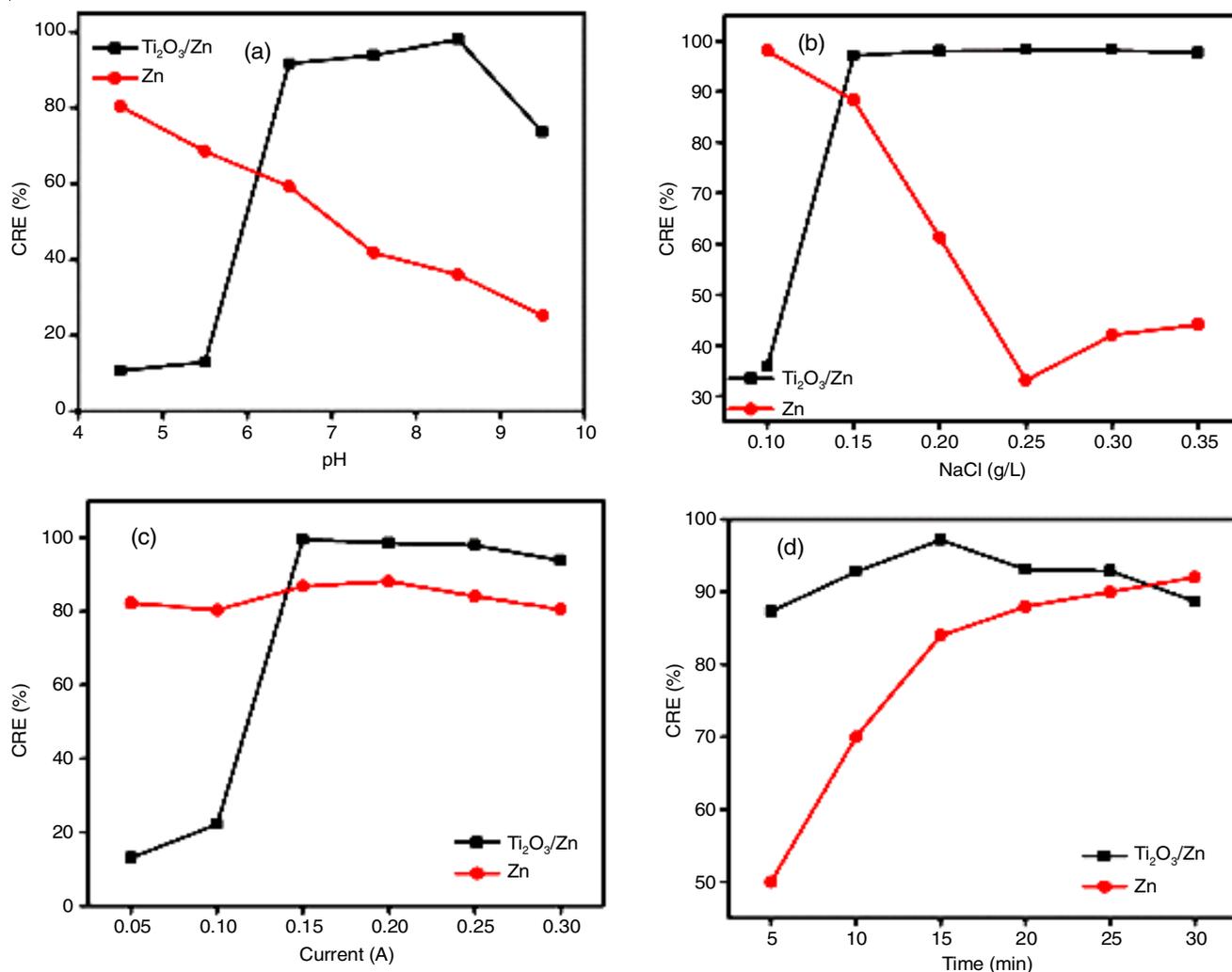
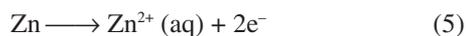
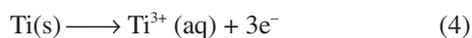


Fig. 3. Effect of varying (a) pH on CRE (%), (b) concentration of NaCl on CRE (%), (c) applied current on CRE (%), (d) time on CRE (%)

hydroxide in the solution. The ability of pollutant removal at certain conditions depends on amount of coagulant spawned with the effect of the conductivity of the solution. Textile and dyeing industries use NaCl in various stages and the wastewater generated from these contain sodium and chloride ions and the solution containing this salt has high mobility thus it requires low voltage for electrocoagulation.

Varying the addition of NaCl from 0.1-0.35g/L, electrocoagulation process were conducted and the CRE removal efficiencies observed during electrocoagulation process are given in Fig. 3b.

The pollutant removal mechanism during electrocoagulation is adsorption of the metal hydroxides due to the formation of metal ions due to oxidation which was maximum at pH 8.5 and 4.5 for 'A' and 'B' electrodes [31].



From the Fig. 3b increasing the electrolyte NaCl 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), the increase in the colour removal efficiency may be due to a change in the strength of ions which increased the conductivity of aqueous medium and a further addition of NaCl up to 0.35 g/L resulted in a moderate but significant retardation of treatment efficiencies in terms of CRE removals in the electrode 'A'. But in the case of Zn electrodes there was a sudden decrease in the CRE as the electrolyte concentration is increased from 0.1 g/L (from 98 % sudden abatement in % of CRE) a additional increase of electrolyte concentration did not improve. As the conductivity increased, chloride anions can affect the anodic surface and increase the anodic dissolution [32]. In both the electrodes, further addition of NaCl resulted in less colour removal efficiency, because of salt film deposition on the electrode surface, which would block the interaction between electrode and wastewater. Thereby there was reduction in the interaction between the dye pollutant and hydroxide free radicals.

Effect of applied current: Electrocoagulation process is strongly affected by the applied current. As current density is the only parameter, which is critical in batch electrocoagulation process [33]. Increasing the applied current, the anodic reaction facilitates the metal ions, which combines with the hydroxyl ions into precipitation and adsorption of the pollutants were also increased, thus leading to an increased efficiency of dye abatement [34-36]. Furthermore, the rate of production of hydrogen increases and their sizes decrease as the applied current increases. All these effects are important for active deduction of dye molecules. Operating at high current may cause many different side reactions in the region around the anode, like the pollutants undergoing direct oxidation or the formation of oxygen, which limits the effectiveness of electrocoagulation. Conversely, a high current causes passivity of the cathode by reduction, leading to a high consumption of energy. Especially regarding economical parameters like electrical energy and electrode consumptions, the best conditions correspond to a low applied current and electrolysis time. To overcome the unnecessary generation of Ti(OH)_n or Zn(OH)_n in wastewater, it is ultimately important to circumvent working

at high current. To optimize the parameter applied current in electrocoagulation process, experiments were carried out at various applied current from 0.05 to 0.30 A under other optimized parameters and the results are furnished in Fig. 3c. As the applied current increased from 0.05 to 0.30A, the anodization followed by floc formation with the Tiⁿ⁺ ions increased, the % CRE was 99.5 at 0.15A and thereafter slight reduction in removal efficiency in the case of electrode 'A' and in Zn-Zn electrodes as the applied current increased there was a steady increase in the CRE removal, maximum CRE was 86 % at 0.15A. This may be explained in electrode 'A' the flocculation was due to the precipitation of Ti³⁺ which forms heavier flocs than and Zn²⁺, whereby at lower applied current highest CRE removal was obtained, moreover it was detected that increasing the applied current above the optimal value decreases the CRE % due to electrolysis of water and oxygen evolution from the formation of hydroxyl free radicals. From the Fig. 3c, it is inferred that the highest percentage removal was at 0.15 A in which 99.5 % removal for the electrodes 'A'. Increasing the current further at 0.3 A reduction in CRE % (93.8 %) which caused the cathode surface with oxide layer which resulted in preventing proper current transfer between the electrodes.

Effect of varying electrocoagulation time: The dye removal efficiency depends on the amount of ions formed both from the anode and cathode which also depends on electrocoagulation time. To study its effect, the electrocoagulation time varied from 5 to 30 min and the other optimized parameters were kept constant. The results obtained are illustrated in Fig. 3d, it was clearly shown that as the time increases the percentage of CRE increased in the case of electrode 'A' (97.2 % in 15 min) 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 min due to energy as well electrode consumption compared to the electrodes 'A' (Fig. 3d).

Metal ions which are produced at the anode, are destabilization agent. Under the low current, fewer metal ions are released from the anode that would not be adequate to destabilize all pollutants which are in the colloidal form or suspended, so dye removal was not efficient in the case of zinc electrodes. When electrocoagulation time changed from 5 to 30 min the energy intake increased from 0.0004966 to 0.00174 kWh/m³ in the case of electrode 'A' and 0.000843 to 0.005227 kWh/m³ for 'B' electrodes (Fig. 4a,b). From these results it is shown that % CRE removal is high with less energy consumption in the case Ti₂O₃/Zn than zinc electrodes. The obtained results infers that the optimum electrolysis time for best removal efficiencies is 15 min for Ti₂O₃/Zn and 30 min for Zn electrodes.

Electrode and energy consumption: The influence of operating parameters electrolysis time for which the electrode and energy consumption was studied and it is represented in Fig. 4a,b. As it happens in all types of electrolytic process, electrode consumption process is considered as a significant economical parameter in the electrocoagulation process. But the efficiency of the electrocoagulation route depends upon the electrode material used. Hence the determination of the electrode consumption not only determines the economic viability of the process but also decides the lifetime of the

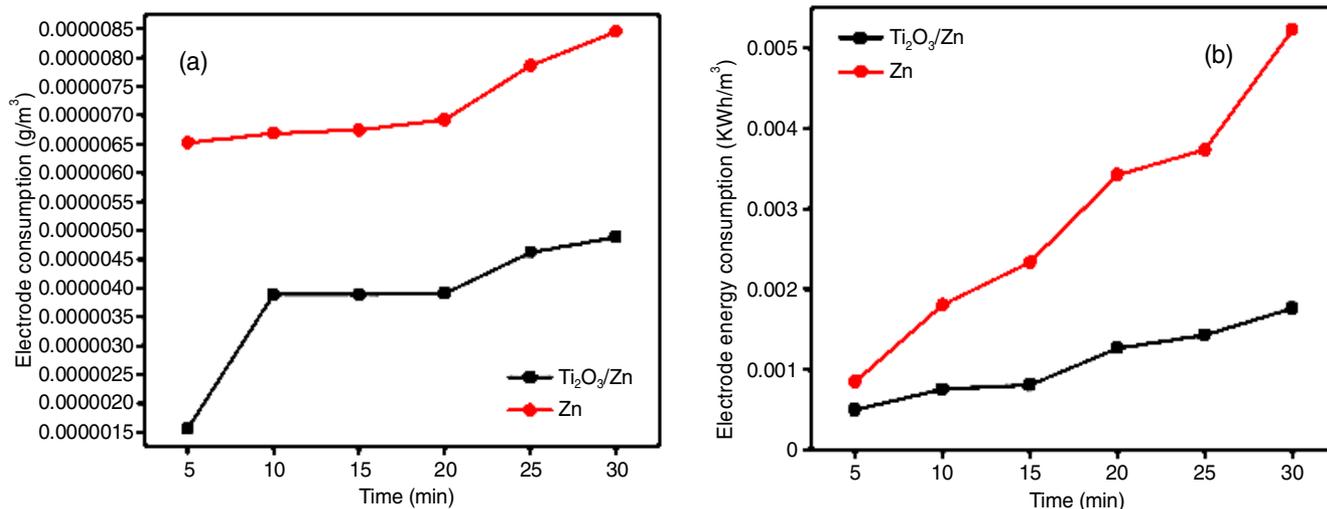


Fig. 4. Electrode & electrical energy consumption for Ti₂O₃/Zn and Zn substrate

electrode. For electrical energy calculation from the operational parameters, electrolysis time alone is taken.

Irrespective of the electrode material, the ingestion of electrode material was dependent on electrolysis time and applied current. Data showed that, at the minimum current supplied at 15 min, 0.15 A current where high CRE % for the electrode 'A', the energy consumption was 0.000802 (KWh/m³) whereas for 'B' electrode it was 0.00233 (KWh/m³). From these results coated electrode consumes 34.42 % less electrical energy in the electrocoagulation process, compared to the bare zinc electrode.

SEM analysis of sludge: The SEM micrograph along with EDS analysis obtained for the sludge is given in Fig. 5. It can be visualized that adsorbed dye molecules (grey or black portion) on the surface of the flaky nature of the precipitates formed from electrocoagulation and the presence of a peak at 4.8 keV in EDS spectra confirms the floc from titanium ions. From SEM and EDS analysis of sludge, it is inferred that first titanium flocs are formed, once it got exhausted from the surface of the electrode, then zinc flocs removed the dye molecules.

Conclusion

The results of this study shows that the colour can be eliminated with high percentages using the newly prepared

Ti₂O₃/Zn electrodes from TiCl₃ by spray pyrolysis method compared with using Zn in electrocoagulation process. In all the experimental parameters, dye removal efficiencies (CRE %) was observed in short period of operational time in using Ti₂O₃/Zn. It is also known that, the increase on the applied current means the increase on energy consumption. So an optimum current density has to be considered due to local discharge limits, energy and electrode consumptions, local energy unit prices and some other limiting factors. In addition, this study showed that high CRE % using Ti₂O₃/Zn was at pH 8.5 but with zinc at acidic pH 4.5. Overall, high colour removal efficiency of disperse dye was obtained using newly modified Ti₂O₃/Zn.

The electrocoagulation process has the merit to treat the textile dyeing wastewater and thereby to reduce the pollution of the surroundings by the dye molecules with the electrode Ti₂O₃/Zn and can also be applied to dyes other than disperse dyes and the real wastewater in dyeing units.

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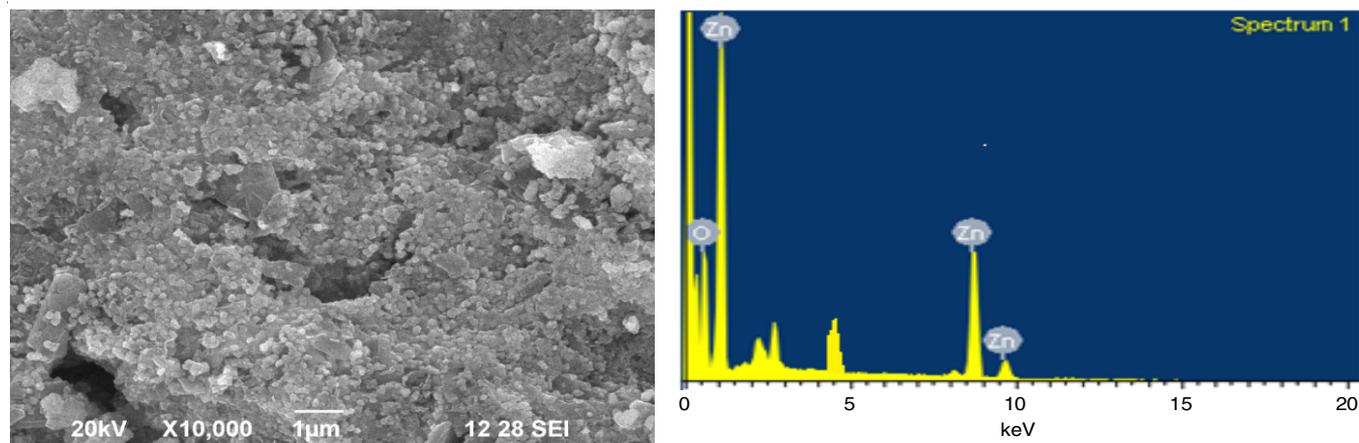


Fig. 5. SEM and EDS of sludge after electrocoagulation

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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