

Electrocoagulation coupled with adsorption for effective removal of eosin yellow and nigrosin dyes in aqueous solution

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Abstract

This paper deals with the study of suitability and efficiency of electrocoagulation (EC) coupled with adsorption to remove dye from synthetic dye solution. The EC cell consisted of mild steel (MS)/copper plates as electrodes and dye solution as electrolyte. The effects of operating time, concentration, supporting electrolyte, current density and pH have been investigated to find out the optimum operating conditions for EC. The concentration of dye was successfully reduced (EY) $\approx 50\%$ and Nigrosin dye $\approx 99\%$ during EC under the optimum operating conditions of initial concentration 0.5ppm, 20ppm, current density 0.04 A/cm², 0.015 A/cm², supporting electrolyte 4g, 4g, electrolysis time 20min, 10min, Eosin Yellow and Nigrosin dye respectively, the removal efficiency of the dyes were found 46.69% and 99%, electrical conductivity were 125.0 S/m and 105.7 S/m and TDS left in the EC treated solution were 82.0 and 69.3 ppt. Further proceedings with solution for adsorption process help to improve the dye removal. Results of the studies are electrical conductivity 20 S/m and TDS 30 ppt for EY, for Nigrosin 64.2 S/m and 42.1 ppt.

Keywords: Adsorption, Current density, Electrocoagulation, Eosin yellow, Nigrosin, Steel and copper electrodes

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INTRODUCTION

Water is the most important component for existence of all living organisms on planet earth. Unfortunately there is only three percentage of water available for drinking and even in that quantity two percentage of water is at North and South Poles as glacier ice and the remaining one percentage of the water is used by humans for their existence. The percentage of portable water is drastically decreasing day by day due to human activities by dumping urban and industrial wastes, viz. dye, chemical, leather, pharmaceutical, metallurgy industries *etc.*, in the water bodies. Deforestation is also one of the reasons for decrease of monsoon level in all over the world. In India monsoon rain is the main source of ground water and drinking water and getting safer drinking water is going to be a big challenge on earth in 21st century. Hence there is a need to develop an efficient and affordable process to convert the waste water to portable water (Nicolaidis S. 1998).

Dyes are the coloring material which is commonly

used on industries such as textile, paint, food industries, reflective stickers, pulp and paper making. Dye industries use too much water, as per the statistics of 2010, in India textile industries using around 1900 Mm³ (Million cubic meters) and effluent water generated was around 75% of its intake. Many of these industries release the untreated effluent into the nearby water bodies such as lake, rivers, ponds *etc.* The chemicals present, especially the dyes, are dangerous to human health and also for the environment since it affects the dissolved oxygen (DO) level in water and demolishes aquatic life. The effluent from dye industry must be treated by some available process such as electrocoagulation, reverse osmosis, filtration, adsorption, bleaching *etc* letting them into water bodies. Among all electrocoagulation is the cheapest and effective treatment method for industrial effluents (Allen RLM 1971).

Electro Coagulation (EC) has been used for treatment of industrial wastewater containing metals at South America and Europe countries in 20th century. It has also been noted that in North America

to treat wastewater from pulp and paper industries. Coagulation is a phenomenon in which the charged particles in colloidal suspension are neutralized by mutual collision with counter ions are agglomerated, followed by sedimentation. EC offers an alternative to the use of metal salts or polymers and polyelectrolyte addition for breaking stable emulsions and suspensions (Yousuf and Mollah, 2000).

MATERIALS AND METHODS

Methodology: Electro Coagulation (EC) is the versatile process to get pure water from industrial waste water. EC technology is a treatment process of applying electrical current to treat and flocculate contaminants without having to add coagulations and reduce the production of residue (Shammas N.K *et al.*, 2010). The percentage of color removal increases with increasing current density the generated H₂ bubbles increase according to Faraday's law (E-S.Z. El-Ashtouky *et al.*, 2010). The amount of metal dissolved by anodic oxidation can be calculated using Faraday's law (Eq. (1)). The mass of metal *m* is, therefore, a function of the electrolysis time *t* and of the electric current *I*.

$$m = \phi \frac{It}{ZF} M \quad (1)$$

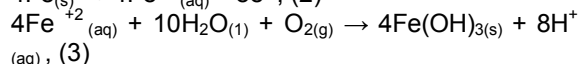
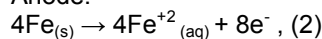
In Eq. (1), *M* is the atomic weight of the electrode material, and *F* is Faraday's constant. However, Faraday's law ($\phi = 1$) is valid only when all the electrons in the system participate only in the metal dissolution reaction at the anode. When parallel reactions occur, a correction factor, denoted current efficiency or faradic yield (ϕ), is used to account for the gap between the theoretical and experimental dissolution of the sacrificial anode (Den .W, Wang. C-J, 2008), (Hu. C-Y, *et al.*, 2007). This value is usually lower than 1, but ϕ may be higher than 1 when the chemical and the electrochemical oxidation mechanism of the metal proceed simultaneously (Gu. Z, *et al.*, 2009). This last situation is frequent with aluminum (Mansouri. K, *et al.*, 2011), (Vepsäläinen. M, *et al.*, 2011). The metal cations released in the bulk undergo various equilibrium reactions that correspond to acid/base, complexation, precipitation and redox reaction in water. The role of these removal mechanisms depends on pollutant species, as illustrated in Table 1.

EC has number of benefits such as compatibility, amenability to automation, cost effectiveness, energy efficiency, safety and versatility. EC combines various mechanisms that can be electrochemical (metal dissolution, reduction of water, pollutant electro-oxidation or electro-reduction...), chemical (acid/base equilibrium with pH change, hydroxide precipitation, redox reaction in the bulk...) and physical (physical adsorption, coagulation, flotation...). These can be sequential and/

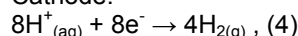
or parallel. Generally on EC iron or aluminum plates are used as an anode for the reaction, and the mechanism for the Fe and Al are as follows (Satish and Chatuevedi, 2013).

For Iron electrode two mechanisms have been proposed

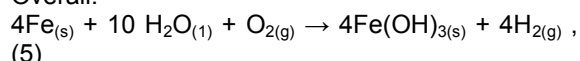
Anode:



Cathode:

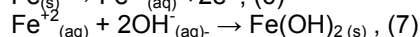
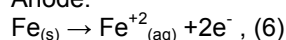


Overall:

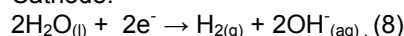


Mechanism 2:

Anode:



Cathode:



Overall:

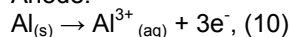


Due to oxidation in an electrolyte system, iron produces in the form of monomeric ions, Fe(OH)₃ and polymeric hydroxy complex such as:

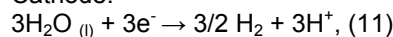
Fe(H₂O)₆³⁺, Fe(H₂O)₅²⁺, Fe(H₂O)₄(OH)₂⁺, Fe(H₂O)₈(OH)₂⁴⁺, Fe(H₂O)₆(OH)₄⁴⁺, depending upon the pH of the aqueous medium.

In the case of Aluminum electrode, reactions are as follows:

Anode:



Cathode:



For aluminum electrodes, formed Al³⁺_(aq) ions will undergo further spontaneous reaction to generate corresponding hydroxide and poly hydroxides. Due to hydrolysis of Al³⁺, Al(H₂O)₆³⁺, Al(H₂O)₅OH₂⁺, Al(H₂O)₄(OH)₂²⁺, Al₂(OH)₂⁴⁺, Al(OH)₃⁴⁺, Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₈(OH)₂₀⁴⁺, Al₁₃O₄(OH)₂₄⁷⁺, Al₁₃(OH)₃₄⁵⁺⁴⁺.

The advantages and disadvantages of the EC process are listed in Table 2 (Bensadok *et al.*, 2008). Even though EC is one among efficient process to remove hazardous materials and industrial effluents from waste water, still it is unable to remove organic waste completely. The summary of the oily waste removed by EC method is given below in the Table 3. Adsorption has been found to be most affordable and vast method to remove the different kind of particles.

Adsorption process mostly carried out by Granular activated carbon (GAC) was used as an adsorbent. Adsorbent are mainly derived from sources such as zeolites, GAC, clays, ores, and other waste resources. Dye or other materials which are adsorbed on the adsorbent is known as adsorbate. GAC can also be prepared from coconut shell, rice husk, petroleum wastes, tannin-rich

materials, sawdust, fertilizer wastes, fly ash, bagasse, blast furnace slag, seafood processing wastes, seaweed and algae, peat moss, scrap tyres, fruit wastes and chitosan, *etc.*, (Janet, *et al.*, 2015). Monolayer adsorption capacity of coconut shell GAC was found to be 90.55 mg of methylene blue/g of GAC and 57.30 mg of methyl orange/g of GAC (Lindsey *et al.*, 2015). From this studies it is evident that adsorption is can be used as efficient process to remove dyes.

Electrocoagulation cell having dimensions of 11 cm x 6 cm x 0.5 cm were specially made and used. Standard volumetric flask, beakers, measuring cylinder, funnel made from the borosilicate material and Eosin yellow (EY), Nigrosin dyes, NaOH, NaCl and H₂SO₄ of Merck Brand were used. Structure of the EY and Nigrosin are given in Fig 1 (Green FJ, 1990), (Porkodi K, 2007) and Fig 2. Application of EY, has been used in hematoxylin and eosin (H&E) staining technique (Clark, 1981; Zhanguo, 2009; Sun, 2012). Ammeter, DC power supply, Stainless steel and copper plates Whatmann40 filter paper and commercially activated charcoal with 60 mesh were used for the Experiments. The charcoal was activated at 100° C in laboratory oven and it was preserved in desiccator for further use.

Mild Steel (MS) and Copper plates of cathode and anode had dimension of 103mm x 52mm x 31mm and 104mm x 51mm x 14mm respectively, were scrubbed manually with emery paper to polish the plates. The total effective electrode area for MS and copper plate was 53.56 cm² 53.04 cm². The stock solutions of dyes eosin yellow (EY) and nigrosin having concentration 100 ppm and 1000 ppm respectively were prepared and stored in amber pet bottles. The spacing between the electrodes was maintained as 1.1cm for both dyes. The electrodes were connected to circuit through crocodile clips shown in Fig 3.

Analysis: The pH and TDS (for Nigrosin) was measured with pen type pH and TDS meter (Bates, R.G., 1973), (Skoog, D.A and West, D.M., 1976). Amount of dye removal was measured by fluorescence spectroscopy (Skoog, D.A and West, D.M., 1980) (for EY) (HIMADZU model RF-5310PC) and OD spectrophotometer (HI A HI U-2000). The concentration of Cu and Na elements were analyzed by using (model AA-6300) AAS (Skoog, D.A and West, D.M., 1980) at wavelength

324.8 nm and 589.0 nm respectively. UV-Vis spectrometer was used to find the maximum absorption wavelength of dye solution (Griffiths, P and De Hasseth, J.A., 2007). FT-IR used to get functional group changes in the dye before and after EC (Kobyas, M., *et al.*, 2006). Surface studies of charcoal before adsorption (BAD) and after adsorption (AAD) were carried out by use of scanning electron microscope (SEM). Percentage of decolourisation was calculated by the following equation.

$$R (\%) = 100 * ([Abs]_i - [Abs]_f) / [Abs]_i \quad (12)$$

Where, [Abs]_i = Initial absorbance of dye (ppm)

[Abs]_f = Final absorbance of dye (ppm)

The experiments were conducted at room temperature (≈ 25°C) with 50 ml synthetic wastewater, supporting electrolyte added, both mixture gently stirred at 250 rpm. Electrodes were placed in cell and current is applied from DC power supply to electrodes through rheostat. The EC process were conducted with various parameters such as concentration of dye, concentration of supporting electrolyte, variation of pH, variation of time, variation of current density to attain maximum removal efficiency. The solution obtained after EC treatment was collected and filtered. The filtrate was again treated with activated charcoal and filtered using whatman40 filter paper. The filtrate was used to study the elements present and water quality parameters of the solution.

RESULTS AND DISCUSSION

Effect of initial concentration on EC: The initial concentration of dye solution is an important operational parameter in EC. In order to study the effect initial concentration of different concentration of the EY dye solutions *viz.*, 0.1, 0.2, 0.3, 0.4 and 0.5 ppm were taken. The EC was carried out at optimum operational conditions (0.04 A/cm²; 4 g of NaCl; pH 4.3; time = 20 min, d=1.1 cm Cu-MS pair). The maximum dye concentration was fixed by using spectrofluorometer and spectrophotometer and the optimum initial concentration of the EY dye solution was found to be 0.5 ppm and the results are shown in the Table 4 and Fig 4. For Nigrosin dye, various concentrations were taken *viz.*, 20, 40, 60, 80 and 100 ppm. The EC was carried out at optimum operational conditions (0.007 A/cm²; 2 g of NaCl; pH 2; 10 min; d = 1.1 cm Cu – MS pair). It was found that when the initial concen-

Table 1. Equilibrium reactions of metal hydroxides with soluble pollutants.

Soluble pollutants	Mechanism of abatement	Reference
Sulfide anions	Precipitation	(De Mello Ferreira. A, <i>et al.</i> , 2013)
Calcium Cations	Co-precipitation	(Lacasa. E, <i>et al.</i> , 2011)
Phosphate anions	Precipitation, adsorption, complexation	(Golder. A.K, <i>et al.</i> , 2006) (Rehbun. M, Lurie. M, 1993)
Organic compounds	Complexation, co-precipitation	(Zhu. J, <i>et al.</i> , 2007)
Fluoride anions	Complexation, precipitation	(Emamjomeh .M Mohammad, <i>et al.</i> , 2011) (Hu. C-Y, <i>et al.</i> , 2014)
Arsenate anions	-	(Vile Kuokkanen, 2016)

Table 2. Major advantages and disadvantages of EC process.

Advantages	Disadvantages
EC over conventional coagulation include economic aspects.	EC is the need to periodically replace the electrodes.
Investment costs for EC systems are low due to their small size.	EC is the need for adequate water conductivity.
No need for very large place.	Natural water and lightly polluted wastewater lack this feature, because of low concentration of metal ions makes less conductivity.
Compared with CC, using EC significantly lowers the volume of sludge produced.	To avoid low conductivity by using supporting electrolyte such as NaCl, it may form toxic chlorinated organic compounds.
EC is the avoidance of chemical additions (excluding possible NaCl), which makes EC "a green technology".	

Where EC = Electrocoagulation

Table 3. Summary of the oily waste removed by EC process and removal percentage.

Waste	Concentration of oil (mg/L)	Electrode	Current density (A/m ²)	Reaction time(min)	Removal efficiency (%)	Reference
Metal processing waste water	60,282-116,128 (COD)	Aluminum	100-200	60	60-90	(El-Nass H. Muf-tah, <i>et al.</i> , 2009)
Petroleum refinery waste water	596 (COD)	Aluminum	130	60	63	(El-Nass H. Muf-tah, <i>et al.</i> , 2014)
Petroleum refinery waste water	3600-5300 (COD)	Aluminum	30	10 mL/min	46	(Nasim Esmaeili-rad., <i>et al.</i> , 2015)
Produced water	>2400	Aluminum and iron	1343	6.8 L/min	0-60	(Nasution., <i>et al.</i> , 2013)
Palm oil mill waste water	50,000(COD)	Aluminum	35.8	480	57.66 (COD)	(Marco Panizza, Giacomo Cerisola., <i>et al.</i> , 2010)
Vehicle cleaning wastewater	572(COD)	Iron, boron-doped	20	6	75	(Rashed. M.N, 2013)

Where, COD = Chemical Oxygen Demand

Table 4. Optimized parameters for Eosin yellow dye.

Optimized parameters		Fluorescence Intensity		OD Value		% of Removal efficiency calculated by	
		Before EC	After EC	Before EC	After EC	Fluorescence Spectrum	OD Spectrum
Concentration	0.5 ppm	906.027	606.276	0.050	0.029	33.08	42
Current Density	0.04 A/cm ²	906.027	612.903	0.039	0.029	32.35	35.89
Supporting Electrolyte	4 g	906.027	414.052	0.039	0.021	54.30	46.15
Electrolysis Time	20 min	906.027	455.756	0.039	0.021	46.69	46.15

Where OD = Optical Density, EC = Electrocoagulation

Table 5. Optimized parameters for Nigrosin dye.

Optimized parameters		% of Removal efficiency calculated by OD	pH	Electrical conductance (S/m)	TDS (ppt)
Concentration	20 ppm	99	10.84	61.3	40.2
Current Density	0.015 A/cm ²	99	9.81	62.8	40.1
Supporting Electrolyte	4 g	99	9.23	105.7	69.3
Electrolysis Time	10 min	98	10.84	61.3	40.2
pH	2	96	9.46	62.3	40.8

Where OD = Optical Density, TDS = Total Dissolved Solids

tration of dye increases the decolorization efficiency decreases. This is due to the insufficient formation of metal hydroxide flocs at higher initial concentrations (Kobyas. M, *et al.*, 2006). The optimum initial concentration of the Nigrosin for EC was 20 ppm and the results are shown in the Ta-

ble 5 and Fig 5.

Effect of current density on EC: The current density is also an important operational parameter in EC as it determines the coagulant dosage rate, bubble production, size growth of the flocs, which can affect the efficiency of the EC. With an in-

Table 6. Functional group frequencies of EY dye before and after EC.

Functional Group	EY dye before EC	EY dye after EC
C-C stretching	1458.08	-
OH stretching	3445.59	3354.94
C=C stretching	1553.55	1639.38
C-Br stretching	574.75	626.82

Where, EY = Eosin Yellow, EC = Electrocoagulation

Table 7. Functional group frequencies of Nigrosin dye before and after EC.

Functional Group	Nigrosin dye before EC	Nigrosin dye after EC
C-C stretching	1588.27	-
N-H bend	1623.95	1606.59
=C-H bend	1004.84	-
N-O asymmetric Stretching	1490.87	1460.98
C-Br stretching	616.21	-
C-Cl stretching	825.48	-

Where, EC= Electrocoagulation

Table 8. AAS study of EY dye solution before and after EC and after AD.

EY dye	Concentration of metals (ppm)	
	Cu	Na
BEC	0.0163	0.7934
AEC	0.0164	0.792
AAD	0.0345	0.4005

Where AAS = Atomic Absorption Spectroscopy, EC = Electrocoagulation, AD = Adsorption, BEC = Before Electrocoagulation, AEC = After Electrocoagulation, AAD = After Adsorption, EY = Eosin Yellow, ppm = Parts per Million

crease in the current density, the anode dissolution rate increases. The effect of current density on EC was studied by considering different current densities viz., 0.01 A/cm², 0.02 A/cm², 0.03 A/cm², 0.04 A/cm², and 0.05 A/cm² for EY dye solution. The EC was carried out at optimum operational conditions (0.5 ppm; 4 g of NaCl; pH 4.3; 20 min, d = 1.1 cm Cu – MS pair). The optimum current density determined for EY dye solution was 0.04 A/cm² and the results are shown in Table 4 and Fig 6. The EC was carried out in different current densities viz., 0.004 A/cm², 0.007 A/cm², 0.011 A/cm², 0.015 A/cm², and 0.019 A/cm² for Nigrosin dye solution. The EC was carried out at

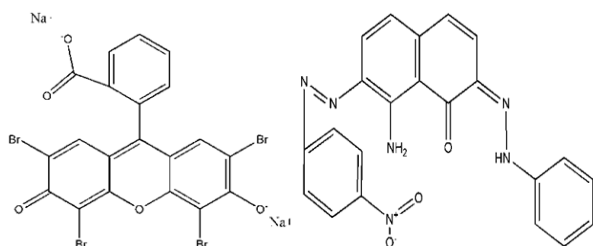


Fig.1. Structure of di So- **Fig.2.** Structure of Nigrosin dye.

Table 9. AAS study of Nigrosin dye solution before and after EC and after AD.

Nigrosin dye	Concentration of metals (ppm)	
	Cu	Na
BEC	0.0823	0.3311
AEC	1.4512	0.5246
AAD	0.0241	0.4822

Where, AAS = Atomic Absorption Spectroscopy, EC = Electrocoagulation, AD = Adsorption, BEC = Before Electrocoagulation, AEC = After Electrocoagulation, AAD = After Adsorption, ppm = Parts per Million.

Table 10. pH, electrical conductivity and TDS of EY dye solution.

Process	pH	Electrical conductivity (S/m)	TDS (ppt)
BEC	4.3	30	20
AEC	7.2	125.0	82.0
AAD	6.9	20	30

Where, BEC = Before Electrocoagulation, AEC = After Electrocoagulation, AAD = After Adsorption, EY = Eosin Yellow, ppm = Parts per Million, TDS = Total Dissolved Substance, ppt = Parts per Trillion.

Table 11. pH, electrical conductivity and TDS of Nigrosin dye solution after adsorption.

Process	% of Decolorisation	pH	Electrical conductivity (S/m)	TDS (ppt)
AAD	100	8.63	64.2	42.1

Where, TDS = Total Dissolved Substance, AAD = After Adsorption, ppt = Parts per Trillion.

optimum operational conditions (20 ppm; 2 g of NaCl; pH 2; 10 min, d = 1.1 cm Cu–MS pair). When the current density increases the anode dissolution rate is increases. An increase in the current density above the optimum current density does not increase in the decolorization efficiency this due to the saturation in the formation of metal hydroxide flocs (Nafaâ Adhoum, *et al.*, 2004) The optimum current density for nigrosin was 0.015 A/cm². The results are shown in the Table 5 and Fig 7.

Effect of Supporting Electrolyte Concentration

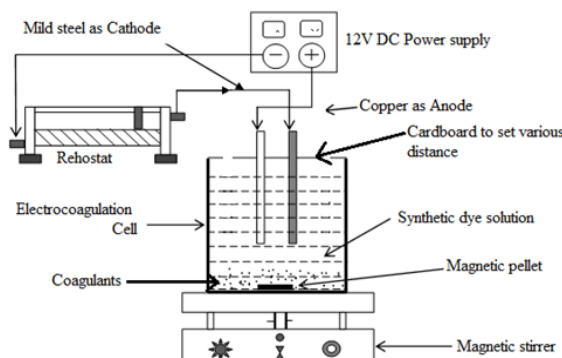


Fig.3. Schematic diagram of Electrocoagulation process.

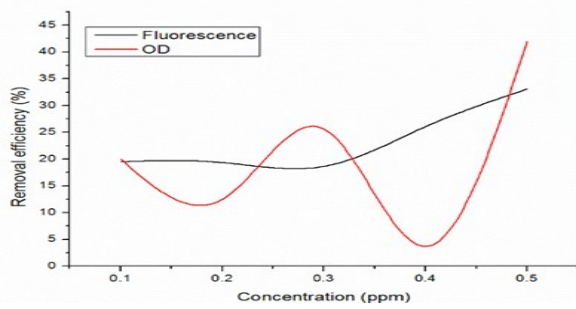


Fig.4. Removal efficiency (%) of EC for different initial concentrations EY dye.

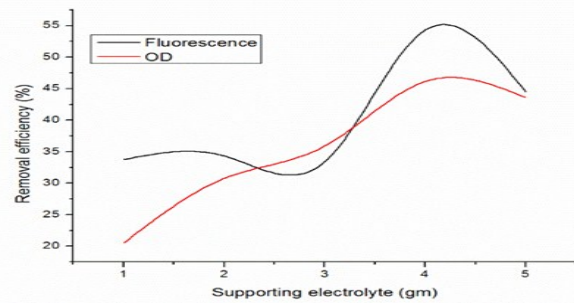


Fig.8. Removal efficiency (%) of EC for various concentrations supporting electrolyte in EY.

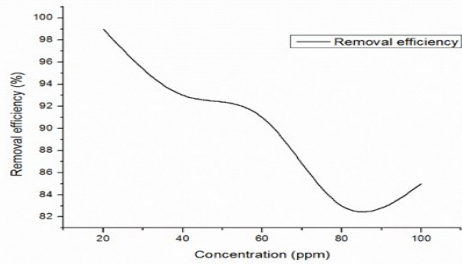


Fig.5. Removal efficiency (%) of EC for different initial concentrations Nigrosin dye.

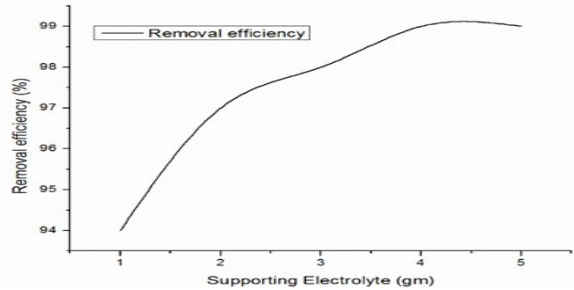


Fig.9. Removal efficiency (%) of EC for various supporting electrolyte concentration in Nigrosin.

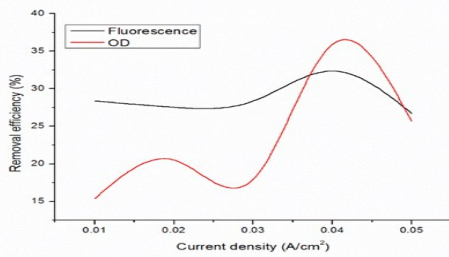


Fig.6. Removal efficiency of EC for various current density of EY dye.

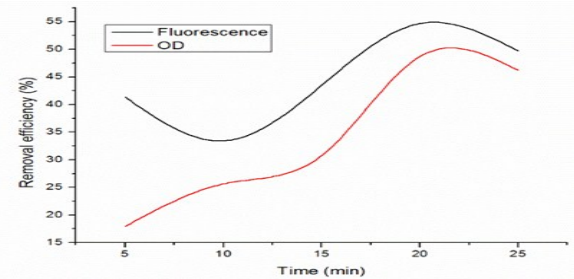


Fig.10. Removal efficiency of EC for different electrolysis time of Nigrosin.

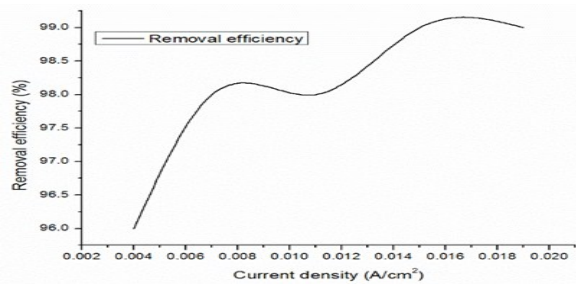


Fig.7. Removal efficiency of EC for various current density of Nigrosin dye.

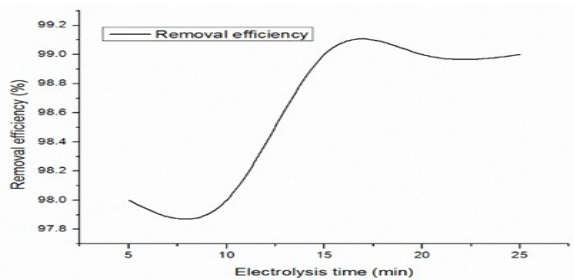


Fig.11. Removal efficiency by EC for different electrolysis time of Nigrosin.

on EC: The concentration of supporting electrolyte (NaCl) is yet another important operational parameter in EC. To study the effect of concentration of supporting electrolyte various concentrations of NaCl were considered for EY dye solution viz., 1 g, 2 g, 3 g, 4 g and 5 g. The EC was carried out at optimum operational conditions (0.5 ppm; 0.04 A/cm²; pH 4.3; 20 min, d=1.1 cm Cu – MS pair). The optimum concentration of the supporting electrolyte for EY dye solution was found to be 4 g and the results are shown in Table 4 and Fig

8. The different concentrations of supporting electrolyte were considered for Nigrosin dye solution viz., 1 g, 2 g, 3 g, 4 g and 5 g. The EC was carried out at optimum operational conditions (20 ppm; 0.007 A/cm²; pH 2; 10 min, d = 1.1 cm Cu–MS pair). When the amount of NaCl increases the decolorization efficiency found increase. This is due to the presence of NaCl in the solution causes the production of hypochlorite ion at anode and leads to increase the decolorization by oxidation of dye molecules. The optimum concentration for

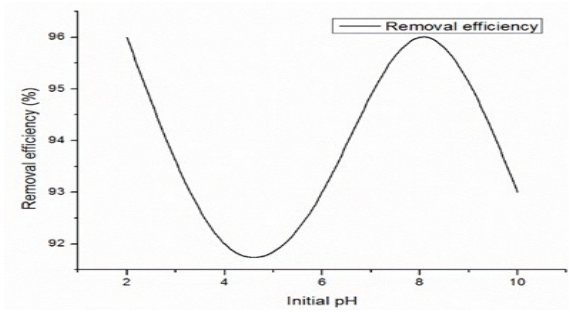


Fig.12. Removal efficiency of EC for various pH of Nigrosin.

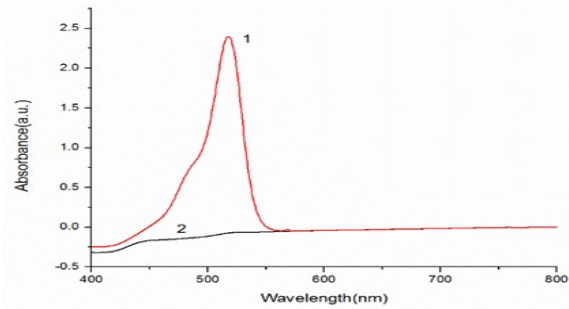


Fig.13. UV-Vis spectrum of EY dye. (1) Before EC and (2) After EC.

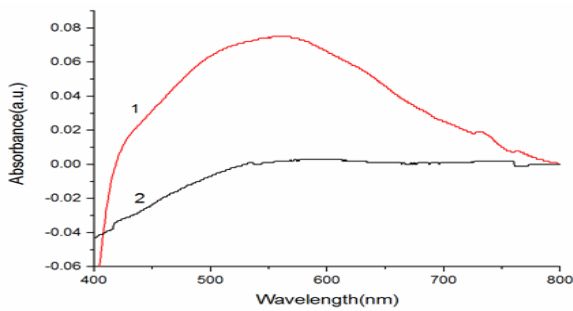


Fig.14. UV-Vis spectrum of Nigrosin dye (1) Before EC (2) After EC.

the supporting electrolyte for Nigrosin dye solution was found to be 2 g and the results are shown in the Table 5 and Fig 9.

Effect of electrolysis time on EC: In order to study the effect of electrolysis time (Khandegar., *et al.*, 2013) on EC different time intervals were considered for EY dye solution *viz.*, 5 min, 10 min,

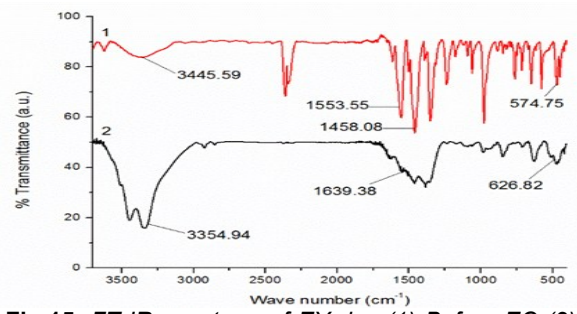


Fig.15. FT-IR spectrum of EY dye (1) Before EC (2) After EC.

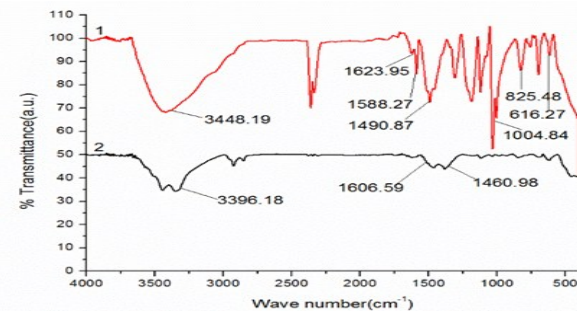


Fig.16. FT-IR spectrum of Nigrosin dye (1) Before EC (2) After EC.

15 min, 20 min and 25 min. The EC was carried out at optimum operational conditions (0.5 ppm; 0.04 A/cm²; pH 4.3; 4 g of NaCl; d=1.1 cm Cu – MS pair). The optimum electrolysis time was obtained at 20 min and the results are shown in Table 4 and Fig 10. The same was carried out for Nigrosin dye solution with different time intervals *viz.*, 5 min, 10 min, 15 min, 20 min and 25 min. The EC was carried out at optimum operational conditions (20 ppm; 0.007 A/cm²; pH 2; 2 g of NaCl; d = 1.1 cm Cu – MS pair). The decolorization efficiency was increased with increase in the electrolysis time. This is due to increase in the generation of flocs. But beyond the optimum time, the decolorization efficiency becomes constant and does not increase further. The results show that the optimum electrolysis time is 10 min and the findings are given in the Table 5 and Fig 11.

Effect of pH on EC: The pH of the solution is an important operational parameter in EC (Verma

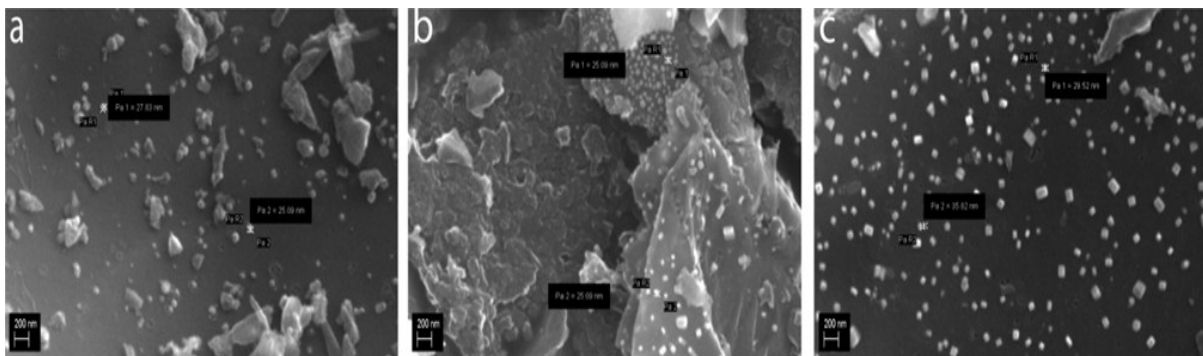


Fig.17. SEM image of GAC (a) Before adsorption (b) EY adsorption (c) Nigrosin adsorption.

S.K., *et al.*, 2013). The maximum dye removal efficiency is obtained at a particular pH called the optimum pH for a particular dye. The precipitation of a dye begins at a particular pH. The pollutant removal efficiency decreases by either increasing or decreasing the pH of the solution from the optimum pH. Hence, different pH of the Nigrosin dye solutions was taken *viz.*, 2, 4, 6, 8 and 10. The EC was carried out at optimum operational conditions (20 ppm; 0.007 A/cm²; 2g of NaCl; 10 min; d = 1.1 cm Cu-MS pair). The maximum decolorization efficiency was obtained at pH. The results are shown in the Table 5 and Fig 12.

Adsorption studies of EC treated dye solutions: The EC treated dye solutions of fully optimized parameters was again treated with GAC of 1g for 10 min and filtered using whatmann-40 filter paper. The filtrate was collected for AAS and pH, TDS, Electrical conductivity studies and the precipitate and GAC (before adsorption) were tested for SEM analysis.

The presence of the concentration of Cu and Na metals in EY and Nigrosin dye solutions before and after EC and after AD were determined and compared using Atomic Adsorption Spectrum. The results obtained are given in the Table 8 and Table 9 respectively.

The water quality parameters such as pH, TDS (Vogel, 1961) and electrical conductivity were studied for EY and Nigrosin dye solutions before and after adsorption. Results are given in Table 10 and Table 11 for EY and Nigrosin dye respectively.

UV-Vis studies of EY and Nigrosin dye before and after EC: The UV-Vis spectral studies show maximum absorbance at 517.50 nm by using water as internal standard in the spectrum of EY dye before treatment and drastic changes are seen in the spectrum of EY dye after the EC and adsorption. It is the evidence for the decolorization and degradation of the dye molecules by using EC and Adsorption processes (Abdurrahman Akyol., *et al.*, 2012). The results obtained from the UV-Vis spectra are given in Fig 13.

The UV-Vis spectral studies (Abdurrahman Akyol., *et al.*, 2012) show maximum absorbance at 562.50 nm for Nigrosin dye in water solvent before treatment and strong changes are seen in the spectrum of Nigrosin dye after the EC and adsorption. The results obtained from the UV-Vis spectra are given in Fig 14.

IR studies of EY and Nigrosin dye before and after EC: The IR spectral studies show the different absorption bands for EY dye before and after electrocoagulation process. From the results it is evident that during EC process dye molecules might have undergone some structural changes (Aoudj, *et al.*, 2010). The band position of the sample dye molecule before and after EC process is given in the Table 6, Fig 15.

The IR spectral studies show the different absorption bands for Nigrosin dye before and after electrocoagulation process. From the results it is evident that during EC process dye molecules might have undergone some structural changes. The band position of the sample dye molecule before and after EC process is given in the Table 7, Fig 16.

SEM studies of GAC: The surface morphology of adsorbents (GAC) were carried out using scanning electron microscopy (SEM) and studies provide useful information regarding textural morphological characteristics of the surface of the adsorbents (Garcia-Morales. M.A., *et al.*, 2013) The SEM photographs of GAC before and after adsorption of EC treated dye solution are shown in Fig.17. For EY and nigrosin dye, the SEM photographs also show that GAC particles are either engulfed (or) adsorbed the dye molecules on the surface.

Conclusion

EC is characterized by simple equipment, easy operation, cost effective, less time consumption and also minimum amount of sludge. EC process for EY dye solution showed maximum removal efficiency of 54.67 % which was verified by fluorescence spectrum and was obtained at optimum operating conditions such as initial dye concentration 0.5 ppm, pH 4.3, current density 0.04 A/cm², NaCl 4 g, electrolysis time 20 min and electrode distance 1.1 cm in Cu-MS electrode pair. EC process for Nigrosin dye solution has maximum removal efficiency of 99 % which was verified by OD spectroscopy and was obtained at optimum operating conditions such as initial dye concentration 20 ppm, pH 2, current density 0.007 A/cm², NaCl 2 g, electrolysis time 10 min, electrode distance 1.1 cm for Cu-MS electrode pair. The EC treated dye solutions was further subjected to adsorption in order to achieve maximum dye removal. The color removal of Nigrosin and EY dye from the aqueous solutions was evident by analyzing water quality parameters such as pH, electrical conductivity, TDS and OD values before and after treatment processes. UV- Vis and IR spectra recorded for dyes before and after EC and also after adsorption indicated that both dyes have undergone some structural changes during treatment processes. The UV-Vis spectra of the dyes solutions after treatment showed a decline in absorbance. The IR spectra of the dyes showed that some of the IR peaks which were present before EC process were missing in after adsorption. AAS studies were also being carried out to determine quantity of copper and sodium ions present in the dye solutions before and after EC and adsorption processes. The study showed an increase in concentration of copper ion which is due to the dissolution of copper anode during electrocoagulation.

SEM images recorded for charcoal to study the efficiency dye adsorption on charcoal showed that GAC particles were either engulfed (or) adsorbed the dye molecules on the surface. Thus, EC process coupled with adsorption may be an effective tool for the removal of dyes from the industrial effluents.

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