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REMOVAL OF COLOUR FROM TEXTILE WASTEWATER BY DIFFERENT METHODS

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Abstract — *Dyes that are used in the industries are the molecules designed to impart colour to the textile fabrics. Wastewater generated by these industries is known to have most polluting molecules both in terms of quality as well as quantity. There are several processes viz. physical, chemical, biological which are widely used for the color removal. Currently, number of absorption process are used for removal of different classes of pollutant especially which are not easily biodegradable. Electrocoagulation proves to be an effective technique for textile wastewater for color and COD removal. Most widely used process used adsorbents are activated carbon, orange peel, activated alumina, silica etc . We have compared the color and COD removal efficiency by electrocoagulation, orange-banana peel powder and chitosan. Color removal by these three techniques was compared by looking at the change in color. COD reduction efficiency for electrocoagulation was found maximum at 8V for 20min detention time which was 92%. Similarly it was found that COD reduction for chitosan was 65% for 3.5 gram dose for detention time of 1hour and for orange-banana peel powder 63.6% for detention time of 1hour of 4gram of orange and 6gram banana peel powder.*

Keywords-*Electrocoagulation, textile wastewater, COD, color removal, chitosan,*

I. INTRODUCTION

The wastewater that is coming out of the dyeing industry is of special concern because of the large number of chemicals present in the wastewater[1]. It generally contains large amount of color molecules which give bad aesthetic to the water and is brown/black in appearance. Conventional method for treating the wastewater generally include the physical, Chemical, and biological process[2]. Due to, large amount of variability of the composition of the wastewater the conventional techniques are becoming inadequate[2,3]. The dye concentration in the wastewater is generally less than that of other chemicals but because of the presence of color it creates aesthetic problem in wastewater disposal, it is therefore necessary to treat the wastewater before discharge. Number of techniques are available for color removal but some may not feasible or some may not be easily available. The electrocoagulation technique is a simple, efficient and reliable treatment without the addition of chemicals thus reducing the amount of load on secondary treatment[2,3,4,5]. The electrocoagulation process has several advantages that makes it attractive for treating various contaminated streams[4]. This treatment is successfully applied for the treatment of many types of wastewater such as landfill leachate, textile wastewater, petroleum refinery wastewater, dairy wastewater etc[4]. Various sorbents are already being used such as mango peel, orange peel, banana peel, neem leaves, tree bark etc. Removal of dyes by using bio-sorbents occurs by the mechanism of reaction with proteinaceous material and due to the affinity to adsorbate species, the latter is attracted and removed [6]. Researchers are still finding new techniques to remove azo dyes from wastewater[6]. Dyes can commonly be classified as per the fibres to which they can be applied, and their chemical nature as: 1. Acid dyes, 2. Reactive dyes, 3. Dispersive dyes[7].

II . TREATMENT METHODS

2.1 Electrocoagulation Process

EDF is a complicated process involving many chemical and physical phenomena that use sacrificial electrodes, such as Al, Fe and others, to supply ions into the water. In the EC process the coagulants generates in situ by dissolving electrically the consumable electrodes (Fe/Al). The metal ions generation takes place at the anode; hydrogen gas is released from the cathode. The water contaminants are treated either by chemical reactions and precipitation or by

physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electro flotation, sedimentation and filtration. The basic process can be summarized in figure.
It is discussed that in the EDF process current is passed through a metal electrode, oxidizing the metal (M) to its (M+) at the anode. $M \rightarrow M^{+} + e^{-}$
At the cathode side, hydrogen gas (H2) and the hydroxyl ion (OH-) are generated by reducing the water.

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

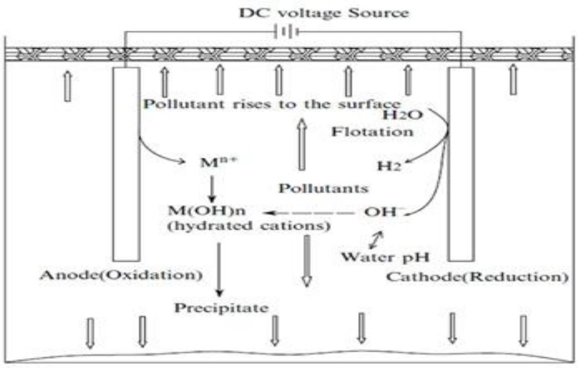

Figure. 1 Reaction at Anode and Cathode

In the solution, the metal cations resulted from the anode oxidation combine with hydroxyl ion (OH^-) resulting from water to form highly charged coagulant. In the case of Aluminium anode, the Al^{3+} reacts with H2O to form Al(OH)3. The destabilization mechanism of the contaminant, particulate suspension, and breaking of emulsion may be summarized as follows:
1. Compression of the diffuse double layer around the charged species by the interactions of ions generated by oxidation of the sacrificial anode.
2. Charge neutralization of the ionic species in the wastewater by counter ions produced by the electrochemical dissolution of the sacrificial anode. The counter ions reduce the electrostatic inter-particle repulsion to the extent that van der waals attraction predominates, thus causing coagulation. In this process a zero net charge results.
3. Floc formation: a sludge blanket is created from the floc that formed as a result of the coagulation process.

A typical electrocoagulation treatment process consists of two electrodes which act as anode and cathode. The electrodes are connected to power source and system is immersed in the aqueous solution. The current is allowed to pass through the solution from electrodes. Simply, an electrolytic cell consists of two electrodes, anode and cathode, immersed in an electrical conducting solution (the electrolyte), and are connected together, external to the solution, via an electrical circuit which includes a current source and control device[1].
The electrocoagulation reactor consisted in a parallel-plate electrocoagulation cell provided with two facing electrodes and with six perforated tubes attached to its bottom to maintain a uniform gas flow and stirring into the cell[3]. .EC, has the advantage of removing small colloidal particles; because of the electric field that sets them in motion. Addition of excessive amount of coagulants can be avoided, due to their in situ generation by electro-oxidation of a sacrificial anode. EC equipment is simple and easy to operate and there is no sludge production[22].
The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity and also on other characteristics such as pH, particle size, and chemical constituent concentrations. In the EC system, there are multiple electrochemical reactions occurring simultaneously at the anodes and cathodes. These mechanisms can be divided into the main mechanisms that cause destabilization of pollutants, and side reactions, such as hydrogen formation.

Electrodes which produce coagulants into water are made from either iron or aluminium. In addition, there can be inert electrodes, typically cathodes, which are sometimes used as counter-electrodes in the system.

Aluminium
The electrolytic dissolution of the aluminium anode produces the cationic monomeric species such as Al^{3+} and $Al(OH)^{2+}$ at low pH, which at appropriate pH values are transformed initially into $Al(OH)_3$ and finally polymerized to $Al_n(OH)_{3n}$ according to the following reactions:

$Al \rightarrow Al^{3+} (aq) + 3e^-$
$Al^{3+} (aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^+ (aq)$
$n\, Al(OH)_3 \rightarrow Al_n(OH)_{3n}$

However, depending on the pH of the aqueous medium other ionic species, such as $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$ and $Al(OH)_4^-$ may also be present in the system. Under appropriate conditions various forms of charged multimeric hydroxo

Al^{3+} species may be formed. These gelatinous charged hydroxo cationic complexes can effectively remove pollutants by adsorption to produce charge neutralization, and by enmeshment in a precipitate.

Iron

Iron upon oxidation in an electrolytic system produces iron hydroxide, $Fe(OH)_n$, where $n = 2$ or 3. Two mechanisms have been proposed for the production of $Fe(OH)_n$.

• Mechanism 1

Anode:

$4Fe(s) \rightarrow 4Fe^{2+}(aq) + 8e^-$

$4Fe^{2+}(aq) + 10\,H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 8H^+(aq)$

Cathode:

$8H^+(aq) + 8e^- \rightarrow 4H_2(g)$

Overall:

$4Fe(s) + 10\,H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 4H_2(g)$

• Mechanism 2

Anode:

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s)$

Cathode:

$2\,H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Overall:

$Fe(s) + 2\,H_2O(l) \rightarrow Fe(OH)_2(s) + H_2(g)$

The $Fe(OH)_n(s)$ formed remains in the aqueous stream as a gelatinous suspension, which can remove the pollutants from wastewater either by complexation or by electrostatic attraction, followed by coagulation. Wastewater containing chromium ions can be removed by the EC technique using iron as the sacrificial anode.
The H_2 produced as a result of the redox reaction may remove dissolved organics or any suspended materials by flotation[34].

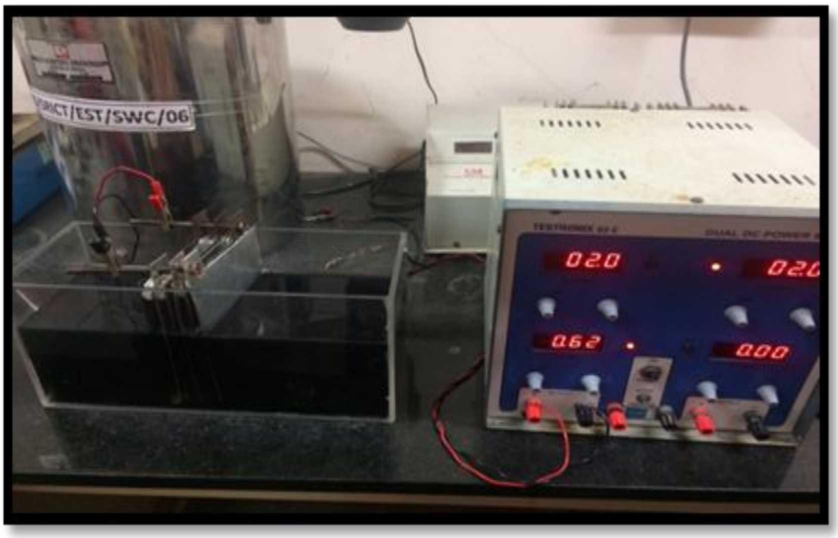

Figure. 2 Experimental Setup

2.1.1 Calculation

Sr No.	pH	Initial COD	Final COD	% COD reduction
At 2V, 0.67 A	6.5	1464	219.6	85%
At 4V, 1.35 A	6.5	1464	190	87%
At 6V, 3.14 A	6.5	1464	146.4	90%
At 8V, 5.67 A	6.5	1464	117.2	92%

2.1.2 COST ANALYSIS

COST OF POWER:
Voltage V = 4v, Current density I/A = 52.94 Amp/m2,Volume = 5L,Treatment time, t = 20 minutes
Current = 0.0255*52.94=1.349 A
Power= 5.399W
Energy = 107.98W=0.0017KWH
Total cost= Rs. 0.0116

COST OF ALUMINIUM:
W=4.739gm/m2
W(active)=0.1208gm/m2
Cost of pure aluminium=Rs.320
Cost of aluminium=Rs.0.0386
Total cost= 0.0386+0.0116=Rs 5.029/m3 of wastewater treated

COST OF IRON:
W=9.79gm/m2
W(active)=0.249gm/m2
Cost of pure iron=Rs.150
Cost of iron=Rs.0.037
Total cost=0.037+0.0116=Rs 4.9/m3 of wastewater treated

2.2 Orange and Banana Peel

Orange and banana are used mainly in orange-juice and soft drinks industries all over the world. They discard a huge amount of orange peels and banana peels. Those discarded peels can be used as an adsorbent for the removal of dyes from the wastewater. Generally waste orange peel and banana peels was obtained from a fruit stall[23].

The removal of various dyes from textile wastewater by adsorption on orange peels has been found to be useful for controlling water pollution due to dyes. From the experiment it is clear that, the adsorption of dyes onto orange peels is influenced by pH values, amount of adsorbents, dye concentration and contact time. Also, the adsorption of dyes onto orange peels follows the Langmuir isotherm model. The efficiency of orange peels as an adsorbent for color removal was observed. Even though the removal efficiency of orange peels is not much higher than other bio-adsorbents, as it is cheaply available. With the help of these cheap and environment friendly adsorbent considerable dye removal can be achieved.

It is observed that the modification of Banana and Orange peel with acid treatment significantly improve colour adsorption capacity as compared to raw Banana and Orange peel. The colour removal efficiency was achieved maximum at very low dose of 0.06 g for Banana peel and 0.05 g of Orange peel within short time of 55 minutes. The adsorption isotherm data was best explained by Langmuir model. The adsorption capacity obtained from Langmuir isotherms for Banana peel and Orange peel was 0.1808 and 0.0647 mg g-1 respectively. The adsorbent was effective at neutral pH. Increasing use of agro based bio adsorbent can be seen in coming decade for removal of dyes from wastewater. Banana and Orange peel have good potential as a low cost adsorbent for improving the effectiveness of waste water treatment[21].

2.2.1 Method of preparation

The banana and orange peels are collected from the restaurants and juice centers; then sun dried and powdered. The powder is activated using 6 N NaOH. The detention of 1 hour is given for the adsorption process. Different dosage of 3+3, 5+5, 4+6 grams of banana and orange peels are taken respectively and 30 ml of the activated mixture is added to the tank for adsorption. Initial and final COD is measured and percentage reduction is calculated.

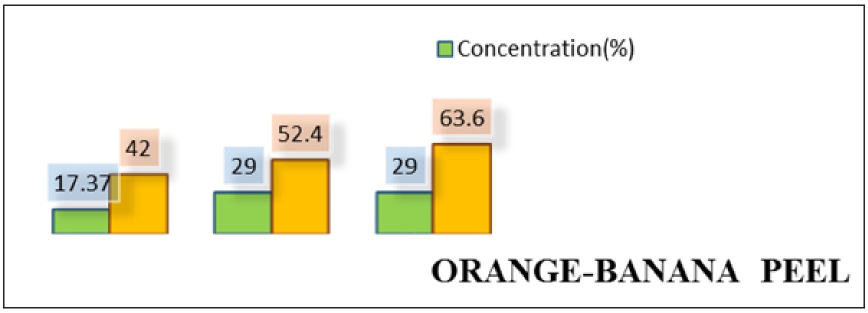

Fig. 3 Graph showing the different removal efficiency with respect to different concentration of the absorbent

2.2.2 Calculation

Sr No.	Concentration(%)	pH	Initial COD	Final COD	% COD reduction
1	2.8	6	1464	512.4	65
2	1.6	6	1464	673.4	54
3	2	6	1464	790.56	46

For Banana + Orange peels, Detention time= 1hr
S1 = (3+3) gm (30 ml)
S2 = (5+5) gm (30 ml)
S3 = (4+6) gm (30 ml)

2.3 Chitosan

Waste shrimp shells were collected from a local restaurant supplier. From these waste shells chitosan was prepared, and the obtained chitosan was used for the experiment without any purification. For the preparation of chitosan the stock solution was prepared by dissolving 2 g of chitosan in 100 ml of 1% HCl acid solution (20000 mg/L). And then this solution was diluted to the desired mass concentrations (from 100 mg/L to 350 mg/L) before being used[29]. It was found that as the chitosan-zinc oxide nanoparticles are low-cost and eco-friendly adsorbent, they can be used for the removal of dyes from aqueous solution. A study on the ability of chitosan to act as an adsorbent produced from waste seafood shells for the removal of five acid dyes, namely, Acid Green 25, Acid Orange 10, Acid Orange 12, Acid Red 18, and Acid Red 73, has been done[30]. According to the utility of cross-linked quaternary chitosan as adsorbent for the removal of Reactive Orange 16 from aqueous solutions showed that the adsorption process was independent of pH, well represented by Langmuir isotherm and a pseudo second-order kinetic model[31]. It was found that the maximum adsorption capacity o chitosan was 1,060 mg/g. Chitosan was proven to be an effective coagulant in the removal of reactive dye such as red 24. The best treatment efficiencies for colour and COD obtained 99.5 and 72.2%, respectively, using a Jar-test experiment[29]. The dye, and the sludge form of dye and chitosan were also characterized by FTIR, suggesting that the prepared chitosan had participated in a complex way with the dye. This is evidence that chitosan has the potential for reducing concentrations of reactive dye in aqueous solution[29]. Chitin, which is a polysaccharide is very similar in structure to cellulose, being composed of poly 2-acetamido-2-dioxy-D-glucose. Chitosan is a well-known derivative of chitin, produced by the deacetylation of chitin which is a natural biopolymer extracted from the shell of arthropod. Chitosan has unique molecular structure, so that it has an extremely high affinity for many classes of dyes, including disperse, direct, reactive, acid, vat, sulphur and naphthol. The only class for which chitosan has low affinity is the basic dyes. The several studies on the use of chitin and chitosan for the removal of dyes was the first one to examine the dye binding properties of chitin and chitosan and found that chitosan had better dye uptake property than chitin. More recently investigated the possibility of using chitosan fibre. Chitosan fibre has amino groups and therefore shows advantage of more adsorption capacity and much easier desorption. A cross-linked chitosan fibre allows the fibres to be used at lower pH which improves the dye binding capacity without solubilising the chitosan and was found to have an Acid Orange II having the binding capacity of about 4.5 mol/kg at pH 3-4[9].

2.3.1 Method of preparation

The chitosan commonly used as coagulant is allowed to check colour removal efficiency. Different weights of chitosan of 3.5 gm, 2 gm and 2.5 gm is taken and activated using acetic acid and water 50 ml solution is prepared. The different concentrations of solution 2.8 gm, 1.6 gm, 2 gm is taken and detention time of 1 hour is provided for colour removal. Initial and final COD is measured and percentage reduction is calculated.

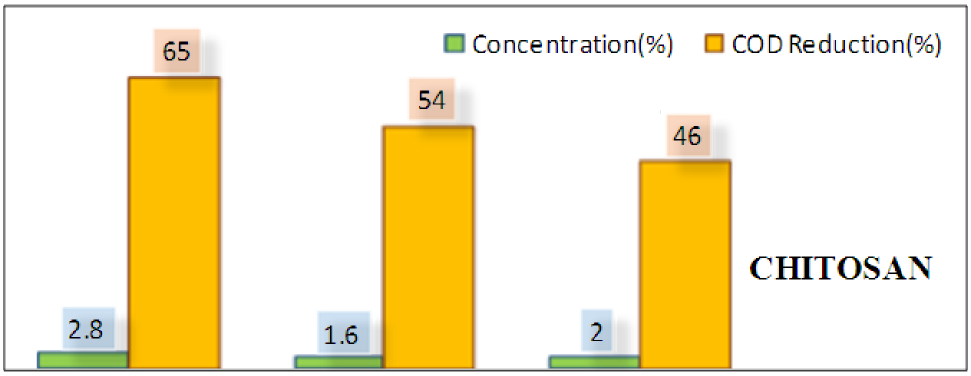

Fig.4 Graph showing the different removal efficiency with respect to different concentration of chitosan

2.3.2 Calculation

Sr No.	Concentration(%)	pH	Initial COD	Final COD	% COD reduction
1	17.37	12	1464	849.12	42
2	29.0	12	1464	696.8	52.4
3	29.0	12	1464	532.89	63.6

For Chitosan, Detention time= 1hr
S1= 3.5 gm (50 ml)
S2 = 2 gm (50 ml)
S3 = 2.5 gm (50 ml)

2.4 ADVANTAGES OF ELECTROCOAGULATION AND OTHER ABSORPTION TECHNIQUES

Process avoids the use of chemicals.

The equipment required for Electro coagulation process is simple, compact and easy to operate and handle the problems encountered during running.

Simple and compact treatment facility results in relatively low cost.

Electro coagulation process has the advantage of removing the smallest colloidal particles because the applied electric field sets them in faster motion thereby facilitating the agglomeration.

It is a low sludge producing process, and the sludge formed during the process tends to be readily settable and easy to dewater, as it is mainly composed of metallic oxides/hydroxides and organic fractions.

The flocks formed during the electro coagulation process tend to be much larger, more stable; therefore can be separated by filtration.

In absorption technique, effluent can be reused with a lower water recovery cost due to the low dissolved solids content as compared with other chemical treatment effluent.

The gas bubbles produced during electrolysis can carry the pollutant on the top of the solution where it can be more easily concentrated, collected, and removed.

The electrocoagulation technique can be conveniently used in rural areas where electricity is not available, as alternative power generated from solar panels can be used as power source.

RESULT

The above figure shows the change in the color removal after performing the electrocoagulation method and by using absorbent. From left to right, i. Effluent sample ii. by using chitosan iii. by using orange-banana peel powder iv. by using electrocoagulation

CONCLUSION

After conducting several experimental runs by using iron and aluminium electrodes and absorbents. The iron and aluminium as sacrificial electrode materials in the treatment of textile wastewater by electrocoagulation has been found to be pH dependent. According to the results of experiments, in acidic medium, pH < 6, COD removal efficiencies of aluminium are higher than those of iron, while in neutral and alkaline medium iron is preferable. Usually high conductivity favours high process performances. The adsorption capacity depends on the type of adsorbent and the nature of wastewater. For the same turbidity or COD removal efficiencies, iron requires a current density of less than of required by aluminium at operating time of 20mins. It was found that the electrocoagulation and absorption methods were highly efficient and relatively fast compared to conventional existing techniques for dye removal from aqueous solutions. Electrocoagulation gave a better color removal efficiencies than the absorbents. Electrocoagulation gave 92% COD removal efficiency at 8V whereas the absorbent gave COD removal efficiency of 65% and 63.6% using orange-banana peel and chitosan peel respectively.

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