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REMOVAL OF COLOUR FROM TEXTILE WASTEWATER BY DIFFERENT METHODS: A REVIEW

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ABSTRACT-*Textile dyes are the molecules designed to impart colour to the textile fabrics. Wastewater generated by the textile industry is known to have most polluting in terms of quality and quantity. Electrocoagulation proves to be an effective technique for textile wastewater. 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. Most widely used process used adsorbent is activated carbon. In this review paper, a comparison of different types of absorbent such as activated carbon, orange peel + banana peel and chitosan along with the conventional electrocoagulation technique is made for removal of color along with COD.*

KEYWORDS- *Electrocoagulation, color removal, COD, textile wastewater*

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]. The amount of COD present in the dyeing wastewater is around 1600mg/l with a strong dark color. 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. 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 find novel methods 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].

Table 1. Exhaustion range of various dye classes[9]

Dye classes	Fibre	Degree of fixation, %	Loss to effluent, %
Acid	Polyamide	80-95	5-20
Basic	Acrylic	95-100	0-5
Direct	Cellulose	70-95	5-30
Disperse	Polyester	90-100	0-10
Metal-complex	Wool	90-98	2-10
Reactive	Cellulose	50-90	10-50
Sulphur	Cellulose	60-90	10-40
Vat	Cellulose	80-95	5-20

II. CONVENTIONAL TREATMENT METHOD

A. Coagulation

The Conventional chemical treatment consists of electrolyte addition to cause coagulation of dyes and other colloidal solids, usually followed by precipitation. Partial Decolourisation is visible and the COD reduces due to suspended solids removal which was observed 40-50%, reduction in BOD was 35-40% colour was reduced to 80%[1]. In Decolourisation by coagulation/flocculation technique using ferrous sulphate and/or lime, lime removes colour by 70-90% and COD reduction is 50-60 %. Moreover, the treatment with ferrous sulphate regulating the pH in the range 9.0±0.5 using lime was equally effective. The tropical peat soil is used as coagulant concluding that Alum, PAC (polyaluminium chloride) and peat soil have 100% color reduction capacity from dispersed dyes , but peat soil can only remove colour from reactive dyes till 94% at 3-5 pH range along with 98% reduction in suspended solids. The coagulant chemicals are either metallic salts (such as alum) or polymers. The polymers are organic compounds made up of a long chain of smaller molecules. Polymers can be either cationic (i.e. positively charged), anionic (i.e. negatively charged), or non-ionic (i.e. neutrally charged)[8].

B. Enhanced Coagulation

Recently, the enhancing coagulation by addition of natural organic matter (NOM) is being studied, although action also dependent on pH. Ferric coagulants removes NOM in 4-5 pH range for aluminium coagulants which has the desirable range of pH of 5 to 6 by combining the electrochemical process with fluidized bio film process and chemical coagulation for the treatment of the textile wastewater[1]. In the case of pilot scale study, fluidized bio film process is used prior to chemical coagulation and electrochemical oxidation processes. Effective COD and color removals of 95.4 % and 98.5 % were achieved by overall combined processes. The degradation of the azo dye is observed by using starch, glucose, lactose. In result the starch was the best source of carbon for decolourization of reactive azo dyes. In presence of 250 mg/L of starch, all the reactive dyes decolorized within 24 hours with the reduction in COD in the range of 75.15–95.9%[1].

C. Adsorption

Colour removal can be achieved by adsorption using (granular activated carbon) GAC in packed bed or (powdered activated carbon) PAC. The dose of PAC is 100 mg/L can provide 90% color removal. The disperse dye is treated by palm ash as adsorbent where several study shows that it can be cheap replacement for commercial activated carbon to get effective colour removal of 59.44% at pH 4 with contact time 120 minute[12].

D. Biological methods

Studies show that dyes are slightly biodegradable, as they are designed to surpass action of body fluids[16]. The textile wastewater is treated in anaerobic baffled reactor to get COD reduction above 90% and colour reduction of 86%[18]. It is assumed that colour reduction is due to adsorption on biomass. The sludge acclimatized to dyes is found to give better colour removal. When studied by several scientist about anoxic/aerobic treatment on reactive azo dyes they found that the rate of COD removal under aerobic conditions was twice the rate under anoxic conditions. The percent COD removal by the anoxic/aerobic process was observed 95% vs. 97% removal by the aerobic control. The percent color removal by the anoxic phase was five times the removal by the aerobic phase[19].

E. 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].

F. 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 (H_2) and the hydroxyl ion (OH^-) are generated by reducing the water.

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

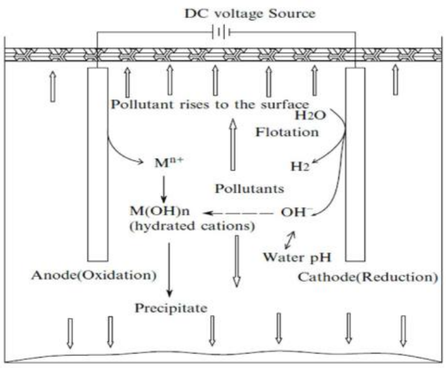

Figure. 1 Reaction at Anode and Cathode

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 H_2O 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. Defluorination of water can be achieved using aluminium electrodes.

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].

Factors affecting EC

There are various parameters which have an effect on the efficiency of the EC in removing the pollutants from water. The factors which are known to have an effect are:

Material of the electrodes can be iron, aluminium and/or inert material (typically cathodes). Iron and aluminium ions and hydroxides have different chemistries and applications.

pH of the solution has an effect on the speciation of metal hydroxides in the solution and also on the zeta potential of the colloidal particles. It also affects the dissolution of aluminium cathodes.

Current density is proportional to the amount of electrochemical reactions taking place on the electrode surface.

Treatment time or electric charge added per volume is proportional to the amount of coagulants produced in the EC system and other reactions taking place in the system.

Electrode potential defines which reactions occur on the electrode surface.

Concentration of the pollutants affects the removal efficiency because coagulation does not follow zeroth-order reaction kinetics but rather pseudo second or first-order kinetics.

Concentration of anions, such as sulphate or fluoride, affects the composition of hydroxides because they can replace hydroxide ions in the precipitates.

Temperature affects floc formation, reaction rates and conductivity. Depending on the pollutant, increasing temperature can have a negative or a positive effect on removal efficiency.

Other parameters, such as hydrodynamic conditions and inter-electrode distance, may have effect on efficiency of the treatment and electricity consumption.

G. 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].

III. 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.

IV. CONCLUSION

India has set up Industry wise minimal national standards (MINAS) for output from treatment plants. The electrocoagulation method shows promising aspects where treatment provides complete colour reduction in all working conditions while varying some parameters like current and voltage applied along with change in type of absorbent. This method provides better alternative than the conventional systems. 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 and turbidity 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 10mins.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.

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