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STUDY OF ORGANIC MATTER REMOVAL FROM INDUSTRIAL WASTEWATER USING COMBINATION OF COAGULATION/FLOCCULATION-ELECTROLYSIS TREATMENT

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ABSTRACT

The existing scenario of industrial wastewater treatment associated with various operational difficulties. Alternative sustainable and techno-commercially feasible treatment techniques need to be explored. Extensive research work has been reported to improve the efficiency of primary and electrolysis process to treat colored wastewater. The present work explored the possibility of combination of primary and electrolysis process to treat colored industrial wastewater. The primary outlet are considered for electrolysis treatment. The wastewater parameters like suspended solids (SS), chemical oxygen demand (COD), turbidity and color has been considered for this study. In primary treatment, performance of various coagulants such as lime, alum, Poly aluminium chloride (PAC) has been studied where lime-PAC dose of 60 ppm found optimal. Similarly, various operational parameters of electrolysis treatment like type of electrode, applied current, electrolyte concentration has been studied. The graphite electrode along with 1.2 g/l of sodium chloride electrolyte concentration and 0.8 amp applied current in electrolysis treatment is found optimal.

The experiments has been conducted for wastewater of commercially operated common effluent treatment plant (CETP) using optimal parameters of primary and electrolysis technique. The results indicate 79.16% reduction of COD, 91.58% reduction of SS, 91.74% reduction of colour and 79.41% reduction of turbidity. Cost estimation has been evaluated for treatment industrial wastewater using combination of primary and electrolysis technique.

I. INTRODUCTION

Industrial waste water treatment is one of the challenging task in the field of chemical and environment engineering. (Mohammad *et al.* 2009) (Avsar *et al.* 2006) It is necessary to treat industrial wastewater properly before disposed it in to water bodies to save environment & ecology. The existing scenario of wastewater treatment mainly focused on primary, secondary and tertiary treatment methods. Even though majority of the water treatment units using these conventional methods, there are several operational issues associated with conventional methods (Altaher *et al.* 2011).

The primary treatment means to removes suspended solid load from wastewater. This is achieved by addition of various chemicals like lime, alum, PAC (flocculating agents & coagulants) followed by settling. (Altaher *et al.* 2011) (Almazan, *et al.* 2012) (Farajnezhad & Gharbani 2013) (Qiao-guang *et al.* 2011). However, appropriate dose of various chemicals to primary treatment is the key for efficient operation. This needs to be decided and observe continuously depending upon characteristic of inlet wastewater. As per open literature, Coagulation/flocculation is a widely used process for industrial wastewater treatment (Renault *et al.* 2009) (Khouni *et al.* 2010) mainly due to the ease of operation, high efficiency, cost effective. (Khouni *et al.* 2010) (Szygula *et al.* 2009).

Similarly, secondary treatment, deals with degradation of the organic matter by using suitable kind of microorganism. (Farajnezhad *et al*. 2013) As microorganism is responsible for the degradation of organic matter. It is highly sensitive operation and needs skilled manpower for its handling, affected by seasonal variations, quality of inlet effluent, retention time etc. Moreover, It is time consuming and costly being energy intensive operation. (Metcalf & Eddy)

Tertiary treatments like adsorption on activated carbon, Ion-exchange, oxidation, biodegradation and membrane filtration are generally used as polishing units to remove suspended load, colour, odour etc.

Even though the existing conventional secondary and tertiary wastewater treatment method are practiced in most of the waste water treatment plants, it is associated certain limitations. The problem becomes more serious in case of common effluent Treatment Plants (CETP) of wastewater treatment. (Jain *et al.* 2006) An alternative technique of electrolysis for treatment of wastewater is emerging. (Mohammad, *et al.* 2009) (Altaher *et al.* 2011) (Almazan *et al.* 2014) (Chatasymeon *et al.* 2006). Electrolysis provides approximately 50 to 95% efficiency in removal of inorganic and organic content from wastewater depending upon its characteristics ((Borazjan *et al.* 2014) (Jain *et al.* 2006). However, we are of the opinion that use of electrolysis alone may not be practically feasible for the treatment of wastewater. It needs to be conditioned properly through primary treatment before sending it to electrolysis. This will not only improve the efficiency of electrolysis process but also reduce suspended load of wastewater.

The systematic study on combination of primary treatment and electrolysis process for the treatment of industrial waste water has not been studied. Therefore the present work focus evaluation of optimal operating parameter for primary treatment followed by electrolysis treatment to achieve stringent regulatory norms.

In the present work wastewater from a commercially operated CETP has been collected and treated using combination of primary and electrolysis technique. The optimal parameters for primary treatment have been evaluated for the given effluent.

II. EXPERIMENTAL

Wastewater Sample Collection

Wastewater was collected from CETP which is situated in Nandesari, Gujarat. Sample characteristic depicted on Table 1.

Chemicals: The work based on treatability studies by combination of coagulation/flocculation with electrolysis technique has been investigated for CETP wastewater. The following chemicals Lime, PAC, Alum were used as coagulants, NaCl was used to supporting electrolyte and HCl was used to remove the impurity on electrode material.

Chemical Characteristics of the Effluent: An initial experiment was carried out to determine the primary characteristic of CETP effluent for the effectiveness of lime, alum and PAC as a coagulant. The characteristic of raw CETP effluent were presented in Table1:

Table 1: Characteristic CETP effluent

Parameter	Raw water
Turbidity (NTU)	680
COD (ppm)	7390
SS (g/l)	218
Colour (Pt/Co)	3920

Coagulant preparation

Stock solutions of Alum, lime and PAC should be prepared before starting the experiment. The solutions were prepared by dissolving 6gm of each substance in distilled water and the solution volumes were increased to 1 liter. They have been prepared in three different concentrations, i.e. 2, 4 and 6 gm/l into distilled water.

Experimental procedure of coagulation/flocculation:

Coagulation and flocculation tests were performed in a standard jar test apparatus consisting of six paddles and equipped with 3 beakers of 1 litre volume. Each beaker was filled with 500 ml of wastewater sample. The performance of the coagulants was compared by adding 20, 40 and 60ppm dose of each one to 500 ml of wastewater. If pH is in acidic side so add lime dose and try to adjust is in neutral condition and if pH is in alkaline so

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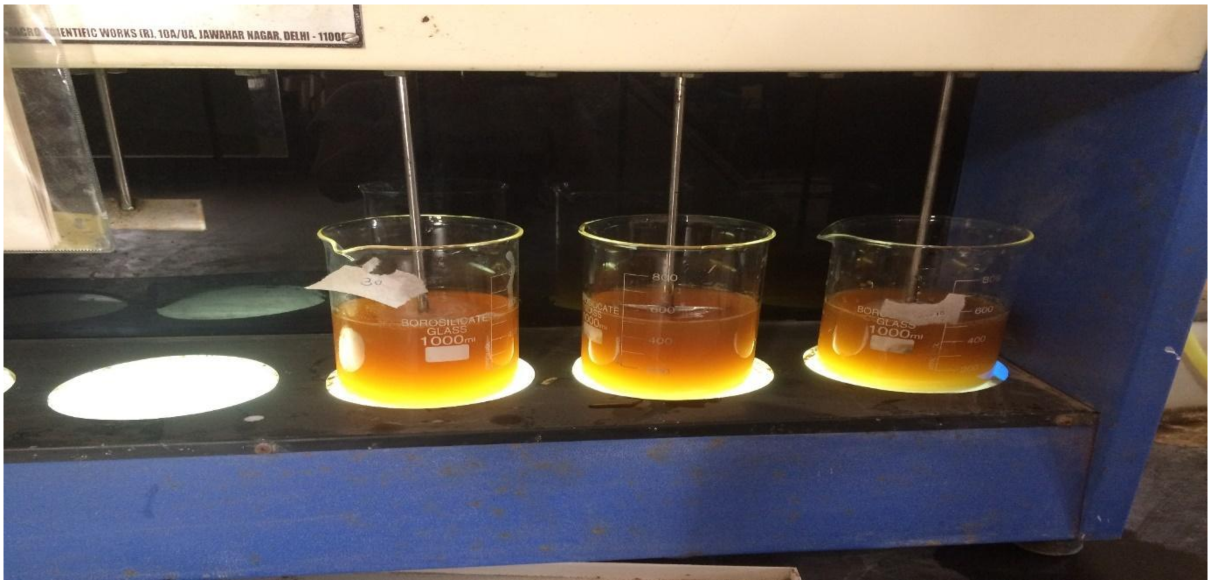
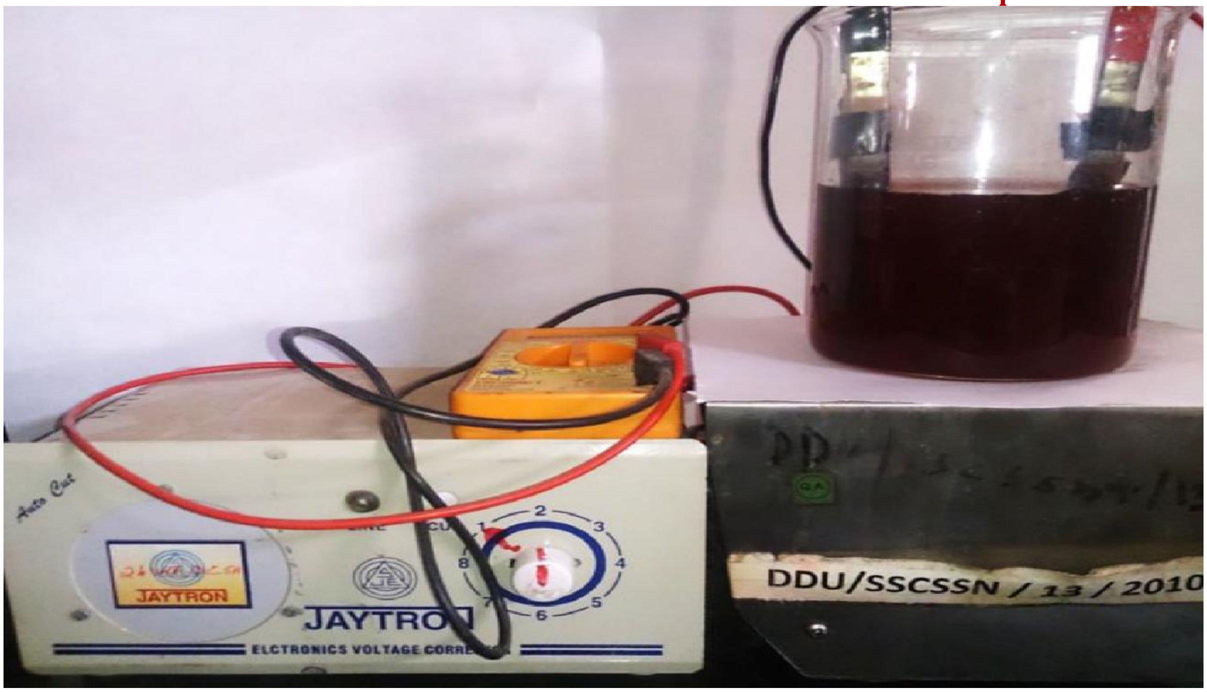
add alum, PAC, $FeCl_3$, $FeSO_4$, and try to adjust is in neutral condition. The samples were agitated at a flash mixing speed of 100 rpm for 1 minutes followed by slow mixing speed of 40 rpm for 15 minutes. At the end of the stirring period the flocs were allowed to settle down for 10 to 20 minutes. All the equipment were calibrated before use.



Experimental Procedure of Electrolysis

Primary outlet are considered for electrolysis treatment. The inter electrode spacing was 3 cm distance at each other. D.C power supply of 0.8 A was used to pass the current, proper agitation done by magnetic stirrer.

The impurities on the surfaces of the electrodes were also removed by dipping for 5 min in a solution which was prepared by mixing 0.1 L of HCl solution (35%) if metal and electrodes were clean with polish paper to remove scale and the electrodes were washed thoroughly with water to remove any solid residues on the surfaces, dried and reweighed. At the end of the run, the solution was filtered. The samples were taken for colour removal analysis, COD, SS and turbidity test. During this processes NaCl (1.2 g/l) was also used as a supporting electrolyte.



The parameters analysed with standard analysis method which is depicted in Table No.4

Sr.No	Parameter Description	Standard Analytical Method
1	Chemical Oxygen Demand	IS 2488 (part 4) 1996
2	Suspended Solid	IS 3025 (part 17) 1984
3	Colour	IS 3025 (part 4) 1983
4	Turbidity	IS 3025 (part 10) 1984

III. RESULTS AND DISCUSSION

Comparision of different coagulant:

The objective of this experiment was to determine best coagulant that can be used to reduce turbidity, SS, COD and colour to the permissible level for such wastewater. Behaviour of coagulant may change from wastewater according to many factors including pH, alkalinity and different constituent of wastewater. (Wang *et al.* 2007) (Girou *et al.* 2002) Fig. 1 depicts the removal efficiency for lime+PAC had superior efficiency in removing colour, SS, COD and turbidity compare with lime+Alum at the specified condition because it produces clear water, floc formed easily and flocs are not broken easily.

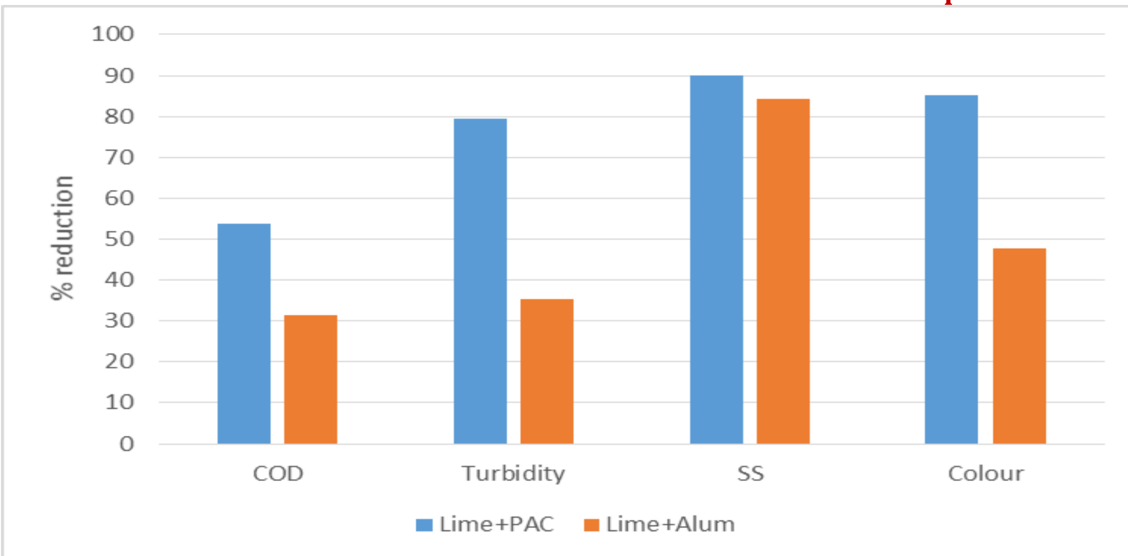


Fig. 1: Comparative statement of coagulants for reduction of organic matter.
(Lime+PAC 60 ppm & Lime+Alum 60 ppm dose, electrode: graphite)

As the results shown in Fig. 1 it can be concluded that the lime + PAC is found to be better compare to lime+alum for treatment of CETP wastewater. Therefore, same is considered for reduction of other parameters like turbidity, SS, COD & colour. In this regard three different coagulant dose of Lime+PAC (20ppm, 40ppm, 60ppm) were carried out

Effect of coagulant dose

As illustrated by **Figure 2**, the highest efficiency of turbidity, SS, COD, and Colour removal to such wastewater was achieved using 60ppm dose of lime+PAC. This dose resulted in turbidity removal efficiency of 31%, SS 31.55%, COD 21.3% and colour 45.5%. Increased the dose of coagulant percentage reduction increase shown in Fig. 2. Then after, the overflow/supernant of primary treatment is treated using electrolysis technique and results obtained are depicted in Fig. 2. The removal efficiency of turbidity, SS, COD and colour obtained was 79.31%, 89.88%, 53.70% and 85.07% respectively. This later value can be accepted from a pre-treatment process for such wastewater taking into consideration it would go through more treatment processes (coagulation/flocculation process followed by electrolysis technique).

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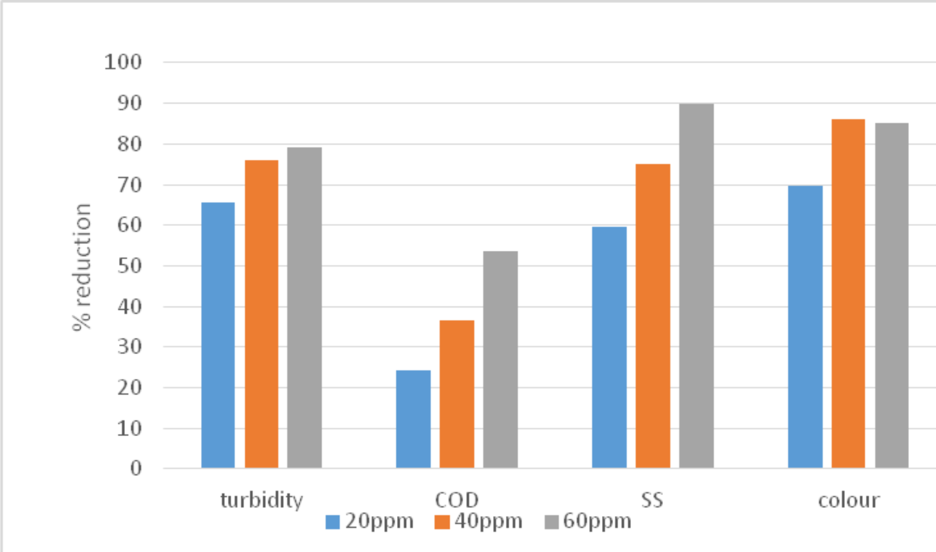

Fig. 2 Combination of primary treatment and electrolysis technique
(Lime+PAC dose 20, 40, 60 ppm Current: 0.8 amp, electrolytes conc.:1 g/l, pH: 7, electrode: graphite, electrolysis time: 1hr)

Effect of Initial Concentration of Electrolytes

The primary outlet are considered for electrolysis treatment. Here, use 60ppm dose of lime+PAC. Wastewater sample with different concentration of NaCl as an electrolyte (0.8 to 1.2 g/l) and pH 7 to electrolysis with potential difference of 0.8 A and removal of COD, SS, Turbidity and colour was a function of electrolysis time. The effect of support electrolyte concentration on COD, SS, Colour and turbidity is shown in Fig. 3. Furthermore, this salt concentration could affect operational parameters in electrolysis such as voltage, current efficiency, and electrical energy. For wastewater sample with 1.2 g/l NaCl 67.93% was removed after 60min of electrolysis. The percentage removal increasing with increasing NaCl concentration. The maximum percent COD removal values, achieved after 60min of electrolysis, were 66.11%, 67.66% and 67.93% for electrolyte concentration containing 0.8, 1 and 1.2 g/l respectively.

The effect of electrolyte concentration on the removal of Colour is shown in Fig. 3. At each NaCl concentration electrolyte concentration increase as the colour removal efficiency also increase. For example, NaCl was 0.8 g/l 66.11%, 1 g/l 73.72 and after 1.2 g/l 82.40 after same electrolysis time.

The effect of electrolyte concentration on the removal of SS is shown in Fig. 3. At each NaCl concentration electrolyte concentration increase as the SS removal efficiency also increase. For example, NaCl was 0.8 g/l 93.12%, 1 g/l 95.17% and after 1.6 g/l 95.87% after same electrolysis time. So prove that base on COD and SS percentage reduction increase as increase the removal efficiency of organic matter. So our further study focus on 1.2 g/l of electrolyte concentration. This concentration removal efficiency of SS, turbidity, COD and colour was 95.87%, 73.8%, 67.93 and 82.40%. Here, use graphite electrode, initial current 0.8 A.

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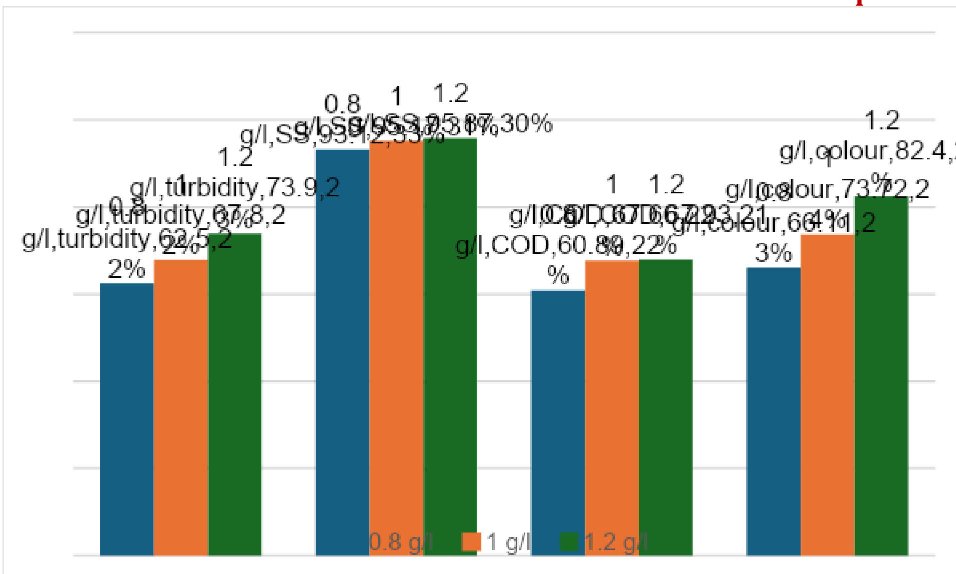

Fig. 3 Effect of electrolytes concentration on removal efficiency of lime+ PAC dose 60 ppm, Current: 0.8 amp, electrode: graphite, distance: 3 cm, electrolysis time: 1hr)

By increasing the concentration of chloride ion, the decomposition rate was also increased. This improvement in decolourization process can be explained by the reaction-taking place at anode (equation 3).

$2Cl^- \rightarrow Cl_2 + 2e$ ………………………………………………………………………………(3)

The generated chlorine can be converted quickly into hypochlorite in solution:

$Cl_2 + H_2O \rightarrow ClO^- + Cl^- + 2H$ ……………………………………………….......................... (4)

The generated hypochlorite in equation 4 can enhance the decolourization of chemical process industry wastewater, while the chloride ion can be recycled and used as the reactant. The generated hypochlorite ions act as main oxidizing agent in the pollutant degradation and were classified as indirect electro oxidation of pollutant. Moreover, the increased NaCl results in a decrease in the operating voltage at constant current.

Fig. 4 primary treatment along with electrolysis technique to reducing organic matter

Effect on different type of Electrode Material

The treatment of wastewater with combination of primary treatment & electrolysis has been conducted. The primary outlet are considered for electrolysis treatment. Use coagulation and flocculation technique for settling of particulates to remove SS, COD, turbidity, colour, etc. Then after, the overflow/supernant of primary treatment is treated using electrolysis technique for different electrode material.

In any electrochemical process, electrode material has significant effect on the treatment efficiency. Therefore, appropriate selection of the electrode material is important. The electrode material for treatment of water and wastewater should also be non-toxic to human health and environment. To investigate the effect of electrode materials on the colour, COD, SS and turbidity removal efficiency, the electrolysis process was carried out using different type electrodes. Studies show Fig. 5 colour, COD, SS and turbidity removal efficiency against electrical potential applied to the electrodes in the electrolysis process. Here, use graphite electrode, copper and aluminium electrode, initial current 0.8 A, electrode concentration 1.2 g/l and distance 3 cm. Aluminium electrode give better removal efficiency shown in Fig. 5. Removal efficiency of COD 39.04%, colour 82.66% and SS 82.91%.

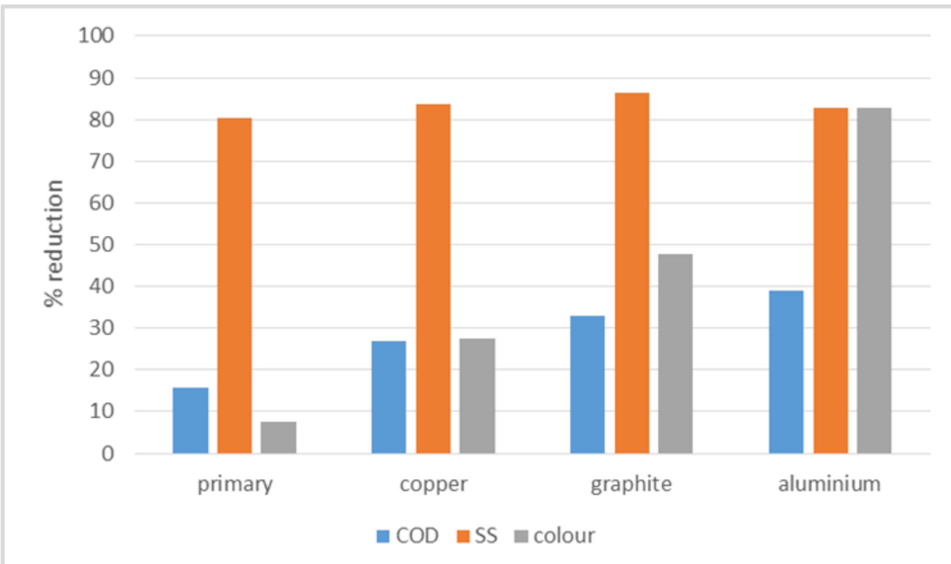

Fig. 5 Effect of different electrode on removal efficiency (Lime dose 60 ppm & PAC dose 60 ppm, Current: 0.8amp, electrolytes conc.:1.2 g/l, pH: 7, electrolysis time: 1hr)

The selection of electrode is important in electrolysis; commonly used metallic and non-metallic electrodes are copper, graphite and aluminium. Shown in Fig. 5 aluminium electrode give better removal efficiency but metal electrodes are dissolved during the electrolysis process, which occurs with coagulant species and metal hydroxides. In metallic electrode metal loss is observed, dissolution of metal in wastewater is more harmful. Metal anode dissolution is accompanied by hydrogen gas evolution at cathodes, the bubbles capturing and floating the suspended solids formed and thus removing contaminants. The investigation of treatment efficiency for copper, graphite and aluminium electrodes was tested for colour, COD, SS, turbidity removal. All experimental studies were carried out under the same conditions, which were initial current 0.8A, electrolyte conc. (NaCl) 1.2 g/l and distance 3cm. Comparison of different electrodes on increase removal efficiency of COD, SS, turbidity, colour.

Effect of electrolysis time

The primary outlet are considered for electrolysis treatment. In any electrochemical process, electrolysis time has significant effect on the treatment efficiency. Electrolysis time increase so reduction of organic matter also increase is shown in Fig. 6. Here, use graphite electrode, initial current 0.8 A, electrode concentration 1.2 g/l and distance 3 cm. To investigate the effect on the colour, COD, SS and turbidity removal efficiency. Studies show Fig. 6 the colour, SS, COD, turbidity removal efficiency against electrical potential applied to the electrodes in the electrolysis process. Highest COD removal is for 80min retention time. Prove that electrolysis time increase as reduction of COD, SS, turbidity, colour also increases. As shown in Fig. 6 removal efficiency of COD 79.16%, colour 91.58%, SS 91.74% and turbidity 79.41% observed after using combination of primary treatment and electrolysis process.

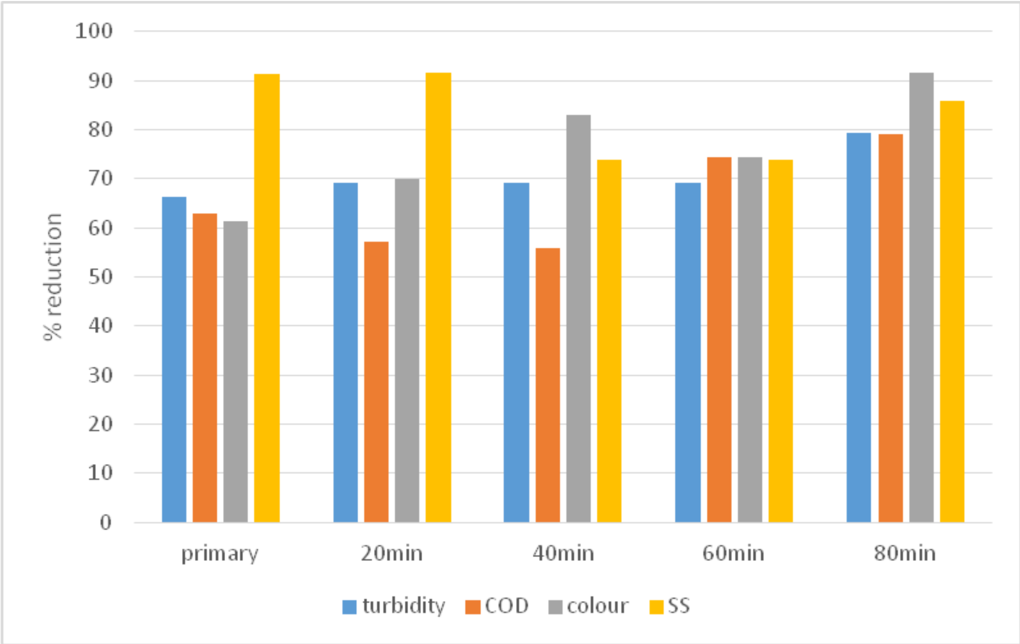

Fig. 6 Effect of electrolysis time on removal efficiency.(lime+PAC dose 60ppm, Current: 0.8amp, electrolytes conc.:1.2 g/l, pH: 6.5, electrode: graphite

Performance of various coagulants such as lime, alum, Poly aluminium chloride (PAC) has been studied where lime-PAC dose of 60 ppm found optimal. Similarly, various operational parameters of electrolysis treatment like type of electrode, applied current, electrolyte concentration has been studied. The graphite electrode along with 1.2 g/l of sodium chloride electrolyte concentration and 0.8 amp applied current in electrolysis treatment is found optimal. We studied all optimum parameter in above section and this parameter give better removal efficiency so in next section we studied all this experiment in above optimum parameter.

Name of Industry: Dye intermediate
Sample: Coloured wastewater

Result and Discussion

As reported in Fig. 7 maximum COD reduction 70.63%, SS reduction 78.44%, turbidity and colour reduction 90.82% was achieved by using coagulation/flocculation followed by electrolysis process. Inlet and outlet sample was analyzed for various parameters and average results obtained are mention In Fig. 7.

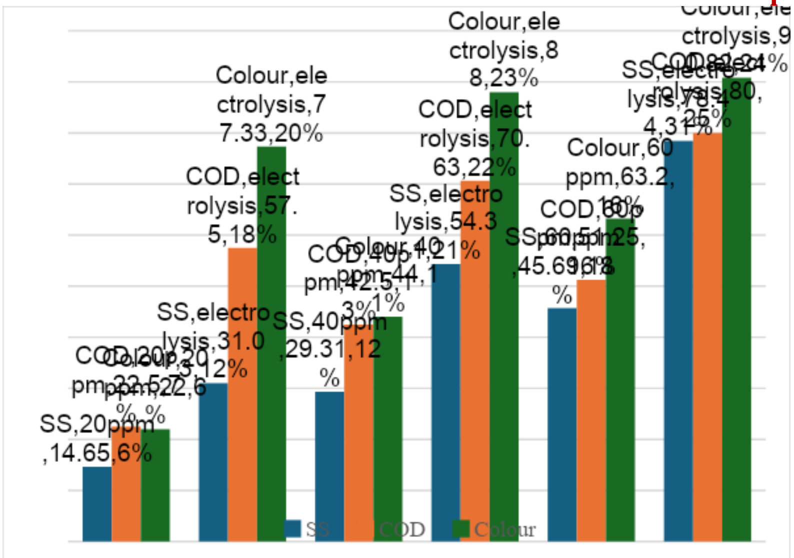

Fig. 7: Effect of lime+PAC with electrolysis
(Lime-PAC dose 20, 40, 60 ppm Current: 0.8amp, electrolytes conc.:1.2 g/l, pH: 7, electrode: graphite)

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Name of Industry: Pharmaceutical Industry
Sample: Coloured wastewater
Result and Discussion:
After coagulation/flocculation technique COD, SS and colour reduced at neutralized pH lime+PAC 60ppm dosing was found to be 2.94%, 36.31% and 38.89% respectively is shown in Fig. 7. The result of combination of coagulation/flocculation and electrolysis techniques shown in Table 5.5. The end result indicates that primary then electrolysis the reduction of COD, SS and colour values are 76.76%, 83.08% and 61.38% respectively is shown in Fig. 7. Looking to increase incoming dose up to 80ppm the effluent reduction also increase COD 91.18%, SS 89.23% and colour 96.67%.

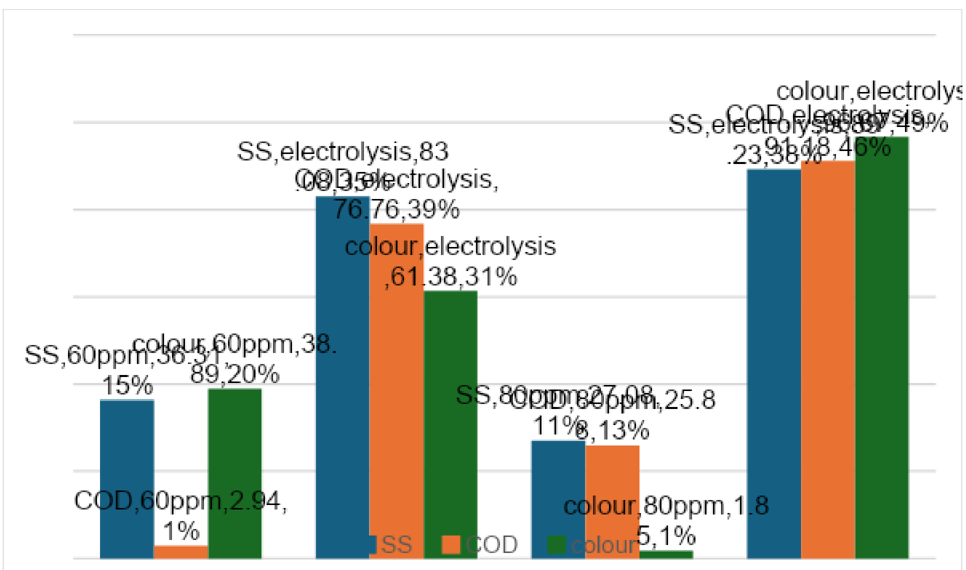

Fig. 5.3: Effect of lime+PAC with electrolysis
(Lime-PAC dose 60 ppm Current: 0.8amp, electrolytes conc.:1.2 g/l, pH: 7, electrode: graphite)

Cost Estimation of Coagulant Dose and Graphite Electrode for industrial wastewater

Operating cost of electrolysis can be calculated by considering electricity price, chemical reagent cost, electrode cost, labor cost, maintenance and equipment cost. However, present study limited by considering electricity cost, electrode material cost and electrolytes cost. The operating cost for electrolysis process is

$C = X^* \, {}^{C}electricity + Y^* \, {}^{C}electrode + Z^* \, {}^{C}electrolyte$

Where, C= operating cost of electrocoagulation process (Rs./m^3 of waste water), ^{C}electricity= specific energy consumption (kWh/m^3 of waste water), ^{C}electrolytes=specific electrolytes (NaCl) consumption (Kg/m3 of waste water), ^{C}electrode= specific electrode consumption (Zinc)(Kg/m^3 of waste water), x= cost of electricity (Rs/kWh), y=cost of electrodes (Rs./kg) and z= cost of electrolytes (Rs./Kg.).

Here, effect of various applied current on electrode consumption and electrolytes consumption as shown in table. The set-up cost or initial cost has not been included in present report.

Applied Voltage	A= Total cost of electricity per cubic meter	B= Total cost of graphite electrode per cubic meter	C= Total cost of electrolyte consumption per cubic meter	Total operating cost per cubic meter
14.67	81.56	5	6	92.5

The operation cost per cubic meter of wastewater treatment was noted at 14.67V (0.8 A) and electrolytes concentration 1.2 gm/lit

Using chemical	Rate of chemical (Rs./kg)	Average chemical dosing (gm/l)	For use 5000m^3/day (kg/day)	Rs. For 1m^3/day	Rs. For 5000m^3/day
Lime+PAC	4+6.5=10.5	(2+2)-(4+4)-(6+6)	42-84-126	0.088-0.18-0.26	441-882-1323
Lime+alum	4+5=9	(2+2)-(4+4)-(6+6)	36-72-108	0.06-0.13-0.19	324-648-972

IV. CONCLUSIONS

The conventional wastewater treatment method practised in the most of the chemical process industries are studied and literatures related to them are reviewed. Most of the units involved in this conventional method associated with operational difficulties, odor nuisance, space problem and cost intensive. The problem becomes more serious in case of common facility of wastewater treatment. An alternative technique of electrolysis for treatment of wastewater is studied. However, use of electrolysis alone will not be practically feasible for the treatment of wastewater. Therefore the current work considered the utilization of basic primary treatment with optimal selection of operating parameters along with electrolysis technique. The treatment of wastewater with combination of primary treatment & electrolysis has been conducted. The optimal dose of chemicals in primary treatment has been evaluated. The primary outlet are considered for electrolysis treatment.

Experimental results indicate that CETP wastewater turbidity, SS, COD and colour removal efficiency of 31%, 31.55%, 21.3% and 45.5% respectively obtained by using 60 ppm dose of lime and PAC. Similarly the electrolysis of the primary outlet yield reduction of COD 79.16%, colour 91.58%, SS 91.74% and turbidity 79.41% by using graphite electrode at 7 pH, with 1.2 g/L of electrolyte at 0.8 A current in 1 hour reaction time.

In Dye intermediate effluent up to 70.63% COD reduction, SS 78.44% and colour 90.82% is obtained at combination of coagulation/flocculation with electrolysis technique.

In Pharmaceutical industry wastewater Up to 76.76% COD reduction, SS 83.03% and colour 61.38% is obtained at combination of coagulation/flocculation with electrolysis technique. After increase dose up to 80 ppm of lime-PAC reduction is also increase COD 91.18%, SS 89.23% and colour 96.67%. The combination of coagulation/flocculation followed by electrolysis has been applied/studied for selected chemical process units in the state of Gujarat. There is need to provide treatment for electrolysis technique.

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