Treatment of Distillery Waste Water using Electro coagulation

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Abstract

Distilleries are one of the most polluting industries generating large volumes of high strength wastewater. These effluents are containing highly colored, COD, BOD, TDS and other organic matter. To meet the environmental standards and regulations, treatment of effluent is must before letting out to the environment. EC treatment has attracted great attention in treating industrial waste water because of versatility and environmental compatibility. A laboratory treatment apparatus was made for the purpose of finding the suitability of electrochemical treatment for the treatment of distillery waste water. Three different electrode material viz. steel, aluminium and iron was utilized to study the relative efficiencies of the electrode materials in removing the impurities present in the distillery wastewater, The distillery wastewater samples were electrochemically treated for 2 hours each with the three different electrode materials under varying voltages of 20V, 35V, 50V, 65V and 80V, since 80V is the maximum capacity of the testing equipment. Iron electrode showed much better results and therefore has higher average performance efficiency. Iron is also cheaper and more easily available than aluminum. Thus it can be concluded that Iron can be suggested as the most desired, amongst the three electrodes for the electro coagulation treatment of Distillery wastewaters.

Keywords: Distillery waste water, electro chemical (EC) treatment, iron electrodes, BOD, COD.

I. Introduction

Distilleries are one of the most polluting industries generating large volumes of high strength wastewater. A distillery industry discharges approximately 100-1000 m³/day wastewater depending on the size of the process India is the fourth largest producer of ethanol in the world and the second largest in Asia (Baskar G., Deeptha V. T. and Rahaman A., 2009). The type of wastewater coming out of a distillery depends on the type of alcohol produced, the processes followed in making the wine and the type of additives used. The volume of wastewater generated from a distillery is usually about 10 times that of ethanol produced. Wastewater from distilleries contains large amounts of organic and inorganic content. For every litre of alcohol, maximum 8-15 litres of spent wash are generated (AIDA, 2008).

Characteristics of Untreated distillery effluent (Manisankar. P, Rani. C and Vishwanathan. S, 2004; Mohanakrishna G, Venkata Mohan S, Sarma PN, 2010).

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Parameter (All values in mg/l except pH)	Range of values	
Ph	3.0-4.5	
BOD ₅	50,000- 60,000	
COD	1,10,000- 1,90,000	
Total Solid (TS)	1,10,000-1,90,000	
Total Volatile Solid (TVS)	80,000-1,20,000	
Total suspended solid (TSS)	13,000-15,000	
Total dissolved solids (TDS)	90,000-1,50,000	
Chlorides	8000-8500	
Phenols	8000-10,000	
Sulphate	7500-9000	
Phosphate	2500-2700	
Total nitrogen	5000-7000	

ISSN: 1007-6735

Various physical, chemical and biological techniques are used for the treatment of distillery spent wash before its discharge to the aqueous ecosystem. In biological treatment, anaerobic treatment is attractive in comparison to direct aerobic treatment due to high organic content of molasses present in spent wash (C. Thakur, V. C. Srivastava, and I. D. Mall, 2009). The basic principle in electrochemical oxidation is that ozone and hydroxyl radicals are produced on the surface of the anode material and they will oxidize harmful compounds. This technique is also environmentally friendly because any chemicals in the oxidation process need be used.

II. Literature Review

Various conventional methods have been adopted such as biological flocculation [18] nanofiltration (Rai et al. 2008; Pandey. R.A., Malhotra. S, Tankhiwale. A, Pande. S, 2003) activated carbons (Panizza, M. and Cerisola, G., 2005) bioelectrochemical process (Mohanakrishna et al. 2010; Piya-areetham P, Shenchunthichai K, Hunsom M, 2006) ozonation-based process (Ponselvan FIA, Kumar M, Malviya J.R., Srivastava V.C., Mall ID, 2009; Lucas et al. 2010; Prasad. R. K and Srivastava. S. N., 2009) Asaithambi et al. 2012; R. A. Pandey, A. Malhotra, S. Tankhiwale, S. Pande, P. P Pathe, and S. N. Kaul, 2003) electro-oxidation (Rai UK, Muthukrishnan M., Guha BK, 2008; Satyawali Y, Balakrishnan M., 2007) membrane-based nanofiltration and reverse osmosis (Satyawali, Y., Balkrishnan, M., 2007) and electrocoagulation (Sreethawong T, Chavadej S, 2008). However, conventional methods found to be techno-economically non-feasible for the treatment of organic pollutant present in the effluent. Hence, it is necessary to investigate an alternative process for effective and economical treatment method.

Many advanced treatments have been studied and electrochemical oxidation has been applied to many kinds of wastewater (Rai UK, Muthukrishnan M., Guha BK, 2008; Satyawali Y, Balakrishnan M., 2007). It is presented as an effective, selective, economical,

ISSN: 1007-6735

and clean alternative for dealing with wastewaters bearing high loads of organic compounds, especially some bio-refractory organic pollutants. Electro coagulation is an efficient method to remove colour and reduce COD. (Manisankar et al; Sushil kumar Shukla, 2014) in their work concludes that by using Graphite - Graphite electrodes 85.2 % COD removed at pH 6.9 – 7.2 and duration is 180 minutes. (Takur C.K., Srivatsava V.C. and Mall I.D., 2009) Reported that by using Al - Al electrode 72.3 % COD removed in 2 hours when pH is 3. (Tezcan Un, U.; and Aytac, E., 2011) State that by using Al - Al electrode 81.3 % COD removed successfully. They also prove that by using Al - Fe electrode 71.8 % COD removed in 2 hour duration when the pH of the solution is 3. (Thakur C, Srivastava VC, Mall ID, 2009) Revealed that 98 % COD removal efficiency was obtained by using Al – Al electrode when the pH of the waste water is 7.2. They also concluded that the electro -coagulation technique can be successfully employed for the treatment of distillery effluent.

Tezcan Un et al. (Y. Yavuz, 2007) employed electrocoagulation method using iron or aluminium as electrodes in the presence of 2.3% H₂O₂ as the oxidant and 0.5 g of polialuminium chloride as the coagulating agent for the treatment of olive mill wastewaters. The performance of the iron electrode was better in comparison to that of aluminium with 62–86% reduction in COD and 100% removal of oil–grease and turbidity. Panizza et al. (Zhang W, Xiong R, Wei G, 2009) compared direct and indirect electrochemical oxidation of a synthetic solution containing the basic dye, methylene blue.

III. Research Design and Objectives

Treatment of Distillery spent wash by Electrochemical Treatment:



Figure 1. Electrochemical Treatment Setup

If a chemical reaction is driven by an external applied voltage, as in electrolysis, or if a voltage is created by a chemical reaction as in a battery, it is an *electro-chemical* reaction. In contrast, chemical reactions where electrons are transferred between molecules are called oxidation/reduction (redox) reactions. In general, electrochemistry deals with situations where oxidation and reduction reactions are separated in space or time, connected by an external electric circuit.

Based on the literature review it was proposed to have the following objectives.

- 1. Learning the process of distillation and how the waste water intended to treat is produced.
- 2. Making a prototype laboratory setup for the electrochemical treatment for the distillery waste water.
- 3. Analyzing the waste water sample for various basic physico-chemical characterististics and elemental Analysis to analyze the presence of Phospherous, Nitrate Nitrogen, Fluorides, Sulphates, Iron, Manganese, Calcium, Magnesium and Cadmium in both the Influent sample and the effluent samples to study the removal efficiencies of the electrodes under investigation.
- 4. Treatment of the waste water with electricity using stainless steel, aluminum and iron electrodes.
- 5. Analyzing the samples after treatment to find out which among the electrode material provides the best treatment efficiency to the distillery wastewater.

IV. Schedule, Tasks and Milestones

1. The major milestones that was proposed to be achieved are:

- 2. The effluent sample collected to be tested for all the water quality parameters as given in Standard methods [40].
- 3. The samples in the appropriate dilutions are then to be treated electrochemically in the apparatus under varying voltages of 20V, 35V, 50V, 65V and 80V.
- 4. The samples after treatment by each electrode material was to be again tested for the parameters above mentioned and the efficiency of the impurity removal by each electrode material and thence the relative efficiencies between the different materials was to be analysed.
- 5. The best performing electrode material would be identified and can be suggested for electro chemical treatment of the distillery wastewater.

V. Materials and Methods

A laboratory treatment apparatus was made for the purpose of finding the suitability of electrochemical treatment for the treatment of distillery waste water. Three different electrode material viz. steel, aluminium and iron was utilized to study the relative efficiencies of the electrode materials in removing the impurities present in the distillery wastewater.





Aluminium

Iron



Steel

Figure 2. Treatment Apparatus and Three Different Electrodes

Based on the principles one apparatus was fabricated and three different electrode materials viz. steel, aluminum and iron was cut to equal sizes, 15 cm x 2.5 cm each. Basic Components of the apparatus included Electrodes (Stainless Steel, Aluminium, Iron), Digital Voltmeter, Beaker, Bar Magnet, Motor, Wooden frame to hold the electrodes and magnetic stirrer and Voltage Regulator. The raw sample was diluted taking 50 ml of effluent in a 1 litre solution. This was necessary because the raw effluent was too concentrated for lab scale treatment.



Figure 3. Wastewater Sample a) Before treatment

Figure 5. b) After Treatment

These samples were electrochemically treated for 2 hours each with the three different electrode materials under varying voltages of 20V, 35V, 50V, 65V and 80V, since 80V is the maximum capacity of the testing equipment. This picture clearly shows the settlement in the sample after treatment.

Analysis of basic parameters like pH, Alkalinity, Acidity, Hardness, Chloride Content, Total Solids, Turbidity, BOD and COD analysis were performed. Elemental Analysis using Atomic absorption spectrometer is conducted to analyze the presence of heavy metals like Iron, Manganese, Calcium, Magnesium and Cadmium and Spectro photo meter was used to analyze the presence of Phospherous, Nitrate Nitrogen, Fluorides, etc in both the Influent sample and the effluent samples to study the removal efficiencies of the electrodes under investigation. Analysis of all parameters mentioned above was done as per the methods given in Standard methods [2].

VI. Results

The distillery wastewater samples after treatment by each electrode material is tested for the parameters mentioned in and the efficiency of the impurity removal by each electrode material and thence the relative efficiencies between the different materials is analysed Parameters measured Vs Voltage applied is plotted and analysed in excel sheets to analyse the specific voltage that gives the maximum removal efficiency





Figure 6. pH Graph

As we can see from the above graph, the three metals when used as electrodes show very different behavior towards the pH of the waste water. Aluminum as well as stainless steel lines shows a general trend of increasing pH with increase in voltage while Iron shows a slight increase followed by a relatively larger dip.It can be concluded that with increasing voltage, aluminum and stainless steel made the waste water more basic and iron made it more acidic. The effect of pH if the voltage is increased further is unclear.

(b) Turbidity concentration in the Influent = 375.2 mg/L



Figure 7. Turbidity Graph

All the three materials show great removal efficiencies in case of turbidity. At around 20V, Al shows least removal but it removal capacity becomes more than steel at 65V. Iron shows maximum removal throughout and has much higher efficiencies.



Figure 8. Turbidity Removal Efficiency Graph

(c) Chloride content of the Influent = 511.75 mg/L



Figure 9. Chloride Content Graph

The chloride content graphs clearly support the conclusion that iron acts as the best electrode out of the three in this case. The removal by Al and steel are almost the same, although when the voltages are increased, steel performs somewhat better in comparison to aluminium.



Figure 10. Chloride Removal Efficiency Graph

(d) Phosphorous content of the influent = 19 mg/L



Figure 11. Phosphorus Content Graph

Aluminium and steel graph lines are almost together in case of phosphorus. All the three electrodes make a straight line showing that the removal efficiency increases continuously with increase in voltage. Although the gap in efficiencies is not too high in this case, iron still shows higher removal then the other two electrodes.



Figure 12. Phosphorus Removal Efficiency Graph

(d) Nitrate Nitrogen concentration in the Influent = 51 mg/L



Figure 13. Nitrogen Content Graph

Nitrogen content graph shows distinct lines that clearly explain the difference in the performances of the three electrodes taken into consideration. Al shows the least removal with the highest amount of nitrogen in the samples after treatment. Steel comes in second but not too far below. Iron shows the highest removal efficiency of all.



Figure 14. Nitrogen Removal Efficiency Graph

(e) Influent Alkalinity = 2016 mg/L



Figure 15. Alkalinity Graph

Alkalinity graph lines follow a similar pattern. The iron graph line is straight, with constant increase in removal with each increasing interval of voltages. Al and steel show a similar pattern, but with variations. The two lines go together almost always except at 65V where steel shows higher removal the Al.



Figure 16. Alkalinity Removal Efficiency Graph

(f) Acidity of the influent = 1350 mg/L



Figure 17. Acidity Graph

Acidity graph also confirms that the removal efficiencies increase with increasing voltages. Here too, iron electrode shows maximum removal, while Al and steel are not too far below. All the average removal efficiencies are above 60 percentages.



Figure 18. Acidity Removal Efficiency Graph

(g) Hardness concentration in the influent = 720 mg/L of CaCO₃



Figure 19. Hardness Graph

The removal efficiency for the hardness in the waste water using Iron electrode is about 7 percentages higher than the other two electrodes. All the average removal efficiencies are above 60 in this case too but iron's is considerably high. The average for Iron is around 68 percentages whereas the other two have around 62 and 63.



Figure 20. Hardness Removal Efficiency Graph

(h) Total Solids in the influent = 7055 mg/L



Figure 21. Total Solids Graph

The amount of settlement seen in the three electrodes varied a lot too. While using Iron as an electrode, the removal efficiencies for total solids were about 8-9 percentages higher than Al and steel electrodes, which is considerably high. Thus it can be concluded that Iron is the most preferred electrode material for removal of total solids in this case.



Figure 22. Total Solids Removal Efficiency Graph

(i) COD of Influent = 1176 mg/L



Figure 23. COD Graph

In case of COD removal, Al shows the highest efficiency. Although the difference in efficiencies is not too high, this confirms with the other studies done in the field. The Al electrode showed around 1 percent higher removal efficiency than the other two. The differences are only in decimals.



Figure 24. COD Removal Efficiency Graph

(j) BOD of the Influent = 42000mg/L





The BOD removal graph lines are all mixed up together and the removal at different voltages follow a rise and fall pattern in all the three electrodes. Although Iron electrode shows slightly better results, further testing is required to form a better conclusion in case of BOD removal.



Figure 26. BOD Removal Efficiency Graph

(k) Flouride concentration in the influent = 3.1 mg/L



Figure 27. Fluoride Graph

Fluoride removal as shown by the graphs tell us that the Iron show higher removal in lower voltages and as we increase the voltages, Al and steel catch up. This leaves us with a question whether the Al and steel electrodes will give higher removal efficiencies than Iron if the voltage is further increased. The answer to this is subject to further testing.



Figure 28. Flouride Removal Efficiency Graph

(1) Sulphate concentration in the Influent = 2750 mg/L



Figure 29. Sulphate content Graph

In case of sulphate removal, the electrodes made out of Al and steel show similar pattern of removal except at 20V. Here too, the removal by Iron is higher than the other two, by around 5 percentages. All the three electrodes show increased removal with increase in voltage.



Figure 30. Sulphate Removal Efficiency Graph

(m) Ferrous content in the influent = 3.029 mg/L



Figure 31. Ferrous removal Graph

Iron electrode shows around 6-7 percentages higher removal of ferrous content in the waste water sample, when compared to AL and Steel electrodes. Steel showed the lowest average of 62.6 percentages. The difference of 6-7 percentages in the removal is considerably high.



Figure 32. Ferrous Removal Efficiency Graph

(n) Manganese content in the influent = 0.141 mg/L



Figure 33. Manganese content Graph

The average manganese removal is almost the same in all the three electrodes, although Iron shows slightly higher removal. Al shows slightly higher removal in lower voltages where as steel overtakes it at 65V and above. All the lines show increasing trend of removal with increase in voltages.



Figure 34. Manganese Removal Efficiency Graph

(o) Calcium content in the influent = 18 mg/L



Figure 35. Calcium content Graph

In case of calcium removal, Iron electrode shows about 5-6 percentages higher removal than Al and steel. Although Iron and Al show continuous increase in removal with increase in voltages, steel does not show a straight line here. The differences in removal are distinct in this graph, with Al having the least removal efficiencies.



Figure 36. Calcium Removal Efficiency Graph

(p) Magnesium content in the influent = 1.468 mg/L



Figure 37. Magnesium content Graph

In case of magnesium too, the electrode made out of Iron shows highest removal efficiency, about 6-7 percentages in average. The Al and steel electrodes show similar removals in lower voltages, but as the voltage is increased, steel electrodes show higher performance than Al.



Figure 38. Magnesium Removal Efficiency Graph

(q) Cadmium content in the influent = 0.08 mg/L



Figure 39. Cadmium content Graph

Although the actual differences are in decimals, the removal efficiencies of Iron electrode in case of cadmium is much higher than Al and steel electrodes, about 9 percentages. Since the actual values are already below the permissible levels, this does not have a huge impact on the conclusion.



Figure 40. Cadmium Removal Efficiency Graph







The removal efficiency of all the electrodes kept on increasing as the voltage was increased. The test could be performed upto 80V only, as that was the maximum capacity of the lab equipment made for this project. Thus, here in this case, 80V gives us the maximum removal efficiency and the removal efficiencies of the three electrodes are analysed at 80V.

In similar studies done in this field, most of the researchers have concluded that Aluminum, as an electrode shows the highest removal efficiency. The simple reason for this being that most of the researchers concentrate only on COD removal. In this project too, aluminum gives slightly higher removal efficiency in case of COD in particular. But when considering the removal efficiencies of all the other impurities, Iron electrode shows much better results and therefore has higher average efficiency. Iron is also cheaper and more easily available than aluminum. Thus it can be concluded that Iron is the most desired, out of the three electrodes in comparison.

Limitations of the work. The test could be performed upto 80V only, as that was the maximum capacity of the lab equipment made for this project.

Future Scope of work. It can also be concluded that further research of larger scale and also at still higher voltages is required before using this method of waste water treatment for practical purposes. Details like voltage, dilution, amount of waste water treated, duration of the treatment etc will have to be optimized but electrochemical coagulation has proved to have potential as a treatment process for distillery waste water.

References

- AIDA (2008). Ethanol opportunities and challenges. [Online] Available: http://aidaindia.org/its08/topics_covered.html
- APHA-AWWA-WPCF, (2005). Standard methods for the examination of water and wastewater. *American Public Health Association*, 21st Edition, New York.
- Baskar G., Deeptha V. T. and Rahaman A., (2009). Root zone technology for compus waste water treatment. *J. Environ. Res. Develop.*, 3(3), 695-705.
- C. Thakur, V. C. Srivastava, and I. D. Mall, (2009). Electrochemical treatment of a distillery wastewater: Parametric and residue disposal study. *Chemical Engineering Journal*, vol. 148, pp. 496-505.
- Manisankar. P, Rani. C and Vishwanathan. S (2004). Effect of Halides in the Electrochemical Treatment of Distillery Effluent. *Chemosphere*, pp. 57-961.
- Mohanakrishna G, Venkata Mohan S, Sarma PN (2010). Bioelectrochemical treatment of distillery wastewater in microbial fuel cell facilitating decolorization and desalination along with power generation. *J Hazard Mater* 177:487–494.

- Nataraj SK, Hosamani KM, Aminabhavi TM (2006). Distillery wastewater treatment by the membrane-based nanofiltration and reverse osmosis processes. *Water Res* 40:2349–2356.
- Pandey. R.A., Malhotra. S, Tankhiwale. A, Pande. S (2003). Treatment of biologically treated distillery effluent a case study. *International Journal of Environmental Studies*, vol. 60, pp. 263-275.
- Panizza, M. and Cerisola, G. (2005). Application of diamond electrodes to electrochemical processes. *Electrochimica Acta*, Vol 51, N°2, pp 191-199, ISSN: 0013-4686.
- Piya-areetham P, Shenchunthichai K, Hunsom M (2006). Application of electrooxidation process for treating concentrated wastewater from distillery industry with a voluminous electrode. *Water Res* 40:2857–2864.
- Ponselvan FIA, Kumar M, Malviya J.R., Srivastava V.C., Mall ID (2009). Electrocoagulation studies on treatment of biodigester effluent using aluminum electrodes. *Water Air Soil Pollut* 199:371–379.
- Prasad. R. K and Srivastava. S. N. (2009). Electrochemical degradation of distillery spent wash using catalytic anode: factor design of experiments. *Chemical Engineering Journal*. V.146, pp. 22-29.
- R. A. Pandey, A. Malhotra, S. Tankhiwale, S. Pande, P. P Pathe, and S. N. Kaul, (2003). Treatment of biologically treated distillery effluent-a case study. *International Journal of Environmental Study*, vol. 60, pp. 263-275.
- Rai UK, Muthukrishnan M., Guha BK (2008). Tertiary treatment of distillery wastewater by nanofiltration. *Desalination* 230:70–78.
- Satyawali, Y., Balkrishnan. M., (2007). Removal of colour from biomethanated distillery spent wash by treatment with activated carbons. *Bioresource Technology*. 98, pp. 2629 2635.

- Sreethawong T, Chavadej S (2008). Color removal of distiller wastewater by ozonation in the absence and presence of immobilized iron oxidecatalyst. *J. Hazard Mater* 155:486–493.
- Sushil kumar Shukla (2014). Fungal decolourization of anaerobically biodigested distillery effluent (ABDE) following coagulant pretreatment. *International Journal of science, Environment and Technology*, Vol 3, N0 2, pp 723-734.
- Tezcan Un, U.; and Aytac, E. (2011). Treatment of Textile Wastewaters by Electrocoagulation Method. 2nd International Conference on Chemical Engineering and Applications, 138-140.
- Yadav S, (2012). Degradation and decolourization of post methanated distillery effluent in biphasic treatment system of bacteria and wetland plant for environmental safety PhD thesis. *School of life science, Pandit Ravi Shankar Shukla University*.
- Zhang W, Xiong R, Wei G (2009). Biological flocculation treatment on distillery wastewater and recirculation of wastewater. *J. Hazard Mater* 172:1252–1257.
- Zhao YG and LI XZ (1999). Advanced treatment of dyeing wastewater for reuse. *Water Sci. STechnol.* 39 (10-11): 249-255.