

Treatment of Distillery Spentwash by Electrocoagulation

V. Khandegar and Anil K. Saroh

Abstract—Effluent from distilleries, known as spent wash, leads to extensive soil and water pollution. Removal of pollutants and color from distillery effluent is becoming increasingly important from environmental and aesthetic point of view. Effluent from distilleries contains certain recalcitrant compounds. In the present work effort were made to reduce chemical oxygen demand (COD) from distillery effluent by electrocoagulation. The maximum COD removal efficiency of 98% was obtained at solution pH of 7.2 with a current density 17.9 mA/cm^2 for electrolysis duration of 3 h. Further experiments were performed using aluminum sulphate as chemical coagulant to compare the COD removal efficiencies obtained by electrocoagulation and chemical coagulation.

Index Terms—Spentwash, electrocoagulation, coagulation, aluminum.

I. INTRODUCTION

Distillery spentwash is the effluent basically generated by fermentation of sugar cane molasses to produce alcohol. For every litre of alcohol, maximum 8-15 litres of spentwash are generated. India is the fourth largest producer of ethanol in the world and the second largest in Asia [1]. Alcohol distilleries are rated as one of the 17 most polluting industries and generate large volumes of high strength wastewater that is of serious environmental concern. Spent wash is characterized by extremely high chemical oxygen demand (COD) (80,000-120,000 mg/L), biochemical oxygen demand (BOD) (40,000-50,000 mg/L), acidic pH, strong odor, nutrients in the form of nitrogen (1660-4200 mg/L), phosphorus (225-3038 mg/L), potassium (9600-17,475 mg/L) can lead to eutrophication of water bodies and dark brown color hinders photosynthesis by blocking sunlight and is therefore deleterious to aquatic life.

Various physical, chemical and biological techniques are used for the treatment of distillery spent wash before its discharge to the aqueous ecosystem [2], [3]. In biological treatment anaerobic treatment attractive in comparison to direct aerobic treatment due to high organic content of molasses present in spent wash [4].

Bio-methanation is employed as a primary treatment step in majority of the distillery units. In this treatment, effluent is usually subjected to anaerobic digestion for removing organic matter and producing biogas which is used as a fuel substitute to produce steam for the fermentation process [5], [6]. The effluent after bio-methanation still contains substantial amount of organic matter and does not remove the color. These difficulties are solved by application of

other treatment like reverse osmosis or ultrafiltration/nanofiltration technique. This technique provides colorless water from spentwash, which can be reused in molasses fermentation. The concentrated spentwash after reverse osmosis treatment has very high BOD and COD and it is difficult to compost or incinerate to achieve zero liquid discharge as desired by pollution control authorities. Hence, there is a need to find out a techno economically feasible treatment method [7]. Many researchers have used electrocoagulation method for the treatment of wastewater. The electrocoagulation treatment is an emerging technology used for the destruction of recalcitrant organics from different synthetic wastewaters [8]-[10] as well as industrial wastewaters [11], [12]. Electrocoagulation (EC) is a simple and efficient method and has been used for the treatment of many types of wastewaters [2], [5], [7], [13], [14]-[16]. Treatment of distillery spent wash has been reported by various authors and summarized in Table I.

II. MATERIALS AND METHODS

In the present study, reverse osmosis reject (ROR) is collected from a distillery was characterized for various parameters and the results are shown in Table II. Chemical oxygen demand (COD), a measure of organic strength of the spent wash, was determined by the dichromate method (open reflux, titrimetric method, APHA, 1998) [17]. It can be noticed that the reverse osmosis reject from distillery industry have very high COD content (52,000 mg/L).

The experiments were conducted in a 500 ml glass beaker in batch mode of operation. Aluminum and iron sheets with dimensions of $150 \text{ mm} \times 32 \text{ mm} \times 1.5 \text{ mm}$ (length \times width \times thickness) were used as electrodes. Experiments were conducted using Al-Al and Fe-Fe combination of electrodes.

The electrodes were connected in a monopolar connection mode. A direct current source (GWINSTEK, GPS 4303 India, 0-3A, 0-30 V) was used for current supply. The contents in the beaker were agitated by a magnetic stirrer (SPINOT 02, India) to avoid concentration gradients. Each experimental run was performed by charging 300 ml of the sample in the glass beaker. The results were evaluated in terms of COD removal efficiency. Repeated experiments were performed to check the reproducibility of the experimental results and the reproducibility was found to be $\pm 3 \%$.

III. RESULTS AND DISCUSSION

A. Effect of pH of the Solution

Initially experiments were conducted at original solution pH 7.2.

Manuscript received May 14, 2013; revised July 17, 2013.

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TABLE I: ELECTROCOAGULATION USED FOR TREATMENT OF DISTILLERY SPENTWASH

Reference	Current density	Time (min)	pH	Anode-Cathode	COD removal efficiency (%)
Khandegar and Saroha (2012)	0.817 A/cm ²	120	3	Al-Al, Al-Fe, Fe-Fe	81.3, 71.8, 52.4
Krishna et al. (2010)	0.03 A/cm ²	120	3	Al-Al	72.3
Prasad and Srivastava (2009)	14.285 mA/cm ²	180	5	(RuO ₂ -Ti)-SS	37
Thakur et al. (2009)	146.75 A/m ²	130	6.75	SS-SS	63.1
Manisankar et al. (2004)	6 A/dm ²	180	6.9-7.2	Graphite-Graphite	85.2

TABLE II: CHARACTERIZATIONS OF THE EFFLUENT

Parameter	Value
pH	7.2
Chemical oxygen demand (mg/L)	52000
Color	Dark brown
Total dissolved solids (mg/L)	82395
Conductivity (mS/cm)	29.6
Salinity (mg/L)	30500

The COD removal efficiency 84.6 % and 76.9 % was obtained at initial pH (7.2), for Al-Al and Fe-Fe electrodes respectively. Further experiments were conducted at different pH of the ROR (4, 5, 6) by aluminum and iron electrodes to study the effect of pH on the EC process and the results are shown in Fig. 1(a) and Fig. 1(b) respectively. The electrolysis was performed for 3 h with a constant current density of 14.7 mA/cm² (0.41 A), agitation speed was kept constant at 500 rpm and the spacing between the electrodes was 3 cm. It can be noticed from Fig. 1(a) and Fig. 1(b) that pH of the spent wash had a significant effect on the COD removal efficiency. For pH < 6, the protons in the solution get reduced to H₂ and thus, the proportion of hydroxide ion produced is less and as a result less COD removal efficiency obtained at low pH [13]. The COD removal efficiency of Al-Al electrodes is higher as compared to Fe-Fe electrodes because the Fe (II) ions generated during the EC process from iron electrodes has high solubility at acidic conditions and are easily oxidized into Fe (III) [5], [18]. Since Fe (III) is difficult to settle, it leads to the decrease in COD removal efficiency for iron electrodes. Further, Al-Al combination of electrodes was found to be most suitable for the treatment of reverse osmosis reject effluent.

B. Effect of Current Density

Experiments were performed at different current densities of 12.5, 14.7 and 17.9 mA/cm² to study the effect of current density on COD reduction. The experiments were conducted for 3 h keeping the electrode distance (3 cm), agitation speed (500 rpm) and the effluent pH (7.2) and the results are shown in Fig. 2(a) and Fig. 2(b). It can be noticed that the maximum COD removal efficiency (Al-Al 98 % and Fe-Fe 84.5 %) was obtained at an applied current density of 17.9 mA/cm² in 3 h electrolysis time.

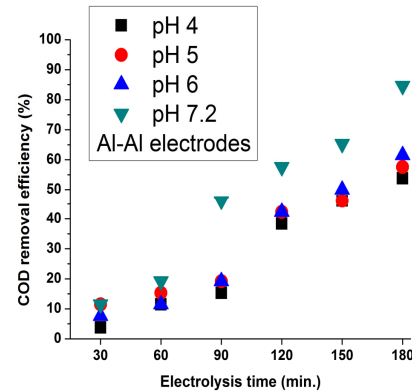


Fig. 1. (a) Effect of pH on the COD removal efficiency, electrodes Al-Al, current density 14.7 mA/cm² (10V), electrode spacing 3 cm, agitation speed 500 rpm, Initial COD 52000 mg/L.

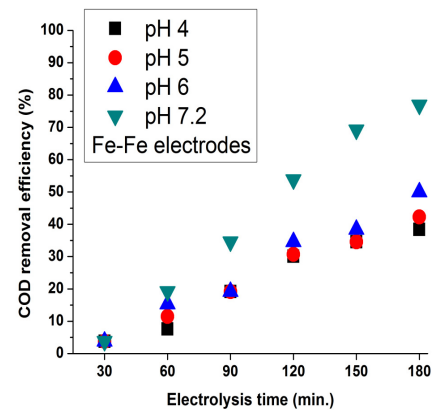


Fig. 1. (b) Effect of pH on the COD removal efficiency, electrodes Fe-Fe, current density 14.7 mA/cm² (10V), electrode spacing 3 cm, agitation speed 500 rpm, and Initial COD 52000 mg/L.

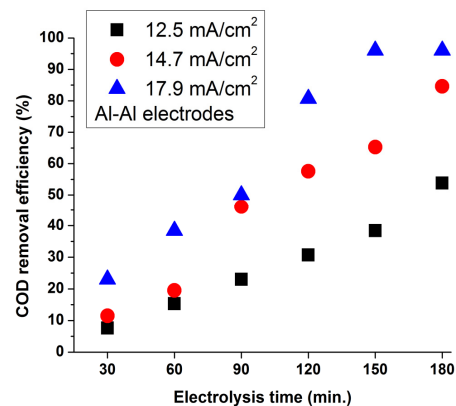


Fig. 2 (a). Effect of current density on the COD removal efficiency, electrodes Al-Al, pH 7.2, electrode spacing 3 cm, agitation speed 500 rpm, Initial COD 52000 mg/L

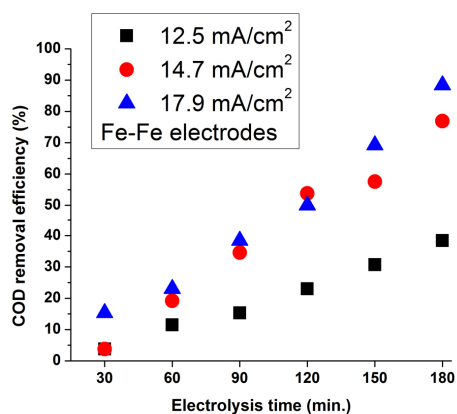


Fig. 2. (b) Effect of current density on the COD removal efficiency, electrodes Fe-Fe, pH 7.2, electrode spacing 3 cm, agitation speed 500 rpm, and Initial COD 52000 mg/L

The COD removal efficiency was found to increase with an increase in the current density. This is due to the fact that with an increase in the current density, the anode dissolution increases due to the Faradays law. Further, with an increase in the current density, there is an increase in the potential needed for the production of chlorine/hypochlorite leading to increased generation of chlorine/hypochlorite at higher current densities [2], [7].

C. Cost Estimation

The operational cost of treatment method is very important criterion for evaluation of the method applicability in industrial use. Electrocoagulation operating cost included mainly cost of energy consumption, cost of the electrode dissolved and the cost of addition of any external chemical (to enhance solution conductivity or varying the pH of the solution).

Calculation of operating cost for initial COD 52000 mg/L.

$$\text{Operating cost} = a \times C_{\text{energy}} + b \times C_{\text{electrode}} + c \times C_{\text{chemical}}$$

In the present study electrode and chemical consumption is very low, so the main operating cost related to only energy consumption.

It was observed that the operating cost increased with the initial COD concentration. It was found that about 375 Rs/m³ is required for the treatment of distillery spentwash containing initial COD concentration of 52000 mg/L.

D. Comparison with Chemical Coagulation

Experiments were conducted to compare the COD removal efficiency of reverse osmosis rejected effluent by electrocoagulation and chemical coagulation techniques. The limitations of coagulation are generation of large amount of sludge and the total dissolved solids are further increased. Aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) was used as the chemical coagulant. Different amounts of coagulant were added (1 to 5 g in 300 mL solution) to vary the coagulant dose. After coagulation the solution was kept for four hours for settling, after which the sediment was separated by filtration. The supernatant liquid was analyzed for COD and the results are shown in Fig. 3. It can be noticed that, the COD removal efficiency obtained by electrocoagulation is much higher as compared to chemical

coagulation technique. The maximum COD of 22 % was obtained at a pH of 7.2 with a coagulant dose of 5 g/300 mL of sample.

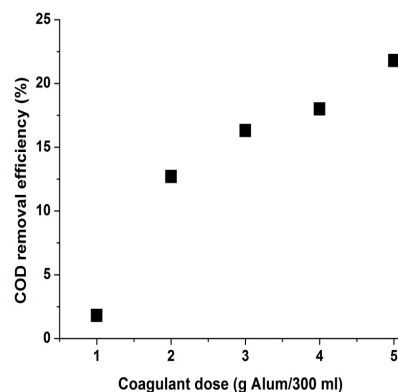


Fig. 3. Effect of coagulant dose on the COD removal efficiency, pH 7.2, Settling time 4 hr, Initial COD 52000 mg/L

IV. CONCLUSIONS

The electrocoagulation of reverse osmosis rejected effluent of distillery was carried out using Al-Al and Fe-Fe electrodes in batch mode of operation and the optimum values of various operating parameters were obtained. The optimum value of current density was found to be 17.9mA/cm² at initial pH of the solution 7.2. A 98 % COD removal efficiency was obtained at an electrolysis time of 3 h using Al-Al electrode. It can be concluded that the electrocoagulation technique can be successfully employed for the treatment of distillery effluent having high organic content.

REFERENCES

- [1] M. S. Chauhan and A. K. Dikshit, "Indian distillery industry: problems and prospects of decolourisation of spentwash," in *Proc. The International Conference on Future Environment and Energy (IPCBE)*, Singapore, 2012, pp. 119-123.
- [2] V. Khandegar and A. K. Saroha, "Electrochemical treatment of distillery spent wash using aluminum and iron electrodes," *Chinese Journal of Chemical Engineering*, vol. 20, no. 3, pp. 439-443, 2012.
- [3] Y. Satyawali and M. Balakrishnan, "Wastewater treatment in molasses-based alcohol distilleries for COD and color removal: A review," *Journal of Environmental Management*, vol. 86, no. 3, pp. 481-497, 2008.
- [4] R. A. Pandey, A. Malhotra, S. Tankhiwale, S. Pande, P. P. Pathe, and S. N. Kaul, "Treatment of biologically treated distillery effluent-a case study," *International Journal of Environmental Study*, vol. 60, pp. 263-275, 2003.
- [5] C. Thakur, V. C. Srivastava, and I. D. Mall, "Electrochemical treatment of a distillery wastewater: Parametric and residue disposal study," *Chemical Engineering Journal*, vol. 148, pp. 496-505, 2009.
- [6] T. Sreethawong and S. Chavadej, "Color removal of distillery wastewater by ozonation in the absence and presence of immobilized iron oxide catalyst," *Journal of Hazardous Material*, vol. 155, pp. 486-493, 2008.
- [7] B. M. Krishna, U. N. Murthy, B. M. Kumar, and K. S. Lokesh, "Electrochemical pretreatment of distillery wastewater using aluminum electrode," *Journal of Applied Electrochemistry*, vol. 40, pp. 663-667, 2010.
- [8] M. Panizza, P. A. Michaud, G. Cerisola, and C. Comninellis, "Anodic oxidation of 2-Naphthol at boron doped diamond electrodes," *Electroanal Chemistry*, vol. 507W, pp. 206-213, 2001.
- [9] N. N. Rao, K. M. Somasekhar, S. N. Kaul, and L. Szpyrkowicz, "Electrochemical oxidation of tannery," *Journal of Chemical Technology and Biotechnology*, vol. 76, pp. 1124-1131, 2001.

- [10] T. C. Wen, "Electro-deposited PbO₂ Anode for the decomposition of low concentration of Cyanide," *Plating and Surface Finishing*, vol. 77, pp. 54-57, 1990.
- [11] A. Akyol, "Treatment of paint manufacturing wastewater by electrocoagulation," *Desalination*, vol. 285, pp. 91-99, 2012.
- [12] B. K. Korbahti, K. Artut, C. Geçgel, and A. Ozer, "Electrochemical decolorization of textile dyes and removal of metal ions from textile dye and metal ion binary mixtures," *Chemical Engineering Journal*, vol. 173, no. 3, pp. 677-688, 2011.
- [13] P. Manisankar, C. Rani, and S. Viswanathan, "Effect of halides in the electrochemical treatment of distillery effluent," *Chemosphere*, vol. 57, pp. 961-966, 2004.
- [14] R. K. Prasad and S. N. Srivastava, "Electrochemical degradation of distillery spent wash using catalytic anode: factorial design of experiments," *Chemical Engineering Journal*, vol. 146, pp. 22-29, 2009.
- [15] S. K. Verma, V. Khandegar, and A. K. Saroha, "Removal of chromium from electroplating industry effluent using electrocoagulation," *Journal of Hazardous Toxic and Radioactive Waste*, vol. 17, no. 2, pp. 146-152, 2013.
- [16] V. Khandegar, A. K. Saroha, "Electrochemical treatment of textile effluent containing Acid Red 131 dye," *Journal of Hazardous Toxic and Radioactive Waste*, (in press).
- [17] APHA (American Public Health Association). (1998). *Standard Methods for the Examination of Water and Wastewater*. 20th Ed. Washington DC.
- [18] N. Modirshahla, M. A. Behnajady, and S. Kooshaiian, "Investigation of the effect of different electrode connections on the removal efficiency of tartrazine from aqueous solutions by electrocoagulation," *Dyes and Pigment*, vol. 74, no.2, pp. 249-257, 2007.



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