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## Electrocoagulation Of Distillery Spentwash For Complete Organic Reduction

V. Khandegar and Anil. K. Saroha\*

Department of Chemical Engineering, Indian Institute of Technology,  
Hauz Khas New Delhi-110016, India

\*Corres. author.: aksaroha@chemical.iitd.ac.in,  
khandegar11@gmail.com

**Abstract:** The aqueous distillery effluent stream known as spent wash is a dark brown highly organic effluent and is approximately 12-15 times by volume of the produced alcohol. It is one of the most complexes, troublesome and strongest organic industrial effluents, having extremely high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) values. Because of the high concentration of organic load, distillery spent wash is a potential source of renewable energy therefore bio-methanation is employed as a primary treatment step in majority of the distillery units. After biomethanation and tertiary treatment, the effluent still contains substantial amount of organic matter and requires further treatment before its discharge to the water body. In the present work effort were made to get completely COD removal from distillery effluent by electrocoagulation. The maximum COD removal efficiency of 100% was obtained at solution pH of 7.2 with a current density 71 mA/cm<sup>2</sup> for electrolysis duration of 1 h. Further experiments were performed using aluminum sulphate as chemical coagulant to compare the COD removal efficiencies obtained by electrocoagulation and chemical coagulation.

**Keywords:** Spentwash; Electrocoagulation; Coagulation; Aluminum; Iron.

### Introduction

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. The characteristics of the wastewater make it cause a few problems with its utilization<sup>1-3</sup>.

**Organic Content:** Wastewater from distilleries contains large amounts of organic and inorganic

content. This makes it have extremely high chemical oxygen demand (COD) and biochemical oxygen demand (BOD). This is in addition to having a strong odor and dark brown color. It contains nutrients such as nitrogen, phosphorus and potassium. These can cause eutrophication of water bodies. This is why water bodies polluted with wastewater from distilleries have little aquatic life<sup>4,5</sup>.

**Acidity:** Wastewater contains a high volume of highly acidic material that presents a lot of disposal and treatment problems. On average, it usually has a pH of 3.8 -- 4.4 and this is due to acidic contents

such as calcium carbonate. This makes the wastewater corrosive to tanks in which it is stored or pipes through which it flows. The acidic waste water causes soil leaching and also interferes with the pH of the soil it washes over. If released untreated into rivers and other water bodies, it can cause death or migration of some organisms. The acidity also makes the recycling process more expensive.

**Molasses Spent Wash (MSW):** Molasses-based distilleries release effluent that contains large amounts of dark brown colored molasses spent wash (MSW). This waste product pollutes the environment in two major ways. First, the dark colored nature of the molasses spent wash blocks out the sunlight on rivers and streams, interfering with normal processes of photosynthesis. This reduces the oxygenation of the water and leads to the death of aquatic life. The molasses spent wash also has a high pollution load which results in eutrophication of contaminated water sources. This waste product makes the rivers and canals produce an obnoxious smell since it contains putriciable organics such as skatole, indole and other sulfur compounds<sup>6-8</sup>.

## Materials and methods

In the present study, distillery spentwash collected from a distillery was characterized for various

parameters and the results are shown in Table 2. Chemical oxygen demand, a measure of organic strength of the spent wash, was determined by the dichromate method (Open reflux, titrimetric method) (APHA, 1998). It can be noticed that the distillery spent wash is acidic in nature with a COD content (3600 mg/L).

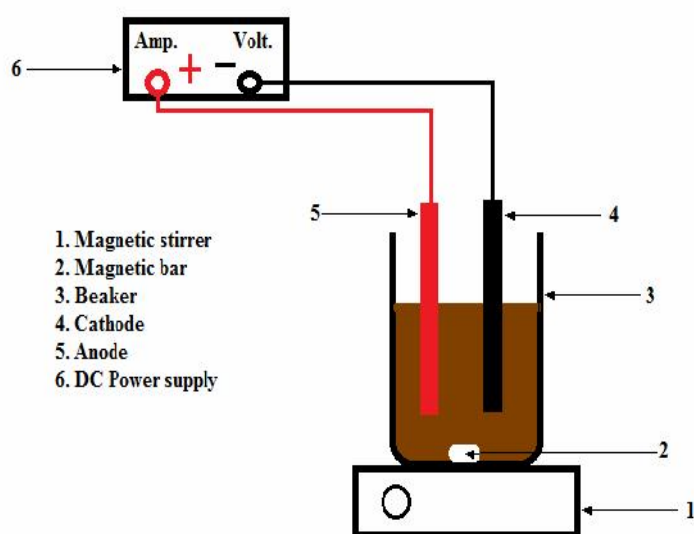
The schematic diagram of the experimental set up is shown in Fig. 1. The experiments were conducted in a 500 ml glass beaker in batch mode of operation. Aluminum and iron sheets with dimensions of 150 mm × 32 mm × 2 mm (length × width × thickness) were used as electrodes. The area of electrodes dipped into the solution was 40 mm × 32 mm. 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.

**Table 1 Distillery spentwash parameter ranges**

Parameters	Values of distillery effluent
pH	3.0–4.5
BOD <sub>5</sub> (mg/L)	50,000–60,000
COD (mg/L)	110,000–190,000
Total solid (TS) (mg/L)	110,000–190,000
Total volatile solid (TVS) (mg/L)	80,000–120,000
Total suspended solid (TSS) (mg/L)	13,000–15,000
Total dissolved solids (TDS) (mg/L)	90,000–150,000
Chlorides (mg/L)	8000–8500
Phenols (mg/L)	8000–10,000
Sulphate (mg/L)	7500–9000
Phosphate (mg/L)	2500–2700
Total nitrogen (mg/L)	5000–7000

**Table 2 Characterization of distillery spent wash**

Parameter	Value
pH	7.5
Chemical oxygen demand (mg/L)	3360
Color	Dark brown
Total dissolved solids (mg/L)	25450
Conductivity (mS/cm)	40
Salinity (mg/L)	23600

**Figure 1** Experimental setup

Each experimental run was performed by charging 300 ml of the distillery spent wash in the glass beaker. The efficiency of the EC process was determined in terms of the COD of the initial and treated sample. The COD removal efficiency was calculated using the following equation:

$$C_R(\%) = \frac{C_o - C_i}{C_o} \times 100 \quad (1)$$

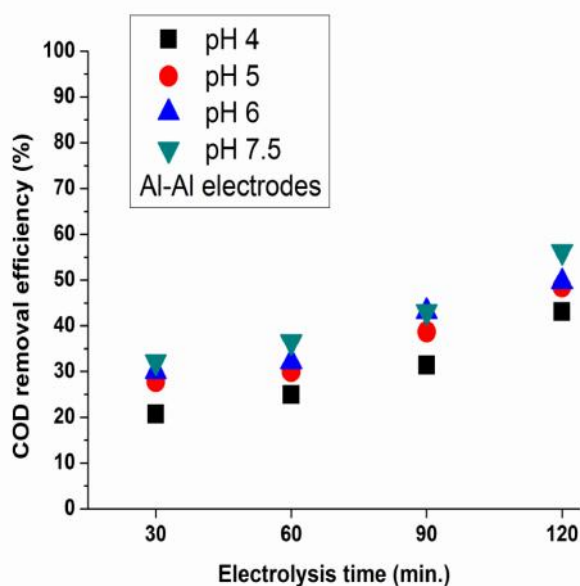
where  $C_R$  is the COD removal efficiency and  $C_o$  and  $C_i$  are initial and final COD of the sample in mg/L. Repeated experiments were performed to check the reproducibility of the experimental results and the reproducibility was found to be  $\pm 3\%$ .

## Results and discussion

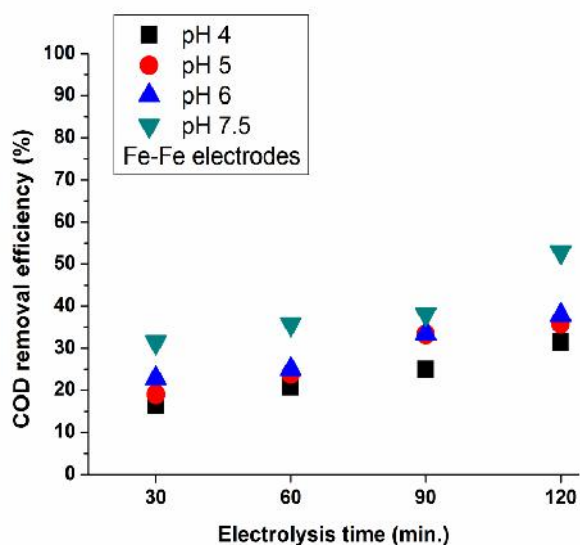
### Effect of pH of the solution

Initially experiments were conducted at original solution pH 7.5. The COD removal efficiency 60 % and 50 % was obtained at initial pH (7.5), for both

Al-Al and Fe-Fe electrodes respectively. Further experiments were conducted at different pH of the wastewater (4, 5, 6) to study the effect of pH on the EC process and the results are shown in Fig. 2(a) and Fig. 2(b) respectively. The electrolysis was performed for 2 h with a constant current density of  $35.9 \text{ mA/cm}^2$  (1 A), agitation speed was kept constant at 500 rpm and the spacing between the electrodes was 3 cm. It can be noticed from Fig. 2(a) and Fig. 2(b) that pH of the spent wash had a significant effect on the COD removal efficiency. The possible reason is that at pH less than 7.2, the protons in the solution get reduced to  $\text{H}_2$ , and thus, the proportion of hydroxide ion produced is less and consequently there is less COD removal efficiency obtained at lower pH values such as 4, 5 and 6.



**Figure 2 (a)** Effect of pH on the COD removal efficiency, current density  $35.9 \text{ mA/cm}^2$  (3 V), electrode spacing 3 cm, agitation speed 500 rpm, Initial COD 3360 mg/L.

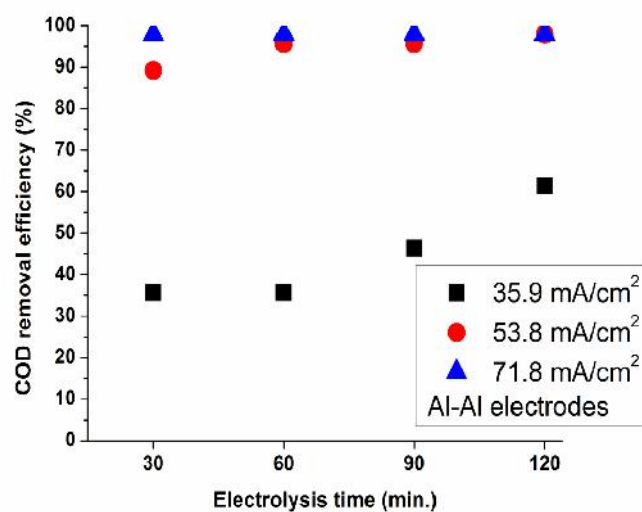


**Figure 2 (b)** Effect of pH on the COD removal efficiency, current density  $35.9 \text{ mA/cm}^2$  (3 V), electrode spacing 3 cm, agitation speed 500 rpm, Initial COD 3360 mg/L.

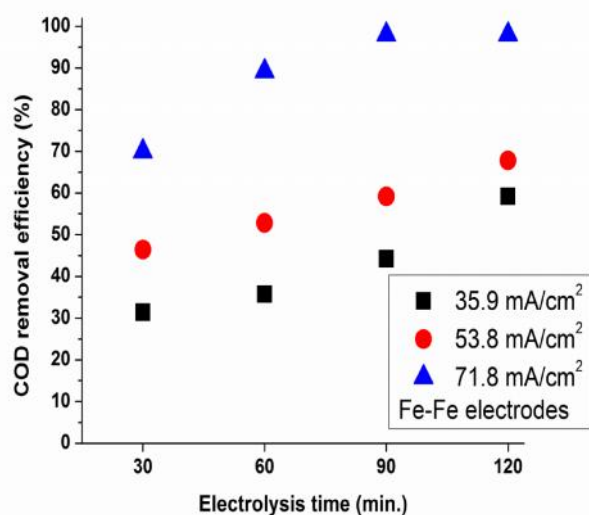
The COD removal efficiency of Al-Al electrodes is higher as compared to Fe-Fe electrodes. The Fe (II) ions generated during the EC process from iron electrodes has high solubility at acidic conditions and are easily oxidized into Fe (III) [9 -11]. Since Fe (III) is difficult to settle, it leads to the decrease in COD removal efficiency for iron electrodes. Further, Al-Al combination of electrodes was found to be most suitable for the treatment of distillery spent wash.

### Effect of current density

Experiments were performed at different current densities of  $35.9$ ,  $53.8$  and  $71.8 \text{ mA/cm}^2$  to study the effect of current density on COD reduction. The experiments were conducted for 2 h keeping constant the electrode distance (3 cm), agitation speed (500 rpm) and the effluent pH (7.2) and the results are shown in Fig. 3(a) and Fig. 3(b). It can be noticed that the maximum COD removal efficiency (Al-Al 99 % and Fe- Fe 88 %) was obtained at an applied current density of  $71.8 \text{ mA/cm}^2$  in 1 h electrolysis time.



**Figure 3(A)** Effect of current density on the COD removal efficiency, Voltage 3V, 5V, 7V, pH 7.5, electrode distance 3cm, agitation speed 500 rpm, Initial COD 3360 mg/L.



**Figure 3 (B)** Effect of current density on the COD removal efficiency, Voltage 3V, 5V, 7V, pH 7.5, electrode distance 3cm, agitation speed 500 rpm, Initial COD 3360 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<sup>8,12</sup>.

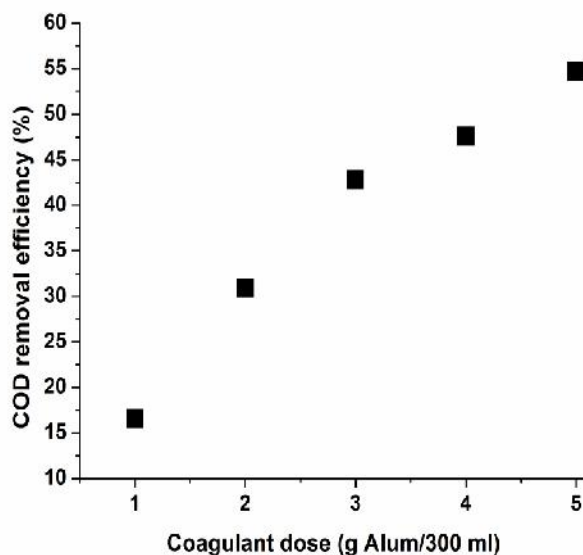
### Comparison with chemical coagulation

Experiments were conducted to compare the COD removal efficiency of distillery spentwash 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. The coagulation experiments were conducted by keeping the agitation speed at 200 rpm for the first hour and 100 rpm for the subsequent two hours. The solution was kept for four hours for settling, after which the sediment was separated

using filtration. The supernatant liquid was analyzed for COD and the results are shown in Fig. 4. 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 55 % was obtained at a pH of 7.2 with a coagulant dose of 5 g/ 300 mL of distillery spent wash.

### Conclusions

The electrocoagulation of distillery spentwash 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  $71.8 \text{ mA/cm}^2$  at initial pH of the solution 7.2. The maximum removal efficiency was obtained at an electrolysis time of 1 h. The maximum COD removal obtained using Al-Al electrodes at the optimized values of the operating parameters was 99 %. It can be concluded that the electrocoagulation technique can be successfully employed for the treatment of distillery effluent having high organic content.



**Figure 4** Effect of coagulant dose on the COD removal efficiency, high agitation speed 200 rpm (1h), slow agitation speed 100 rpm (2h), Settling time 4h.

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