"Degradation of Colour and COD from distillery spent wash by aluminium and zinc-titania composite electrodes"

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Abstract-*Distillery industries are considered as one of the most environmentally polluting and noxious industries with extremely high brown colour, total organic carbon, TDS, COD and low pH. The direct discharge of distillery effluent is not recommended into rivers or land without treatment. Electro coagulation technique is one of the most important and commonly used methods for the removal of colour and COD from distillery spent wash. The present study is mainly focused on the treatment of distillery spent wash by electro coagulation method using pure alluminium and zinc-titania composite electrodes for different pH, voltage and distance of the electrodes. Both were compared for the efficiency in removing colour and COD from distillery effluent. The colour removal is 99% from aluminium electrodes and 59% from zinc-titania composite electrodes were obtained. The 85% and 90% of COD removal was obtained with aluminium and zinc-titania composite electrodes respectively with optimum pH, voltage and distance of the electrodes and also high COD removal was observed for both aluminium and zinc-titania composite electrodes.*

Key words: *Distillery Spent Wash, Zinc-titania, COD, Aluminium, Colour, Composite*

1. Introduction

Distillery industries are profit gaining industries all over the country even though it is cost-effective. In alcohol industries molasses is used as raw material and it is byproduct of sugarcane industries (prakash *et al.* 2014). In India, there are 579 sugar mills producing 2.71 billion litres of alcohol and 295 distilleries generating 40 billion litres of spent wash in a year (mantha et al. 1987). Out of 295 distilleries in India, 129 have completed the construction of biomethanation digester for primary treatment of effluent (Roopa *et al.* 2013). Distillery spent wash refers to the effluent generated from alcohol distilleries. On an average of 8-15 L of effluent is generated for every liter of alcohol produced.

Nanotechnology is a promising technology with hygienic bright future and the use of nanoparticles in many applications such as textile production, medical devices, cosmetics and many other fields. Nowadays nanoparticles are using to treatment of industrial wastewater process (Kudakwashe *et al.* 2014). Use of several nanomaterials such as titanium dioxide, zinc oxide, ceramic membranes, polymer membranes, nanowire membranes, carbon nanotubes, submicron nanopowder and magnetic nanoparticles are also to determine the problems connected to quality of water in natural sources (Karishma *et al.* 2015).

There are various techniques such as electrochemical oxidation, photo catalytic, electro catalytic, adsorption and electro coagulation methods are resolve the problems connecting to water quality in natural atmosphere (Karishma *et al.* 2015). Among all these techniques, electro coagulation is one of the simpler techniques and it makes use of electrochemical cell where a direct current or voltage is applied to the electrodes. Also, the electrochemical co-deposition of zinc with nanoparticles composites (Chandrappa *et al*. 2012) and nickel with metal oxides composites (Chandrappa *et al*. 2012) are resolve the problems connected to quality of water.

1.1 Impact of Distillery Spent Wash on Environment

- Disposing of distillery effluent containing high total dissolved solids will produce adverse effect on aquatic life; make the water unsuitable for drinking purpose and corrosion of water system.
- Reduces photosynthetic activity since no sunlight penetrates in to the water body because of its high turbidity and suspended solids.
- High amount of biological oxygen demand contain in distillery spent wash when left to water without treatment reduce dissolved oxygen contain in water there by effecting the reproduction system of fishes and growth of aquatic plant.

- Presence of high sulphate compound pollutes the air by realising hydrogen sulphate gas to the atmosphere.
- Decreases soil fertility because of it's highly acidic in nature and make land unfit for agricultural purpose (Sohail *et al.* 2014).

1.2 Uses and effects of nanoparticles on Environment

- Environmental monitoring and protection: To check a nuclear seep out faster and more accurate at nuclear power plant by utilizing advanced nanotechnology.
- Biological application: nanoparticles develop small ultra probes on planetary surfaces and also control quality of soil, air, and water contamination.
- The amount of waste reduced by adopting high precision manufacturing method.
- The nanotechnology can be used to removal of gases from green house and other pollutants from atmosphere.
- Environmental damages can be reduced with the help of nanotechnology
- The major problem of nanoparticles is the analysis method
- It is very difficult to detect the nanoparticles in air use full for environmental protection.
- The demand of energy is high for synthesizing of nanoparticles.
- Recovery and recycling rates are not that good in the case of nanoparticles.

In the present study, we focus on the removal of colour and determination of COD in distillery spent wash by electro coagulation route. The removal of colour efficiency and estimation of COD percentage for both alluminium and zinc-titania composite electrodes were proposed. Also the effects of pH, voltage and distance between the electrodes are examined.

2. Materials and Methods

2.1 Materials

The distillery spent wash was collected from shamanur distilleries located in Duggavati, Davangere, Karnataka. Aluminium, Zinc and Mild Steel plates were purchased from Kavitha Chemicals Bangalore, Karnataka. Also, zinc sulphate ($ZnSO_4$), sodium sulphate ($Na_2(SO_4)_3$), sodium chloride (NaCl), sodium lauryl sulphate (SLS) and titanium dioxide (TiO_2) nanoparticles (30.09 nm) were brought from mahajan chemicals Bangalore, Karnataka, India.

2.2 Methods

2.2.1 Electro coagulation

In typical technique, the electrochemical cell consists of two bare aluminium electrodes (4 cm x 4 cm x 0.3 cm) are immersed in a distillery spent wash, which is taken in a 1 L volume of a beaker. The experiments were conducted in different distances of aluminium electrodes. The cleaned and dried electrodes are connected to positive and negative terminals of DC power supply. The electro coagulation was carried out for about 1 h under potentiostatic conditions where the constant voltage was drawn from a DC power supply (model LD 3202 potentiostat/galvanostat 32V/2A supplied by Aplab Regulated Dual DC Power Supply, India) with constant stirring. The pH of distillery spent wash was recorded before and after electro coagulation. The effect of pH, voltage and distance between the electrodes are studied. Each experiment is a batch operation, for every 1 hour the samples were drawn and COD is determined. At the end of each experiment, the sample was transferred into another beaker and kept undisturbed for 30 minutes in order to allow the flocs that formed during electro coagulation to settle down.

2.2.2 Fabrication of Zn–TiO_2 composite thin films on mild steel by electro deposition

The plating solution was prepared by dissolving 180 g/L zinc sulphate, 30 g/L sodium sulphate, 10 g/L sodium chloride, 0.0044 mM/L sodium lauryl sulphate (SLS) and 1 g/L titanium dioxide nanoparticles in 1000 mL of demineralised water and the pH of electrolyte bath was adjusted to 2.5. The bath solution containing 1g/L of titanium dioxide was stirred 1 hour for uniform concentration. The zinc and mild steel plates were dipped in 10% of sulphuric acid for few minutes and finally rinsed with water. The zinc plate (anode) and mild steel plates (cathode) were polished mechanically and degreased with sand paper and followed by water wash and after it is well dried immediately. The electro deposition was carried out at current density of 2A/dm² for 10 minute, 20 minute and 30 minutes under stirred condition with magnetic stirrer speed of 800 rpm. After electro deposition, the coated plates are removed from the solution and washed with water and dried. The titania nanoparticles were characterized by SEM and XRD measurements in Indian Institute of Science Bangalore.

2.2.3 Determination of Optimum parameters

To determine the optimum pH, the pH was adjusted by using 0.1N NaOH or 0.1N HCl. Also, to determine optimum voltage and distance between the electrodes in electro coagulation process were carried out, the voltage and electrode distance are fixed based on the previous experiments. After that the samples were analyzed for colour degradation and COD measurement.

3. RESULTS AND DISCUSSION

3.1 X-ray Diffraction Analysis

Figure 1 shows the XRD patterns of purchased TiO_2 nanoparticles. The peak position and intensities graph obtained from XRD analysis and the 2ɵ values ranging from 5.00 and 100. It can be seen from Figure. 1, the six main peaks appeared at 2ɵ of 25.5°, 38.2°, 48.1°, 54.2°, 55.4° and 62.9° values corresponds to characteristic peaks of titanium dioxide. The actual size of nanoparticles was found by taking the highest peak value of FWHM (full wavelength half maximum) using schrrer formula. In this figure each peak position was found to be shifted by a constant 2ɵ value of 5 degree which may be due to some instrumental zero error. The mean crystallite size was evaluated using Scherrer's formula and it was found to be around 30.2 nm.

$$D_P = \frac{0.9\lambda}{\beta Cos 2\theta}$$

Where, D_P =Average crystallite size, β =Line broadening in radians
θ =Bragg angle, λ = X-ray wavelength (1.54056)

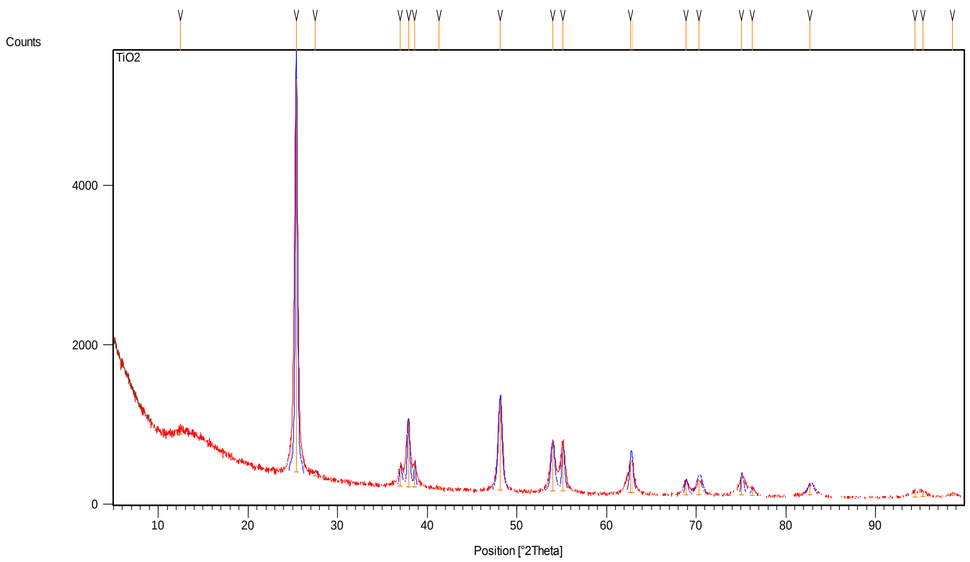

Fig – 1: XRD patterns of TiO_2 Nanoparticles

3.2 Scanning electron microscopic analysis

Figure 2. Shows the scanning electron micrographs of TiO_2 nanoparticles. As we observed that in figure 2(a), 2(b) the particles were well defined urchin-like TiO_2 nanoparticles. Figure 2(c) and 2(d), shows the well defined pebbles shape of nanoparticles with different diameters. All the micrographs are well defined structure with different sizes TiO_2 nanoparticles.

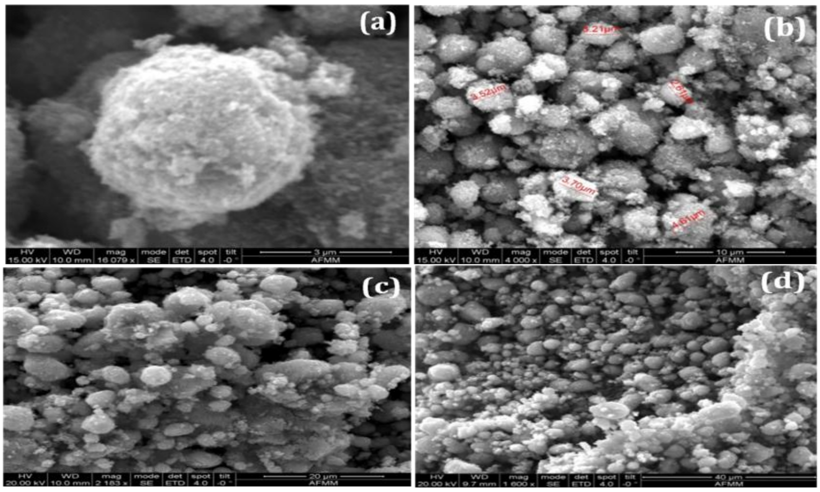

Fig -2: SEM images of TiO_2 nanoparticles (a) 3 µm (b) 10 µm (c) 20 µm and (d) 40 µm

3.3 Initial characteristics of distillery spent wash

The characteristics and experimental results on treatment of distillery spent wash using pure alluminium and zinc-titania composite electrodes by electro coagulation method. The initial characteristics such as pH, COD, Turbidity, Colour, BOD, TDS, TSS, EC, as shown in Table-1.

Sl no	Parameters	Unit	Values
1	pH	-	3.83
2	COD	g/L	186930
3	BOD	mg/L	60000
4	TDS	Ppm	14580
5	TSS	mg/L	14050
6	Turbidity	NTU	7860
7	EC	mS/cm	26.51
8	Colour	Pt.co	589000

Table-1: Initial Characteristics of Distillery Spent Wash

3.4 COD and colour reduction by electro coagulation using pure aluminum electrodes with Variation of H at constant distance and voltage.

Table 2 and Figure 3, shows the removal of COD and colour efficiency for optimum results obtained from the electro coagulation process using pure aluminum electrodes with pH variation at electrode distance and voltage.

Table-2: Reduction of COD and colour with electro coagulation using aluminum electrodes

pH	Distance (cm)	Voltage (volt)	COD (mg/L)	% removal efficiency of COD	Colour (Pt.Co)	% removal efficiency of colour
5	3	5	40000	78.60	27300	95.36
7	3	5	33333.3	82.17	4575	99.22
8	3	5	26666.67	85.73	1699	99.71

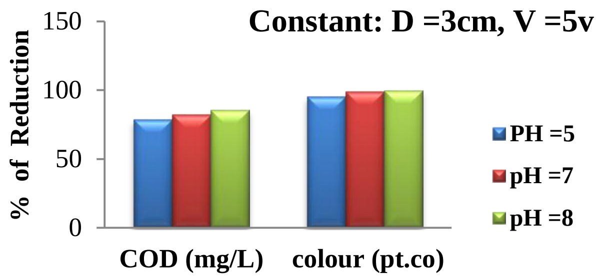

Fig -3: Reduction of COD and colour with electro coagulation using aluminum electrodes

3.5 COD and colour reduction by electro coagulation using zinc-titania composite electrodes at different electrolysis time

Table 3 and Figure 4, shows the removal of COD and colour efficiency for optimum results obtained from the electro coagulation process using zinc-titania composite electrodes with optimum pH of 8, electrode distance is 3cm and voltage of 5V with variation of time.

Electrolysis time in (min)	Distance (cm)	Voltage (volt)	pH	COD (mg/L)	% removal efficiency of COD	Colour (Pt.Co)	% removal efficiency of Colour
10	3	5	8	23456	87.45	268995	54.33
20	3	5	8	22123	88.16	257487	56.28
40	3	5	8	20689	88.93	241824	58.99
60	3	5	8	18476	90.11	239814	59.28

Table-3: Reduction of COD and colour with electro coagulation using zinc-titania composite electrodes

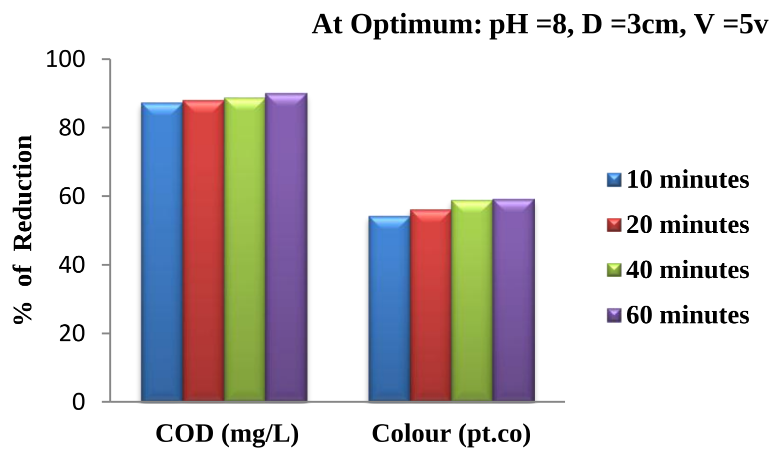

Fig-4 : Reduction of COD and colour with electro coagulation using zinc-titania composite electrodes

The obtained results shows that better COD removal efficiency was obtained when the distance between electrodes are less and the pH of spent wash was alkaline. The COD removal efficiency was found to increases with an increase in pH. Electro coagulation using aluminum electrode was carried out for three different pH values, constant distance and voltages. The maximum removal of COD and colour was found with pH =8, D =3cm and V =5v. It indicates that alkaline condition is more suitable for the treatment of distillery spent wash. In this condition chlorine is present in the form of hypochlorite ion and it is prevalent for alkaline condition.

The initial pH of the solution was set to 5, 7, and 8. The peak performance was achieved at pH value of 8, at which highest percentage removal of COD and Colour from the spent wash, 85.73%, and 99.71% respectively. Optimum pH is 8, distance of electrodes is 3cm and voltage of 5v, it is revealed that in acidic condition, the protons present in the solution gets reduced to H_2 gas and thus the proportion of hydroxide ion produced is less and consequently there is less removal efficiency. The optimum electrode distance is 3cm lowering the spacing of electrode distance results to higher % COD and colour reduction because of attraction between generated ions is stronger, there by resulting in the high movement of ions in sample (Dayaca R.A et al, 2015).

Distance between electrodes is low (3cm), attraction between generated ions is more, resulting in the high movement of the ions. The generated ions continuously keep on colliding due to availability of less space and preventing formation of flocs required to coagulate the organic content. On further increasing the distance between the electrodes (3cm to 5cm), the resistance between electrodes increases and generation of ions decreases for a constant current. The movement of ions becomes slower and ions get sufficient time and space to form flocs required for settling of the organic matter. The coagulation of organic matter will keep on increasing with an increase of electrode distance till an optimum distance between the electrodes is reached. On further increasing distance between electrodes beyond the optimum value, the amount of anode dissolution decreases and ions have to travel a longer distance for interaction between the electrodes to form flocs. This will reduce the formation of flocs leading to a reduction in the COD removal efficiency of the spent wash (Khandegar V et al, 2012).

4. CONCLUSION

- Distillery spent wash, molasses and wastewaters are more potential for environmental pollution. Electro coagulation is the efficient method used in the treatment of distillery spent wash.
- Using of aluminium electrodes in electro coagulation method resulting in high efficiency colour and COD removal of 99.71% and 85.73% was observed.
- Zinc-titania composite electrodes are subjected to electro coagulation of distillery spent wash found to remove the COD with efficiency of 90.11% but lesser colour removal was observed.

- Colour removal was high with aluminum electrodes and higher COD removal by zinc-titania composite electrodes.
- It has been found that, an increase in COD and colour reduction efficiency was obtained by decrease in pH, voltage and electrode distance.
- It has been concluded that, the electro coagulation technique can be successfully employed for the treatment of distillery spent wash (effluent) having high COD and colour content.

BIOGRAPHIES

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