



Removal of organics from bilge water by batch electrocoagulation process



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ABSTRACT

A batch electrocoagulation study was conducted using aluminium electrodes to check the treatability of synthetic bilge water. The studies were conducted to investigate the effect of various operational parameters on the treatment efficiency. At a pH of 7, applied voltage of 10 V, spacing of 1 cm and effective electrode area of 45 cm², a maximum soluble COD (COD_s) removal efficiency of 85% was obtained after an electrolysis time of 120 min. The second order rate constant was derived and a maximum rate constant of 3×10^{-6} L/mg-min was observed at optimum experimental conditions. COD_s experimental measurements give an acceptable fit for both Langmuir model and Freundlich isotherm models. A comparative study between electrocoagulation and chemical coagulation was performed and chemical coagulation showed only 59.3% removal efficiency. The sludge formed after the electrocoagulation process was characterized for mineral composition and functional groups. XRD and FTIR results represent the formation of aluminium hydroxide during electrocoagulation process and the presence of hydrocarbons and heavy metals in the sludge indicates the removal of these pollutants from bilge water by electrocoagulation process. Among different electrode combinations of aluminium and iron, Al–Al combination showed maximum removal efficiency. A case study on real bilge water was conducted and a maximum removal of 89.84% was obtained at optimum conditions using aluminium electrodes.

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1. Introduction

In recent years the increase in sea transportation has brought along marine problems. The major pollutants in the aquatic environment are oily wastes. According to the report prepared by EPA on cruise ship discharge assessment [1], bilge water is the mixture of seawater, oily fluids, lubricants, cleaning fluids, and other similar wastes. These get accumulated in the lowest part of the vessel from a variety of different sources. The sources of bilge water throughout the spaces of a vessel are the main and auxiliary engines, boilers, evaporators and related auxiliary systems, equipment and related components, machines and other operations. Metals present in bilge and ballast water cannot be removed through treatment or environmental degradation. If these metals are ingested, they can cause various human health problems such as lead poisoning and cancer [2]. The structure and functions of marine communities and ecosystems can be disrupted by the oil present in bilge water. The chemical contaminants in oil ultimately

impacts the survival rates of the affected species by poisoning marine life, disrupting feeding, causing chronic diseases, reproductive failures and deformities [1].

The electrocoagulation (EC) technology being more flexible, compact and fairly less expensive, promises better treatment of bilge water. EC is an economical and robust technology, a technical solution to numerous environmental pollution problems and has widely grown over the last few decades. The conductivity of bilge water is high due to the high chloride concentration and this makes it appropriate to treat by EC and it demands only low energy consumption and less chemical usage. An increased current intensity combined with decreased voltage and energy costs is obtained due to high conductivity [3].

This study investigates the applicability of electrocoagulation process to remove the organics from bilge water and the efficiency was calculated in terms of organics removal. The effect of different operational parameters was studied. The sludge generated after electrocoagulation process was characterized. The kinetic study, adsorption isotherm study and mass transfer study were carried out. A comparison between electrocoagulation and chemical coagulation was done and also the performance of different electrode

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combinations of iron and aluminium on electrocoagulation was checked. The applicability of electrocoagulation process on real bilge water was tested.

2. Materials and methods

2.1. Synthetic bilge water preparation

A synthetic bilge water (SBW), a highly stable and homogeneous oil-in-water emulsion was prepared by mixing deionized water, polysorbate (Tween 40[®]) as emulsifying agent, motor oil SAE 30, acrylic paint, sodium chloride, and metallic salts (Zn²⁺, Cu²⁺ and Ni²⁺). A Flash mixer (Remi motor, Rjendra Elec. Ind. Ltd) was used for the homogeneous mixing of all components. Andrade [4] reported that the Tween 40[®] dose for the highest possible emulsified oil concentration is 5000 mg/L and the same concentration was considered for the present study. After 24 h of preparation, the free oil fraction was separated from the prepared synthetic wastewater, which kept under quiescent conditions in the lab. Then, the resulting stable oil-in-water emulsion extracted from the bottom of the sample container and analyzed to determine the emulsified-oil fraction. A maximum of 1280 mg/L out of 5000 mg/L of oil was remained emulsified in the SBW after adding 2500 mg/L of Tween 40 to this mixture, representing an emulsified-oil fraction equal to 0.26. The SBW composition included this amount of motor and emulsifying agent, plus acrylic paint to add coloured colloidal particles, and metallic salts for conductivity, thus simulating actual bilge water. The resulting SBW composition and its initial characteristics are given in Tables 1 and 2, respectively. The pH of the synthetic bilge water was measured using Ion Analyzer (Thermo) and electrical conductivity of the synthetic bilge water by conductivity metre (Eutech). Turbidity was measured using turbidity metre. Total solids, total suspended solids and total dissolved solids are analyzed based on gravimetric method as per standard methods [5]. The sludge content was measured using the imhoff cone and quantified. Soluble COD (COD_S) was chosen as the principal parameter to define effluent treatment as analysis of other components, namely, O&G, and C10–C50 hydrocarbons was laborious. In order to get the soluble fraction, the sample was filtered through 0.45 μm glass filter paper using Vacuum pump. Hach 200 was used as the digester for the measurement of COD by closed reflux method.

2.2. Experimental

An acrylic reactor of size 10 cm × 10 cm × 15 cm and was used for the entire batch electrocoagulation of SBW. A working volume of 1.0 L was considered for the entire experiments. The required initial pH of the working solution was adjusted by 1 N HCl and 1 N NaOH. Aluminium plates of thickness 0.4 cm were used as electrodes (both anode and cathode) and were placed vertical and parallel to each other. The total effective electrode area and the spacing between electrodes were fixed as 30 cm² and 3 cm, respectively. The anode and cathode were connected to a DC sup-

Table 1
Synthetic bilge water composition [4].

Constituent	Concentration (mg/L)
Total oil (SAE 30)	5000
Tween 40	2500
Sodium chloride	600
Acrylic paint	200
Copper chloride dehydrate	5
Zinc chloride	2.5
Nickel chloride hexahydrate	1.5

Table 2
Characteristics of synthetic bilge water.

Parameter	Values
pH	7
Conductivity	1026 μS/cm
Turbidity	2870 NTU
Total COD	21,120 mg/L
Soluble COD	17,600 mg/L
Total solids	7260 mg/L
Total dissolved solids	2670 mg/L
Total suspended solids	4590 mg/L
Total fixed solids	580 mg/L
Total volatile solids	6680 mg/L

ply unit (30 V/5 A), in which required voltage was fixed. All the reactor setup was kept above a magnetic stirrer for giving proper agitation and a constant speed of 300 rpm was kept during the electrocoagulation process. To remove the oxide and/or passivation layer from the electrodes, the electrode surfaces were grinded with sandpaper and rinsed with 1 N HCl before each experiment. An aliquot of 5 ml from the middle of the EC cell was collected using pipette for every 15 min up to 120 min and filtered (2.5 μm) to remove flocs. Then the sample was allowed to settle for 30 min. After settling the sample was analyzed for soluble COD removal.

The soluble COD removal efficiency (Y_t , %) was calculated from equation,

$$Y_t = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

where C_0 is the initial soluble COD of synthetic bilge water before electrocoagulation (mg/L), and C_t is the soluble COD of synthetic bilge water after 't' min of electrocoagulation (mg/L).

The amount of the sludge produced was calculated after drying and ignited at 105 °C for 24 h and 550 °C for 15 min, respectively. Obtained sludge was also characterized using FT-IR and X-ray diffraction techniques.

3. Results and discussions

3.1. Effect of solution pH

The effect of solution pH on COD removal efficiency of electrocoagulation process was investigated in the initial pH range from 3 to 10 and the results are depicted in Fig. 1. It was found that the aluminium electrodes have higher efficiency near to neutral pH. At a pH of 7, the removal efficiency of electrocoagulation process was optimum with a removal efficiency of 77.6%, after 120 min of electrolysis. The low efficiency at lower pH values is mainly due to the lesser amount of aluminium insoluble precipitates generation in the electrolytic system. At lower pH values, aluminium species will be predominated in the form of Al³⁺ and Al(OH)₂⁺. Also, the hydroxide ions formed at the cathode were neutralized by the protons, results in lesser amount of aluminium hydroxide formation [6]. Therefore, the effective coagulation of pollutant not occurred at highly acidic ranges. When pH is between 4 and 9, the Al³⁺ and OH⁻ ions generated by the electrodes react to form various monomeric species such as Al(OH)₂⁺, Al(OH)₂⁺, and polymeric species such as Al₆(OH)₁₅³⁺, Al₇(OH)₁₇⁴⁺, Al₁₃(OH)₃₄⁵⁺ that finally transform into insoluble amorphous Al(OH)₃(s) through complex polymerization/precipitation kinetics [7]. These insoluble precipitates are responsible for the effective coagulation at these pH values. When pH is higher than 10, the monomeric Al(OH)₄⁻ anion concentration increases at the expense of Al(OH)₃(s). In addition, the cathode may be chemically attacked by OH⁻ ions generated together with H₂ at high pH values [8]. So, for acidic pH different aluminium monomeric species or protons will be adsorbed [9], whereas for aluminium at alkaline pHs both monomeric

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