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Simultaneous removal of oil and grease, and heavy metals from artificial bilge water using electro-coagulation/flotation

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ABSTRACT

US and international regulations pertaining to the control of bilge water discharges from ships have concentrated their attention to the levels of oil and grease rather than to the heavy metal concentrations. The consensus is that any discharge of bilge water (and oily water emulsion within 12 nautical miles from the nearest land cannot exceed 15 parts per million (ppm). Since there is no specific regulation for metal pollutants under the bilge water section, reference standards regulating heavy metal concentrations are taken from the ambient water quality criteria to protect aquatic life.

The research herein presented discusses electro-coagulation (EC) as a method to treat bilge water, with a focus on oily emulsions and heavy metals (copper, nickel and zinc) removal efficiency. Experiments were run using a continuous flow reactor, manufactured by Ecolotron, Inc., and a synthetic emulsion as artificial bilge water. The synthetic emulsion contained 5000 mg/L of oil and grease, 5 mg/L of copper, 1.5 mg/L of nickel, and 2.5 mg/l of zinc. The experimental results demonstrate that EC is very efficient in removing oil and grease. For oil and grease removal, the best treatment and cost efficiency was obtained when using a combination of carbon steel and aluminum electrodes, at a detention time less than one minute, a flow rate of 1 L/min and 0.6 A/cm^2 of current density. The final effluent oil and grease concentration, before filtration, was always less than 10 mg/L.

For heavy metal removal, the combination of aluminum and carbon steel electrodes, flow rate of 1 L/min, effluent recycling, and 7.5 amps produced 99% zinc removal efficiency. Copper and nickel are harder to remove, and a removal efficiency of 70% was achieved.

1. Introduction

In the United States, bilge water production is estimated in the millions of cubic meters per year (there is not a national report on the actual amounts of bilge water produced in the US). As a reference, cruise ships operating in Southeast Alaska produce around 5–20 m^3 of bilge water every 24 h, that is 1800 to 7200 m^3 per year (Alaska Department of Environmental Conservation, 2000).

The Environmental Protection Agency, (EPA) in conjunction with the Department of Defense (DoD), the Secretary of State, the Secretary of Commerce and several Federal Agencies, is developing the Uniform National Discharge Standards (UNDS), organized in three phases, for incidental liquid discharges from vessels of the US Armed Forces. From the Nature of Discharge Report for Surface Vessels Bilge Water, the annual mass loading of heavy metals in bilge water produced by US aircraft carriers is about 116 kg of copper, 57 kg of nickel, 299 kg of zinc, and 160 kg of iron (EPA, 1999).

Even though the discharge of bilge water is strongly regulated, both inside and outside the country, the regulations have been focused more on controlling the discharge of oil and oily mixture than on the discharge of heavy metals. All vessels generate bilge water and most commissioned Armed Forces vessels are fitted with oil water separator (OWS) systems designed to prevent the discharge of oil in excess of 15 mg/L within 22.2 km (12 nautical miles), in accordance with OPNAVINST 5090.1B.

In London, in 1973, the International Convention for the Prevention of Pollution from Ships (MARPOL, 1973) met and enforced, in 1978, the Regulation 16th, which states that any discharge of bilge water (and oily water emulsion) cannot exceed 15 parts per million (ppm) of oil content if the discharge is at 22.2 km (12 nautical miles) from the nearest land.

The Unites States accepted the MARPOL Protocol and passed laws to enforce it, such as: the Clear Water Act (CWA, 1972; 33 U.S.C.

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Symbols and abbreviations

APPS	Act to Prevent Pollution from Ships
ASTM	American Standard Test Method
Co	initial concentration
DC	direct current
DMC	dissolved metal concentration
DO	dissolved oxygen
DoD	Department of Defense
E	energy consumption (kWh)
EC	electrocoagulation
EPA	Environmental Protection Agency
HEM	hexane extractable materials
I	current intensity (Amps)
IR	infrared
ISE	ion selective electrode
m	mass of contaminant (g)
MARPOL	International Convention for the Prevention of Pollution from Ship
NMSA	National Marine Sanctuaries
NTU	Nephelometric Turbidity Unit
OPA	Oil Pollution Act
OPNAVINST	Office of the Chief of Naval Operations Instruction
ORP	Oxidation–Reduction Potential
PFR	plug-flow reactor
RPM	revolutions per minute
SAE	Society of Automotive Engineers
SBW	Synthetic Bilge Water
SEC	Specific Energy Consumption
TDS	total dissolved solids
TOC	total organic carbon
TPH	total petroleum hydrocarbons
TSS	total suspended solids
U	Voltage (V)
UNDS	Uniform National Discharge Standards
W	power (kW)

§ 1301), which establishes the basic structure for regulating discharges of pollutants into the waters of the United States and regulating quality standards for surface waters; the National Marine Sanctuaries Act (NMSA, 1988; 16 U.S.C. § 1431 et seq.), a law that protects marine resources and ecosystems, such as coral reefs, sunken historical vessels, or unique habitats, from degradation while facilitating public or private uses compatible with resource protection; the Oil Pollution Act (OPA, 1990; 33 U.S.C. § 2702 et seq.), that streamlined and strengthened EPA's ability to prevent and respond to catastrophic oil spills; and the Act to Prevent Pollution from Ships (APPS, 2000; 33 U.S.C. § 1901 et seq.), federal law that implements those provisions of MARPOL in United States. In addition, the Coast Guard has the primary responsibility to prescribe and enforce the regulation necessary to implement APPS 2000 in the United States and has regulations pertain to management of the discharge of oil or oily mixtures into the sea from ships.

In summary, bilge water discharges are well controlled with regard to oil concentrations but are lacking in specific heavy metal concentration limits. Since there is no specific regulation for metal pollutants under the bilge water section, reference standards regulating heavy metal concentrations are taken from the ambient water quality criteria to protect aquatic life (65 FR 31682 (EPA, 2009)).

With impending future stringent regulations concerning the levels of heavy metal and oil and grease that can be discharged in continental waters, enhanced treatment methods with high removal efficiency, low operation costs, short operation times and reduced use of additional chemical products are required. In the present article, electro-coagulation (EC) is discussed as a method to treat bilge water, with a focus on oily emulsions and heavy metals (copper, nickel and zinc) removal efficiency.

The objectives of this research include conducting experiments with a continuous flow EC reactor to determine the factors affecting the oil and metals (copper, nickel and zinc) removal efficiency using a synthetic bilge water. These factors included flow rate, electrode material, flotation unit configuration and current intensity. Operational costs of this type of treatment are also discussed.

2. The electro-coagulation (EC) process

The EC process involves many chemicals and physical factors, where electrical current is applied to consumable electrodes that generate, in the primary stage, coagulants due to electrolytic oxidation of the electrode. Immediately, in the secondary stage, contaminant destabilization, particulate suspension, and breaking of emulsions occur; after that, the ultimate stage, the formation of flocs, takes place due to the aggregation of destabilized particles (Mollah et al., 2004a,b). EC stages are detailed as follows (Chen et al., 2000a,b; Kobya et al., 2003; Chen, 2004; Mollah et al., 2004a,b; Heidmann and Camano, 2008; Merzouk et al., 2009; Thella et al., 2008):

The generation of metal ions in the EC process takes place as follows:

At the carbon steel anode:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad (1)$$

$$Fe_{(s)} \rightarrow Fe^{3+}_{(aq)} + 3e^- \quad (2)$$

At the aluminum anode:

$$Al_{(s)} \rightarrow Al^{2+}_{(aq)} + 2e^- \quad (3)$$

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (4)$$

Metal ions are hydrolyzed forming hydroxides like $Al(H_2O)_6^{3+}$, $Al(H_2O)_5OH^{2+}$, $Al(H_2O)_4OH^{2+}$, $Fe(OH)_3$ and these hydrolysis products can produce $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$ $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, $Al_{13}(OH)_{34}^{5+}$, $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2^+$, $Fe_2(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{4+}$.

Due to salinity in the water stream, chlorine is released according to Eq. (6):

At the anode:

$$2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^- \quad (5)$$

$$2Cl^- \rightarrow Cl_2 + 2e \quad (6)$$

At the cathode: