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HYDROCARBONS REMOVAL FROM BILGE WATER BY ADSORPTION ONTO ACTIVATED BIOCHAR FROM POSIDONIA OCEANICA

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The normal operations carried out on the boats during navigation generate waste waters such as oily bilge water. The latter is the aqueous mixture of potential pollutants of different origins and types: oily fluids, lubricants and greases, cleaning fluids and other wastes that accumulate in the lower part of the vessel [1,2]. The current legislation provides that they can be discharge directly into the sea if the concentrations of some components are below the expected limits. In particular, with regard to oil / hydrocarbons contamination, the current regulatory limit is 15 mg L⁻¹ of total hydrocarbons. The present work starts from a public/private partnership funded by a grant of the Ministry of Economic Development (MiSE). Among the aims of the project, novel methods shall be tested for the reduction of hydrocarbons concentration at values below 5 mg L⁻¹. Moreover, instrumental techniques able to quickly measure the required low hydrocarbons concentration were tested. Among the different steps of bilge water treatment in pilot plant (coagulation, flotation, centrifugation, adsorption etc.), the latter requires the use of adsorbent materials able to reduce the oily concentration below the legal limits. Here we have chosen, optimized and tested materials obtained from bio-oil production waste, a biochar obtained by pyrolysis of Posidonia oceanica, a marine plant widespread in the Mediterranean sea.



Figure 1. Benchtop pilot system for hydrocarbon/oil fraction removal from bilge water type dispersion.

The biochar has been characterized and adsorption experiments were carried out with the pristine biochar (not activated) and with two chemically activated biochars (BCB and BCA) by

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means of acid or alkali treatments. Moreover, a commercial activated carbon (Filtrasorb 400) has been used for comparison purpose. Synthetic bilge waters were prepared following the reference standards [3] for the preparation of test fluids (used to test the bilge separator plant), containing DMA (distillate marine fuel) and SLS (sodium lauryl sulfate).

Batch adsorption isotherms were carried out without ionic medium and at different ionic strengths in NaCl in order to evaluate the effect of salinity on the adsorption ability of adsorbent materials. The same adsorbents were tested by column experiments. In particular, a bench pilot system was built (Figure 1.) and breakthrough curves were obtained changing amount of adsorbent material in column, flow rate, initial DMA and surfactant concentrations.

Several instrumental techniques (turbidimetry, TOC, HPLC-QQQ and HPLC-FLD) have been used to measure surfactant and hydrocarbon concentrations in experimental samples.

The batch experimental data were fitted with the most used isotherm models (Langmuir, Freundlich, Sips) and important considerations were made on the breakthrough curves of column experiments.

References

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THERMODYNAMICS OF INTERACTION BETWEEN RISEDRONIC ACID AND METAL CATIONS: INVESTIGATIONS IN SOLUTION AND IN THE SOLID STATE

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Risedronic acid (see Figure 1) belongs to the class of biphosphonates (BP), widely used in the medical field to treat bone disorders. Bisphosphonates (BPs, e.g., alendronate, risedronate, and ibandronate) help to maintain bone mass, to inhibit osteoclast-mediated bone resorption, and to reduce the risk of both vertebral and non-vertebral fractures. The clinical efficacy of BPs is mainly based on two key properties: their capacity to strongly bind hydroxyapatite crystals of bone, and their inhibitory effects on osteoclast precursors and mature osteoclasts. Interaction of risedronate with metal cations is poorly investigated. Qualitatively, it is indicated that adsorption of risedronate is inhibited when the drug is taken with mineral water containing high levels of calcium or magnesium, but chemico-physical results are missing.

In this work, the interaction of risedronate with Ca²⁺, Cu²⁺, Pb²⁺ and Zn²⁺ is investigated by means of potentiometric and calorimetric measurements to determine thermodynamic parameters (Δ G, Δ H and T Δ S). The most important species resulted to be the M₂L and variously protonated MH_iL (with i from 0 to 2) depending on the specific metal cation considered. During all the measurements, the formation of a sparingly soluble species has been noted starting from very acidic pH values (~ 3.5). Thus, four solid samples have been properly prepared and characterized by means of surface spectroscopic techniques (μ XRF, XRD, Raman and ATR-IR) and thermal analysis (TG-DTA). In addition, the solubility of these compounds has also been determined by the shake-flask method followed by differential pulse-anodic stripping voltammetry at different NaCl concentrations, to determine Setschenow and activity coefficients. Preliminary results show that the solubility of lead and copper risedronate increases with chloride concentration, probably due to the formation of chloro complexes with Pb²⁺ and Cu²⁺.



Figure 1. Chemical structure of Risedronic acid