

REMOVAL OF OILY XENOBIOTIC COMPOUNDS FROM SLOPS ORIGINATED FROM OIL TRANSPORTATION BY TANKERS

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ABSTRACT

Petroleum products such as diesel fuels may be released into the marine or coastal environment by discharges of slops, ballast and bilge waters, dry dock activities, and tanker and non-tanker accidents. Many of these fluids are very stable emulsion, which make chemical treatment difficult and normal separation processes alone (gravity, flocculation, skimming) are rarely effective. The conventional methods for treatment of emulsified oily wastewater is chemical de-emulsification followed by secondary clarifications, which requires the use of a variety of chemicals such as sulphuric acid, iron and alumina sulphates, ect.. Coagulation is widely used in water and wastewater treatment. The water phase from chemical treatment has usually to be further treated to meet today's effluent standard for discharge into the environment. This can be achieved by granular activated carbon (GAC) filtration. When GAC become saturated in pollutant it needs to be regenerated with costly thermal or chemical treatment. Very little work has been done on the potential bioregeneration of GAC saturated by salty mixtures of biodegradable and non-biodegradable compounds. Basing on these issues this research work investigated the feasibility of coupling physical, chemical and biological processes to optimize the treatment while reducing the costs. Specifically this study focus on the role of a mixed culture of microorganisms on bioregeneration of GAC loaded with a mixture of compounds occurring in slops.

1 INTRODUCTION

Many industrial sectors are likely to generate highly saline wastewater. These include the agro-food, petroleum and leather industries. The discharge of such wastewater containing at the same time high salinity and high organic content without prior treatment is known to adversely affect the aquatic life (*Atlas, 1995*). These issues are particularly critical in Mediterranean Sea that has been defined as a "Special Area" by the international Law MARPOL 73/78 (IMO, 1973/1978) that strictly forbids any mineral oil or oily mixtures

to be directly discharged to the sea by oil tankers. Saline effluents are conventionally treated through physico-chemical means, as biological treatment is strongly inhibited by salts (mainly NaCl). However, the costs of physico-chemical treatments being particularly high, alternative systems for the treatment of organic matter are nowadays increasingly the focus of research. Even though biological treatment of carbonaceous, nitrogenous and phosphorous pollution has proved to be feasible at rather high salt concentrations, the performance obtained depends on a proper adaptation of the biomass or the use of halophilic organisms. Oily wastewater and oil-water emulsion are two of the main pollutants discharged to water environment, often with high level of salinity. Oily wastewater are generated by ships mainly in engine-rooms (bilge waters) and by washing oil tanks (slops) in amounts of millions of tons annually. Many of these fluids are very stable emulsion, which make chemical treatment difficult and normal separation processes alone (gravity, flocculation, skimming) rarely effective. The conventional methods for treatment of emulsified oily wastewater is chemical de-emulsification followed by secondary clarifications, which requires the use of a variety of chemicals such as sulphuric acid, iron and alumina sulphates, ect. Coagulation is widely used in water and wastewater treatment. *Shut'ko* (1986) investigated the treatment of industrial wastewater from petroleum refineries by using metal salts containing coagulants. The water phase from chemical treatment has to be further treated to meet today's effluent standard for discharge systems. This can be achieved by biological treatment (*Soltani et al., 2010*) or granular activated carbon (GAC) filtration. Granular activated carbons (GACs) are either in the form of crushed granules (coal or shell) or of pellets prepared by agglomerating pulverized powders with binders such as coal tar pitch. Particle sizes in the range of 12/42 mesh are advantageous for liquid phase adsorption. GAC filters are widely used in drinking water and ground water treatment to adsorb Synthetic Organic Chemicals (SOCs). Once a GAC column is exhausted, the GAC must be replaced (*Ha et al., 2000*) and disposed of or recycled in some way (i.e., landfilling, incineration, or thermal reactivation). Replacement and disposal of exhausted GAC is quite expensive. A process of biodegradation—where one or more of the SOCs are biodegradable—could lengthen the GAC service life for some SOC mixtures. Specifically, GAC bioregeneration is the recovery of adsorption capacity of activated carbon by the biodegradation of adsorbed organic molecules on the carbon (*Rice and Robson, 1982*). It has been generally accepted that bioregeneration involves desorption of the adsorbed compounds from activated carbon to bulk solution, followed by biodegradation. This in turn, induces further desorption of the compounds into the bulk solution (*Hutchinson and Robinson, 1990; Jonge et al., 1996*). Much research has been done on the adsorption of mixtures of SOCs and the biodegradation and adsorption of mixtures of biodegradable SOCs (*Lefebvre and Moletta, 2006; Putz et al., (2005); Aktas and Cecen, 2007*). however very little work has been done on the biodegradation and adsorption of salty mixtures of biodegradable and non-biodegradable SOCs.

Focusing on these issues the research work investigated the feasibility of a complete treatment including:

- (i) A simple separation (on board) by gravity as a pre-treatment;
- (ii) A chemical coagulation as a primary treatment;
- (iii) A filtration on activated carbons as secondary treatment
- (iv) The bio-regeneration of the exhaust carbons (GAC) in order to reduce the GAC regeneration costs.

The research has also led to a proper characterization of the specific wastewater typologies as available scientific data are incomplete or too scattered.

2 MATERIALS AND METHODS

2.1 Water Sampling and characterization

Grab samples were collected from a floating tank (Figure1a) of an oil costal deposit in the Augusta harbour (Sicily). A simple gravity separation (2 h) was carried out on site (Figure1b) to reduce the effluent concentration of floating oil. About 1000 liters of the clarified wastewater were stored in a fridge at 4°C, in order to inhibit any biological activity. Water characterization was carried out according to Standard Methods (APHA, 2005). Analytical characterization and most of the experiments were carried out in the Environmental Engineering laboratory of the University Kore of Enna (Sicily).

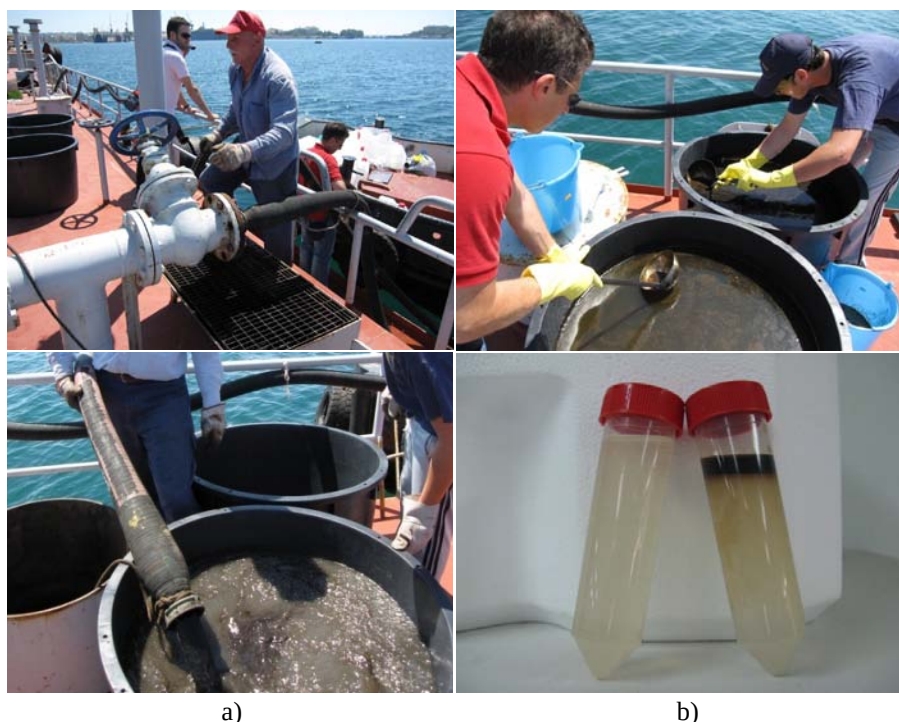


Figure 1. Water sampling a) and pre-treatment on board b) - Please see the acknowledgments

2.2 Primary treatment

The coagulation process was considered feasible for these wastewaters and investigated through several Jar tests. Ferric chloride was selected as coagulant on the basis of preliminary tests (not reported) and as it is known to be effective over a wide range of pH. The goal of the Jar test was to determine the optimum doses at which the coagulant and polyelectrolyte (Polidal A57) should be introduced to the wastewater. Various doses (between 30 and 200 mg/l) were investigated at natural pH values. The settleability of the

wastewater was tested in accordance with the procedure outlined in the Standard Methods (APHA, 2005). The test requires a multiple stirring apparatus running at the same speed, which can be varied. The test procedure was carried out by filling beakers with 1500 ml of the wastewater to be treated, after measuring pH, TPH, TOC and COD of the wastewater. The contents of the beakers were mixed at high speed (120 rpm) for 1 minute followed by a lower speed (40 rpm) for 20 min. Agitation was stopped and flocs were allowed to settle (1 h). Samples of supernatant were collected and pH, TPH, TOC and COD of the supernatant were determined on the supernatant in accordance with Standard Methods (APHA, 2005).

2.3 GAC saturation

Saturation of GAC was carried out through continuous flow column filtration. The standard experiment utilized a column filled with GAC (23 cm of length) with an empty bed contact time (EBCT) ranging from 18 to 21,7 minutes in the different experiments. In each experiment the 3,2-cm diameter column was packed with 20-30 mesh PicaHydro S23 GAC or Picabiol GAC. The flow rate ranged from 50,1 to 62,8 ml/min in the experiments. Because of the difficulties encountered in measuring COD, in these very high salinity waters, the TOC parameter was mainly used as an indicator of the total organic contamination throughout the prosecution of the GAC saturation experiments. An alternative approach to organic content analysis was the use of gas chromatography/mass spectrophotometry (GC/MS) techniques for the identification of petroleum hydrocarbons in the H-alkane form which was however limited to the control of the TOC and COD values accurateness. It should be noted that the GAC saturation procedure was carried out using a different slop source from the previous one utilized in the Jar test, being this last, characterized by a lower organic load (in terms of COD). As a results, COD discharge limit was not achieved by the considered GAC columns filtration conditions. However the main goal of these experiments was the GAC saturation in order to perform and verify the potential of the following GAC bioregeneration (Figure 2 a).

2.4 Respirometric tests

In the very early steps some respirometric batch tests were performed in order to investigate the biological degradation of TPH in the high salinity slops. These experiments were carried out in strict collaboration with some University of Palermo colleagues (*Torregrossa et al., 2010*). The effects of slops addition to the respiration rates of biomass withdrawn from a CAS process (Palermo municipal wastewater treatment plant) was investigated as well as the behaviour of halophilic biomass taken from a full scale plant treating high salinity petrochemical wastewater (conductivity ≈ 14 mS/cm). Respirometric batch experiments were performed using a “flowing-gas/static-liquid” type as batch respirometer (*Spanjers et al., 1996*) in order to verify the potential for the sludge from the conventional WWTP to be used in GAC bioregeneration. The biomass samples were eventually diluted with tap water in order to obtain a MLSS concentration in the range of 2000-3000 mgVSS/L. Further, they were moved into the batch respirometer and aerated until endogenous conditions were reached before running the respirometric test. The samples were maintained at a constant temperature of $20 \pm 1^\circ\text{C}$ with a thermostatic cryostat (JULABO). Agitation was provided by magnetic stirrer (FALC), and samples were intermittently aerated using aeration pumps. The dissolved oxygen concentration was measured with an oxygen probe and oximeter (WTW MULTI340i), while the

aeration control and data acquisition were managed by the OURsys software. The aeration intervals were set from 3 to 6 mgO₂/L. The OURsys software provided the respirograms generation.

2.5 Biorigeneration experiments

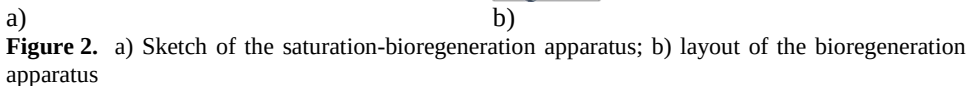
2.5.1 Specifically selected microorganisms

Different halophiles/halotolerans bacteria, able to oxidize hydrocarbons in the salty slops were considered in the research. In marine oil-polluted sites two predominant bacteria were identified (Atlas, 1995), by oligonucleotide probes and quantitative fluorescence dot-blot hybridization techniques: the aromatic hydrocarbon decomposer *Cycloclasticus pugetii*, estimated to make up 23-25% of the total bacteria population in sea water, and the aliphatic hydrocarbon decomposer *Alcanivorax borkumensis* which formed 4-7% of the bacteria population. In marine water, other investigators (Kargi, 2002; Putz et al., 2005; Yakimov et al., 2007) suggested further bacteria: *Halobacterium* (extreme halophile), *Marinobacter*, *Thalassolituus*, *Oleispira*, *Pseudomonas* sp., *Rhodococcus rhodochrous*. For present GAC bioregeneration tests, the ubiquitous bacteria *Alkanivorax borkumensis*, an obligate hydrocarbonoclastic one (OHCB), was initially considered. This bacterium is able to grow, at 28°C and aerobic conditions, on many saturated petroleum fraction constituents: straight-chain and branched alkanes, isoprenoids and long side-chain alkyl compounds (e.g. alkylmonocycloalkanes, alkylbenzenes and organic alkyl-sulfuric compounds). After the revitalization of the collection strain, the *A. borkumensis* cells were cultured over a period of two weeks. To allow the bacteria acclimation in laboratory (Ha et al., 2000), different cultures in scalar dilution in tubes of culture broths (marine broth DIFCO 2216 with 1% of sodium pyruvate) and wastewater (raw water filtered with a 0,45 micron filter) were prepared. The acclimation steps were: preparation of liquid culture (10⁸ cells) in physiological solution, inoculum of 500 µl of bacterial suspension in tubes, incubation at 28°C for 5 days. *A. borkumensis* grew in all the dilutions prepared. *A. borkumensis* acclimation allowed either bacterium adaptation to oily wastewater and verification of its ability to grow with minimal nutrients.

2.5.2 Batch experiments

Batch bioregeneration tests were carried out by a combination of activated sludge sampled from the MBR section of the oily contaminated groundwater treatment plant of Gela Refinery (Sicily) and the *Alcanivorax borkumensis* bacterium (DSMZ 11573), which was added to the rather high salinity sludge (conductivity ≈14 mS/cm).

Batch bioregeneration were carried out in a mixture of buffered nutrient (urea and biphasic ammonium <30% and vegetable substances <65%) slop, acclimated microorganisms and sludge from the treatment plant. Slops contained microbial community naturally occurring. A layout of the experimental bioregeneration setup is shown in Figure 2b. Loaded GAC was directly subjected to the recirculation of the mixture preemptively filtered on sand.



3.1 Slops characterization

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Table I. Slops water characteristics

3.2 Chemical pre-treatment

Figure 3 show the results of the chemical pre-treatment tests carried out through Jar test apparatus (Figure 3 a).

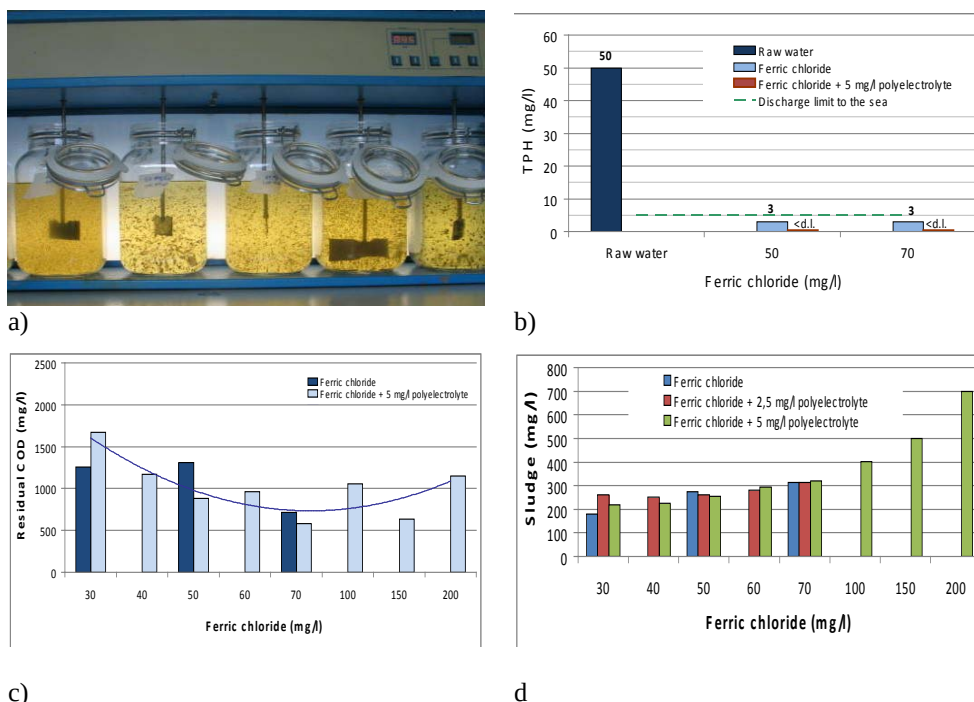


Figure 3. Jar test results: a) Sketch of the apparatus, b) TPH removal efficiency, c) COD removal efficiency, d) sludge production

Figure 3 b and Figure 3 c respectively show the effects of coagulant dosage on the TPH and TOC pretreatment removal efficiency. The pre-treatment, at natural pH, was found to reduce TPH from about 50 mg/l to values well below the discharge limit (resulting in a 99% removal efficiency), and to reduce COD from about 1100 to 584 mg/l (resulting in a 47% removal efficiency).

The optimum ferric chloride dose, also considering sludge and costs minimization (Figure 3 d), was recognized to be 70 mg/l plus 5 ml of polyelectrolyte. Results showed, in general, that COD removal increases with the increase in coagulant dose till it reaches an optimum value beyond which the COD removal efficiency starts to decrease. This can be attributed to restabilization of colloidal particulates that may occur due to the reversal of charges when coagulants are used at dosages higher than the optimal one (Jekel, 1986).

3.2.1 Results from preliminary respirometric tests

In a preliminary stage, respirometric tests carried out on sludge from a municipal CAS process, slowly acclimated to the slop (Figure 4).

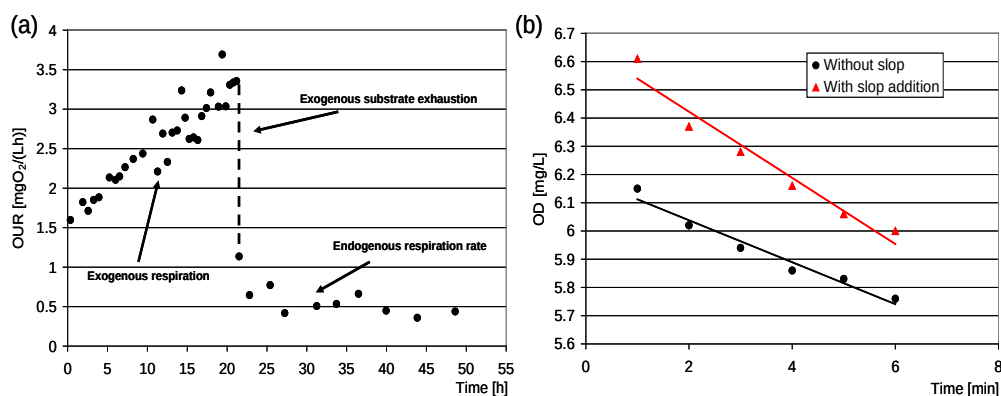


Figure 4. Respirogram of biomass from a CAS process acclimated to slop (a) and respirometric batch test of halophilic bacteria fed with slop (b).

High percentages of salt are known to compromise the correct operation of conventional aerobic wastewater treatment processes above chloride concentrations of 5–8 g l⁻¹ (Ludzack and Noran, 1965). In spite of the detrimental effect of salt on microbial activity, moderate acclimation of activated sludge to high salinity was possible.

Acclimation implies the exposure of non-salt-adapted micro-organisms to increasing salt concentrations in order to permit the obtainment of satisfactory effluent treatment performance at a given salt concentration. The success of such adaptation depends on several factors, such as the type and growth phase of micro-organisms, as well as the rapid or gradual increase of salt concentration during acclimation. OUR pattern in Figure 4 a indicates a moderate increase of biomass respiration rates as a consequence of sodium acetate addition (exogenous substrate). Such a result gave a preliminary indication of the potential biodegradability of the considered high salinity wastewater. However, respirometric rates were too low compared to that of activated sludge fed with municipal wastewater (Strotmann et al., 1999). For this reason, other sludge sources with different characteristics were investigated in the prosecution of the research. Indeed, when feeding the sludge collected from a saline groundwater treatment plant with slop, it resulted in a fast growth phase indicating the chance of a potential acclimatization of the biomass (Figure 4 b). This inoculum was then utilized for the GAC bioregeneration experiments.

3.3 GAC Saturation and bio-regeneration results

Figure 5 a shows a typical result of GAC treatment (saturation) phase obtained through a continuous flow column filtration. With the respect to TOC values the GAC was considered saturated after about twelve liters.

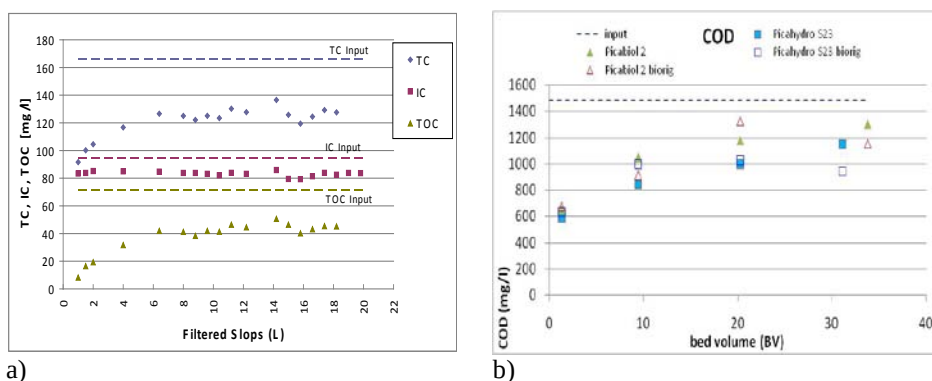


Figure 5. a) GAC behaviour in a typical saturation experiment and b) a comparison of the virgin and bio-regenerated GACs.

GAC renewal of adsorptive capacity consisted in re-circulating the mixture of acclimated bacteria, nutrients and dissolved oxygen in the described closed batch system. According to *Goeddertz et al. (1988)* the offline process for activated carbon bioregeneration was preferred to the bioregeneration process occurring during the BAC treatment because of the limitations of the BAC process for availability of nutrients and dissolved oxygen, the persistence of many organic compounds and operational difficulties including hydraulic short circuiting and excessive head loss.

In the case of offline systems, where pre-loaded activated carbon is consecutively biologically treated, it also could appear easier to determine the extent of bioregeneration. However only very few studies, reporting quantitative measurements of bioregeneration, are described in the literature (*Aktas and Cecen, 2007*) and no one deals with salty wastewater. Bioregeneration of activated carbon can be quantified either by the direct measurement of substrate loading on the activated carbon, or by the indirect measurement of substrate consumption such as CO_2 production using either a radiochemical analysis technique or instrumental measurement of respiration. In this study bioregeneration was directly quantified through the comparison of the equilibrium adsorption capacities of fresh and bio-regenerated GAC.

The biodegradation of hydrocarbons by natural occurring bacteria and fungi in the acclimated sludge involves the oxidation of the substrate by oxygenase enzymes, for which molecular oxygen was required. In this process, alkanes are converted to carboxylic acids that are then biodegraded via β -oxidation, while aromatic hydrocarbon rings are hydroxylated to form diols, the rings are then cleaved with the formation of catechols which are degraded to intermediates of the tricarboxylic acid cycle (*Atlas, 1995*).

Results from the bioregeneration tests (a typical trial is reported in Figure 5 b) showed a good recovery of the adsorptive capacity of the biologically treated GAC.

Two mechanisms are involved in the bioregeneration of granular activated carbon (GAC): bioregeneration due to a concentration gradient and bioregeneration due to extracellular enzyme reactions. Concentration gradient mechanism (*Aktas and Cecen,*

2007) involves organic compounds released from the activated carbon following desorption due to a concentration gradient between bulk liquid and activated carbon surface: organic compound released into the liquid phase are then degraded by microbial activities, causing a lowering of the organic compound concentration in the liquid phase. Extracellular enzyme reactions mechanism involves exoenzymes excreted by microorganisms diffuse into activated carbon pores and react with adsorbed substrates; hydrolytic decay of the substrate may occur or desorption of the resulting enzyme metabolite may take place due to the weaker adsorbability of this metabolite.

4 CONCLUSIONS

Large quantities of oils may be released into the environment by discharges of slops, bilge and ballast waters from tankers and non-tankers, as well as from incidents such as explosion, collision, groundings and contacts. In addition, dry dock activities in harbors are also a potential source of similar oil pollution. In this paper the feasibility of treating an emulsified oily wastewater (slop) of high salinity, TPH and COD values was investigated. Pre-treatment of wastewater was best achieved when 70 mg/l of ferric chloride and 5 mg/l of polyelectrolyte were dosed at natural pH. At optimum conditions, (including the sludge and process costs minimization) the TPH and COD of the wastewater were reduced by 99 and 47 per cent, respectively. The TPH level of the treated wastewater was well below the discharge limit set by the regulatory authority, but this result was not achieved with COD. The considered wastewater thus required further treatment by GAC adsorption. Tests on bioregeneration of exhaust GAC, carried out in batch units gave encouraging results in terms of TPH removal from saturated GAC. Although biological treatment is usually inhibited by high salt concentrations, results from the present research proved the feasibility of using salt-adapted microorganisms capable of degrading the main pollutants contained in these salty contaminated waters. The selection of salt-tolerant micro-organisms involved an adaptation of a specifically selected sludge joined to *Alcanivorax borkumensis* to high salt concentrations. Although the contribute of the specifically added *Alcanivorax borkumensis* was not evident, the salt-tolerant strains, after a proper adaptation, have proved capable of removing efficiently the organic matter adsorbed on the GAC. Bioregeneration of GAC loaded by TPH from slops can thus increase the service-life of the GAC and, not requiring the GAC to be removed from the filter, it can allow a further reduction in GAC management costs. Several other factors including biodegradability, adsorbability and desorbability of the different sorbates, characteristics of activated carbon and process configuration, still need to be optimized by varying the operational conditions. Starting from the present results further study of bioregeneration systems of GAC treating slops are thus needed to understand the potential economic and process performance benefits of this technology.

Acknowledgments. This project was partially funded by the Italian Ministry of Education, University and Research (MIUR), through the program “Research Program of

Relevant National Interest”, PRIN 2007PM3TJM_002 (Project title: *Water bodies protection from xenobiotic compounds: new methods for the analysis, the control and the treatment in civil and industrial wastewaters*).

The authors sincerely wish to thank the Pontoni S.r.l. service staff, operating in the Augusta Harbor (Sicily), for their kind and essential cooperation. The authors especially want to honour “The Chief”, Domenico Settipani (the man with the red hat in Figure 1) who died in an unexpected accident on work on Monday, 23rd May 2011.

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