Small improvements in the treatment of oily wastes from marine transportation

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A B S T R A C T

Purpose. The main goal of this research was to investigate the treatment of high salinity slops and dockyards waste(water)s through physical, chemical and biological treatments.
Methods. The work specifically focus on the feasibility of treating these wastes by chemical coagulation and sedimentation followed by a granular activated carbon (GAC) filtration including the on-line bioregeneration of the exhaust carbons by the obligate marine hydrocarbonoclasticus bacterium (OHCB) Alcanivorax borkumensis SK2.
Results. Optimum coagulant dosages were provided for both the two waste(water)s in the pre-treatment phase. The selected GAC was proved to be effective in the finishing process allowing to respect the discharge limits.
Tests on on-line bioregeneration of exhaust GAC gave some encouraging results in terms of adsorption capacity recovery.
Conclusions. This process, without removing GAC from the filter can increase the column service-life with a consequent reduction of management costs. Although biological treatment is usually inhibited by high salt concentrations, results from the present research proved the feasibility of using marine micro-organisms capable of degrading the main pollutants contained in these oily and salty contaminated waters.

Keywords:
Slops, dockyard wastewaters, cost, high salinity, biological, activated carbons

1. Introduction

Most of the international trade in goods is transported by sea. Thus, ocean shipping plays a central and essential role in the world economy and in world trade. Maritime trade is generally divided into three broad categories: liquid-bulk, dry-bulk, and general cargo. Petroleum alone accounts for nearly all of the liquid-bulk trade and for almost half of the total world tonnage shipped. Tons of barrels travel everyday all around the world, and even more will travel in the next years because of the increasing demand of emerging countries. 8 millions of barrels pass only through the Mediterranean sea by 3000 routes every year. Considering that almost the 30% of the world refining capacity is focused in the Mediterranean routes are expected to intensify.

This important trade path causes a heavy risk exposition of marine pollution associated with accidental events (oil spills) and routine operations like tank cleaning (slops), dirty ballast, sewage and bilge water management [1,2].

An other considerable contribution to marine pollution, is due to boatyards activities, produced both in the construction and the repair/wash phases. For example, sandblasting, that is used to remove biofouling from the hull also causes the partial removal of the antibiofouling paints so releasing organic-metallic and oily compounds in the yards wastewaters [3].

Most of the ports, however suffers from the lack of suitable reception facilities and treatment plants for these waste(water)s often giving rise to undesirable behaviours both from the ships and dockyards staff. In order to restrict marine pollution it could be useful to propose sustainable treatment processes at an affordable cost.

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 high salt concentrations, the performance obtained depends on a proper adaptation of the biomass or the use of halophilic organisms.

The standard 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, etc [4, 5]. Coagulation is widely used in water and wastewater treatment. 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 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 and disposed of or recycled in some way (i.e., landfilling, incineration, or thermal reactivation) [6]. 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. GAC bioregeneration is the recovery of adsorption capacity of activated carbon by the biodegradation of adsorbed organic molecules on the carbon [7-13].

Much research has been done on the adsorption of synthetic mixtures of SOCs and on the biodegradation and adsorption of mixtures of biodegradable SOCs [14, 15]. However very little work has been done on the biodegradation and adsorption of real salty and oily waste(water)s [16-18].

Oil hydrocarbon degradation mainly proceeds by marine micro-organisms, and the microbial community of marine ecosystems involved in this process have been extensively studied [19]. Different authors have showed that marine communities of oil-degrading bacteria are composed of indigenous members able to degrade mixtures of hydrocarbons [20].

In marine oil-polluted environment two predominant bacterial genera were identified [20 - 23] by oligonucleotide probes and quantitative fluorescence dot-blot hybridization techniques: the polycyclic aromatic hydrocarbon decomposer *Cycloclasticus* sp, and the aliphatic hydrocarbon decomposer *Alcanivorax* sp. In marine water, other investigators [19, 24, 25] suggested also further bacteria belonging to the *Halobacterium* (extreme halophile), *Marinobacter*, *Thalassolituus*, *Oleispira*, *Pseudomonas*, *Rhodococcus* genera.

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

(i) A simple separation 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.

2. Materials and methods

2.1 Source of waste(water)s

Two different waste(water)s were considered in the experiments: slops (ex diesel) and dockyard waste(water)s. Slops were directly sampled from the barges transiting in the industrial port of Augusta (Sicily) (Fig. 1). Dockyard waste(water)s were collected from the storage tanks of the *'Cantiere Navale di Augusta'* Society (Sicily). A simple gravity separation (2 h) was carried out to separate floating oil from both the wastes. The clarified samples were stored in a fridge at 4°C, in order to inhibit any biological activity.

a) b)

Fig. 1 Water sampling a) and slop pre-treatment on board b)

2.2 Analysis of physic-chemical parameters

The wastewater were analysed for various physic-chemical parameters, such as pH, COD, TOC, chlorides and TPH. The measurements of pH were performed according to the APHA Standard methods [26] with the aid of a multiparameter device model "SevenGo Duo Pro" of Mettler Toledo, equipped with a glass electrode, combined with suitable reference electrode, which operates in the range of 0-14 units pH, with a resolution of 0.001 pH units. The measurements of COD were conducted according to the APAT CNR IRSA 5130:2003 method using, if necessary, precautions needed for samples with elevate chlorides concentrations to reduce interferences. The determination of TOC was obtained according to the UNI EN 1484:1999 method. Analysis of TPH were performed according to the EPA 5021A:2003 + EPA 8015D:2003 and EPA 3510C:1996 + EPA 8015D:2003 for light and heavy hydrocarbons respectively. Chlorides concentrations were measured according to UNI EN ISO 10304-1:2009 method.

2.3 Chemical coagulation and flocculation

The coagulation process was considered feasible for these wastewaters and investigated through several jar tests. Ferric chloride ($FeCl_3$), aluminum sulfate ($Al_2(SO_4)_3$) and polyaluminum chloride ($Al_2(OH_3)Cl_3$) were used for the coagulation process of slops while only ferric chloride was tested on the dockyard waste(water)s.

The ferric chloride, hydrated with $6H_2O$, is produced by EMSURE and it was supplied in powder form, of a yellowish color. The aluminum sulfate $Al_2(SO_4)_3$•$16H_2O$ was supplied by BDH as a white powder. The polyaluminum chloride ($Al_2(OH)_3Cl_3$) was provided by Auk Chemistry in solution at 18% by weight. Coagulants were prepared in a concentrated solution of 100 mg/l, to simplify the addition during the jar-tests. In order to control the pH of the solution to the desired values, sodium hydroxide (NaOH) and sulphuric acid (H_2SO_4), were used during the tests. The NaOH is produced by Carlo Erba and it was supplied in white powder, anhydrous pure (100%). Two solutions respectively of 0.1 M and 1 M were used to obtain a quick achievement of the desired pH. The sulfuric acid was supplied by Sigma Aldrich in concentrated solution (95-97%). A solution of H_2SO_4 0.1 M, was also prepared to obtain a more gradual variation of the pH value.

The goal of the jar test (Jar-test apparatus, model FC6S, Velp Scientifica) was to determine the optimum dose at which the coagulant should be used for the pre-treatment while minimizing the sludge production. The optimal own pH range for each coagulant was previously investigated at set coagulant doses. 1.5 liter beckers were filled with sampled waters and then introduced to the Jar-test apparatus. Jar test conditions, for all the tests, were the following:

- a rapid mixing stage (coagulation): shaking at 120 rpm for 1 min. [5];
- a slow mixing step (flocculation): stirring at 30 rpm for 20 min. [27, 28];
- a gravity separation step: residence time of 90 min. [5].

Before starting the jar-tests pH was tested.

2.4 Sludge production

The volumetric measurement of settled sludge after the sedimentation process was performed according to APHA Standard methods [26]. The settled sludge were determined through Imhoff. Operationally the process starts with filling the Imhoff cone with a water sample vigorously stirred and leaving it to settle continuously monitoring the amount of the settling sludge at 30 , 60 and 90 min time intervals, carefully removing the solids along the wall of the cone with a glass rod imprinting at the same time a slight twisting motion. The measurement of the volume (ml) occupied at the bottom of the graduated cone from the sediment provides the value of the settleable solids expressed in ml/l.

2.6 GAC saturation

Saturation of GAC was carried out through continuous flow column filtration. The standard experiment utilized columns of 100 cm length filled with 10 g of GAC (about 23 cm) with an empty bed contact volume (EBCV) of 18 ml. In each experiment the 1-cm diameter columns were packed with Filtrasorb 400 GAC (Calgon Carbon Corporation) a mesoporous carbon (Tab 1). The flow rate ranged from 6.7 to 7 ml/min between the different saturation experiments. Although the significant difficulties encountered in obtaining stable measurements of COD in these real very high salinity waste(water)s, this parameter was utilized during the experiments as it is the critical one for the respect of the discharge limits. Saturation experiments were replicated three times. A fourth column was operated in order to measure microbiological parameters variation in the saturated GAC.

Table 1 Main characteristics of the Filtrasorb 400

Parameter	Value	Units
Iodine Number	1000	mg/g (min)
Effective Size	0,55-0,75	mm
Moisture by Weight	2%	max
Uniformity Coefficient	1,9	max
Screen Size by Weight, US Sieve Series	On 12 mesh	5% (max)
	Through 40 mesh	4% (max)
Apparent Density	0.54	g/cm^3
Water Extractables	< 1	%
Non Wettable	< 1	%

2.7 Microorganism under study and growth conditions

A strain of *A. borkumensis* SK2^T (Y12579) was used in the bio-regeneration tests. Strain used in this study belong to a bacterial collection hold at IAMC-CNR of Messina and was isolated from natural seawater in previous researches [29].

Started cultures were prepared by inoculating one loop of microbial cells into 10 ml of ONR7a mineral medium based on the composition of seawater [30]. Nitrogen was provided in the form of NH_4Cl, and phosphate was provided in the form of Na_2HPO_4. Medium ONR7a contained (per liter of distilled water) 22.79 g of NaCl, 11.18 g of $MgCl_2$*$6H_2O$, 3.98 g of Na_2SO_4, 1.46 g of $CaCl_2$, - $2H_2O$, 1.3 g of TAPS0 {3-[N-tris(hydroxymethyl) methylamino]-2-hydroxypropanesulfonic acid}, 0.72 g of KCl, 0.27 g of NH_4Cl, 89 mg of Na_2HP0_4 * $7H_20$, 83 mg of NaBr, 31 mg of $NaHCO_3$, 27 mg of H_3B0_3, 24 mg of SrCI*$6H_20$, 2.6 mg of NaF, and 2.0 mg of $FeCl_2$*$4H_20$. To prevent precipitation of ONR7a during autoclaving, three separate solutions were prepared and then mixed together after autoclaving when the solutions had cooled to at least

50°C; one solution contained NaCl, Na_2S0_4, KCl, NaBr, $NaHCO_3$, H_2B0_3, NaF, NH_4Cl, Na_2HPO_4, and TAPSO (pH adjusted to 7.6 with NaOH), the second solution contained $MgCl_2$, $CaCl_2$, and SrCI, (divalent cation salts), and the third solution contained $FeCl_2$; 0.1% (w/v) sterile tetradecane ($C_{14}H_{30}$, Sigma-Aldrich, Milan, Italy) was used as only energy and carbon source. After growing in a rotary shaker (New Brunswick C24KC, Edison NJ, USA; 150 rpm) at 25°C for two days, 500 μl of the seed culture broth were transferred into a 250 ml Erlenmeyer flask containing 100 ml of ONR7a medium supplemented with 1% (w/v) sterile tetradecane. The culture was incubated in a rotary shaker (New Brunswick C24KC, Edison NJ, USA; 150 rpm) at 25°C for 5 days.

2.8 Microbial measurement in batch bioregeneration tests

Sub-samples of GAC, after saturation with slops, were taken aseptically from the fourth column and subjected to batch bioregeneration tests, for 10 days, to evaluate the effects of the addition of the specialized culture and nutrients on microbial growth. In the experiment identified as "BIO", carried out in natural seawater [sterilized by filtration through a 0.2-μm syringe filter (Sartorius)] the previous selected bacterial culture was added together with inorganic nutrients with higher concentrations than those occurring in the natural sea water (final concentrations: KH_2PO_4 0.077 g l^{-1}, NH_4Cl 0.2 g l^{-1} and $NaNO_3$ 0.1 g l^{-1}). Oxygen was continuously supplied to the system.

A negative (abiotic) control (CONT) test was carried out, in comparable conditions, without the addition of bacteria and nutrients. Measures of direct bacterial count (DAPI) and cultivable fraction (CFU) were carried out, in triplicate, with the following methodology:

Total Bacterial Abundance (DAPI Count)

Prior to dispersion, the GAC samples were incubated for at least 15 min with Tween 80 (final concentration, 1 mg L^{-1}). According to Kuwae et Hosokawe [31] an ultrasonic cleaner bath (*Branson 1200 Ultrasonic Cleaner*, Branson USA) was used for the bacterial dispersion from the carbons (10 min). After centrifugation (8 min at 8000 xg) and collection of water-Tween 80 phase, cellular counts were performed by DAPI (Sigma-Aldrich S.r.L., Milan, Italy) staining on samples fixed with formaldehyde (2% final concentration). Samples were prepared as previously reported [20, 32]. All results were expressed as number of cell gr^{-1}.

Plate counts (CFU count)

For enumeration of cultivable hydrocarbon-degrading bacteria, GAC samples were prepared as described above. Samples were serially diluted in sterile physiological solution and plated on ONR7a [33] and ONR7a added with sterilized crude oil (Arabian Light Crude Oil, 100 μl) as unique energy and/or carbon source. Culture media and crude oil were autoclaved separately for 20 min at 120°C. All agar plates were incubated at 25±1°C for 7 days.

2.8 GAC bioregeneration (Columns experimental set-up)

On line bioregeneration tests were carried out through the use of a simple bio-reactor containing the microbial culture (Fig.2) and subjected to a slight forced aeration. At the beginning (T_0) of the experiments selected microorganism was added, in the bio-reactor, at a final density of 10^3 cell ml^{-1}.

Loaded GAC was then subjected to the counter-current recirculation of the mixture pre-emptively filtered on sand. Layout of the experimental setup is shown in Fig. 3. The columns were bio-regenerated at 25 ± 1 °C for 10 days. The experiments were carried out three times.

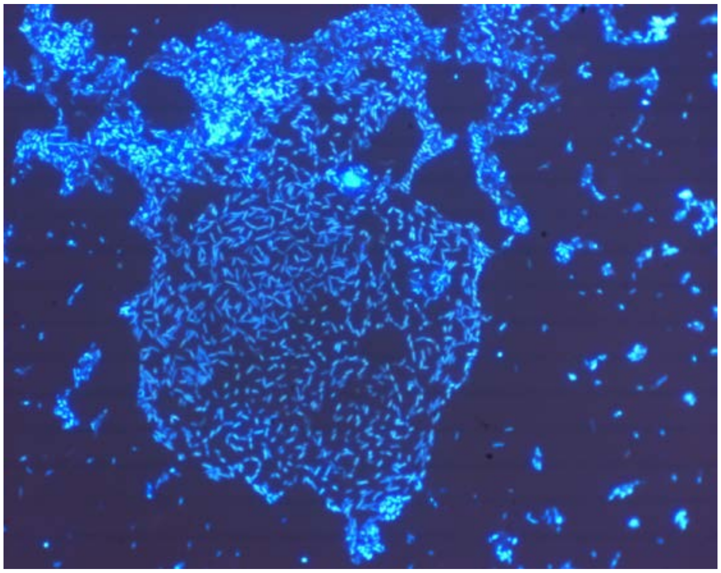

Fig. 2 Photography in fluorescence microscopy (DAPI staining) of A. borkumensis SK2 during the growth in crude oil

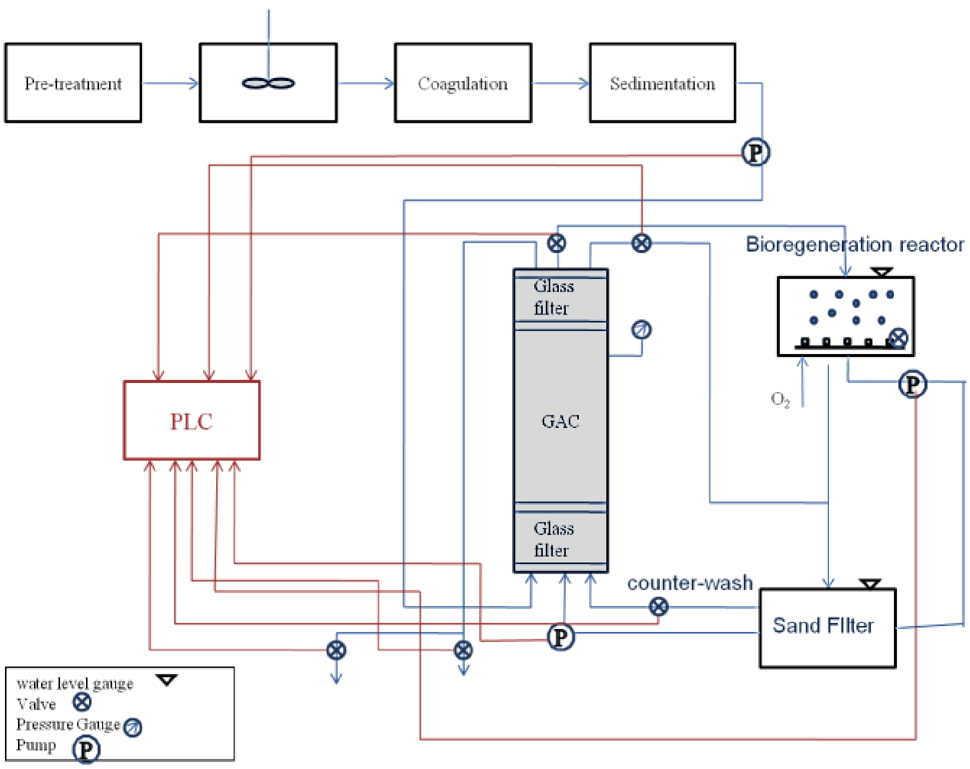

Fig. 3 Schematic representation of bio-regeneration system proposed in this work.

3. Results and discussion

3.1 Characteristics of waste(water)s

The slops from the barge and the dockyard waste(water)s collected from the waste deposit were found to have the general characteristics summarised in Table 1. From the table, it is clear that both these wastewaters, having an almost neutral pH value, have Total Petroleum Hydrocarbons and COD values higher than discharge limits to the sea (5 and 160 mg/l respectively). With regards to the last two parameters that are critical for the respect of the discharge limits, COD and TPH values of ex diesel slops treated in this research have shown significant lower concentrations than those analysed in previous researches from the authors. Of particular concern was also the high concentration of chloride in the slops. At such elevated conditions, current analytical methods for organic content analysis are obstructed as concentrations above 2000 mg/1 (as) interfere with chemical oxygen demand (COD) and total organic carbon (TOC) analytical procedures by the formation of precipitates and acids, respectively [26].

Table 1 Main characteristics of the sampled waste(water)s.

Parameters	**Units**	**ex diesel slops**	**dockyard waters**
pH		7.0	7.4
Light hydrocarbons from C6 to C10	(mg/l)	< 0.01	0.80
Heavy hydrocarbons from C > 10 to C20	(mg/l)	6.66	143.99
Heavy hydrocarbons from C > 20 to C30	(mg/l)	2.72	72.00
Heavy hydrocarbons from C > 30 to C40	(mg/l)	0.49	74.57
Heavy hydrocarbons from C > 40 to C50	(mg/l)	< 0.006	3.52
Sum of heavy hydrocarbons from C > 10 to C50	(mg/l)	9.88	294.09
TPH from C6 to C50	(mg/l)	9.88	294.89
TOC	(mg/l)	114.8	478.5
COD	(mg/l)	301.0	930.0
Chlorides Cl^-	(mg/l)	20320.0	809.0

3.2 Effects of pH on COD removal

Typical pH ranges for each coagulant have been investigated (data not reported) to determine the optimal pH value for both waters samples: a pH range of 4.0-9.0 for ferric chloride [34], a pH range of 5.5-8.0 for alum [35] and a pH range of 4.0-9.0 for poly-aluminum chloride [28]. Results from these tests have shown no significant differences so justifying the choice to operate with the original pH.

3.3 Determination of optimum dosage for COD removal

Ex diesel slops

When using $FeCl_3$ as coagulant for treatment of slops (ex diesel) at pH 7, the higher COD removal efficiency occurred with doses of 50.0 mg/l of coagulant, obtaining a COD final concentration of about 260 mg/l (Fig. 4). The reduced efficiency is however influenced by the low initial COD value. Enhanced efficiency were observed in previous research [16,18] on heavier polluted slops. The production of sludge shows an upward trend with increasing dose of ferric chloride, except in the range from 70.0 to 90.0 mg/l, where it remained almost constant. The precipitation of solids (data not reported) showed a volume decrease with increasing of the settling time, due to the compression of settled flocs after 90'. Only in the case of the lower dose (50.0 mg/l) there was an inverse trend due most likely to the lower size of the flocs formed during flocculation, which caused a slower settling velocity during the compression phase of the solids. As a consequence a dosage around 50.0 mg/l of $FeCl_3$ was indicated as the best performing one causing the higher decrease of COD and the lower sludge volume production (7.3 ml/l after 90') (Fig. 5).

Through the use of $Al_2(SO_4)_3$ at pH 7, instead, the best removal of COD occurred for the dosage of 90 mg/l (26%) with a concentration value of 222.0 mg/l (Fig. 4) at the end of the treatment tha is still far from the legal limit of 160 mg/l imposed for the discharge to surface (sea) waters. Furthermore we can observe abatement percentages between 14% and 22% for the dosages ranging between 60 and 80 mg/l of aluminum sulfate. A low production of sludge was noted after 30' for the lower coagulant doses up to 80 mg/l. Higher dosages favoured the formation of heavier flocs and their resulting faster precipitation. The trend in the amount of settled solids after 90' is closely related to the dosage of coagulant, with the gradual increase of the volume of the sludge with increasing dose (Fig. 5).

Through the use of $Al_2(OH)_3Cl_3$ at pH 7, the best COD removal, slightly higher than 15%, occurred with the dosage of 40 mg/l of coagulant and final concentrations of approximately 254 mg/l of COD were obtained (Fig. 4). An almost linear increase of sludge production followed the increase in the coagulant dose, with a good precipitation registered already after 30' (data not reported). At the higher doses, in the transition, a significant compaction of the sludge occurred during the settling time from 30' to 90'. The settled sludge volume for coagulant doses of 40 and 50 mg/l resulted as high as 60 and 90 ml/l respectively (Fig. 5). For this reason a concentrantion of polyaluminum chloride around 30 mg/l was considered as the optimal dosage in this process.

With regard to the removal efficiency of COD from the investigated waste(water)s the best performing coagulant was aluminum sulfate while the ferric chloride and the polyaluminum chloride did not achieve equivalent performance. In addition, for the polyaluminum chloride, despite the lower dosages tested, high sludge production was observed that signicantly affect the economy of the process.

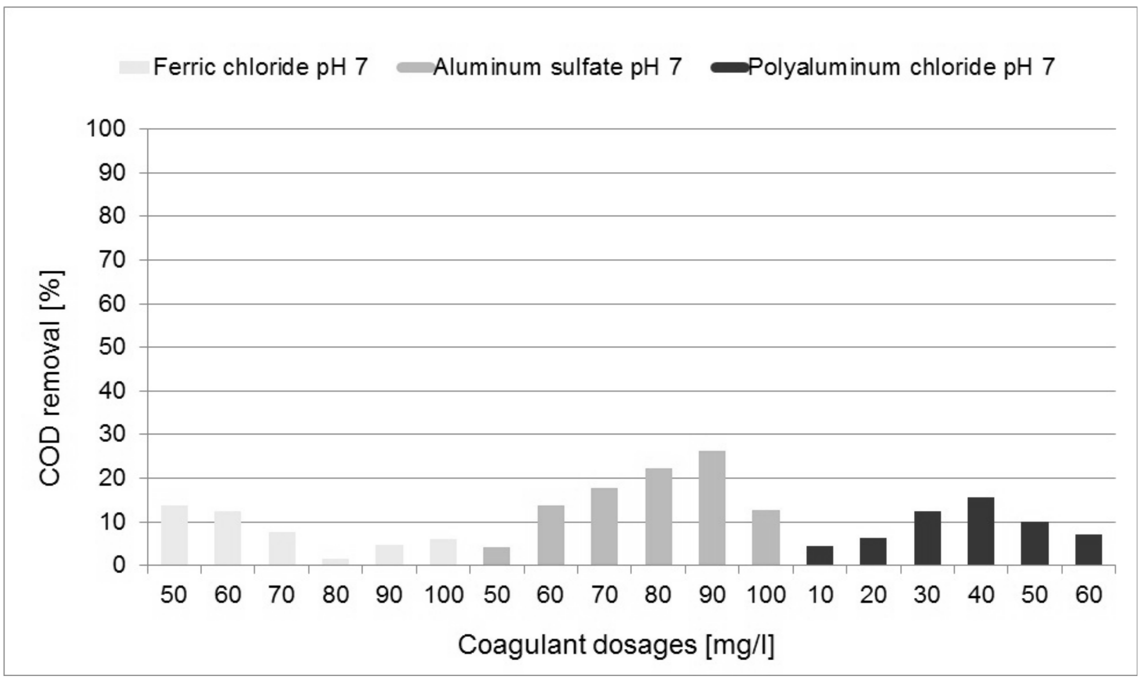

Fig. 4 COD removal efficiency, in the ex diesel slops, at various doses of the coagulants (ferric chloride, aluminium sulfate and polyaluminum chloride)

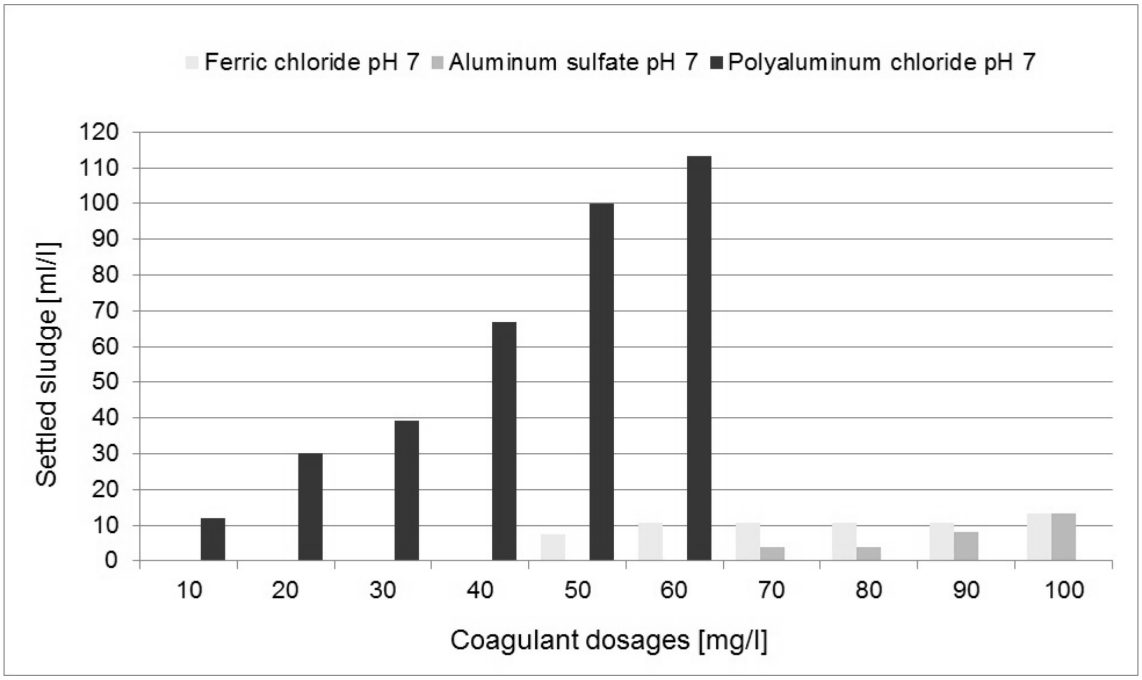

Fig. 5 Sludge production in the ex-diesel slops coagulation with ferric chloride, aluminium sulfate and polyalumin chloride

Dockyard waste(water)s

Test conducted with a broad range of ferric chloride concentration on dockyard wastewaters indicated the chance to use smaller amounts of coagulant in comparison with the slops. Fig. 6 shows that the best COD removal efficiencies (above 70%) were obtained by using 90 and 110 mg/l of coagulant, but also a 30 mg/l and 50 mg/l $FeCl_3$ concentrations had showed a very good efficiency (63% and 68% respectively) with lower sludge production. Also for this sample of waste(water)s, it was observed a substantial linearity of sludge production with coagulant concentration, increasing with a minimum value of 6 ml/l at 10 mg/l concentration up to a maximum value of 27 ml/l at 110 mg/l concentration (Fig. 7).

Tests conducted with aluminum sulfate in previous research on these wastewaters (data not reported) showed almost same COD removal efficiency but with a lower settling kinetics, while those conducted with polyaluminum chloride had produced great amounts of sludge.

For this reason, it was made the choice to use only ferric chloride as pre-treatment for the subsequent GAC filtration tests, considering the two dosages of 30 mg/l (with slightly lower COD removal effectiveness and sludge production) or 50 mg/l (with slightly higher COD removal effectiveness and sludge production) the optimal choice for this process.

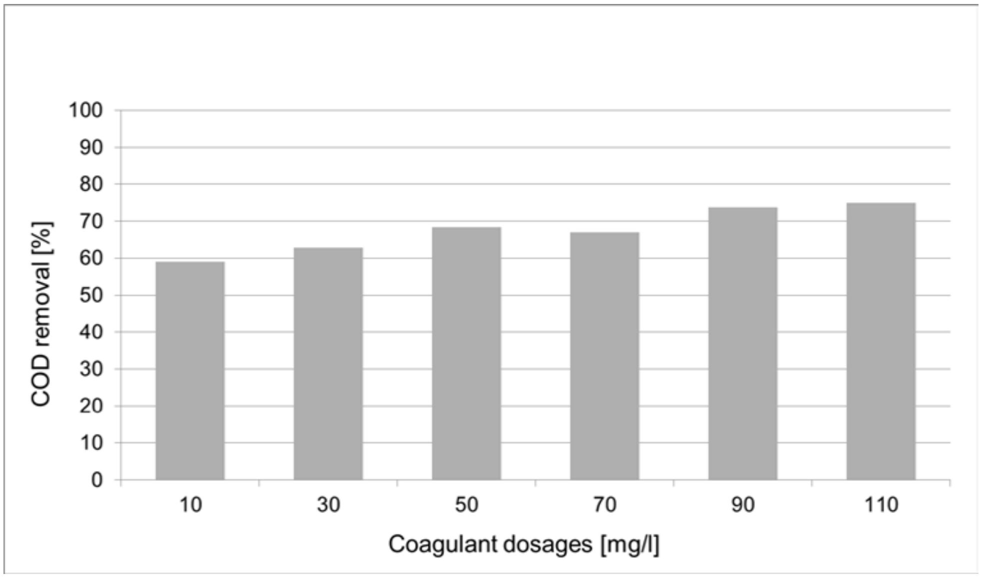

Fig. 6 COD removal efficiency by ferric chloride coagulation at various doses in the dockyard waste(water)s

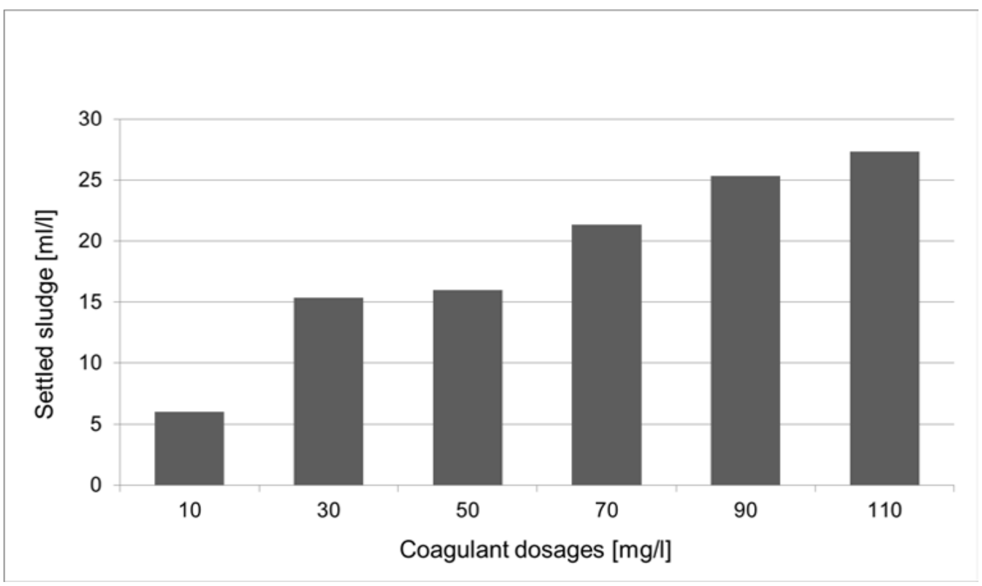

Fig. 7 Sludge production in the dockyard waste(water)s coagulation with ferric chloride

3.5 Batch bioregeneration test: DAPI and CFU count

Measures of direct bacterial count (DAPI) and cultivable fraction (CFU) were carried out on saturated carbons (batch experiments) with the following results.

Total Bacterial Abundance (DAPI Count)

Measures of microbial abundance (measured by DAPI count, Fig. 8) in the carbons saturated by slops filtration at the end of experimental period (T_{10}) showed values of ~10^3 cells ml^{-1} for the control (CONT); by contrast in the bio-regenerated GAC (BIO) it was possible to observe values higher than two logarithmic orders (~10^5 cell ml^{-1}).

Plate counts (CFU count)

At the end of the experimental period, counts of oil-degrading bacteria capable of grow in plate showed values of ~10^2 CFU ml^{-1} for the control (CONT) while in the bio-regenerated GAC values up to 31 x 10^4 CFU ml-1 were detected (Fig. 8).

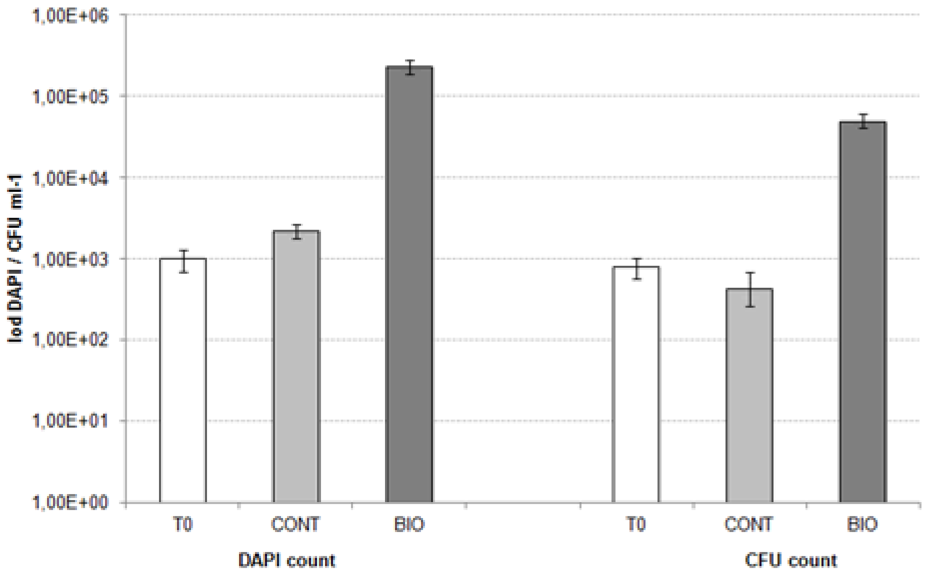

Fig. 8 Bacterial densities determined by DAPI staining and measure of cultivable bacteria (CFU). Concentration of the cells observed at the begging of experiment (T0, white bars) and after ten days in control (grey bars) and bioregeneration (BIO, dark bars) experiments on carbons saturated by slops.

3.5 GAC Filtration and comparison of virgin and bio-regenerated GAC

GAC renewal of adsorptive capacity consisted in re-circulating the mixture of acclimated bacteria, nutrients and dissolved oxygen in the described closed batch system. As described in the methods and according to Goeddertz et al. [36] 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 could appear easier to determine the extent of bioregeneration. However only very few studies, reporting quantitative measurements of bioregeneration, are described in the literature [13] and no one deals with salty wastewater. Bioregeneration was here directly quantified through the comparison of the equilibrium adsorption capacities of fresh and bio-regenerated GAC through columns filtration tests. Results from the bioregeneration tests (Fig. 9 and 10) showed (mean values) an appreciable recovery of the adsorptive capacity of the biologically treated GAC for both the two waste(water)s. Similar result were obtained by [37]. Fig.11. shows the qualitative improvement of the dockyard waste(water)s over the complete process.

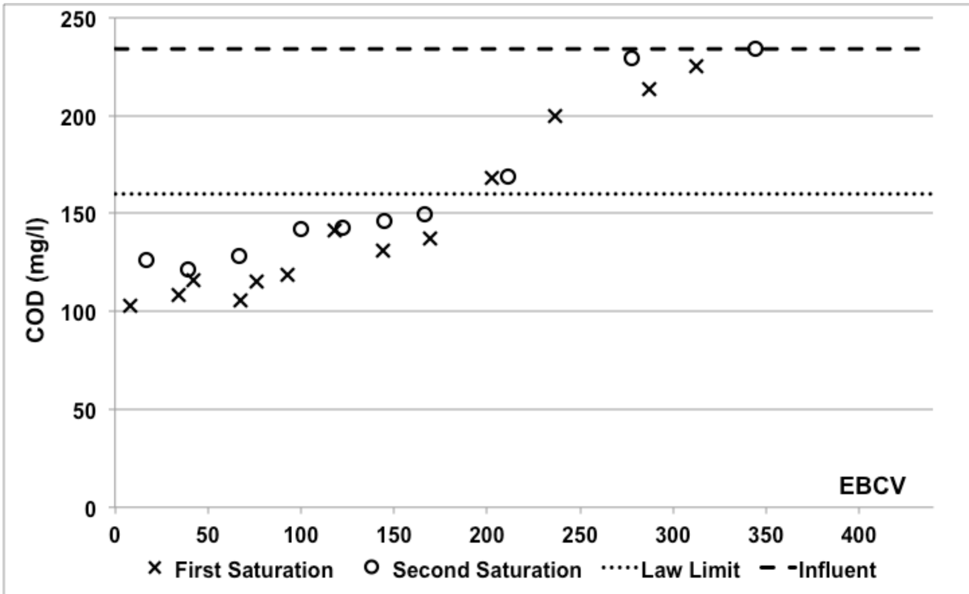

Fig. 9 Comparison of virgin and bio-regenerated GAC in the column filtration of slops

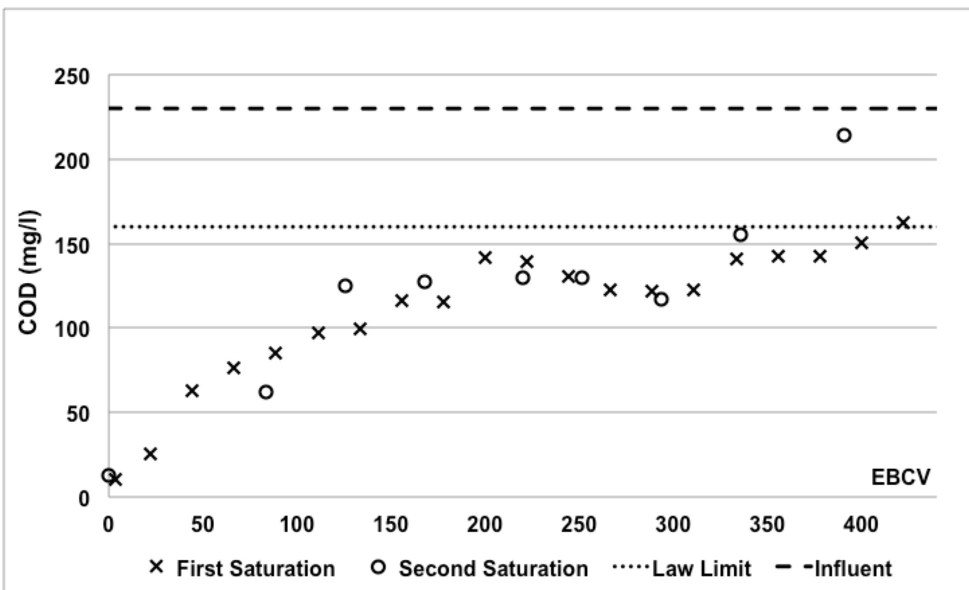

Fig. 10 Comparison of virgin and bio-regenerated GAC in the column filtration of dockyard waters

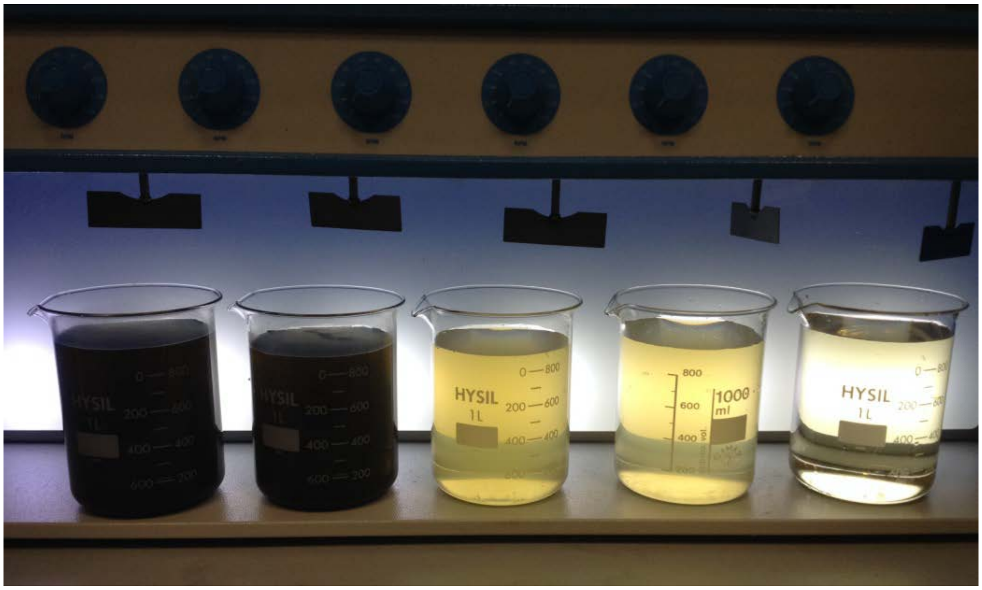

Fig. 11 Qualitative improvement of the dockyard waste(water)s over the full process (from the left: raw waste(water), de-oiled, after coagulation, after sand filtration, after GAC filtration)

The biodegradation of hydrocarbons by natural occurring bacteria involves the oxidation of the substrate by oxygenase enzymes, for which molecular oxygens is 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 [21].

Two main mechanisms are here proposed to explain the bioregeneration of the granular activated carbon: bioregeneration due to a concentration gradient and bioregeneration due to extracellular enzyme reactions.

Concentration gradient mechanism [13] involves organic compounds relased from the activated carbon following desorption due to a concentration gradient between bulk liquid and activated carbon surface; According to this theory, organic compound released from the carbons into the liquid phase are degraded by microbial activities, causing a lowering of the organic compound concentration in the liquid phase. As a consequence, the adsorbed organics are desorbed due to the concentration gradient between the activated carbon surface and bulk liquid [38, 10, 39].

Extracellular enzyme reactions mechanism involves exoenzymes excreted by microorganisms which 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 [39, 40, 41].

However, other investigators believe that desorption is a prerequisite for bioregeneration and nondesorbable compounds cannot be bioregenerated [10, 38, 42, 43].

According to Xiaojian et al. [9], the enzyme molecules are larger than the sizes of micropores and thus cannot access to the adsorbed substrate. They estimated that for an enzyme to actively catalyze a reaction inside a pore, the pore diameter must be at least three times greater than the enzyme size. Considering that the average molecular diameter of a monomeric enzyme (molecular weight between 13,000 and 35,000) is above 31–44A˚, they concluded that the pore diameter must be larger than 10nm which exclude the micropores (≈2 nm) and some of the mesopores (≈ 2–50 nm) of activated carbons.

4. Conclusions

In this paper the feasibility of treating two emulsified oily waste(water) was verified through a coagulation pre-treatment followed by GAC filtration. To treat the high salinity slop, a selection of salt-tolerant micro-organisms was performed involving an adaptation of the specialized Alcanivorax borkumensis SK2 to the high contaminants concentrations. The same process was also applied to the dockyard waste(water)s. Bioregeneration was quantified through the comparison of the equilibrium adsorption capacities of fresh and bio-regenerated GAC through columns filtration tests. On-line bioregeneration gave encouraging results in terms of adsorption recovery of the saturated carbons thus increasing the service-life of the GAC without removing the carbon from the filter (with consequently reduced management costs). Although biological treatment is usually inhibited by high salt concentrations, results from the present research proved, for the investigated slops, the feasibility of using salt-adapted micro-organisms capable of degrading the main pollutants contained in these oily and salty contaminated waters.

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