CHEMICAL ENGINEERING TRANSACTIONS Volume 20, 2010
Editors Enrico Bardone, Aurelio Viglia
 ISBN 978-88-95608-12-9 ISSN 1974-9791
DOI: 10.3303/CET1020046

Chemical-physical and biological treatment of high salinity wastewaters contaminated by oily xenobiotic compounds

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Wastewaters contaminated by xenobiotics of oil-bearing origin, generated by various sources and subsequently discharged into the natural environment create a major ecological problem throughout the world because of the persistence and accumulation of these compounds.

The main goal of this research is to investigate the effectiveness of a removal process composed of several treatments including physical, chemical and biological phases. Considered wastewater are wash-waters originated from the cleaning of ships' fuel tanks (slops). Beside the presence of refractory compounds, these waters show extremely high salinity levels (up to 25.000 p.p.m.), that limit the possibility of discharge to sewers and address the disposal to the sea. This severely lowers the concentrations limits for most of the "sensible" parameters, such both COD and xenobiotic hydrocarbons, thus requiring a higher level treatment. The research has also led to a proper characterization of the specific wastewater typologies as available scientific data are incomplete or too scattered.

The main objective of this work was to investigate the feasibility of treating slop wastewater by sedimentation and chemical coagulation followed by granular activated carbon (GAC) filtration and offline bioregeneration of exhaust carbons. Previous research is far from provide a complete understanding of process design, operation, and performance of GAC bioregeneration systems treating mixtures of biodegradable and nonbiodegradable SOCs such slops are. Experiments on bioregeneration are still in progress and results are thus incomplete and only methods are here presented.

Introduction

Oily wastewater and oil-water emulsion are two of the main pollutants discharged to water environment. 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 standard methods for treatment of emulsified oily wastewater is chemical de-emulsification followed by secondary clarifications, which requires the use of a

Please cite this article as: Mancini G., Lanciotti E. and Bruno M., (2010), Chemical-physical and biological treatment of high salinity wastewaters contaminated by oily xenobiotic compounds, Chemical Engineering Transactions, 20, 271-278
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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 purificated to meet today's effluent standard for discharge systems. This can be achieved by granular activated carbon (GAC) filtration. GAC is often 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). Replacement and disposal of exhausted GAC is quite expensive. Encouragement of biodegradation—where one or more of the SOCs are biodegradable—should 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 (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 compound into the bulk solution (Hutchinson and Robinson, 1990; Jonge et al., 1996).
In this paper treatment of an emulsified oily wastewater is investigated using sedimentation and coagulation, GAC adsorption and off line biorigeneration of exhaust carbons. Much research has been done on the adsorption of mixtures of SOCs and on the biodegradation and adsorption of mixtures of biodegradable SOCs. Beside very little work has been done on the biodegradation and adsorption of salty mixtures of biodegradable and nonbiodegradable SOCs. This lack of research is particularly problematic because such salty SOC mixtures are widespread in the environment, and many nonbiodegradable SOCs may cause adverse health effects. This study examines the role of a mixed culture of microorganisms on bioregeneration of GAC loaded with a mixture of compounds occurring in slops wastewater.

Materials and methods

Wastewater pre-treatment

Grab samples were collected from a floating tank of an oil costal deposit in the Augusta harbour (Sicily). The samples were stored in a fridge to prevent any biological activity. For the pre-treatment study, jar tests were conducted. Ferric chloride was used as coagulant as it is known to be effective over a wide range of pH.). The objective 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 of coagulant (between 30 and 200 mg/l) were studied at natural pH values. Samples of supernatant were collected and pH, TPH, TOC and COD of the supernatant were determined on the surnatant in accordance with Standard Methods (APHA, 2005).

GAC treatment

Saturation of GAC was carried out through continuous flow column filtration (30g). A column of 17 cm length was run with an emptybed contact time (EBCT) of 10 minutes. The 3-cm diameter column was packed with 20-30 mesh PicaHydro S23GAC GAC. The flow rate of the column was between 13.3 and 16.7 ml/min.

Biorigeneration experiments

Microorganisms
The ability of halophiles/halotolerans bacteria to oxidize hydrocarbons in the presence of salts is useful for the biological treatment of saline ecosystems contaminated with petroleum products. In literature (Atlas, 1995), in marine oil-polluted sites two predominant bacteria were identified, 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 also further bacteria: *Halobacterium* (extreme halophile), *Marinobacter, Thallassolituus, Oleispira, Pseudomonas* sp., R*hodococcus rhodochrous*. In this bioregeneration test it was chosen the ubiquitous bacteria *Alkanivorax borkumensis*, obligate hydrocarbonoclastic bacteria (OHCB). This bacterium grows at 28°C, in aerobic conditions, and it is able to grow 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).

Batch experiments
Bach bioregeneration was carried out by *Alcanivorax borkumensis* bacterium (DSMZ 11573), which was added to the high salinity wastewater. 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 considered. The acclimation steps were: preparation of liquid culture (10^8 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 to verify its ability to grow with minimal nutrients.
Batch bioregeneration was carried out in a mixture of buffered nutrient seawater, acclimated microorganisms and saturated GAC at natural pH. Seawater contain microbial community naturally occurring. A diagram of the experimental setup is shown in Figure 3. Loaded GAC was placed into two bottles (10 g each one), one for bioregeneration batch and another one for control batch (Figure 1). 500 ml buffered nutrient seawater was added to each bottle. The bioregeneration batch was inoculated with an inoculum (10^8 cells) of the colture of *Alcanivorax borkumensis*, acclimated to a mixture of slops and nutrients (urea and biphasic ammonium <30% and vegetable substances <65%). A control batch was employed to identify the desorption of the adsorbed compounds without contribution of the selected microorganism. Small samples of GAC were taken before and after the bioregeneration phase, The TPH loading on the GAC was measured (EPA 3545A) by dichloromethane extraction in ASE (high temperature and pressure extractor). Samples of the dichloromethane solution were diluted and analyzed by gas chromatography.

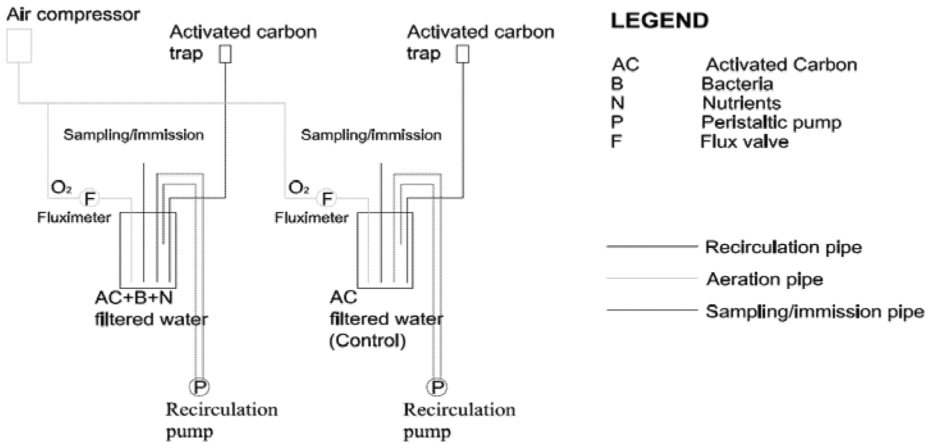


Figure 1 Bioregeneration experimental setup.

Results and discussion

Slops collected from the oil deposit were found to have the general characteristics shown in Table 1. From the table, it is clear that these wastewaters have THP (50 mg/l) and COD (1110 mg/l) values higher than discharge limits to the sea (5 and 160 mg/l respectively).

Table 1 Slops water charachteristics

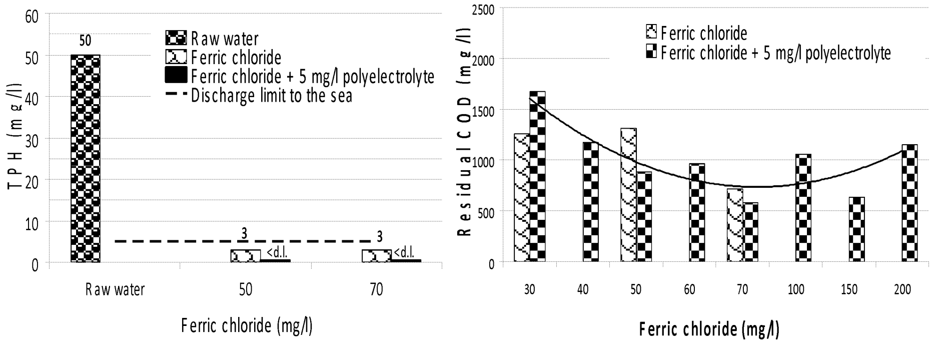
Parameter	M. U.	Value	Parameter	M. U.	Value
pH	-	7.5	Sulphate SO_4^{-2}	mg/l	1970
COD	mg/l	1110	Conductivity	mS/cm	107.5
Suspended solids (SS)	mg/l	26	Total organic carbon	mg/l	65,7
Total dissolved solids	mg/l	55000	Total carbon	mg/l	161,7
TPH	mg/l	50	Inorganic carbon	mg/l	95,9
Chloride Cl^{-1}	mg/l	17760	Anionic surfactant	mg/l	2.65

Figure 2(a) and 2(b) 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 below detection limit, resulting in a 99% removal efficiency, and to reduce COD from about 1100 to 584 mg/l resulting in a 47% removal efficiency.

Mechanismis of bioregeneration

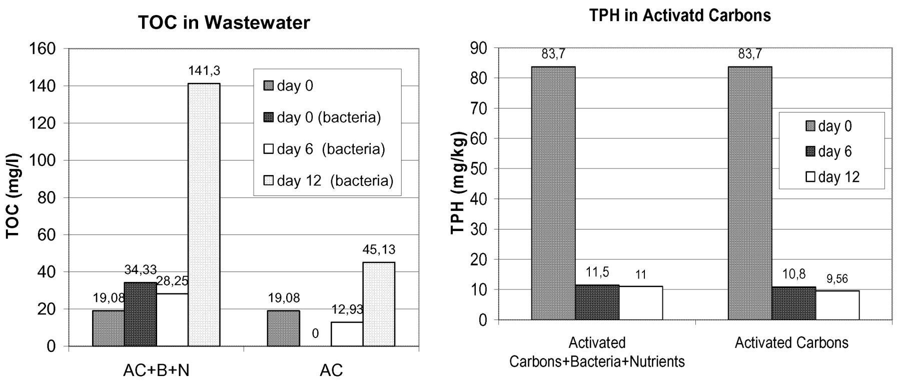
An increase in turbidity was observed in both the reactors due to the growth of a microbial community as also indicated by the increase in TOC values (Figure 3a). The increase was higher in the reactor where also nutrients were added. Initial amounts of TPH adsorbed on saturated GAC in the reactors was about 80 mg/kg. In the batch control bioregeneration unit, after 1 weeks incubation, the TPH concentrations on the

GAC was about 11 mg/kg with efficiency of 86% (Figure 3b). No significant variation was observed after two weeks treatment.



(a) *(b)*

Figure 2 Jar test results: (a) TPH removal efficiency; (b) COD removal efficiency.



a) b)

Figure 3 Batch bioregeneration test results

Mechanismis of bioregeneration

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Two mechanisms are proposed to explain bioregeneration of granular activated carbon (GAC): bioregeneration due to a concentration gradient, bioregeneration due to extracellular enzyme reactions. Concentration gradient mechanism (Aktas and Cecen, 2007) involves organic compounds relased from the activated carbon following desorption due to a concentration gradient between bulk liquid and activated carbon surface: 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. 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.

Conclusions

The investigation looked into the feasibility of treating an emulsified oily wastewater of high salinity, TPH and COD values. 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, the TPH and COD of the wastewater were reduced by 99 and 47 per cent, respectively. A further treatment consisted of a GAC column adsorption process. Tests on bioregeneration of exhaust GAC, carried out in batch units give some encouraging results in terms of TPH removal from saturated GAC. However the contribute of the specifically added Alcanivorax borkumensis was irrelevant. Further study of bioregeneration systems of GAC treating slops is needed to fully understand the potential economic and process performance benefits of this technology.

References

APHA, 2005, Standard Methods for the Examination of Water and Wastewater.

Aktas O., Cecen F. Bioregeneration of activated carbon: a review International Biodeterioration & Biodegradation 59 (2007) 257-272.

Atlas R.M., Pertroleum biodegradation and oil spill bioremedation. 1995. Marine Pollution Bulletin. 31:178-182.

Ha S-R., Vinitnantharat S., Ozaki H. Bioregeneration by mixed microrganisms of granular activated carbon loaded with a mixture of phenols. 2000. Biotechnology Letters 22:1093-1096.

Hutchinson D.H. and Robinson C.W., 1990, A microbial regeneration process for granular activated carbon-II regeneration studies, Water Res. 24, 1217-1223.

Jekel M., 1986, The stabilization of dispersed mineral particles by adsorption of humic substance, Water Research 20(12), 1543-1554.

Jonge R.J., Greure A.M., Van Andel J.G., 1996, Bioregeneration of powdered activated carbon (PAC) loaded with aromatic compounds. Water Res. 30, 875-882.

Kargi F. Enhanced biological treatment of saline wastewater by using halophilic bacteria. 2002, Biotechnology Letters 24:1569-1572.

Laat J., Bouanga F., Dore M. and Mallevialle J., 1985, Influence of bacterial growth in granular activated carbon filters on the removal of biodegradable and of nonbiodegradable organic compounds, Water Res. 19(12), 1565-1578.

Putz A.R.H., Losh D.E., Speitel G.E.Jr. Removal of nonbiodegradable chemicals from mixtures during granular activated carbon bioregeneration. 2005. J. Environ. Eng. 131 (2): 196-205.

Rice R.G. and Robson C.M., 1982, Biological Activated Carbon Enhanced Aerobic Biological Activity in GAC Systems. Michigan: Ann Arbor Science Publishers.

Shut'ko A. P., 1986, Treatment of industrial wastewater from petroleum refineries by using aluminum-containing coagulants, Neftepererab. Neftekhim 8, 5.

Yakimov M.M., Kenneth N.T., Golyshin P. Obligate oil-degrading marine bacteria. 2007. Current Opinion in Biotechnology 18:257-266.