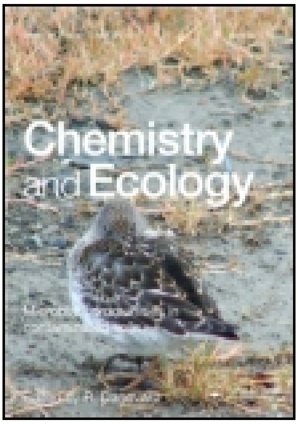

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Effect of acidification and modified Fenton treatment on a contaminated harbour sediment

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This study presents the results of laboratory experimental oxidation treatments conducted on marine sediments highly polluted with hydrocarbons. The purpose of the study was to compare the effect of a modified Fenton treatment conducted with acidified stabilised H_2O_2 with one of simple acidification with H_2SO_4 used as control to evaluate the potential of heavy metal mobilisation. The H_2O_2 initial concentration was 0.62 M and $KH_2PO_4 = 1.15\,g{\cdot}L^{-1}$. To evaluate changes in the solid and liquid phase, chemical oxygen demand (COD), thermogravimetric analysis (TGA) and differential thermal analysis (DTA) under O_2 atmosphere analyses were performed on the solid, while total organic carbon (TOC), COD, pH and Eh were measured on the liquid. Evaluation of the heavy metal mobilisation was performed using sequential extraction procedures. Results indicate that the treatment was able to change the organic matter to a less hydrophobic state, to destroy part of the carbon and to lower the COD of the sediment. In addition, the treated sediment showed easier-to handle characteristics, reduced caking and lower aggregation capacity. However some mobilisation of Cu occurred while the concentration of Fe lowered.

Keywords: marine sediments; chemical oxidation; heavy metals; metals mobilisation; sequential extraction

1. Introduction

The sediments of harbours situated in industrial areas may be highly polluted with a great quantity of hazardous compounds, such as heavy metals, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), dioxins, furans, polychlorinated biphenyls (PCBs), pesticides and herbicides, depending on the type of activity present in the area [1]. Marine sediments are a mixture of different materials including the shells of aquatic organisms, transported soil particles, organic matter from sewage, industrial wastes, dead and rotting vegetation and animals, other organic and inorganic materials and chemicals. The interaction between sediment particles and contaminants is affected by the constituents of sediment such as clay, organic matter, iron and manganese oxides, and associated characteristics, such as particle size, pH and oxidation–reduction conditions [2].

In this study, the modified Fenton treatment was applied to treat a marine sediment highly contaminated with hydrocarbons. Because the sediment used was not artificially contaminated, this study could provide more information on the impact of oxidation treatments on such complex matrixes.

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The application of concentrated H_2O_2 solutions in the presence of Fe-containing minerals proved to be effective in the remediation of soils contaminated by different pollutants [3–13], providing a highly reactive matrix made of different species with the potential to transform a wide range of organic contaminants [14]. In particular, the hydroxyl radical is capable of non-selectively oxidising a variety of organic contaminants. Few studies have evaluated the possible collateral effects of remediation using Fenton processes. Some authors observed increased dissolution of organic matter and the increase of water solubility of hydrophobic compounds such as DDT above the limits imposed for water [15]. Because the conditions generated during the treatment change the pH and redox potential, the dissolution of heavy metals may occur, causing environmental risk. Therefore, the concentrations of two metals, Cu and Fe, were measured both in the leachate solution and performing sequential extraction procedures on the treated sediment.

To discriminate between the effects of the lowering of the pH on heavy metal release and of the oxidation treatment, control tests were performed using acidified distilled water with H_2SO_4.

The attention was also focused on the sediment's thermal behaviour, because modified Fenton oxidation could also become a pre-treatment of a successive thermal treatment. In our case, the pre-treated sediment would have easier-to-handle characteristics limiting problems to the processing equipment due to the tightly aggregation and adhesiveness of the untreated particles.

2. Materials and methods

The sediment used in this study was a mixture of different sediments collected at 30–50 cm depth in an industrial harbour in Sicily, Italy. Selected sample characteristics are listed in Table 1. These analyses were executed according to the Italian Environmental Regulation [16] methods.

The treatment was carried out in triplicate on sediment slurries. The oxidation procedure was as follows: samples of ∼10 g of dry sediments were weighed and placed in 120 mL Pyrex flasks with Teflon caps. Then, 100 mL of a solution of water and stabilised H_2O_2, with KH_2PO_4, were added. The oxidant versus contaminants weight ratio was 10 : 1 where, as contaminants, we considered the organic contamination of hydrocarbons $C > 12$. The following initial concentration was used: $H_2O_2 = 0.62$ M and $KH_2PO_4 = 1.15\ g{\cdot}L^{-1}$. The pH of the solution was adjusted to 1.5 and 0.75 with H_2SO_4. Control experiments were conducted using distilled water acidified with H_2SO_4. The slurries were stirred on an orbital shaker (Heidolph Unimax 1100) at 250 rpm for 10 min, then the stirring was diminished to 100 rpm and reactions were kept going until the concentration of H_2O_2 was detectable. To prevent possible explosions due to gas accumulation in the tubes, the caps were not sealed during reaction time to permit evacuation of the generated gas. At the end of reaction, the liquid fraction was separated by vacuum filtering on 0.45 µm Whatman filters.

The following parameters were analysed on the filtrate: the chemical oxygen demand (COD) determined by back-titration of residual potassium dichromate with ferrous ammonium sulfate

Table 1. Selected sediment characteristics.

1	Selected sediment characteristics	
Granulometry	Fraction $x > 2$ mm	2.3%
	Fraction $2 > x > 0.063$ mm	17.5%
	Fraction $x < 0.063$ mm	80.2%
Specific weight	1.31	$kg{\cdot}dm^{-3}$
Organic contamination	Hydrocarbons $C > 12$	21258.9 ppm
	PAH	20.6 ppm
Metals	Al	16368.2 ppm
	Fe	39762.6 ppm
	Cu	358.9 ppm

(Italian Environmental Regulation) at the end of reaction time; the total organic carbon (TOC) with a Shimadzu TOC-5000 analyser; the residual H_2O_2 with a Merk RQ-flex reflectometer, the concentrations of the anions acetate, formate, and oxalate by ionic chromatography on a Dionex DX 120 ion chromatograph equipped with a IONPAC AS12A column (200 mm, 4 mm i.d.) and guard column (50 mm, 4 mm i.d.). The concentrations of Cu and Fe were monitored through flame atomic absorption spectrometry. The solid fraction was dried at 105 °C overnight and analysed for COD. Its thermal behaviour was analysed through simultaneous thermogravimetric and differential thermal analyses (TGA–DTA) using a Stanton, STA-780 TGA-DTA analyser. The TGA operating conditions were the following: temperature ramps at 20 $°C \cdot min^{-1}$ from 20 to 900 °C. The analyses were conducted under an O_2 (incineration) atmosphere with a 5 $mL \cdot min^{-1}$ gas flow. Elemental analysis was also performed on the solid with a EuroEA Elemental Analyser. Sequential extractions were then performed following the Tessier protocol. All reagents were ACS grade and supplied by Carlo Erba Reagents, Milan, Italy.

3. Results and discussion

The sediment showed a strong buffering capacity (Figure 1a) and although the initial solution pH for was between 0.5 and 1.75, by the end of the reaction, the slurries had a pH between 6.2 and 6.7. The sediment pH of a distilled water control (without acidification) reached pH 7.3. When oxidant was employed, a lower final pH value was observed, indicating the formation of acid species in the oxidised samples. The reduction of pH during oxidation treatments is attributed to the generation of acid species such as CO_2, H^+, carboxylic and β-keto acids that is usual in oxidation treatments [12,17].

Immediately after the addition of the oxidant, a greater redox potential was measured, as expected. Its value then lowered because of the consumption of H_2O_2 (Figure 1b,c). It was observed that lower pH allowed longer H_2O_2 lifetimes.

In Figure 1d, variations in TOC over time are presented. A greater TOC concentration was observed in samples treated with hydrogen peroxide. The measured TOC may depend on the

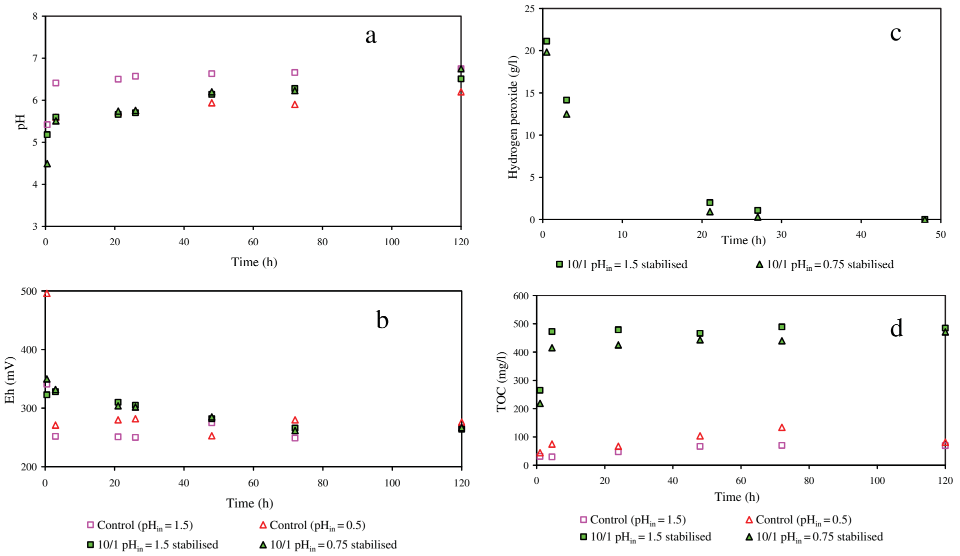

Figure 1. Measurements of: (a) pH, (b) Eh, (c) H_2O_2 and (d) TOC of the supernatant liquid.

direct desorption of soluble parts of organic matter from the sediment or on the desorption of initially hydrophobic matter that has become soluble as a result of the reactions [18]. Oxidation reactions lead to a consumption of TOC and to its final conversion to CO_2. In our case, the increase in TOC could be due to the partial conversion of hydrophobic matter to more soluble compounds as a consequence of the oxidation reactions. In effect, and as already observed [19], oxidation can result in the release of smaller parts of organic matter from larger molecules and in the change of natural organic matter to a less hydrophobic status [15]. Once formed, the $^{\bullet}OH$ generated from H_2O_2 may readily non-selectively interact with a broad range of organics, the most common reactions being H-atom abstraction from C–H or O–H bonds and addition to aromatic ring in aromatic compounds or to alkenes [18]. This results in an overall decrease in hydrophobicity and in enhanced dissolution in the aqueous phase. The lowering of pH increased slightly the TOC removal in the control experiments.

The results of COD measurements on the filtered liquid and on the sediment at the end of the reactions showed that the COD of the solution augmented, when the oxidant was used, from around $508\,\mathrm{mg{\cdot}L^{-1}}$ and $764\,\mathrm{mg{\cdot}L^{-1}}$ of the control at pH 1.5 and 0.75, respectively, to 1004 and $1077\,\mathrm{mg{\cdot}L^{-1}}$ in the 10 : 1 $\mathrm{pH_{in}}$ 1.5 and 10 : 1 $\mathrm{pH_{in}}$ 0.75 experiment, thus indicating the solubilisation from the matrix of newly formed organic and/or inorganic species. When the pH was lower, a greater COD was measured in the presence of the oxidant. Comparing these results with others discussed elsewhere [20], the presence of acid lowered the COD with respect to the control with distilled water only. This may be due to the oxidising power of H_2SO_4 solutions. The COD of the sediment diminished more consistently in the oxidised samples, as expected, and greater diminutions were observed at lower pH. This can be attributed to the combined effects of the oxidising power of the acid, of the increased stability of H_2O_2 (increased H_2O_2 lifetime as also observed in Baciocchi et al. [7]) and of an increased solubility of the Fe species that catalyse the decomposition of H_2O_2 in reactive species. In effect, the catalytic activity of Fenton systems can be related to the activation of H_2O_2 by Fe ions leached from the solid material and acting as homogeneous catalysts, or to the combined and pH-dependent effects of metal leaching and direct heterogeneous catalysis [12,21–23]. Phosphates could increase the rate of mineral-catalysed Fenton-like reactions. Therefore, the degradation probably occurred both in the aqueous phase, mainly for the species that undergo desorption [6,23], and directly on the surface of the iron minerals [3,24].

Figure 2 presents the results for the concentrations of the anions acetate, formate and oxalate in the solution at the end of reaction. These three ions were detected only in the treated samples and are common by-products of oxidation treatments, being almost recalcitrant to further oxidation. The TOC originating from their contribution was ∼30% of the total measured TOC. The concentration of acetate was lower in the more acidic sample, whereas there were only slight differences in the concentrations of the other ions.

In Figure 3 the TGA and DTA analyses of the samples are presented. In TGA analysis, variations in the mass of the sample are recorded as a function of time, whereas in DTA the differences in temperature between the sample and a reference material are recorded as a function of time. This type of analysis enables identifications of endothermic (dehydration, dehydroxylation, evaporation, decomposition, etc.) and exothermic reactions (oxidation, combustion and certain decompositions). The initial weight loss observed at the beginning of the TGA curves, which corresponds to an endothermic reaction, was surely due to initial dehydration phenomena below 200 °C. Conversely, the presence of organic matter produced a strong exothermic oxidation, with an associated huge peak around 300 °C. The presence of another exothermic peak of little amplitude around 550 °C was also observed. Secondary exothermic peaks might be due to the combustion of different and more recalcitrant classes of organic matter [25], and/or the formation of oxalates, which are common by-products of the oxidation of organic matter and were evidenced in the liquid fraction (see Figure 2). With respect to the untreated sample, all treatments provided a reduction

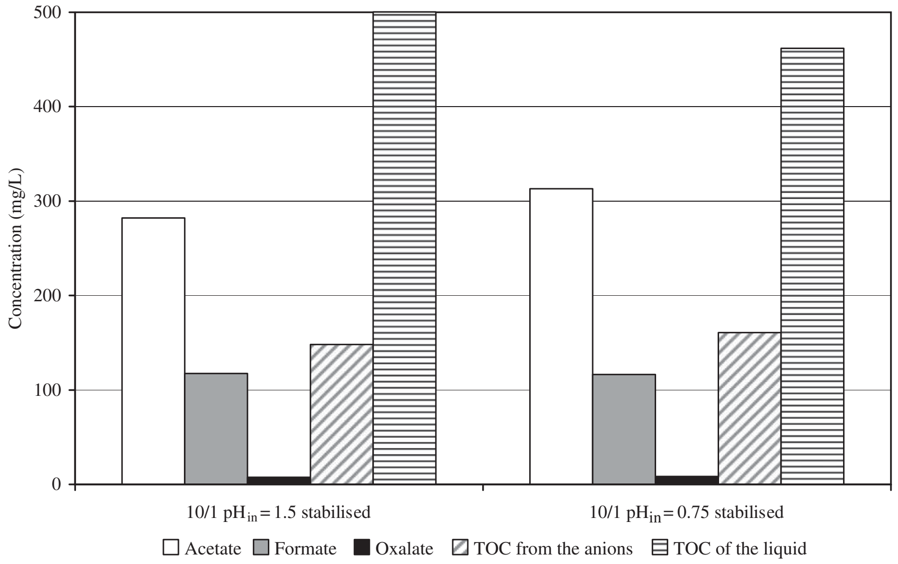

Figure 2. Concentrations of the ions: acetate, formate and oxalate in the filtered liquid at the end of reaction.

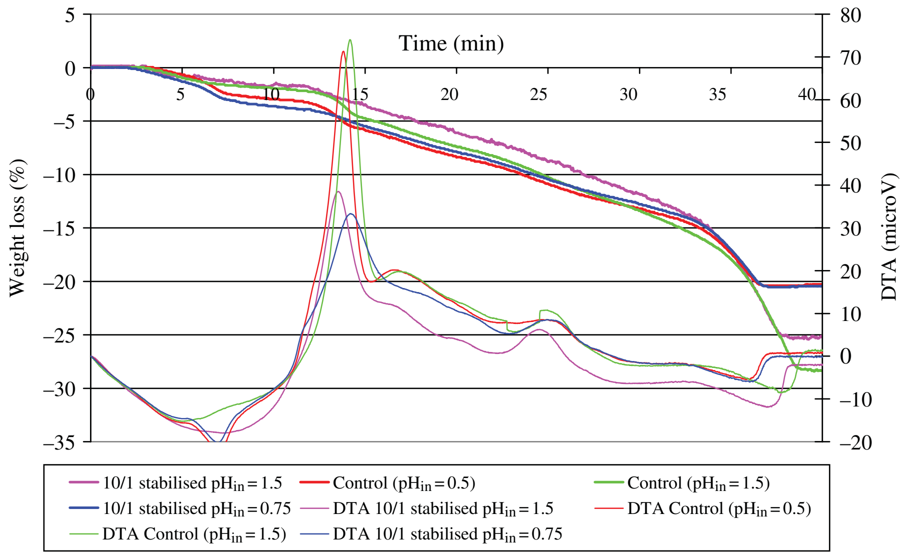

Figure 3. TGA and DTA analyses of the acidified samples and of the oxidised samples (heating rate: 20 °C·min^{-1}, O_2).

in the intensity of the DTA exothermic peak. This reduction was more evident when the oxidant was used and is consistent with changes in sample composition after treatment [26]. The acidic treatment destroyed part of the carbonate fraction decomposing above 650 °C.

The mass loss observed in TGA was divided into four intervals according to Lopez capel: labile organic matter (200–400 °C), recalcitrant (400–550 °C), refractory (550–650 °C) and carbonates (650–900 °C). Although this was a simplification, it could be helpful, considering the considerable amounts of organic contamination involved, that this is a marine sediment and that the modified Fenton treatment reacts mostly with organic compounds. Whereas the labile pool is more reactive and susceptible to degradation, the recalcitrant pool has low degradation rates and the refractory pool that is composed of either artificial chars or highly aromatic compounds, may remain in sediments for centuries [25]. The oxidation treatment reduced the weight losses observed under O_2 in the 200–400 °C and in the 400–550 °C range ($\sim$30% between 200 and 400 °C, and 10% between 400 and 550 °C). Lower influence was observed in the 550–650 °C range, as also observed in another study [20]. The refractory fraction seemed to be affected more by the diminution of reagent pH, rather than by the presence of the oxidant. The introduction of oxygen during oxidation treatments, in the natural organic matter of some soils, was observed during TGA analysis by Dell'Abate et al. [27].

The results of elemental analysis performed on the treated sediment were compared with a calculated value of carbon obtained by adding to the organic C (mass loss during TGA in the 200–650 °C interval), the inorganic C calculated from the mass loss due to the decomposition of carbonates. The result of this calculation was consistent with those of the elemental analysis, although it is evident that this number may be greater than or equal to that from elemental analysis (and in our case, was always greater). The presence of the oxidant and the decrease in the pH of the reagents, lowered the total C of the sediment, in agreement with the other performed analyses.

To assess possible collateral effects of the treatment, the concentration of Cu and Fe in the solution was measured. Results indicated that the treatment enhanced the dissolution of Cu, especially in the oxidised samples. Concentrations of Cu in the liquid were up to 1.02 $mg{\cdot}L^{-1}$ in the 10 : 1 stabilised pH_{in} 0.75 experiment, whereas in the control acid experiments, they reached a maximum of 0.12 $mg{\cdot}L^{-1}$ at pH_{in} 0.75. The concentration of Fe was below the detection limit. The treatment may facilitate the dissolution of metals linked to organic matter (that could be destroyed) or through the formation of complexes in the aqueous phase (because of the increased TOC), as also observed by Villa et al. [15].

Figure 4 presents the results of sequential extraction procedures performed following the Tessier procedure. The amount of Cu bound to organic matter diminished slightly, and the easy exchangeable fraction increased, especially in the oxidised samples. Also, the fraction of Cu linked to the carbonates increased, whereas the fraction bound to the oxides decreased. This could be due to the presence of the stabiliser acting as a precipitating agent for metals in solution. pH seemed to be of lower importance in the release of Cu. Also the amount of Fe bound to organic matter diminished, but as in the solution its concentration was undetectable, it seemed to be redistributed mostly in the oxides fraction.

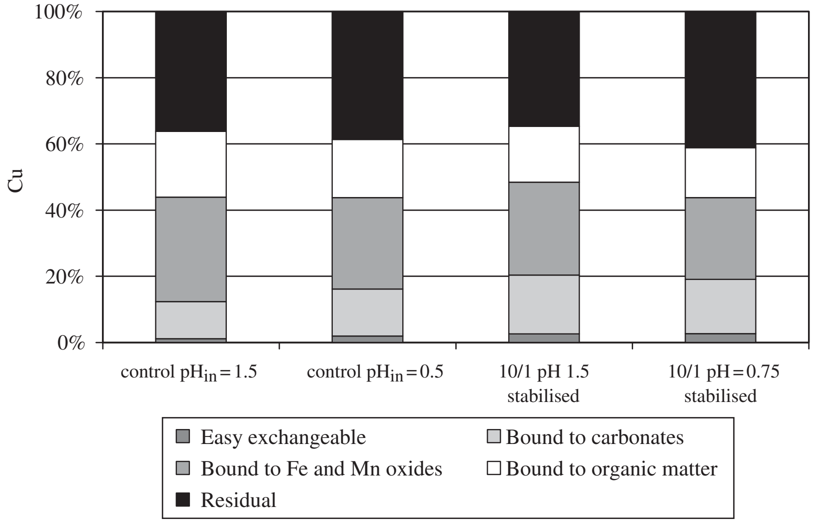

Figure 4. Selective extraction following the Tessier protocol of Cu from the treated sediment.

4. Conclusions

In this study, the effect of a Fenton-like treatment conducted in a marine sediment slurry was evaluated. The results indicate that the treatment was able to change the organic matter to a less hydrophobic state, to reduce the COD of the sediment, to destroy part of the most labile carbon in the 200–400 °C region and, to a lesser extent, of the recalcitrant carbon in the 400–550 °C region. The treatment, however, can be strongly affected by sediments' heterogeneity.

Among possible collateral effects, the oxidation treatment resulted in some Cu mobilisation and in an increase in the easy exchangeable fraction, which is the most mobile. Cu release could be attributed to the destruction of organic matter and, to a lesser extent, to the lowering of pH. Some redistribution of Cu and Fe in the solid phase also occurred.

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