



## Clay mineral-enhanced bioremediation of marine oil pollution

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### ABSTRACT

Three year old laboratory mixtures of Prestige oil, Atlantic sea water and various types of clay mineral powder (Na- and Ca-smectites, palygorskite, synthetic mica-montmorillonite and a low defect kaolinite) contained significantly lower concentrations of extracted oil than the non-clay containing control. As no significant quantities of oil could be detected in the clay samples following solvent extraction, and no expansion of the viscous oil-treated smectite interlayers could be detected by X-ray diffraction, the measured hydrocarbon content is suggested to provide a reasonable estimate of the total oil present. The observed decrease in the concentration of oil over the reaction period is attributed largely to bacterial digestion rather than to hydrocarbon adsorption, with denser populations of cultured oleophilic bacteria in the more strongly digested samples. Overall, the smectites with high specific surface areas and cation exchange capacities induced the highest degree of oil breakdown, and also stimulated the digestion of the heavier aromatic and resin-asphaltene compounds. The presence of bivalent cations at interlayer sites and hydrated surfaces, including abundant  $Mg^{2+}$  derived from sea water, is suggested to minimize the thickness of the diffuse ion layer and thus enhance both inorganic and organic nutrient supply from mineral surface to bacterial cell. Adding clay minerals to marine oil pollution is therefore suggested as an effective and economically interesting way of enhancing the bacterial digestion of contaminating spills.

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### 1. Introduction

Marine oil spills resulting from industrial pollution, accidents and acts of war continue to pose a major environmental threat to the ecosystem and represent a loss of billions of Euros to the global economy (Massoud et al., 1996; Patin, 1999). After the November 2003 Prestige spillage off the coast of NW Spain, there was little chance of physically removing, dispersing or isolating the now estimated ~63,000t of leaked crude oil before being washed up along the Atlantic coastline under the rough sea conditions (Whitfield, 2003). In such cases, attempts to clean up the fuel quickly are often limited and restricted to manual removal from sandy beaches or to using hot pressurized water on boulders and man-made structures.

Although little applied in the Prestige disaster, absorbing or dispersing agents can also be used to help clean up oil spillage (Bayat et al., 2005). Well known are the beneficial properties of clay minerals, which are the most abundant minerals formed during water–rock interaction on Earth. Their charged, large specific surface areas ( $m^2 g^{-1}$ ), and interlayer spaces can potentially adsorb a variety of polar and non-polar organic substances as well as toxic metals (Sposito et al., 1999). As a result, clays and clay minerals find thousands of industrial applications

and are increasingly used for environmental protection and remediation purposes (Murray, 2000; Churchman et al., 2006). In hydrocarbon polluted aqueous systems, colloidal sized clays are additionally known to aid dispersion (Meyers and Quinn, 1973; Owens and Lee, 2003). They increase surface area and accelerate the processes of physical and chemical disaggregation by micelle formation and reduction in the size of oil globules.

An additional property of some clay minerals, which is not so well understood, is their ability to increase the rate of bacterial growth and enhance the degradation of hydrocarbon compounds (Stotzky and Rem, 1966; van Loosdrecht et al., 1990; Chaerun and Tazaki, 2005). It has been suggested that the buffering ability of smectites and their ability to adsorb protons released during hydrocarbon breakdown play an important role in maintaining optimal pH conditions and sustaining bacterial growth (Stotzky and Rem, 1966). Some kaolinites have also been shown to increase the rate of oil breakdown by bacterial digestion (Chaerun and Tazaki, 2005). Here, the formation of C–O–Na–Si complexes on the surfaces of bacterial cell walls associated with particle dissolution is suggested to aid nutrient adsorption by the cell and hence stimulate bacterial activity. Although there is general agreement that mineral surfaces provide favorable conditions for bacteria activity, in many cases the precise mechanisms by which this is achieved remain enigmatic and the experimental observations are not always considered to be consistent (van Loosdrecht et al., 1990).

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