Journal of Hazardous Materials 207–208 (2012) 128–135

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Use of microwaves for in-situ removal of pollutant compounds from solid matrices

A.A. Barba[a,*], D. Acierno[b], M. d'Amore[a]

[a] Dipartimento di Scienze Farmaceutiche e Biomediche, Università degli Studi di Salerno, Via Ponte don Melillo, 84084 Fisciano (SA), Italy
[b] Dipartimento di Ingegneria dei Materiali e della Produzione, Università degli Studi di Napoli "Federico II", P.le Tecchio, 80, 80125 Napoli, Italy

ARTICLE INFO

Article history:
Received 9 January 2011
Received in revised form 19 March 2011
Accepted 19 July 2011
Available online 9 August 2011

This work is dedicated to the memory of Dr. Pino Marucci.

Keywords:
Microwaves
Pollutant removal
Process intensification
Microwaves applicator

ABSTRACT

Thermal treatments are the most used methods to remediate contaminated solids. However, they may seriously damage the otherwise recoverable matrices, especially when mild operating conditions cannot be used. Microwaves recently raised as a powerful tool in industrial engineering for their ability, among other advantages, to offer a selected heating, thus allowing to treat and remove only the undesired components of a matrix. This work approaches the microwave assisted thermal treatments of waste from a physical–chemical point of view. Two recovering operations have been performed, respectively, on a soil contaminated by volatile organic compounds and on a ceramic filter spoiled by soot, using two specially designed prototypes, both realized on pre-pilot scale. The heat and mass transfer balances have then been analyzed in their more general form, and terms related to the use of microwaves outlined. Solutions of the differential equations have been applied to interpret the effects of microwaves on rate and efficiency of the remediation processes.

1. Introduction

The current way to treat wastes is their thermal disposal in special plants [1,2]. Expired drugs in pharmacy as well as hospital waste and contaminated food are destroyed by high temperature treatments in dedicated apparatuses, with afterburning of the exhaust to oxidize possible secondary compounds generated in the first step of the incineration process. Municipal wastes are incinerated, once the humid and the re-usable fractions are separated to increase their calorific value. Once again, an afterburner is required to clean up the exhaust. Thermal treatments are also frequently applied to remediate contaminated soils and groundwater.

Since several decades the potential use of microwave technology as an energy-efficient alternative to current heating technologies in waste-streams was investigated [3–5]. Microwave energy is an innovative tool for heating processes, although microwaves have been firstly adopted for communication purposes [6,7]. Reasons for the growing interest in their applications shown by both Academies and Industries can be found in the occurrence of benefits such as improved products uniformity and yields, reduction in manufacturing costs due to energy saving and shorter processing times (process intensification), unique microstructures and properties of the treated materials and synthesis of new materials that otherwise would be difficult to be produced. These advantages focused the attention on the use of electromagnetic energy in many applications, ranging from materials processing (foods, polymers (curing), wood, ceramics and composites), to mineral treatments and, finally, as reported above, to environmental remediation processes (soil remediation, toxic wastes inertization, and so on) [8–10]. Whether microwaves act in a thermal or a chemical way is still under discussion. As a matter of fact, very interesting results have been obtained, so as to extend their field of application even to drug production in pharmaceutics. Key of all processes above is the energy transfer. In conventional heating processes energy is transferred to materials by convection, conduction and radiation phenomena through the external body surfaces in presence of temperature gradients [11]. In contrast, microwave energy is delivered directly to the materials through interactions between the molecules and the electromagnetic field applied.

Examples of researches on microwave applications in environmental remediation are reported in [4,12–16]. In particular, in Remya and Lin [4] a review of current status of microwave application in wastewater treatment is presented; in Robinson et al. [12], Yuan et al. [13], Huang et al. [14], studies on remediation processes assisted by microwaves of soils contaminated with heavy- and light-hydrocarbons and with poly-halogenated-phenyl compounds, respectively, are discussed to emphasize feasibility and importance of in-situ microwave heating. In Abramovitch

* Corresponding author. Tel.: +39 089969240; fax: +39 089969206.
E-mail address: aabarba@unisa.it (A.A. Barba).

0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2011.07.123

et al. [15], preliminary studies on decontamination process of soils contaminated by toxic metal ions have shown the possibility to immobilize the latter by microwave irradiation, making them virtually unleachable. Finally, in Kulkarni and co-workers [16] a review on current remediation technologies, which included microwave heating, of dioxin polluted soil and sediment is discussed.

All applications above are linked together through the heating step performed by microwave irradiation. Physical and mathematical descriptions of the thermal processes of remediation can be trivial as the tools used are partial differential equations of heat and mass balances, whose terms are consolidated by prolonged and successful applications in engineering, chemistry and physics. Difficulties may arise when new terms have to be introduced into the equations due to other phenomena driving or triggering the processes. Chemical reactions with related heat release, or heat generation caused by electromagnetic fields may thus deeply modify the equations, dramatically changing the results. Therefore, the coupled balance equations of heat and mass transfer, and the electromagnetic field propagation equation have to be simultaneously solved to interpret phenomena occurring during microwave irradiation, in order to attain the final goal of designing and realizing microwaves apparatuses (applicators) able to perform the desired operations.

This work intends to show how microwaves can greatly modify the thermal remediation processes, helping in reducing times and improving efficiencies. The two "case studies" reported refer to both a purely physical process, i.e. the microwave remediation of a soil contaminated by VOCs (volatile organic compounds), and a process with chemical reaction, i.e. the microwave regeneration of a soot trap ceramic filter used to clean up the exhausts of industrial diesel engines. Both applications are currently at the pre-pilot phase of the scale-up process. Energy transfer by microwave irradiation is the actor of the processes, so as the complex permittivity of the irradiated materials is the key parameter governing the processes in their entirety.

The basic equations holding have been analyzed and solved. The heat and mass transfer equations are modified due to the presence of electromagnetic field induced energy dissipation. The modified equations are used to improve design and performance of microwave assisted remediation processes.

2. In-situ remediation thermal processes: Heat and mass transfer aspects

Logistics is one of the crucial points in remediation operations. Often, contaminated sites have large extensions, remarkable amounts of materials to be processed, significant operation costs. Sometimes, the way of working ex-situ can be adopted, transferring solids to chemical plants equipped for decontaminations. However, this implies a number of issues, including operational strategies, safety risks, personnel expertise and money. In some cases the in-situ option is strongly desired: in industrial remediation operations, the possibility of recovering a material without any plant stopping or dismounting gives a tremendous added value to a process.

Whenever a contaminant may be separated from a solid matrix, remediation may be performed, and the easier the separation, the larger the number of usable methods. Among them, thermal treatments have always been of great interest for the number of ways they can be applied and for the easiness of the applications. Possibility of local heat generation induced by an electromagnetic field definitely opened new perspectives. In particular, in-situ treatments are possible using electrical energy, radio frequencies, microwaves. As long as the irradiated material is susceptible of dissipating the ingoing energy flux, the heat may be generated inside and the decontamination may be really performed in-situ.

Starting from this premise, two processes (named case study 1 and case study 2) have been examined from the same point of view: to carry out in-situ remediation by microwaves thermal treatments using pilot-scale applicators, based on both results obtained on lab scale as well as the solutions coming from the mathematical models formulated.

Basically, three equations have been considered to describe mathematically a microwave induced thermal process: the equation of energy, the conservation of mass equation and the Maxwell equations accompanied by the materials' constitutive equations. For all of them, simplified forms have been used.

For each case under consideration, the more general equation of energy can be simplified to the one of temperature (T) variation, provided that the viscous term is negligible, the pressure derivative is zero and Fourier's equation holds. The equation then becomes:

$$\rho C_p \frac{D}{Dt}T = -K\nabla^2 T + \sum_i \Delta H_i r_i + \sum_j \dot{Q}_j \tag{1}$$

where t is the time, ρ is the density, C_p is the specific heat, K is the thermal conductivity; $\sum_i \Delta H_i r_i$ and $\sum_j \dot{Q}_j$ are, respectively, the sums of the terms of heat generations due to phase change/chemical reaction (ΔH_i latent heat, r_i rate of state change/reaction) and heat supplied/removed due to external causes ($\dot{Q}_j$). The latter term can represent the energy dissipation induced by microwave radiation. In particular, starting from the Poynting complex vector, introducing the constitutive equations for isotropic temporally non-dispersive materials and the Maxwell equations, through the use of the Gauss/Green theorem of divergence, the energy dissipation can be calculated by [3,5]:

$$\dot{Q} = \frac{1}{2}\omega\varepsilon_0\varepsilon''\left|\underline{E}\right|^2 \tag{2}$$

where ω is the angular frequency ($\omega = 2\pi f$, f frequency), ε_0 is the vacuum permittivity, ε'' is imaginary part of the material permittivity (loss factor) and E is the electric strength. It is important to note that Eq. (2) quantifies the heat flux dissipated during the microwave irradiation, for given electric field and permittivity of the material.

Finally, for a binary system with constant density (ρ), if Fick's equation holds, the mass variation of the generic A component is:

$$\frac{\partial}{\partial t}\rho_A + \underline{v}\cdot\underline{\nabla}\rho_A = D_{AB}\nabla^2\rho_A + r_A \tag{3}$$

where D_{AB} is the diffusivity of the component A in a B phase, $\underline{v}$ is the velocity field and r_A the consumption rate of A.

3. Experimental

3.1. Materials and instruments

3.1.1. Case study 1

A commercial gardening soil is used as a porous soil model and naphthalene is selected as a model soil contaminant. Methanol is used both as a solvent for contaminant solution (naphthalene is insoluble in water) and as the liquid-phase extractor.

Dielectric properties of soil–water mixtures are measured by an HP 851907B vector network analyzer with dielectric probe meter HP 85070B.

A Soxhlet extractor system and an HP 5890 gas chromatograph are used to extract and to assay the contaminant, respectively.

3.1.2. Case study 2

Soot powder deposition on a trap filter is carried out at the exhaust of a gas-oil burner. A commercially available gas-oil is used; the soot generator apparatus is described in details elsewhere [17]. A ceramic foam with 92% in porosity is used as an inert trap filter for diesel soot (*DS*). The trap filter has a cylindrical shape (76 mm in