Mechanochemical Treatment of Contaminated Marine Sediments for PAH Degradation

F. CANGIALOSI, G. INTINI, L. LIBERTI, M. NOTARNICOLA, T. PASTORE and S. SASSO

Department of Environmental Engineering and Sustainable Development, Technical University of Bari, 8 v.le Turismo, 74100 Taranto (Italy)

E-mail: g.intini@poliba.it

Abstract

Mechanochemical (MC) treatment for degrading recalcitrant harmful PAH compounds (namely, anthracene and benzo[a]pyrene) adsorbed on marine sediments was investigated in laboratory. Optimal operating conditions (*i.e.*, mill rotation speed, milling time, milling-to-milled mass ratio), together with explanation of their physical effects on sediment particle size and specific surface area were assessed, leading to fast (30–60 min) and very effective (>98 %) degradation of both contaminants under the experimental conditions investigated. Attempts carried out through HPLC analysis and DTA checks before and after MC treatment permitted to envisage likely pathways for chemical reactions occurring during the process, yielding amorphous carbon as final product. Further research is planned to exclude the formation of noxious gaseous by-products.

INTRODUCTION

Concern over pollution by polyaromatic hydrocarbons (PAHs) increases worldwide due to the acknowledged carcinogenic nature of some of them, in particular benzo[a]pyrene (B[a]P) [1].

Among commonly proposed methods for eliminating PAHs from contaminated solids (soil, sludge, sediments *etc.*), incineration is often considered environmentally hazardous and expensive, sanitary landfilling simply transfers the threaten to future generations, cost-effective bioremediation requires long reaction times (years) and finds poor application to hydrophobic aromatic compounds like PAHs [2].

Mechanochemistry (MC), a technique proposed since 1902 [3], is today effectively used in several fields, *e.g.* for producing catalysts [4], functional ceramics [5], special-purpose materials [6, 7], hydrogen-storing materials [8] *etc.* It has also been suggested in the last decade for decontaminating organic wastes [9–11]. Contaminated marine sediments are one of them.

Indeed, large amounts (megatons) of marine sediments, partly contaminated by toxic recalcitrant organics like PAHs and polychlorobyphenyls (PCBs) as well as by heavy metals and other inorganic pollutants, will be produced from 2007 during extensive dredging operations recently planned at the industrial harbour of Taranto (Italy).

A systematic experimental investigation was accordingly initiated in order to ascertain MC potentialities to that aim [12–14]. This paper reports the results achieved with PAHs while those obtained with PCBs are described elsewhere [15].
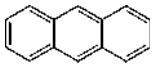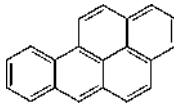
MATERIALS AND METHODS

Representative uncontaminated marine sediments sampled from Taranto's harbour (Table 1) were physically characterized for their grain size distribution (mod. Mastersizer 2000 laser scattering apparatus by Malvern, UK), and for specific surface by BET low-temperature N_2 adsorption (mod. HM 1200 by Mountech, Japan). Chemical composition of matrix was determined by ICP-OES (mod. OPTIMA 2100 DV by PerkinElmer, USA).

Unpolluted sediment samples were artificially contaminated with selected PAHs by standard procedure [16]. To this aim, approx. 400 g of

TABLE 1

Physicochemical characteristics of Taranto's sediments

Compound	Content, %	Udden−Wentworth classification, %	
SiO_2	50.64	Sand	28
CaO	21.31	Silt	20
Al_2O_3	12.32	Clay	52
MgO	3.77	Granulometric size distribution, μm:	
Fe_2O_3	3.46	D_{10}	18.2
Na_2O	3.24	D_{50}	89.5
Loss on ignition (LOI)	1.3	D_{90}	492.1

TABLE 2

Physicochemical characteristics of selected PAHs

Characteristic	Anthracene	Benzo(a)pyrene
Structure		
Molecular mass	178.2	252.3
Solubility at 25 °C, μg/l	59	3.8
Vapour pressure, mm Hg	$2.4 \cdot 10^{-4}$	$5.5 \cdot 10^{-9}$
Log K_{OW} (log k_{OC})	4.5 (4.15)	6.06 (5.74)
Toxicity	NC	HC
Sublimation temperature, °C	340	310−312

Note. NC − no carcinogenic, HC − highly carcinogenic.

sediment were suspended in methylene chloride and the slurry was progressively added with Anthracene (ANT) and B[a]P, adequately representative of PAHs family (Table 2). After two weeks of gentle stirring to achieve adsorption equilibrium and complete solvent evaporation, a contamination degree of 47.5 and 45 mg PAH/ kg_{sed} was measured for ANT and B[a]P, respectively. Chemical analysis of these latter in the sediments was carried out according to USEPA [17]. PAHs were desorbed from the polluted sediment by ultrasonic extraction (mod. Sonica 3200 by Soltec, Italy) using methylene chloride as solvent and anhydrous Na_2SO_4 as drying agent. The extract was then cleaned up on specific solid phase extraction columns and PAHs were determined by high pressure liquid chromatography (mod. 1100 HPLC by Agilent, USA) previously calibrated with a standard mixture of 16 PAH compounds.

A laboratory Fritsch Pulverisette 6 monoplanetary mill was used (Table 3).

Major milling parameters like mill rotation speed ω_p and milling-to-milled mass ratio $R_{b/p}$ (*i.e.*, the total mass of steel balls per unit mass of sediment) were varied as shown in Table 4, keeping ball diameter (6 mm) and sediment mass (50 g) to be milled in each test constant.

Thermogravimetric analysis of sediments was carried out using a mod. 409 EP TG/DT Analyzer by Netsch (D) in a 20 to 1000 °C temperature range with a single ramp at 10 °C/min heating rate in air.

TABLE 3

Fritsch Pulverisette 6 monoplanetary mill technical characteristics

Parameter	Symbol	Value
Vial radius, mm	r_v	50
Vial depth, mm	h_v	70
Vial net volume, ml	V	550
Plate radius, mm	r_p	60.8
Speed ratio	$R = \omega_v/\omega_p$	−0.82

TABLE 4

Milling tests plan

Parameter	Test set							
	1: Variable speed ω_p			2: Variable ratio $R_{b/p}$				
Test #	1.1	1.2	1.3	2.1	2.2	2.3	2.4	2.5
$\omega_{p,}$ rpm	450	200	300			450		
$R_{b/p}$		10		5	10	15	20	27.5

RESULTS AND DISCUSSION

Physical effects during MC treatment

Mechanochemical treatment allows chemically stable large organic molecules to react at relatively mild operating conditions due to the mechanical energy transferred during grinding in special milling apparatuses (planetary, nutation, vibratory, jet, etc.) [18]. Mechanical energy transferred through solid state collisions among milling bodies (usually steel balls) and reactant material may promote both physical and chemical modifications of this latter. Part of the energy is converted to heat, yielding bulk temperature in the vial 100 °C and local (at micro and even nanolevel) temperature 1000 °C, which supplies the activation energy for the chemical transformation required [19]. Remaining mechanochemical energy causes fractures, jams and sliding to macro, meso and microscopic levels, which modify the solid (crystalline) structure of the reactant material [20]. It was demonstrated that primary mechanism of MC demolition of recalcitrant aromatic molecules in planetary mills relies on gradual break of benzene rings by milling energy [21]. Breaking-up phenomena following collisions during milling can be explained as follows: the surface of the material passes from "elastic" to "plastic" state, then the crystalline structure of polymer molecules is subjected to deformation by increasing inner stress until fractures occur. Smaller grains produced by initial milling undergo further breaking-up at higher speed (due to their lower size and larger total surface area) and the process continues until structural changes and chemical reactions are completely achieved in a fast and technically effective manner [22]. This was expected to occur also with PAHs in the present investigation.
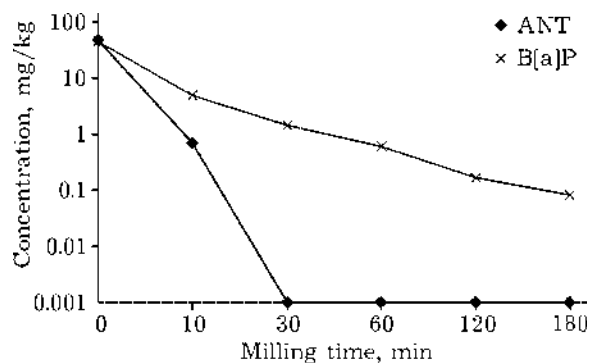

Fig. 1. Mechanochemical degradation kinetics of anthracene and benzo[a]pyrene.

Figure 1 shows that PAH degradation in the sediments examined achieved by MC treatment is very fast, reaching 1 mg/kg concentration (i.e., >98 % removal) after approx. 10 and 45 min for otherwise chemically stable ANT and B[a]P, respectively. The relatively lower degradation rate of B[a]P may be explained by its larger structural complexity than ANT (5 vs. 3 benzene fused rings). Both molecules, however, may be considered totally degraded in practice (residual concentration in sediment 10^{-3} and 10^{-1} mg/kg) after approx. 0.5 and 3 h for ANT and B[a]P, respectively.

Figure 2 shows the modification of grain size distribution as well as the significant reduction of mean grain size of the investigated sediments after MC treatment (60 min milling). The untreated sample is characterized by a principal peak around 70 μm whereas the treated sample shows a lower mode and two central peaks corresponding to 5 and 40 μm, respectively, typical of MC treatments [23].

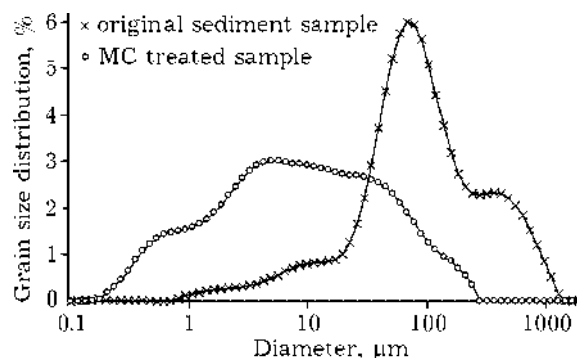Specific surface area (SSA) of the sample also varied significantly with milling, although
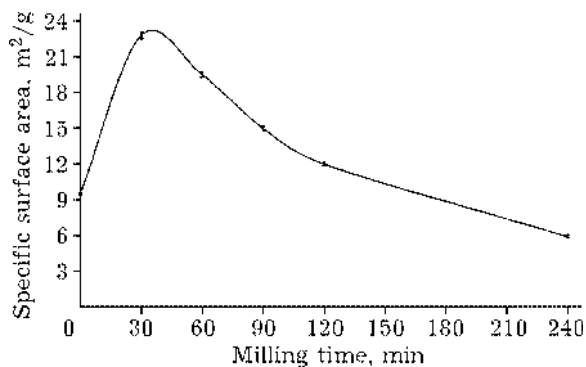

Fig. 2. Granulometric size evolution.

Fig. 3. Specific surface area evolution with MC treatment of marine sediments investigated.

Fig. 5. PAH abatement with MC milling-to-milled mass ratio ($R_{b/p}$): *1* − ANT, 10 min; *2* − ANT, 30 min; *3* − B[a]P, 10 min; *4* − B[a]P, 30 min.

not in a straightforward way, as shown in Fig. 3. SSA increases almost regularly initially, reaching a top after approx. 30 min grinding, and that favours demolition of aromatic compounds into lighter hydrocarbons (see Fig. 1). Prolonged grinding causes SSA rapidly decreasing to almost its initial (or even lower) value, probably due to electric charging (aggregation phenomena) or syntherization of solid particles [24].

The influence of two other major process parameters on MC treatment was also investigated, namely mill rotation speed (ω_p), and milling-to-milled mass ratio ($R_{b/p}$). As expected, Fig. 4 indicates that PAH degradation rate increased with rotation speed under the conditions investigated during tests set #1. This may be easily explained considering that higher mechanical energy is transferred when ball-to-particle collision occurs at higher speed.

Figure 5 shows the results obtained during tests set #2, when the ratio $R_{b/p}$ was varied from 5 to 27.5 with milled mass kept constant at 50 g of sediments and ball diameter at 6 mm.
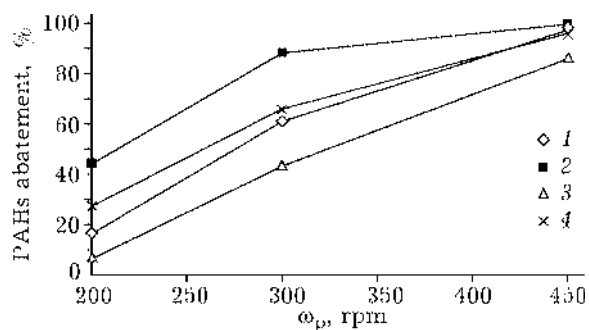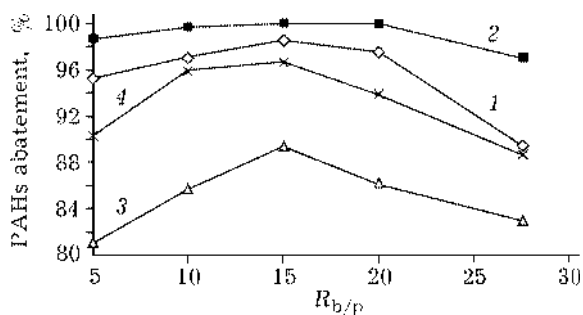
It can be easily seen that there is an optimal $R_{b/p}$ value, ranging between 10 and 20 under the experimental conditions investigated. This optimal range corresponded to 550 and 1050 g overall mass (sediment + balls) loaded into the vial, *i.e.*, accounting for their densities, an optimal vial volumetric filling around 30 %, in full agreement with previous results [15]. As previously explained, below this range MC energy is prevailingly dissipated in ineffective ball-ball collisions while over this range (where vial is flooded by excess milling balls) energy is increasingly wasted in ball-ball friction interactions.

On the basis of the experimental results achieved under the conditions investigated (shown in Figs. 1−5), it may be concluded that physical effects during MC degradation of ANT and B[a]P polluting marine sediments are optimised at grinding duration T = 30 min, mill rotation speed ω_p = 450 rpm and milling-to-milled mass ratio $R_{b/p}$ ~ 15. Under these conditions MC degradation reached over 99 and 90 % for ANT and B[a]P, respectively.

Chemical decomposition during MC treatment

As already stated, the most interesting transformation taking place during milling process deals with structural demolition of aromatic compounds into lighter hydrocarbons, although the chemical pathways of such a transformation are not totally clarified yet [25]. Few attempts are reported in the literature to explain ANT degradation enhanced by external energy (*e.g.*, solar radiation [26] or electromagnetic energy provided by UV rays [27]).

Fig. 4. PAH abatement with MC mill rotation speed (ω_p): *1* − ANT, 10 min; *2* − ANT, 30 min; *3* − B[a]P, 10 min; *4* − B[a]P, 30 min.

In order to throw more light on it, present PAH chemical transformation onto the sediments during MC treatment was checked through chromatographic and DTA analyses. Mallakin *et al.* [26], explaining a complete ANT photomodification pathway, suggested that in the presence of oxygen and under solar radiation ANT reacts initially to form endoperoxides, which are further degraded into different by-products including quinones or diones.

It is similarly suggested now that, due to MC energy, ANT is oxidized to its 9,10-endoperoxide, subsequently oxidized to 9,10-anthraquinone (ANQ) with concomitant generation of hydrogen peroxide, according to following reactions (Schemes 1 and 2).

Figure 6 confirms this initial pathway, showing quantitative evolution of ANT to ANQ with milling.

As for pathway of B[a]P reaction with milling, chromatographic analyses indicate that it is degraded into two isomeric by-products (benzo(k)fluoranthene B[k]F and benzo(b)-fluoranthene B[b]F), according to following reaction (Scheme 3).

As shown in Fig. 7, indeed, curve *1*, related to untreated sediment, confirms B[a]P presence only (peak *a*); curve *2* (after 10 min grinding) shows its transformation into B[k]F (peak *b*) and B[b]F (peak *c*) intermediates; curves *3* and *4* (after 30 and 60 min grinding, respectively) in-
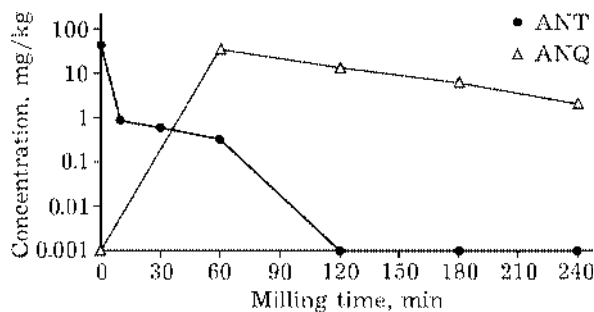

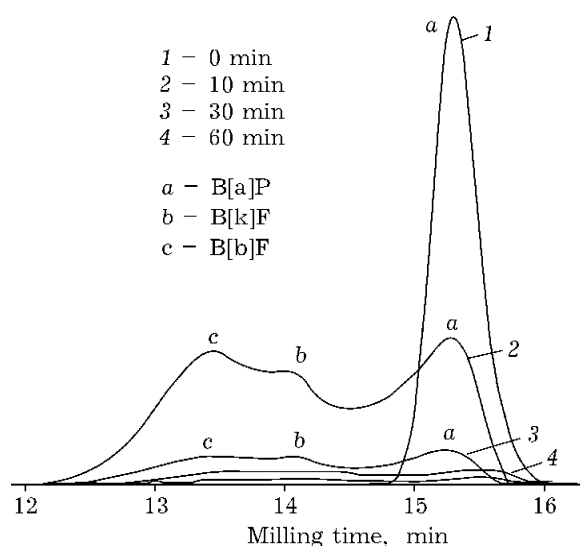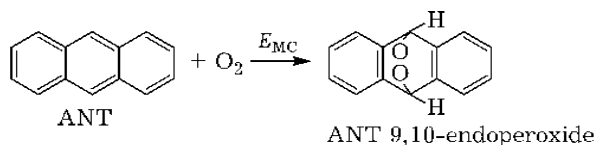Fig. 6. Chemical conversion of anthracene to 9,10-anthraquinone during MC treatment.
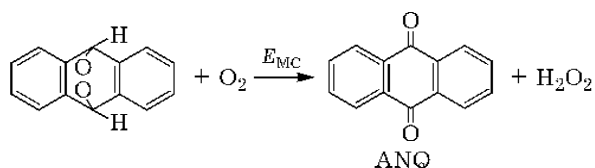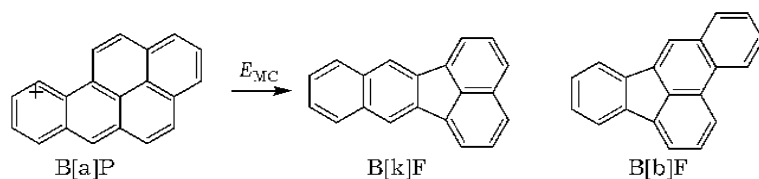

Fig. 7. Chromatografic analysis (HPLC) of B[a]P chemical degradation during MC treatment.
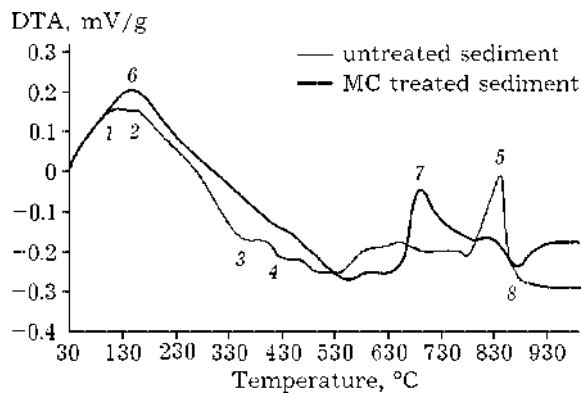

Scheme 1.

Scheme 2.

Scheme 3.

DTA, mV/g

Fig. 8. DTA analyses before and after MC treatment. For design. see text.

dicate that both B[a]P and the above by-products disappeared at the end MC process, to yield (presumably) lighter hydrocarbons.

It was demonstrated [21] that prolonged grinding (over 70 h) shall lead to further complete degradation of ANT by-products to elemental graphite.

Precious information on further degradation pathways of PAHs, yielding finally elemental C, was obtained by DTA investigation, as shown by thermograms in Fig. 8 obtained after 7 h grinding.

a) Untreated sediment:

− two endo-reactions (points *1, 2*) occur from 120 to 155 °C, attributable to the presence of light hydrocarbons;

− two exo-reactions (points *3, 4*) occur from 300 to 430 °C, probably due to combustion of more complex hydrocarbon molecules;

− a typical calcination process may be observed at 840 °C (point *5*).

b) Treated sediment:

− one endo-peak only occurs (at 140 °C), due to release of volatile organic compounds into which PAHs degraded by MC treatment (point *6*);

− carbonation of residual calcite (point *7*) is observed at lower temperature (695 °C) than with untreated sediment (point *5*), due to the transformation of mineralogical composition of this latter after MC treatment;

− in agreement with Zolin [28] one exo-peak finally occurs at 874 °C (point *8*), probably due to combustion of graphite, final product of PAH degradation after MC treatment.

CONCLUSIONS

The following conclusions may be drawn from the results of a laboratory investigation on degradation of selected PAHs (benzo[a]-pyrene, and anthracene) contaminating marine sediments, when submitted to mechanochemical treatment:

1. Optimal set of MC operating parameters requires the highest possible mill rotation speed (450 rpm) and finite milling time (~30 min) in order to decrease granulometric size and increase specific surface area of the particles as well as moderate milling-to-milled mass ratio (10 to 20 to achieve vial volumetric filling ~30 %) under the conditions investigated with 50 g of milled sediment and 6 mm milling ball diameter.

2. Under these conditions MC treatment provided fast (30 min) and effective (>98 %) degradation of both contaminants, ANT and B[a]P, although this latter required longer treatment (1−3 h) for complete decomposition (>99.9 %).

3. Differential thermal analysis (DTA) indicated that both contaminants were completely degraded to graphite after extensive MC treatment (7 h)

4. Chemical identification (HPLC) carried out along milling permitted to throw more light on reaction pathways of MC degradation of both pollutants, some derivatives and by-products of which were identified.

Further studies are in progress to better ascertain this last aspect and to exclude the formation of noxious by-products, eventually released to the air in gaseous form during MC treatment of PAHs.

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