

# Mechanochemical Treatment of Contaminated Marine Sediments for PCB Degradation

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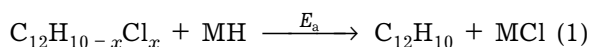
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## Abstract

Results of a laboratory investigation aimed at determining technical efficiency as well as kinetics of chemical degradation of PCBs contaminating marine sediments by mechanochemical treatment with  $\text{NaBH}_4$  are presented. Optimization of operating conditions allowed PCBs degradation to be achieved in very effective (>98 %) and fast (<30 min) manner. A kinetic approach to PCBs degradation accounting for variation of reaction rates for different PCB congeners was developed and a mathematical model useful for scaling-up MC treatment was convincingly achieved.

## 1. INTRODUCTION

Contamination of marine sediments represents a critical health threaten for coastal ecosystem. Hydrophobic contaminants like PCBs, in particular, arriving *via* rain, flood, river discharge *etc.*, tend to accumulate therein partitioning between dissolved and particulate phases [1, 2]. Microbiological PCB dechlorination in contaminated sediments may occur naturally, although very slowly [3]. Chemical PCB degradation by typical nucleophilic reaction may be represented as:



where  $\text{C}_{12}\text{H}_{10-x}\text{Cl}_x$  is a generic polychlorobiphenyl (PCB) congener ( $1 < x < 10$ ), MH is the hydrogen donor metal hydride, MCl is a salt,  $E_a$  is the activation energy.

Reaction (1) was studied in organic solvents showing slow kinetics at ambient temperature [4] and acceptable reaction rate for temperatures in the 120–350 °C range without [5] or with [6] metal catalysts. However, decontamination of soils or sediments from PCBs by alkali metal reductive dehalogenation cannot be achieved in a cost-effective way using organic solvents, due to the cost of these latter. Hence, technologies for allowing dechlorination reaction to occur at solid state are welcome.

Mechanochemical (MC) treatment, where solid-to-solid reactions are activated at room temperature by collisions with milling bodies (usually steel balls) in special high energy milling devices (shaker, vibratory, centrifugal, jet, nutational or planetary mills), reportedly allows for PCB degradation according to reaction (1) to occur at appreciable reaction rate under non-drastring conditions [7–14].

As in classic collision kinetic theory, main steps involved in a MC treatment are [15]:

1. Effective collision among reagent molecules and milling bodies to form an activated complex.
2. Transformation of the activated complex into reaction products.

MC effectiveness depends on collision energy, which in turn is related to operating conditions such as mill rotational speed, ball size, milling-to-milled mass ratio, volumetric mill filling factor *etc.* [16–19].

Several theoretical and experimental studies were aimed at describing kinematics and energetics of high energy milling [20, 21] and correlating grinding conditions and calculated impact energy [22, 23]. Attempts to correlate the energy developed by different mills to size reduction [24] and to structural changes of milled material [25] are also reported.

General theoretical methods for correlating dechlorination rate with milling parameters,

however, are still missing. To that aim, using a computer assisted simulation [8] developed a relationship for PVC dechlorination by MC that could be used for large scale high energy milling apparatuses. They treated dehalogenation as a first order irreversible reaction with a single lumped reaction rate, but this cannot represent adequately the mechanism involved in dechlorination of complex mixtures like PCBs.

By reference to these extremely toxic contaminants, found also in sediments dredged from the industrial and Navy's harbour of Taranto (Italy) [26], the present investigation was carried out with the aim of: 1) establishing technical effectiveness of PCB degradation in marine sediments by MC treatment; 2) investigating MC kinetics and how it correlates to main operating parameters in order to define process scale-up criteria.

## 2. EXPERIMENTAL

### 2.1. Sample preparation and PCBs analysis

Uncontaminated sediment sampled from Taranto's harbour, mainly made by silt (58 %) and clay (37 %), was spiked with Aroclor 1260 (Supelco, PA, USA), a mixture of 209 PCB congeners, containing approx. 12 %  $C_{12}H_5Cl_5$ , 38 %  $C_{12}H_4Cl_6$ , 41 %  $C_{12}H_3Cl_7$  and 8 %  $C_{12}H_2Cl_8$  for an average Cl content of 60 %. The mixture was dissolved in hexane and the solution was poured on sediment samples [27] to yield 300 ppm PCB concentration, representative of maximum contamination level detected at Taranto's harbour. The sample was then added with hexane until complete wetting and then homogenized by 1 h gentle stirring in a glass bottle. Hexane was then allowed to evaporate in a rotavapour for 48 h. As suggested by [28], analysis of PCBs in contaminated samples was carried out by Soxhlet® extraction with hexane, extract concentration, clean-up from organic interferences by means of silica gel, florisil and sulphuric acid and final PCBs analysis with GC/MS (Varian CP 3800)

### 2.2. High energy milling experiments

Pulverisette 6 (Fritsch, Germany), a small-scale laboratory monoplanetary mill, was used

TABLE 1

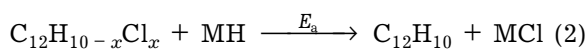
Fritsch Pulverisette 6 mill characteristics

Parameter	Symbol	Value/range
Vial radius, mm	$r_v$	50
Vial depth, mm	$h_v$	100
Plate radius, mm	$r_p$	60.8
Speed ratio	$R = \omega_v/\omega_p$	-0.82

(see technical characteristics in Table 1) with a 500 ml net volume AISI 304 stainless-steel vial and AISI 420C steel balls.

Main mill parameters such as rotation speed, milling times and intermittent stops for heat dissipation can be adjusted and programmed. The mill operated in air and milling treatment was stopped for 10 min every 30th minute to avoid excess temperature increase.

$NaBH_4$  in large excess for sediments contaminated by 300 ppm PCB (14 : 1 on a H : Cl atomic ratio [9]) was used as nucleophilic reducing reagent to carry out the dechlorination reaction:



After preliminary tests had shown that the degradation process is almost over after 1 h (Fig. 1), samples were taken at 10, 20, 30 and 60 min to adequately investigate reaction kinetics.

Main experimental conditions influencing MC dechlorination process [20] were allowed to vary largely as follows:

- mill rotation speed ( $\omega_p$ ): 20 to 50 rad/s;
- balls diameter ( $d_b$ ): 6 and 10 mm;
- balls number ( $N_b$ ): 36 to 1000;
- overall milling bodies mass ( $M_b$ ): 500 to 1350 g;
- sediment mass ( $M_p$ ): 50 to 125 g;
- milling-to-milled mass ratio ( $R_{b/p}$ ) constant at 10

according to the experimental plan shown in Table 2.

## 3. RESULTS AND DISCUSSION

### 3.1. Experimental analysis

Figure 1 shows a typical PCBs degradation profile with time during MC treatment. As anticipated, although the reaction is over after approx. 1 h, its largest part occurs in

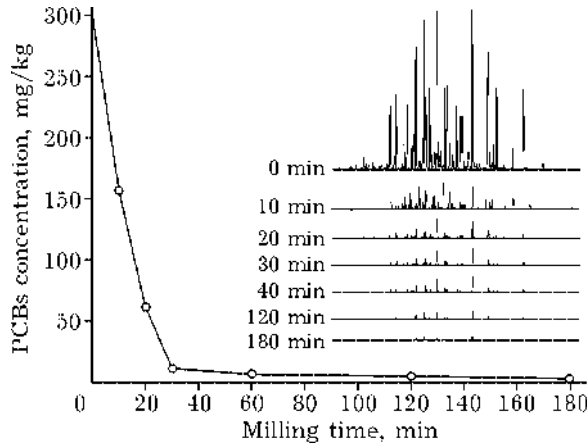


Fig. 1. PCBs concentration vs. milling time and corresponding gas chromatograms.

half that time. As shown by differential disappear of gas-chromatogram peaks, however, it is worth pointing out that each PCB congener in the Aroclor-1260 mixture (corresponding to a specific chlorination degree with its own activation energy and reaction rate) should presumably respond to the treatment

in different ways: the one observed hence is the integral reaction rate of PCBs degradation by MC under the conditions investigated.

In order to assess the influence on MC performance of main operating parameters, these latter were individually investigated.

Figure 2 shows the influence of mill rotation speed on PCB percent decrease, expressed as:

$$\text{PCB}_{\text{dec}}(t) = 1 - \frac{[\text{PCB}]_t}{[\text{PCB}]_0} \quad (3)$$

As expected, PCB degradation improved significantly with mill speed within the experimental range investigated, especially during the first 30 min when the reaction is not over yet (see Fig. 1). This should be clearly related to the increasing energy transferred at higher speed throughout ball-sediment collisions [20, 29, 8].

Figure 3 shows that the variation of PCBs degradation with milled mass (*i.e.*, the amount of contaminated sediment loaded into the mill vial) at constant milling-to-milled mass ratio ( $R_{b/p} = 10$ ) reaches a maximum and then de-

TABLE 2

Milling tests plan

Test set	Tests	$R_{b/p}$	$\omega_p$ , rad/s	$d_b$ , mm	$M_p$ , g	$M_b$ , g	$N_b$
1: Variable speed	1.1.	10	50	10	50	500	124
	1.2.	10	40	10	50	500	124
	1.3.	10	30	10	50	500	124
	1.4.	10	20	10	50	500	124
2: Variable milling mass	2.1.	10	50	10	50	500	124
	2.2.	10	50	10	75	750	187
	2.3.	10	50	10	100	1000	249
	2.4.	10	50	10	125	1250	310
3: Variable 3.1. milling-to-milled ratio	3.1.	5	6	50	250	287	
	3.2.	10	50	6	50	500	575
	3.3.	17	50	6	50	845	1000
	3.4.	27	50	6	50	1350	1585
4: Variable ball diameter	4.1.	10	50	5	50	500	1000
	4.2.	10	50	6	50	500	575
	4.3.	10	50	10	50	500	124
	4.4.	10	50	15	50	500	36

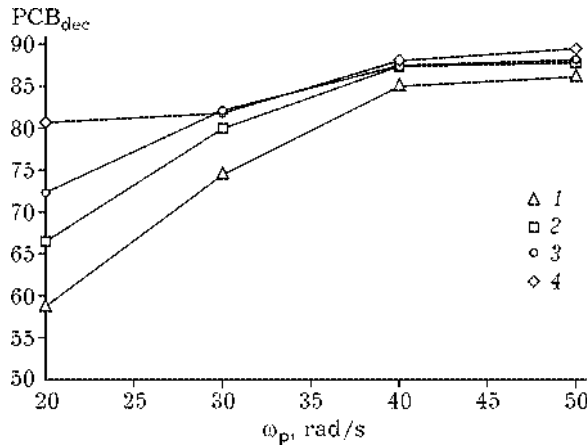


Fig. 2. Tests carried out with variable mill rotation speed ( $\omega_p$ ). Here and in Figs. 3–5: milling time, min: 10 (1), 20 (2), 30 (3), 60 (4).

creases. It should be considered that increasing the sediment mass (with a corresponding ten-fold increase of milling balls mass) occupies a higher volume of the vial.

By reference to the concept of vial volumetric fill factor  $\Phi$  (*i.e.*, the ratio of the vial volume occupied by the balls plus the material to the whole vial volume [30]), one may easily surmise that under the experimental conditions investigated there is an optimal volumetric filling of the vial ( $\Phi \sim 0.3$ , reached with approx. 75 g of sediments and 750 g of balls, *i.e.*, with an overall mass of 825 g loaded into the vial). At lower values the vial appears underloaded (*i.e.*, sediments fill dead space of the vial and do not impact milling bodies) while at larger val-

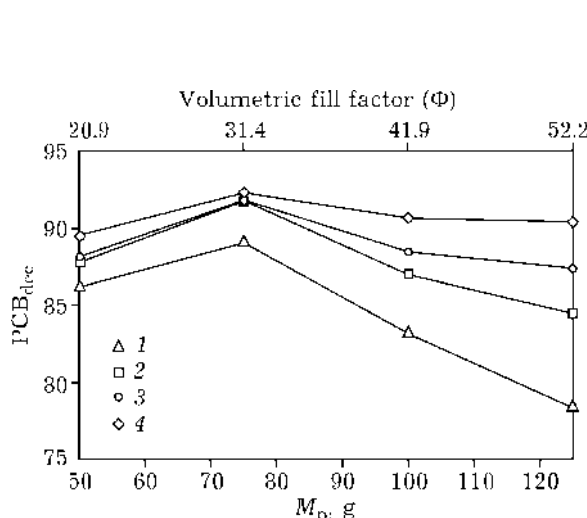


Fig. 3. Tests carried out with variable milled mass ( $M_p$ ). For design. see Fig. 2.

ues it appears overloaded (*i.e.*, an increasing balls number dissipates part of the energy in the attrition process during ball-ball interactions). In this case, less energy would be available to activate the reductive dehalogenation reactions during collisions between the balls and the sediments layered on the vial wall, which is considered the primary mechanism of MC activation in planetary mills [19].

Figure 4 shows the influence of milling-to-milled mass ratio ( $R_{b/p}$ ) varied from 5 to 27 with milled mass set constantly at 50 g.

Again it can be seen that there is an optimal range for  $R_{b/p}$  value, varying between 10 and 20 under the experimental conditions investigated. This optimal range corresponds to 550 to 1050 g overall mass loaded into the vial, *i.e.*, to an optimal vial volumetric fill factor  $\Phi$  around 0.3, in full agreement with previous results (see Fig. 3).

As explained before, below this range milling energy is dissipated in ineffective ball-ball collisions the frequency of which increases with balls number ( $N_b$ ). Over this range, where vial filling is due prevalingly to a higher load of milling bodies, useful MC energy is wasted in ball-ball friction interactions.

Figure 5, finally, shows the influence of balls diameter, varying between 5 and 15 mm. Also with this parameter an optimal range seems to exist, centred around 6 mm. This should be explained by focusing on the mechanism relating ball diameter to impact energy.

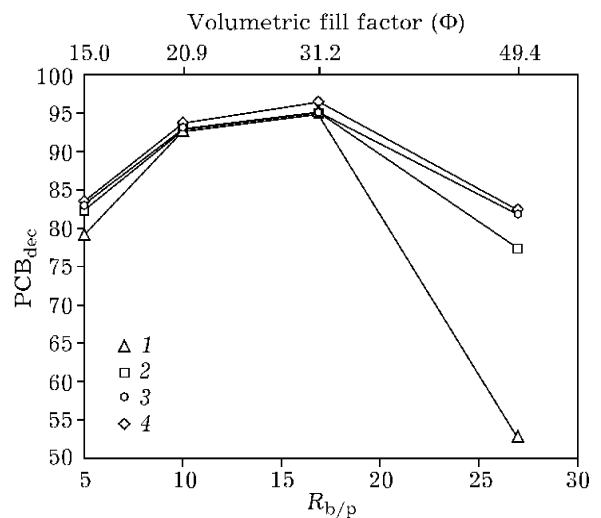


Fig. 4. Tests carried out with variable  $R_{b/p}$ . For design. see Fig. 2.

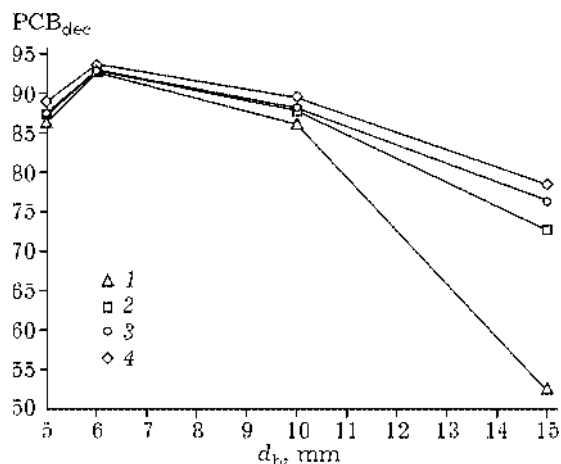


Fig. 5. Tests carried out with different balls diameter ( $d_b$ ). For design, see Fig. 2.

One would expect that the energy supplied in a single impact, at fixed  $\omega_p$  and  $R_{b/p}$  (hence, volumetric vial fill factor  $\Phi$ ), depends on the ball size  $d_b$ , as larger balls would provide more energy to allow PCBs degradation to occur. Figure 5 seems to disagree with such an expectation. To explain this finding, one must take into account the concept of total impacts frequency  $f_t$  (i.e., total number of impacts among balls and vial walls per unit time) [20]. Assuming that impact frequency of a single ball ( $f$ ) is independent on diameter,  $f_t$  can be taken as  $f$  times the ball numbers contained in the vial  $N_b$ . By increasing ball diameter, at constant vial fill factor, the number of the balls decreases and so the total impact frequency does, resulting in less total energy transferred to the milled mass.

The experimental part of this study permitted to evidence conclusively the following influence of main operating parameters in laboratory PCB degradation by high energy milling under the conditions investigated:

- mill speed ( $\omega_p$ ) enhances significantly and directly PCBs degradation efficiency;
- both milling-to-milled mass ratio ( $R_{b/p}$ ) (hence, volumetric vial fill factor  $\Phi$ ) and ball size ( $d_b$ ) exert a critical influence and should be accurately selected in a given range for optimal results, depending on experimental conditions adopted for the system investigated;
- under optimal experimental conditions investigated, MC treatment allowed PCBs degradation to be achieved in very effective (>98 %) and fast (<30 min) manner.

### 3.2. Theoretical analysis

The second part of this study aims at correlating experimental information on the influence of operating parameters with theoretical analysis on PCB dechlorination kinetics in order to define a mathematical model useful for scaling-up MC treatment.

**Kinetics of PCBs degradation.** PCB degradation with  $\text{NaBH}_4$  is a typical aromatic nucleophilic substitution following the second order kinetics according to  $\text{S}_{\text{N}}2$  reaction [31]. Taking into account that a residual concentration ( $\text{PCB}_r$ ) was observed after 1h in all tests (see Fig. 1), reaction rate can be expressed by:

$$\frac{d[\text{PCB}]_t}{dt} = -k([\text{PCB}]_t - [\text{PCB}]_r)[\text{NaBH}_4] \quad (4)$$

Rate parameter  $k$  depends on milling conditions (rotation speed, sediment mass, milling-to-milled mass ratio, balls diameter). Accounting for the large stoichiometric excess of  $\text{NaBH}_4$ , used in these experiments (14 : 1 on a H : Cl molar basis),  $[\text{NaBH}_4]$  term may be neglected in Eq. (4), which assumes the form of a pseudo-first-order reaction rate the solution of which in dimensionless units is:

$$\frac{[\text{PCB}]_t - [\text{PCB}]_r}{[\text{PCB}]_0 - [\text{PCB}]_r} = \eta = e^{-kt} \quad (5)$$

If a single point value is assumed for the reaction parameter  $k$ , the chemical reaction can be referred to as Single First-Order Reaction model (SFOR), stating that each PCB congener (characterized by a given chlorination degree) reacts with the same reaction rate. As pointed out when discussing the chromatograms in Fig. 1, this seems not realistic in the present situation, where a mixture of 209 PCB congeners has been used, each presumably characterized by its own dechlorination activation energy (i.e., its own reaction rate). In the presence of a PCBs mixture (occurring most frequently in practice) dechlorination rate may be better described by a Multiple First-Order Reaction model (MFOR) that considers a distribution of reaction rates. According to MFOR model, independent parallel dechlorination reactions occur, each characterized by its own reaction rate parameter  $k_i$ , described by:

$$\frac{[\text{PCB}_i]_t - [\text{PCB}_i]_r}{[\text{PCB}_i]_0 - [\text{PCB}_i]_r} = \eta = e^{-k_i t} \quad (6)$$

where  $[\text{PCB}_i]$  is the concentration of the  $i$ -th PCB congener ( $1 < i < 209$ ) and  $\eta_i(t)$  represents the  $i$ -th fraction of the mixture not degraded at time  $t$ .

Previous works, carried out in other fields of chemical engineering [32, 33], assumed the reaction rate parameter  $k_i$  to be related to its activation energy  $E_{a(i)}$  by an Arrhenius-like expression. Furthermore, the variability of reaction rate was ascribed to activation energy only, considering all reactions to proceed with a common pre-exponential factor. Galwey *et al.* [34] demonstrated that solid state reactions (like in the present situation) do not necessary follow an Arrhenius-like expression relating  $k$  to activation energy. Hence it was decided to use the MFOR model in a straightforward way, introducing a distribution function for reaction rate.

According to this approach, the dependence of the kinetics from single  $k_i$  was replaced by a continuous dependence, substituting  $k$  by an opportune continuous distribution,  $f(k)$ . The fraction  $dN/dN_0$  of PCB congeners with reaction rate parameter between  $k$  and  $k + dk$  is then given by:

$$\frac{dN}{dN_0} = f(k) dk \quad (7)$$

where  $N_0$  is the total number of congeners.

During the milling process, the continuous distribution of  $k$  (hence the degradation kinetics) changes because some congeners are completely degraded. The overall reactivity of PCBs mixture can then be seen as the sum of independent parallel reactions described by Eq. (6) the linear combination of which, occurring with a rate parameter  $k$  distributed according the  $f(k)$  function, yields the experimentally measured dimensionless residual PCBs  $\eta$ :

$$\eta(t) = \int_0^{\infty} e^{-kt} f(k) dk \quad (8)$$

The above mathematical problem is a Fredholm integral equation of the first kind, the solution of which with respect to  $f(k)$  is an **ill-posed** inverse problem, encountered in many fields of chemical engineering [35, 36]. To solve

Eq. (8) with respect to  $f(k)$  we applied CONTIN method [37], a general purpose constrained regularisation method that finds most parsimonious solution consistent with prior knowledge and experimental data. Indeed *a priori* information is very important to solve an ill-posed problem, enhancing the chance to solve or even to convert it into a **well-posed** one.

In the present case, some hypotheses were made on the form of  $f(k)$  function. First, it was considered that  $f(k)$  is a distribution function (*i.e.*, it is normalized to 1 over the  $[0, \infty]$  integration domain). Second, it was assumed that  $f(k)$  has one peak corresponding to a specific reaction rate value. In fact, the Aroclor mixture used in this study shows a peak in the mass distribution of congeners with a degree of chlorination 7. Moreover, it was considered that dechlorination rate parameter  $k$  decreases with the number of Cl atoms in PCB molecules, as reported elsewhere [38]. On these premises one can expect that reaction rate distribution function  $f(k)$  has a maximum; its position depends on the shape of the function correlating  $k$  to the number of Cl atoms. On the basis of such observations and taking into account that such a function must be defined for positive value of  $k$ , a gamma distribution was initially chosen as trial function for solving Eq. (8).

In the present case, *a priori* knowledge on Fredholm equation solution was sufficient to use the CONTIN algorithm for fitting the coefficients by the non-linear least square method.

Preliminary test with a gamma distribution had shown that such a function is able to describe experimental data [39, 40]. However the location of the maximum was very close to zero, indicating that an exponential function could have been a more parsimonious choice for representing  $f(k)$ :

$$f(k) = \frac{1}{\bar{k}} e^{-k/\bar{k}} \quad (9)$$

An exponential distribution for  $f(k)$  is also meaningful in the sense that one distribution parameter ( $\bar{k}$ ) represents the weighted average of PCBs mixture's reaction rate parameters. When using the distribution function defined by Eq. (9) and the Kernel  $\exp(-kt)$  in Eq. (8), the non-linear least square algorithm allows to calculate  $\bar{k}$  for each test of the experimental plan.

In Figure 6 the experimental data obtained in test set 3.1 are compared with calculated values from SFOR and MFOR models. As shown, taking into account a distribution of reaction rates according to Eq. (9), MFOR model achieves an acceptable agreement with experimental results.

Average reaction rate parameter  $\bar{k}$  in test 3.1 conditions resulted in  $62.8 \text{ h}^{-1}$ . As stated above, the physical meaning of  $\bar{k}$  is strictly related to PCBs mixture composition and to operating conditions, both influencing reaction activation energy.

**Correlation of average reaction rate parameter with mill operating conditions.** When MC treatment operating conditions were optimised to achieve higher PCBs reduction, higher reaction rates were also observed, *i.e.* the fraction of congeners with higher  $k$  values increased. This occurrence implies a shifting of exponential  $f(k)$  distribution towards higher  $k$  values, described by an increase of  $\bar{k}$ . Since  $\bar{k}$  can be considered a good indicator of MC degradation kinetics, a non-linear multiple regression was used to correlate  $\bar{k}$  with mill operating conditions. To this aim, the relationship among  $\bar{k}$  and  $\omega_p$ ,  $d_b$  and  $\Phi$  was sought. Before introducing the mathematical form of regression equation, it is opportune to review qualitatively the fundamental mechanisms involved in MC treatment in planetary mills.

It is known that MC reactions depend on the mechanical action during milling, *i.e.*, the

energy supplied through ball-sediment impacts. The following discussion assumes that any mechanism responsible for a change in the energy transfer during impacts is directly associated to a variation in the reaction rate distribution and hence to  $\bar{k}$ , as in MC treatment of particulate solids the rate of transformation is determined mainly by energetic conditions. Therefore, the qualitative analysis of reaction rate dependence on process parameters is equivalent to the analysis, presented below, of the influence of process parameters on total energy transferred from the milling bodies to the contaminated sediment.

As shown when discussing the role of ball diameter (see Section 3.1), in order to define a relationship between  $\bar{k}$  and  $d_b$  two competing mechanisms must be accounted for, one expressing the increased energy transferred during ball-sediment contacts due to higher mass and the other representing a dumping factor resulting from a decrease in  $f_t$  with exceeding ball size. However, the relationship between total impact energy and  $N_b$  is not straightforward (*i.e.* increasing balls number does not necessarily imply an increase in energy *efficiently* transferred to the milled mass). If the ball number increases (at fixed ball diameter) one expects that total energy (proportional to  $f_t$  and, hence, to  $N_b$ ) should increase proportionally. Nevertheless, increasing  $N_b$  causes a reduction of the available vial volume: the number, as well as the efficiency, of ball-sediment impacts would decrease as a consequence of more frequent ball-ball attrition with dissipation of energy. On such a basis, an increase in energy with  $N_b$  should be expected when the dominant mechanism is the enhanced total impact frequency  $f_t$  (*i.e.*, for low values of  $N_b$ ); when  $N_b$  exceeds an optimal value, energy transfer becomes less **efficient** as more balls in the vial means less effective contacts with the mass to be milled.

In order to generalize such considerations (making them independent on the particular dimensions of the vial used in the present experiments),  $N_b$  can be made dimensionless by normalizing it to the number necessary to completely fill up the vial, expressed by the filling factor  $\Phi$  [20].

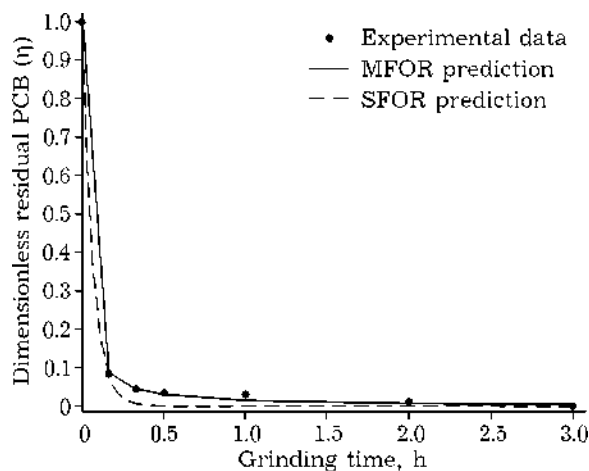


Fig. 6. Calculated and experimental PCBs dechlorination rate. Test set 3.1:  $R_{b/p} = 5$ ;  $\omega_p = 47 \text{ rad/s}$ ;  $d_b = 5 \text{ mm}$ ;  $M_p = 50 \text{ g}$ .

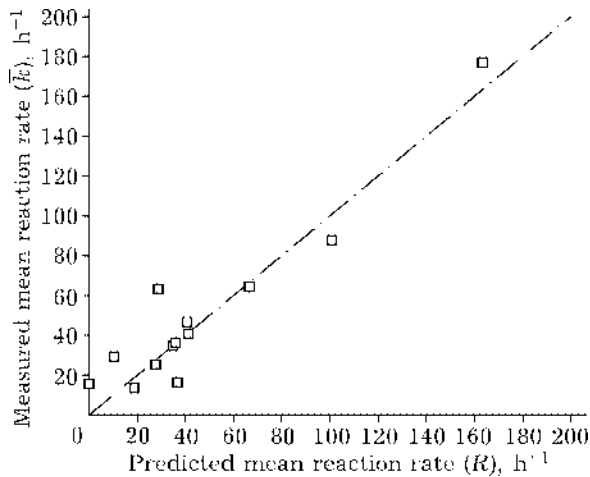


Fig. 7. Comparison between predicted and measured average reaction rate parameter ( $\bar{k}$ ).

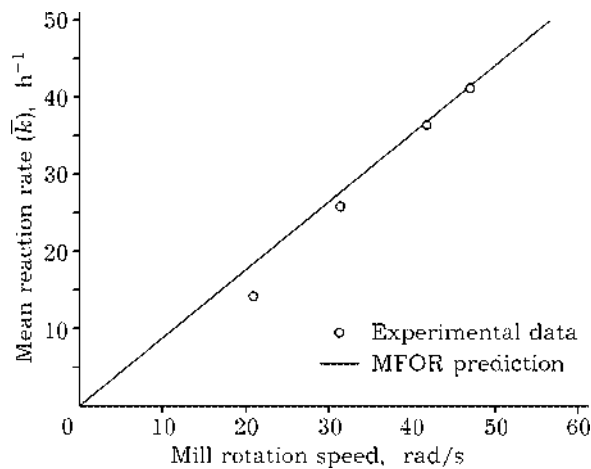


Fig. 8. Predicted and measured dependence of average reaction rate parameter ( $\bar{k}$ ) on mill rotation speed ( $\omega_p$ ).

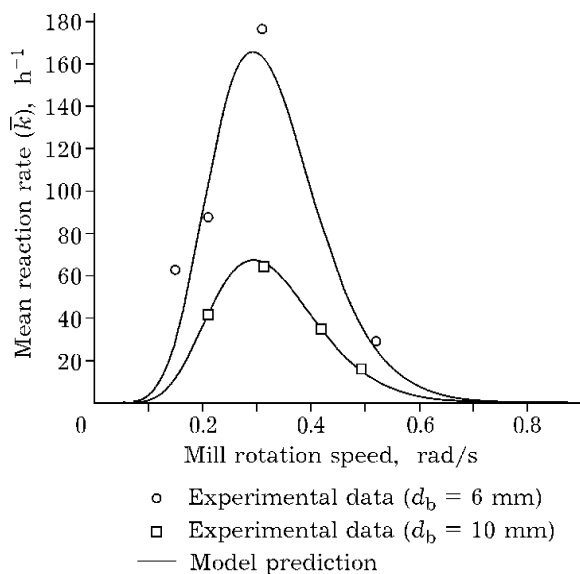


Fig. 9. Predicted and measured dependence of average reaction rate parameter ( $\bar{k}$ ) on vial volumetric filling for 2 ball diameters.

TABLE 3

Values of regression coefficients in Eq. (10)

A	n	a	b	$\alpha$	$\beta$
6.82	1	2113	2.92	9.45	3204

The considerations described above, *i.e.*, the increasing energy efficiently transferred when  $d_b$  and  $\Phi$  are sufficiently low and, viceversa, the predominance of dumping mechanisms when  $d_b$  and  $\Phi$  exceed an optimal range of values – may be described by the following expression:

$$\bar{k} = A\omega_p^n d_b^a \exp(-bd_b) \Phi^\alpha \exp(-\beta\Phi) \quad (10)$$

where  $A$ ,  $n$ ,  $a$ ,  $b$ ,  $\alpha$  and  $\beta$  coefficients depend on mill characteristics. In the above expression a proportional relationship was assumed between  $\bar{k}$  and  $\omega_p$ , as the higher the mill rotation speed, the higher the kinetic energy of the ball. Although this kind of approach is not based on the first principle laws, it uses both experimental data and physical explanation of the mechanisms involved, so that it can give a physical insight into the dechlorination process being involved in MC treatment.

Table 3 reports  $A$ ,  $n$ ,  $a$ ,  $b$ ,  $\alpha$  and  $\beta$  value obtained by non-linear regression fitting of data derived from all test sets carried out in this work.

Using the values in Table 3, Fig. 7 shows the good agreement achieved between  $\bar{k}$  calculated by Eq. (10) and derived from the analysis of global PCBs reaction rate.

According to Eq. (10) and Table 3, a linear dependence of  $\bar{k}$  on  $\omega_p$  should be expected, as clearly confirmed by Fig. 8.

Figure 9 confirms the critical dependence of  $\bar{k}$  on fill factor  $\Phi$  for two ball diameters. As experimentally found in this study, the surmised antagonistic mechanisms lead to optimal  $\bar{k}$  value around 30 % vial filling with both ball diameters as well as with 6 mm compared with 10 mm ball diameter.

#### 4. CONCLUSIONS

After a laboratory investigation on technical efficiency, kinetics and scale-up possibilities of MC decontamination of PCBs adsorbed



on marine sediments, the following conclusions may be drawn:

– under the best operating conditions fast (<30 min) and very effective (>98 %) PCBs degradation may be achieved;

– the best operating conditions must be assessed carefully, as MC treatment efficiency increases linearly with mill rotation speed but discrete values have to be selected for other main parameters like vial filling, milling-to-milled mass ratio and ball diameter;

– a kinetic model based accounting for multiple parallel reactions of different PCB congeners was satisfactorily introduced, characterized by an exponential distribution function yielding a mean reaction rate parameter ( $\bar{k}$ ) correlated to main operating parameters;

– based on these achievements, a mathematical model was developed useful for scaling-up MC treatment.

This approach allows for elucidating the changes in energy transfer for a given MC apparatus at different scales, thus enabling to ease the correlations needed for defining more general scale-up criteria for MC process. Further studies are in progress along these directions.

### List of symbols

$A, n, a, b, \alpha, \beta$  – Regression coefficients

$d_b$  – Balls diameter, mm

$E_a$  – Activation energy, kJ/mol

$E_{a(i)}$  –  $i$ -th congener dehalogenation activation energy

$f$  – Impact frequency of a single ball, Hz

$f(k)$  – Continuous distribution of reaction rates

$f_t = fN_b$  – Total impacts frequency, Hz

$h_v$  – Vial depth, mm

$k$  – Dehalogenation reaction rate,  $h^{-1}$

$k_i$  –  $i$ -th congener dehalogenation reaction rate,  $h^{-1}$

$\bar{k}$  – Mean of exponential distribution,  $h^{-1}$

$M_b$  – Milling bodies mass, g

$M_p$  – Milled sediment mass, g

$N$  – Congeners number

$N_0$  – Initial congeners number

$N_b$  – Balls number (–)

$PCB_{dec}$  – Decrease in PCBs concentration (–)

$R = \omega_v/\omega_p$  – Mill speed ratio (–)

$R_{b/p} = M_b/M_p$  – Milling-to-milled mass ratio (–)

$r_p$  – Mill plate radius, mm

$r_v$  – Vial radius, mm

$S_{N2}$  – Bimolecular nucleophilic substitution

$t$  – Time, h

$x$  – Chlorination degree (–)

$\eta$  – Dimensionless residual PCB concentration (–)

$\eta_i$  – Dimensionless residual PCB<sub>*i*</sub> concentration (–)

$\Phi$  – Vial fill factor (–)

$\omega_p$  – Mill rotation speed, rad/s

$\omega_v$  – Vial rotation speed, rad/s

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