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Influence of inorganic soil components and humic substances on the mechanochemical removal of pentachlorophenol

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The influence of the presence of humic acids of different origin on the catalytic transformation of pentachlorophenol (PCP) by two metal oxides, ferrihydrite and birnessite, using mechanochemical contact was studied. The mechanochemical dry contact with light grinding of PCP and birnessite was more effective than that observed in the presence of ferrihydrite (approximately 70 and 40% of PCP removal after 20 days, respectively). The removal of PCP by birnessite and ferrihydrite was significantly enhanced in the presence of humic acid (HA). The different origin of humic acids (agricultural, forest and commercial) showed a slight influence on the overall reaction. The commercial HA, when mixed with birnessite, was more effective in reducing PCP concentration compared to the others two HAs investigated. The transformation process in the presence of birnessite with and without HA was accompanied by the release of four chlorides per molecule of PCP transformed. © *2004 Kluwer Academic Publishers*

1. Introduction

Pentachlorophenol (PCP) has been listed as priority pollutant by the environmental protection legislation and banned in different countries. This pollutant, which is known to be an endocrine disrupter, has been used as biocide in many agricultural and industrial applications. In a very complex system, like the soil, PCP is known to be transformed (oxidized or reduced) through degradation by several bacterial and fungal species as well as by heterogeneous catalysis by soil colloids. The results of the abiotic degradation of PCP have been obtained almost always from laboratory studies conducted in batch experiments and they cannot be easily applied for the remediation of contaminated soils.

Reactions of hydrolysis, oxidation and polymerization catalyzed by clay minerals and metal (hydr)oxides dominate the abiotic transformation of xenobiotics in soil. The efficiency of the catalytic process depends on structure, chemistry, and surface reactivity of minerals and on structure and properties of the xenobiotic as well as on the reaction conditions [1–8].

Manganese and iron oxides, in particular birnessite (δ-MnO_2), a non-stoichiometric manganese oxide, and ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$), a metastable very reactive iron oxide, are able to oxidize a number of organo-chlorinated pollutants such as phenols and aromatic amines releasing oxidation products in aqueous solution by oxidative coupling reaction mechanisms [4, 7, 8].

The mechanochemical method has recently attracted attention in the degradation of organo-chlorinated molecules [9–11]. The solid contact of the modified surface with the xenobiotic seems to induce the production of radicals, which are involved in subsequent oxidative coupling reactions. Moreover, the mechanochemical procedure could furnish a tool to start the reaction between highly hydrophobic xenobiotics and the minerals without any interference of organic solvents.

The reaction of organo-chlorinated compounds (PCP, chloroanilines, and PCBs) with synthetic birnessite, ferrihydrite or ferruginous-smectite and the comparison of the degradation efficiency between mechanochemical and batch procedures has been carried out [12]. In the removal of the pollutants mechanochemical procedure was more effective than the batch one and the degradation ability of the mineral surfaces was independent on the pH. Moreover, the technique has the potentiality of a sound technological application for the remediation of contaminated soils and sediments.

It is well known that soil organic matter, in particular humic substances, plays important roles in transformation processes of organic pollutants *via* a variety of interactions, including solubilization, adsorption and oxidation [13–15]. Information concerning the influence of the presence of soil organic matter, such as humic substances in association with minerals, on the mechanochemical treatment efficiency would be extremely useful for a potential application in remediation

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strategies. In this study experiments were conducted to examine the effects of soil organic matter, and in particular humic acids of different sources (agricultural, forest and commercial), on the removal of pentachlorophenol by metal oxide surfaces of birnessite and ferrihydrite using a mechanochemical dry treatment process.

2. Experimental procedures

2.1. Materials

The birnessite was synthesized starting from $KMnO_4$ and HCl according to the method outlined by McKenzie [16]. The ferrihydrite was synthesized by dissolving $Fe(NO_3)_3{\cdot}9H_2O$ in distilled water and adding KOH 1 M to raise the pH to 7.5, according to the procedure of Krishnamurti [17]. The synthesized oxides were characterized by X-ray diffraction analysis that confirmed the crystallization of birnessite (reflections at approximately 0.728 and 0.244 nm) and ferrihydrite (reflections at approximately 0.245 and 0.201 nm).

Analytical grade pentachlorophenol was purchased by Sigma Chemical Co. and used without further purification.

The humic acids were extracted from an agricultural soil (Azienda Pantanello, Policoro, Italy), reported as AHA, and from a forest soil (Foresta Umbra, Puglia, Italy), reported as FHA, by a 0.5 M NaOH-0.1 M $Na_4P_2O_7$ mixture under N_2. Extracts were then separated and purified following the IHSS standard procedure [18]. The same extraction and purification procedures were applied to a commercial potassium humate (Humin Tech, Düsseldorf, Germany), reported as CHA.

Purified HAs were characterized with respect to moisture content, ash, functional groups and elemental analysis according to conventional methods [18] (Table I). Additional spectroscopic characterizations of HAs were done by FT-IR analysis.

2.2. Methods

Following our previous experiments [12], PCP (8 mg) and birnessite or ferrihydrite (192 mg), in the presence or absence of different HAs (10 mg of AHA, FHA, or CHA), were manually ground for 10 min using an agate mortar and pestle. Duplicate aliquots of each mixture (10 mg) were immediately extracted with 4 ml of methanol under stirring at room temperature for 20 min and considered as starting samples ($t = 0$). The remaining mixtures were incubated at 30°C in capped porcelain cups. Methanol extractions were again carried out on 10 mg samples after different incubation times. Methanol extracts were centrifuged at 31000 g for 30 min and the supernatants filtered through 0.2 μm regenerated cellulose filters before HPLC analysis. In the case of incubation with HAs, supernatants were purified by Sep-Pak C_{18} cartridges (Waters).

The extent of transformation was evaluated on the basis of the overall disappearance of PCP in the extracts by HPLC analysis. Control experiments, using the grinding technique, were carried out with the three HAs and PCP (without any oxide).

At the same time intervals, 10 mg of each ground mixture were also dispersed in 4 ml of distilled water and stirred for 20 min at room temperature to extract soluble chlorides. Suspensions were filtered and the filtrates were analyzed by ion exchange chromatography (IE-HPLC) for chloride content.

Dry aliquots of mixtures (~90 mg) were also subjected to 8-h soxhlet extractions with 50 ml of a hexane-acetone mixture (1:1 v/v). The resulting extracts were filtered and extraction solvents exchanged with methanol in a rotary evaporator. All experiments were performed in duplicate.

TABLE I Functional acid groups content, ash and moisture contents and elemental composition of the humic acids of different origin

	Commercial HA (CHA)	Forest HA (FHA)	Agricultural HA (AHA)
Total acidity (meq g^{-1})	6.00	5.46	3.99
COOH (meq g^{-1})	4.12	3.27	2.76
Phenolic OH (meq g^{-1})	1.88	1.66	1.23
Ash (%)	2.5	1.2	2.3
H_2O (%)	14.1	8.4	4.1
C (%)	54.1	50.3	50.0
N (%)	1.3	3.7	3.9
H (%)	3.9	4.8	4.7
S (%)	0.4	3.0	0.3
O (%)	40.3	38.2	41.1

2.3. Analytical methods

PCP extracts were analyzed using a Perkin-Elmer LC Mod. 410 high-performance liquid chromatograph, which was operated at a flow rate of 1 ml min^{-1}, a 3.9×150 mm C-18 column and a diode-array detector (Perkin-Elmer, Series 200) set at 220 nm. The mobile phase was a mixture of an aqueous solution of 0.05% phosphoric acid and acetonitrile. The following acetonitrile gradient was used: 30% for 2 min, 30–90% for 10 min before returning to initial conditions.

The concentration of chlorine ions in solutions were measured by ion exchange HPLC using a Dionex DX 500 system equipped with the GP40 gradient pump, the ED40 electrochemical detector working in conductimetry, and the 4×250 mm ion pac AS14A column. The isocratic elution was conducted at a flow rate of 1 mL min^{-1} using a solution 8 mM Na_2CO_3 and 1 mM $NaHCO_3$ as mobile phase.

The elemental composition of HAs was determined by a C H N analyzer (model EA 1108 of Fisons Instruments) in triplicate analysis of each sample. FTIR measurements were made on a Fourier Transform Nicolet 5 PC infrared spectrophotometer using KBr pellets on a spectral range of 400–4000 cm^{-1}.

3. Results and discussions

Since the recovery of PCP was the same both from solvent and soxhlet extraction methods, the easier solvent extraction method was used for all samples.

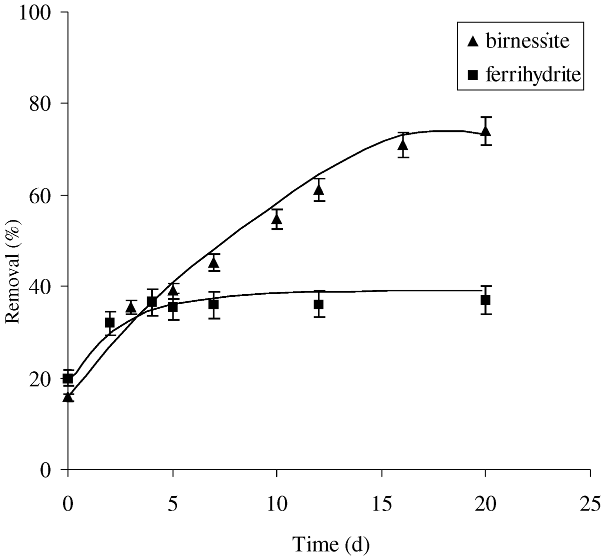

Figure 1 Removal of PCP in presence of birnessite or ferrihydrite.

The removal of PCP by birnessite and ferrihydrite with the mechanochemical treatment is reported in Fig. 1. The reaction catalyzed by birnessite was faster than that catalyzed by ferrihydrite. Approximately 75 and 36% of PCP was removed by birnessite and ferrihydrite, respectively, after 20 days of incubation. Previous experiments conducted with the same catalysts and PCP in methanol suspension resulted in much lower extent of removal of the xenobiotic [12]. Moreover, HPLC chromatograms of extracts from birnessite samples showed the presence of reaction products at lower and higher retention time than that of PCP, which increased during the incubation time, as PCP was removed during the course of the reaction. Otherwise, no products peaks were found in the reaction of PCP with ferrihydrite. Probably, other stable reaction products may be formed, which are not detected with the analytical method employed.

Fig. 2 presents time courses for PCP transformation in the presence of birnessite and the three selected HAs.

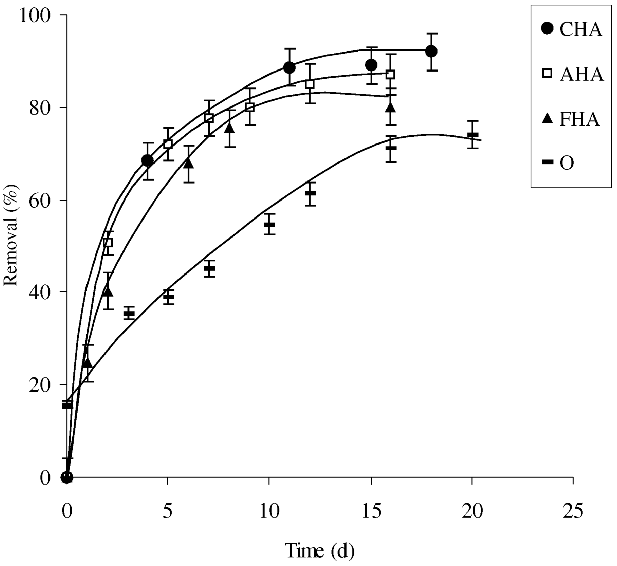

Figure 2 Removal of PCP with birnessite in the absence (O) and in the presence of humic acids: CHA, AHA, FHA.

The rate and extent of reactions were always higher in the presence than in absence of HAs. It is worth mentioning that the mechanochemical interaction of PCP with HAs in the absence of inorganic catalyst did not produce any removal of pollutant after 20 days of incubation. So, mere sorption mechanisms of PCP on humic samples have to be excluded.

The transformation of PCP with birnessite acting alone was 16% at starting time reaching 74% after 20 days of incubation. In the presence of the three selected humic acids together with birnessite, the removal was zero at starting time and reached 92% for CHA, 87% for AHA and 80% for FHA, after 16 days of incubation. Moreover, the removal kinetics was much faster as evidenced by the steeper curve slopes. The influence of HAs on the PCP removal was observed also in the presence of ferrihydrite. In comparison of the oxides alone the ferrihydrite-HA mixture increased the PCP removal from 36.5 to 43.8% after 16 days of incubation (data not shown).

The chemical and spectroscopic results reported in Table I suggest different properties of the three HAs employed in these experiments. The main differences between AHA and FHA samples are the higher acidity and degree of humification of the latter, as evidenced by atomic ratios C/N or C/H, acidic functional groups contents. Compared to the samples FHA and AHA, the CHA showed different characteristics: its high acidity, as pointed out also by the FT-IR spectra, the high C/N and C/H ratios suggest higher stability and condensation degree and an extended humification degree [19].

In spite of differences in chemical and spectroscopic properties of the HAs investigated, the results obtained evidenced that the synergistic effect of HAs on PCP removal seems to be independent on their specific characteristics. Only a slightly higher effect of commercial HA can be appreciated.

Conceivably, the role of organic matter in enhancing the mechanochemical transformation of PCP in the presence of birnessite or ferrihydrite could be explained by an increase in free radicals production promoted by humic acids and mechanochemical grinding. Support for this interpretation is provided where one considers that free radicals are produced in the first step of the reaction between chorophenols and manganese or iron oxides [6] and that humic acids contain indigenous organic free radicals that may be involved to various extent in several chemical processes [20]. However this field of research is open and warrants further study.

With a view to examining the likely release of chlorine atoms from PCP during the reaction, the aqueous extracts were analyzed by ionic chromatography and the pattern of dehalogenation determined. Fig. 3, where the data are presented as μmol of PCP transformed and μmol of chloride released, shows that during the time course of the reaction the overall amount of PCP decreased whereas chloride increased both in presence and absence of humic acid, confirming that catalytic process by inorganic components may result in the dehalogenation of the chlorinated substrate [21]. The chloride released/PCP transformed ratio (μmol/μmol) averaged around 4 both in the presence and absence

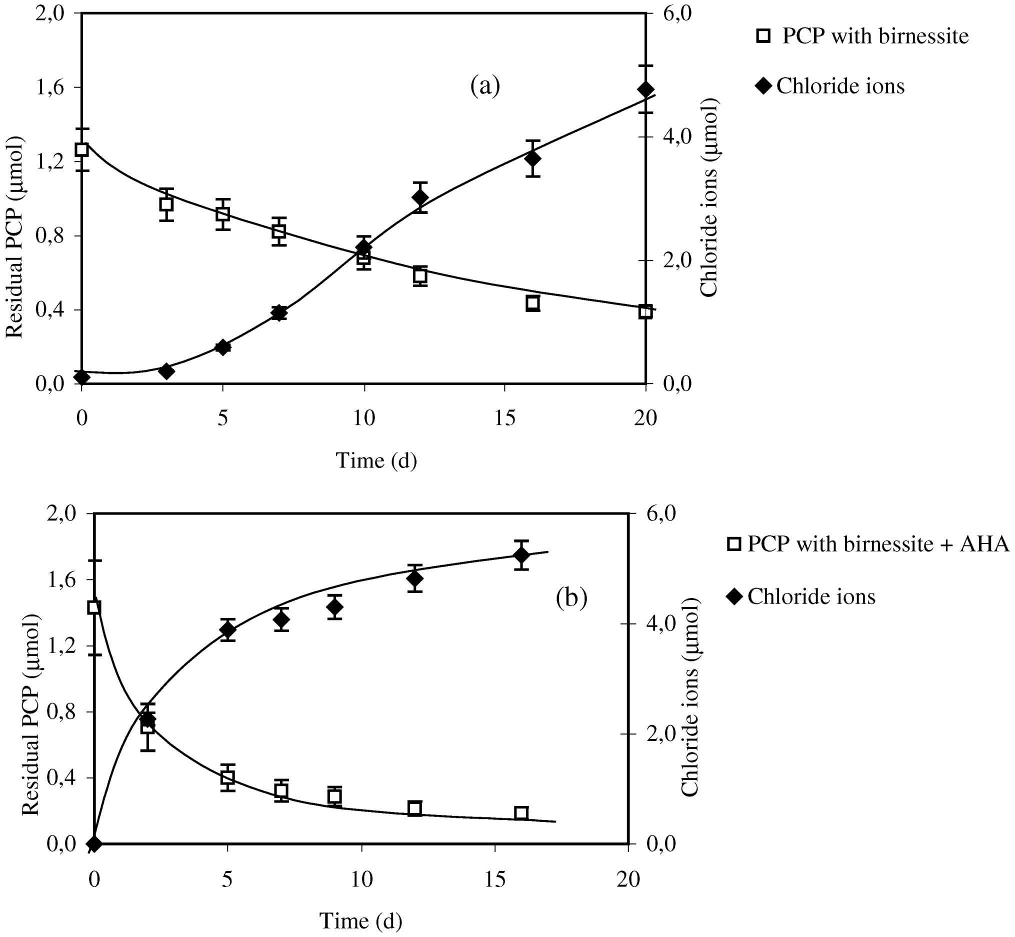

Figure 3 Effect of incubation time on the transformation and dehalogenation of PCP by (a) birnessite and (b) birnessite + AHA.

of HAs. This observation, together to the presence of similar peaks of reaction products observed in the chromatograms let suppose the same reaction mechanisms with and without HAs.

4. Conclusions

To our knowledge, the mechanochemical transformation reactions, which we have suggested via the birnessite- or ferrihydrite-humic acids mixtures, are novel and so far unreported in the chemical literature. The disappearance of the PCP during the reaction is accompanied with an intense dechlorination (four chloride in average are released per molecule of PCP transformed). The presence of humic acids of different origin together with birnessite or ferrihydrite increases the rate and extent of removal reaction. This suggests that humic substances promote generation of radical intermediates by oxidation reaction of PCP with inorganic components. Further experiments will deal with the identification of reaction products in order to study reaction mechanisms involved. The one presented here proves to be a promising technique for decontamination purposes.

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