Solvent extraction of chlorinated compounds from soils and hydrodechlorination of the extract phase

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ABSTRACT

The remediation of soils contaminated with chlorinated compounds was investigated. The process consists of solvent extraction followed by catalytic hydroprocessing (hydrodechlorination) of the extract phase. A mixture of ethylacetate–acetone–water (E–A–W) was adopted as solvent in the extraction process. Tests of extraction of chlorobenzene from a model contaminated soil were carried out and the Langmuir adsorption equation was characterized. The solvent, contaminated with different chlorinated compounds was then hydrotreated with a Pd/C catalyst. The chlorinated compounds tested are: chlorobenzene, hexachlorobenzene and hexachloroethane at various initial concentrations. The reaction runs were carried out at room temperature and at a hydrogen pressure of 1 bar. Hydrotreating of these compounds takes place according to a Langmuir–Hinshelwood mechanism whose kinetic parameters were determined. The experiments show that high destruction efficiencies may be reached in reasonably short times, particularly for hexachloroethane. Longer times are necessary for the aromatic compounds (chlorobenzene and hexachlorobenzene) for which the C—Cl bond is much stronger than that in the aliphatic compound. Time for a 95% destruction efficiency for all experimental runs was determined. A noteworthy finding is that ethylacetate and acetone do not undergo any reaction during hydrotreating. Thus the treated extract solution may be recycled inasmuch as it conserves its full extracting capacity towards chlorinated compounds. A limitation in recycling is the inhibiting effect of benzene on the HDCl rate: benzene produced by HDCl of chlorinated compounds, accumulates in the solvent mixture in the event of recycling. Simulation of the process with the recycling of the solvent was carried out, accounting for the inhibiting effect of benzene.

1. Introduction

Solvent extraction is an ex situ separation and concentration process in which a non-aqueous liquid is used to remove contaminants from soils. The pollutants that can be removed by this technique are apolar or slightly polar: aliphatic hydrocarbons, polynuclear aromatic hydrocarbons, chloro-organic compounds and metal compounds. Extraction efficiency is affected by solvent type and several solvents have been tested for different contaminants. Organic compounds generally have a higher solubility in moderately polar solvents. However, to obtain an efficient contact with the soil, allowing the application of solvent extraction in wet soils, without the need of soil drying, hydrophobic solvents are mixed with an amount of hydrophilic co-solvent. Therefore, solvent mixtures are generally binary or ternary systems. Several solvents (ethanol, 2-propanol, acetone and 1-pentanol) have been tested for the remediation of soils contaminated by polycyclic aromatic hydrocarbons (PAHs). The highest extraction efficiencies were obtained using a ternary mixture composed by 5% 1-pentanol, 10% water and 85% ethanol [1]. A hexane with acetone mixture was tested for its suitability to extract Aroclor 1016 from soil, obtaining an extraction efficiency above 94%. Results suggest that, compared to hexane alone, the 5% acetone mixture extracts approximately 20–30% more Aroclor 1016 from soil than pure hexane [2]. Solvent washing with water–ethanol mixtures was evaluated as a method to remove pentachlorophenol from soils contaminated with wood treating wastes. The 50% ethanol solution proved to be as effective as more concentrated solutions of ethanol. An extraction efficiency up to 87% was obtained at a 1/4 (g/ml) soil/solvent ratio and three crosscurrent wash stages [3]. High extraction efficiency (77–99.9%) of several organic contaminants: chloro-aliphatic, chlorobenzenes, polynuclear aromatic hydrocarbons, PCBs using a ternary system single-phase of ethyl acetate, acetone and water (E–A–W) are reported [4]. The same solvent mixture (ethyl acetate, acetone and water) was adopted for remediation of soils contaminated with hydrocarbons, because it consists of environmentally friendly solvents, which form, for certain compositions, a single phase mixture [5]. Extraction efficiency was evaluated as a function of the

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Nomenclature

c_c	catalyst concentration in HDCl runs (g of catalyst/g of solution)
c_i	concentration of any compound in HDCl runs (g of compound i/g of solution)
c_i°	initial concentration of any compound in HDCl runs (g of compound i/g of solution)
k	kinetic constant (min^{-1})
k_1, k_2	kinetic contants in the network of Eq. (12) (min^{-1})
K	Langmuir constant for the adsorption of chlorobenzene on soil (g of solution/g of chlorobenzene)
K_B	adsorption constant of benzene on catalyst (g of solution/g of benzene); see Eq. (11)
K_{BCl}	adsorption constant of chlorobenzene on catalyst (g of solution/g of chlorobenzene); see Eq. (11)
K_{Cl}	adsorption constant on catalyst of chlorinated compounds (g of solution/g of chlorinated compounds)
m_{cat}	mass of catalyst loaded in the reactor (g)
m_i	mass of reactant BCl, BCl_6 or ECl_6 loaded in the reactor (g)
m_ℓ	mass of solution (E–A–W) loaded in extraction runs (g)
m_s	mass of soil loaded in extraction runs (g)
m_{sol}	mass of solution (E–A–W) loaded in the reactor in HDCl runs (g)
r_i	HDCl reaction rate of compound i (g of i/g of solution × min)
r_1, r_2	HDCl reaction rates in the network of Eq. (12) (g/g of solution × min)
t_{95}	time for a destruction efficiency = 95% (min)
w_{eq}	concentration of chlorobenzene in the extract phase at equilibrium with the solid (g of chlorobenzene/g of solution)
w_s	solubility of chlorobenzene in the solvent (g of chlorobenzene/g of solution)

Greek symbols

α	liquid/solid ratio in extraction runs (g of solution/g of soil)
ω_{eq}	concentration of chlorobenzene on soil at adsorption equilibrium (g of chlorobenzene/g of soil)
ω_{max}	maximum concentration of chlorobenzene on soil at adsorption equilibrium (g of chlorobenzene/g of soil)
ω°	initial concentration of chlorobenzene (or chlorinated compound) on soil (g of chlorobenzene/g of soil)

composition of the E–A–W mixtures. The best choice is a mixture of 50% ethyl acetate, 40% of acetone and 10% of water which assures both high extraction efficiency and the existence of a single liquid phase.

However, in the above papers attention is focused on the efficiency of the extraction process but no mention is made as to how to reduce the toxicity of the extracted phase, in which the contaminants were transferred. The solvent extraction method needs to be integrated with complementary technology suitable for the specific contaminants, to be proposed as a soil remediation process. Due to their stability and low biodegradability many chlorinated organic compounds are classified as recalcitrant compounds. Various technologies such as bioremediation, phytoremediation, physical and thermal processes, chemical oxidation and chemical reduction [6]

are under development for remediation of soils contaminated by chlorinated organic compounds.

As reported by the authors of this paper, catalytic hydrodechlorination (HDCl) is a valid process for detoxifying chlorinated hazardous chemicals both in oily media (e.g. [7,8]) and in aqueous phase (e.g. [9,10]). Catalytic hydrodechlorination is a chemical process analogous to processes widely applied in industry for hydrorefining petroleum. In hydrorefining processes the heteroatoms like nitrogen, sulfur and oxygen present in petroleum products are substituted, through a catalytic reaction, with hydrogen. The corresponding processes are named HDN (hydrodenitrogenation), HDS (hydrodesulfurization) and HDO (hydrodeoxygenation). The result is a fuel free of heteroatoms. By-products are: NH_3, H_2S and H_2O, respectively. In the case of HDCl the by-product is HCl. Since in petroleum components chlorine is rarely present as a heteroatom, HDCl is of little interest in the petroleum industry. By contrast, it is of great interest in toxic waste treatment: the toxicity of many organic wastes (chlorinated solvents, pesticides, PCBs, PCDDs) depends on the presence of the chlorine atoms. Their substitution with hydrogen through HDCl produces an organic molecule whose toxicity is generally absent or much lower than the original chlorinated compound. Therefore, HDCl has been studied and proposed as an alternative industrial process to incineration for the treatment of chlorinated toxic wastes [11,12]. If chlorinated compounds to be treated are in a oily phase HDCl adopts the same catalysts developed for HDN, HDS and HDO. NiMo catalysts supported on Al_2O_3 and pretreated by sulphidation generally show excellent HDCl activity [13]. Operating conditions are typically $250\,^\circ\text{C} < T < 350\,^\circ\text{C}$ and $40\,\text{bar} < P_{H_2} < 100\,\text{bar}$. If the chlorinated compounds are in aqueous phase the HDCl process is promoted by noble metal catalysts (Pt, Pd, Rh) and the process can be carried out at low temperatures ($20\,^\circ\text{C} < T < 50\,^\circ\text{C}$) and low pressure ($P = 1\,\text{bar}$) [9,10]. Among the noble metal catalysts palladium showed the highest activity. The support is generally carbon.

The aim of the present paper is to investigate the possibility of applying soil extraction followed by catalytic hydrodechlorination as a remediation technique for soils contaminated by organic chlorinated compounds. To our knowledge, no information is available on the feasibility of the HDCl process for the contaminated solvent after the extraction process. We first studied the extraction efficiency of chlorobenzene from a contaminated standard soil using a E–A–W solution. Then E–A–W solutions, contaminated with various chlorinated compounds (chlorobenzene, hexachlorobenzene and hexachloroethane) at different concentration levels, were treated in a HDCl reactor using a Pd/C catalyst (palladium supported on carbon).

2. Methodology

In this paper the results of two different types of experiments are reported:

- Solvent extraction runs (or extraction runs).
- Hydrodeclorination runs (or hydrotreatment runs).

2.1. Extraction runs

The extraction runs were performed using an uncontaminated sand from the estuary of the Volturno river. The cumulative-distribution curve (from screen analysis) for this soil is represented in Fig. 1. Soil samples were contaminated with chlorobenzene (BCl), thoroughly mixed, and left undisturbed for 24 h. Then a given quantity of solvent was mixed to the contaminated sample (soil). The sample was agitated for about 10 min using a labshaker
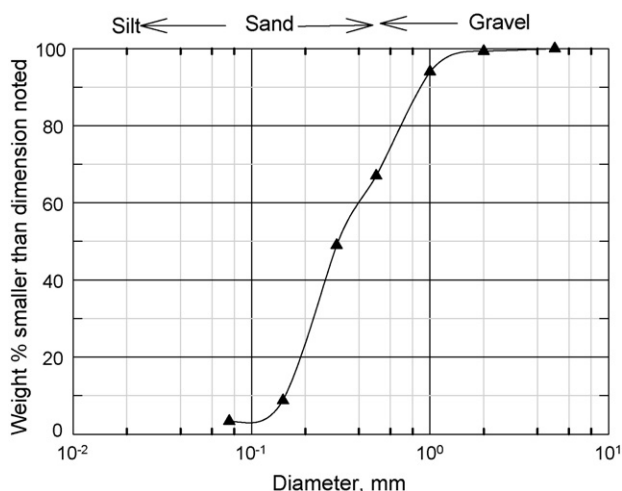
Fig. 1. Cumulative-distribution plot for screen analysis of Volturno river sand.

Fig. 2. Experimental apparatus of HDCl runs.

and then centrifuged at $300 \times g$ (Hettich, mod. Rotanta 460R with rotor 5624). All runs were performed at a fixed liquid/soil ratio ($m_\ell/m_s \cong 2$) and varying the initial concentration of chlorobenzene adsorbed on the soil in the range 1.3×10^{-4} to 4×10^{-3} g of chlorobenzene/g of soil. The liquid/soil ratio ($m_\ell/m_s \cong 2$) ensures at the same time a high efficiency of the extraction process with a limited amount of solvent [5].

Liquid samples of the extract were filtered through Millipore membranes and analyzed by GC-FID (HP 6890) equipped with a fused silica capillary column (HP-ULTRA2, length 50 m, i.d. 0.2 mm, film thickness 0.33 μm). The solvent is the ternary system ethylacetate–acetone–water (E–A–W) which is reported to be particularly suitable for extracting organic contaminants from soils both due to its high extraction efficiency and because it consists of environmentally safe chemicals forming a single phase mixture in a large range of concentrations [4,5]. The composition diagram of this ternary system may be found in [4,5]. The composition of the mixture (wt.%) used in our experiments was: ethylacetate = 40%, acetone = 45% and water = 15% (density = 0.82 g/cm^3). This composition is very similar to the optimized one proposed (ethylacetate = 50%, acetone = 40% and water = 10%) in the case of extracting hydrocarbons [5] but further outside the two-phase region of the ternary system.

2.2. Hydrodechlorination runs

Hydrodechlorination (HDCl) runs were carried out in a 1.5 l stirred glass reactor at constant temperature (20 or 30 °C) and hydrogen pressure ($p_{H_2} = 1$ bar). The reactor was set in a thermostatic bath and equipped with a manometer to measure and control the hydrogen pressure in order to maintain it at the set value. Purge gas (nitrogen) or reacting gas (hydrogen) were fed to the reactor through a sparger at the bottom of the reactor (Fig. 2). A commercial Pd/C was adopted (Escat 11; 5% Pd; Enghelard) to promote the HDCl reactions. The model chlorinated compounds used in the experiments were chlorobenzene (BCl), hexachlorobenzene (BCl$_6$), and hexachloroethane (ECl$_6$), the first two representing compounds with the strongest C−Cl bond strength, the third as a compound with lighter bond strength. Moreover, chlorobenzene is representative of molecules with only one chlorine atom per molecule while hexachlorobenzene and hexachloroethane are representative of molecules with a higher number of Cl atoms on the molecule. These compounds were not hydroprocessed simultaneously but in separate runs. Before each run the following operations were
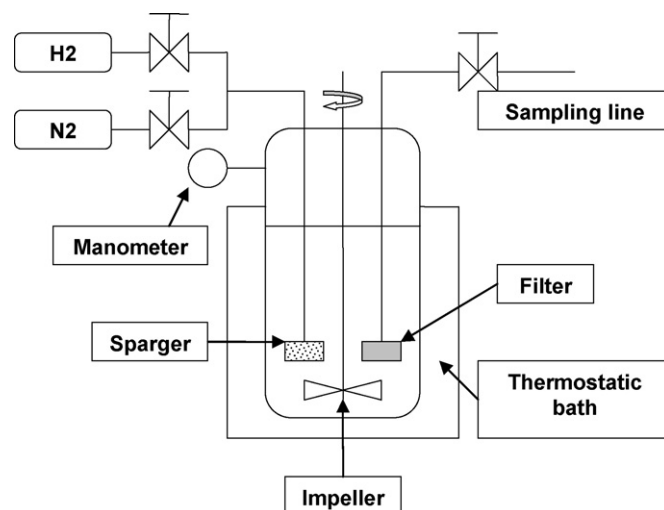
accomplished: (i) loading the solvent (E–A–W) in the reactor; (ii) purging the head space with nitrogen; (iii) loading the chlorinated compound (either BCl or BCl$_6$ or ECl$_6$) followed by its dissolution in the liquid; (iv) loading the catalyst; (v) loading the hydrogen (time $t = 0$ of the reaction). During the run samples of the reacting mixture were withdrawn through a sampling line, filtered, and analyzed by GC. Operating conditions of the HDCl runs are reported in Table 1. In the caption of the same table we also report the solubility of the compounds in the solvent mixture as measured. As run 1 was carried out in the absence of the catalyst, it is a blank run.

3. Results and discussion

3.1. Extraction runs

Extraction runs were carried out to obtain the Langmuir isotherm represented by the following equation:

$$\omega_{eq} = \frac{\omega_{max} K w_{eq}}{1 + K w_{eq}} \tag{1}$$

where ω_{eq} is the concentration of chlorobenzene on soil at adsorption equilibrium (g of chlorobenzene/g of soil), ω_{max} is the maximum concentration of chlorobenzene on soil at adsorption equilibrium (g of chlorobenzene/g of soil), w_{eq} is the concentration of chlorobenzene in the liquid phase at equilibrium with the solid (g of chlorobenzene/g of solution) and K is the Langmuir constant for the adsorption of chlorobenzene on soil (g of solution/g of chlorobenzene). Best fitting procedure was carried out after linearization of Eq. (1). Fig. 3 shows the fitting of experimental data after linearization of Eq. (1) by plotting the ratio w_{eq}/ω_{eq} versus w_{eq}. The values of parameters are: $\omega_{max} = 0.035\,g_{BCl}/g_{soil}$ and $K = 30.3\,g_{sol}/g_{BCl}$. The correlation coefficient is $R^2 = 0.66$. Having determined the Langmuir adsorption isotherm it is possible to determine the extraction efficiency. The mass balance on the system soil/liquid at equilibrium is:

$$m_\ell w_{eq} + m_s \omega_{eq} = m_s \omega^\circ \tag{2}$$

where m_ℓ is the mass of liquid phase [g], m_s is the mass of soil [g] and ω° is the initial concentration of chlorobenzene on soil (g of chlorobenzene/g of soil). Combining Eqs. (1) and (2) one obtains the quadratic equation:

$$K\alpha w_{eq}^2 + (\alpha + K\omega_{max} - K\omega^\circ)w_{eq} - \omega^\circ = 0 \tag{3}$$

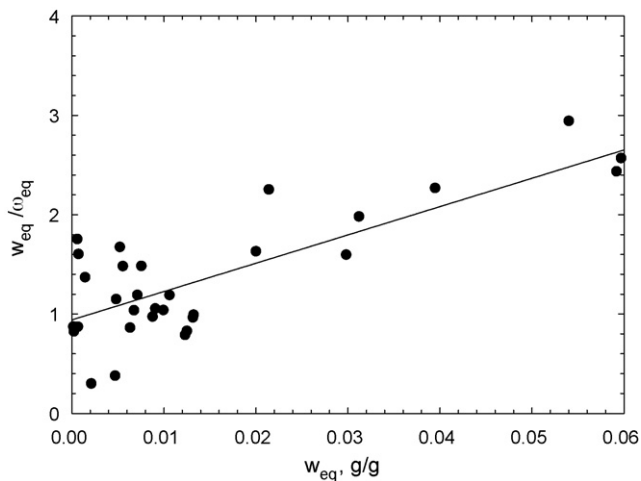where $\alpha = m_\ell/m_s$ is the liquid phase/solid phase mass ratio.

Fig. 3. Linearization of Langmuir adsorption isotherm: $\omega_{max} = 0.035\,g_{BCl}/g_{soil}$; $K = 30.3\,g_{soil}/g_{BCl}$ and $R^2 = 0.66$.

The applicable solution of Eq. (3) is:

$$w_{eq} = \frac{-(\alpha + K\omega_{max} - K\omega^\circ) + \sqrt{(\alpha + K\omega_{max} - K\omega^\circ)^2 + 4K\alpha\omega^\circ}}{2K\alpha}$$

(4)

The efficiency of the extraction process is evaluated through the percent extraction efficiency defined as: $E\%$ = (mass of chlorobenzene in liquid phase at equilibrium/mass of chlorobenzene on soil at $t = 0$) × 100. Hence it is:

$$E\% = \alpha \frac{w_{eq}}{\omega^\circ} \times 100$$

(5)

A simplified solution can be obtained when $w_{eq} \to 0$. Indeed, the Langmuir equation becomes approximately linear ($Kw_{eq} \ll 1$) and Eq. (1) becomes:

$$\omega_{eq} = \omega_{max} K w_{eq}$$

(6)

By substitution of Eq. (6) in Eq. (2) we obtain in place of Eq. (4):

$$w_{eq} = \frac{\omega^\circ}{\alpha + \omega_{max} K}$$

(7)

and from Eq. (5):

$$E\% = \frac{\alpha}{\alpha + K\omega_{max}} \times 100$$

(8)

With the values already obtained of $\omega_{max} = 0.035\,g_{BCl}/g_{soil}$, $K = 30.3\,g_{sol}/g_{BCl}$ and substituting w_{eq} from Eq. (4) into Eq. (5) the percent extraction efficiency ($E\%$) is calculated as a function of the liquid/solid ratio $\alpha = m_\ell/m_s$ for different values of the initial mass
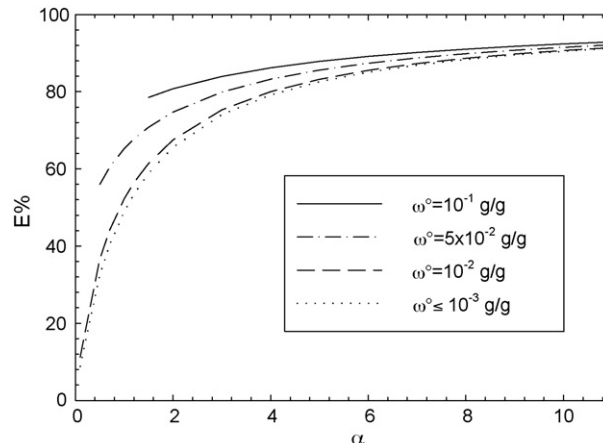

Fig. 4. Extraction efficiency of chlorobenzene for various initial concentrations. The x-axis is the liquid soil ratio $\alpha = m_\ell/m_s$.

fraction concentration ω° of chlorobenzene in the soil (Fig. 4). It must be noted that at larger $\alpha(w_{eq} \to 0)$ and according to Eq. (8) the extraction efficiency tends to be independent of the initial concentration of chlorobenzene in the soil.

Furthermore, it must be considered that chlorobenzene has a limited solubility in the solvent. Namely at $20\,°C$ the solubility is $w_s = 6.5 \times 10^{-2}\,g/g$ (4.74×10^2 mM). Therefore, for any ω° there exists a minimum value of α for which the solubility of chlorobenzene in the solvent would be exceeded. Let α_{min} be this value. Then for $\alpha < \alpha_{min}$ Eq. (4) would produce values of $w_{eq} > w_s$. In this instance the extraction efficiency must be calculated as:

$$E\% = \frac{\alpha w_s}{\omega^\circ} \times 100$$

(9)

Values of $E\%$ in Fig. 4 are reported for $\alpha \geq \alpha_{min}$.

3.2. Hydrodechlorination of chlorobenzene

The hydrodechlorination (HDCl) of chlorobenzene takes place through the substitution of the single chlorine atom with a hydrogen atom and formation of benzene and hydrochloric acid [13]:

$$C_6H_5Cl + H_2 \to C_6H_6 + HCl$$

(10)

Operating conditions of HDCl runs are reported in Table 1. Analysis of liquid samples withdrawn during run 1 indicate that HDCl does not take place at all in the absence of the catalyst. In runs 2–4 HDCl of chlorobenzene is promoted by the catalyst with the formation of benzene. In Fig. 5, as an example, the pattern of chlorobenzene and benzene concentrations, in the presence of a catalyst, is reported versus t for run 4 where the initial concentration of chlorobenzene in E–A–W ternary system is $c^\circ_{BCl} =$

Table 1
Operating conditions of HDCl runs

Run	Reactant	T [°C]	p_{H_2} [bar]	m_{sol} [g]	m_{cat} [g]	m_i [g]	c_c [g/g]	c°_i [g/g]	c°_i [mM]	t_{95} [min]
1	BCl	20	1	4.03×10^2	0	0.46	0	1.14×10^{-3}	8.32	n.a.
2	BCl	20	1	4.03×10^2	0.25	0.46	6.2×10^{-4}	1.14×10^{-3}	8.32	25
3	BCl	20	1	4.00×10^2	0.25	2.00	6.2×10^{-4}	5.00×10^{-3}	36.4	105
4	BCl	20	1	4.07×10^2	0.25	4.40	6.1×10^{-4}	1.08×10^{-2}	78.8	253
5	BCl$_6$	30	1	7.06×10^2	0.50	0.40	7.1×10^{-4}	5.67×10^{-4}	1.63	42
6	BCl$_6$	30	1	7.03×10^2	0.50	1.00	7.1×10^{-4}	1.42×10^{-3}	4.10	93
7	ECl$_6$	20	1	4.93×10^2	0.25	0.51	5.1×10^{-4}	1.20×10^{-3}	3.58	10
8	ECl$_6$	20	1	5.28×10^2	0.25	5.19	4.7×10^{-4}	9.83×10^{-3}	34.1	34

The solubilities of the compounds in the solvent are: chlorobenzene, 6.5×10^{-2} g/g (4.74×10^2 mM) at $20\,°C$; hexachlorobenzene, 1.14×10^{-3} g/g (3.28 mM) at $20\,°C$, and 2.03×10^{-3} g/g (5.84 mM) at $30\,°C$; hexachloroethane, 7.45×10^{-2} g/g (2.58×10^2 mM) at $20\,°C$.
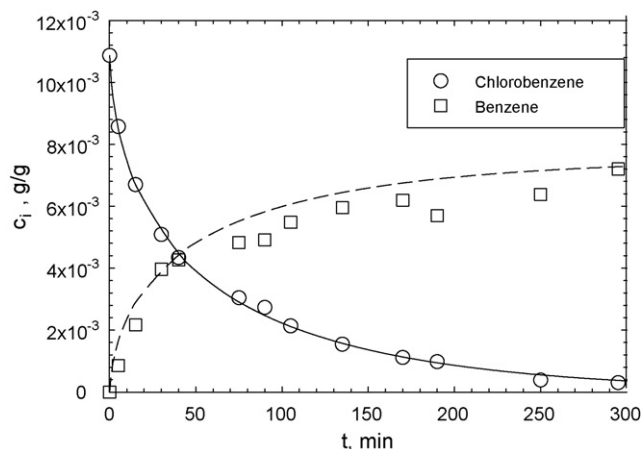
Fig. 5. HDCl of chlorobenzene. Run 4 ($T = 20\,°C$, $p_{H_2} = 1$ bar). Fitting curves are from Eq. (11).

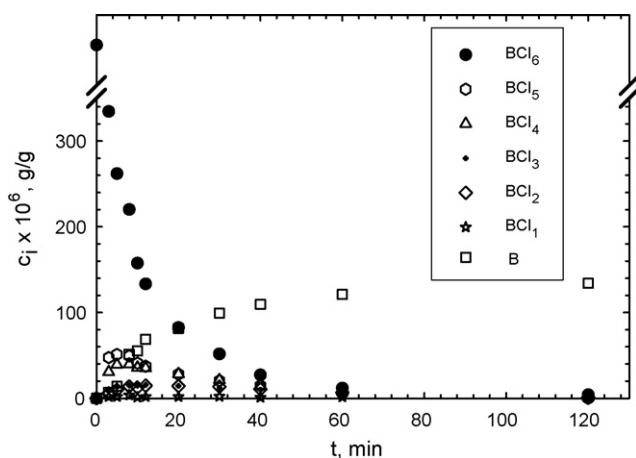**Fig. 6.** Plot of the distribution of reaction products of hexachlorobenzene HDCl as a function of reaction time for run 5 $T = 30\,°C$, $p_{H_2} = 1$ bar.

1.08×10^{-2} g/g (78.8 mM). At lower initial concentration (i.e. run 2 at $c_{BIC}^{\circ} = 1.14 \times 10^{-3}$ g/g or 8.32 mM) the process is much quicker. In a previous paper [9] the kinetics of HDCl of chlorobenzene in water were shown to follow a Langmuir–Hinshelwood mechanism. Even in the present case where the solvent is the E–A–W ternary system the reaction rate follows a L–H mechanism. The overall analysis of the reaction data for runs 2–4 allowed us to determine the kinetic equation as:

$$r_{BCl} = -\frac{k c_{BCl}}{1 + K_{BCl} c_{BCl} + K_B c_B} \tag{11}$$

where r_{BCl} is the reaction rate of chlorobenzene $r_{BCl} = (dc_{BCl}/dt)\,g_{BCl}\,min^{-1}$, k is the kinetic constant (min^{-1}), K_{BCl} (g_{sol}/g_{BCl}) and K_B (g_{sol}/g_B) are the adsorption constants on the catalyst of chlorobenzene and benzene, respectively. Values of these parameters obtained by fitting experimental data with Eq. (11) are reported in Table 2. The solid curves through the data in Fig. 5 are obtained from the kinetic model corresponding to Eq. (11).

3.3. Hydrodechlorination of hexachlorobenzene

The HDCl of hexachlorobenzene takes place according to a complex reaction network, as shown in Fig. 6, which refers to run 5. The reactant (BCl_6), the intermediates (BCl_5; BCl_4; BCl_3; BCl_2; $BCl_1 \equiv BCl$)

and the product B are all detected on the GC chromatograms. Complex reaction networks have been already observed when polychlorinated molecules are treated by the HDCl process [8]. Indeed, the HDCl process proceeds mainly through the substitution of a single chlorine atom for each reactive step, while simultaneous substitutions do not occur or occur to a limited extent [8,13]. Moreover, when more than one Cl atom is present on the reacting molecule the selectivity of the HDCl attack is not high. Therefore, all possible products obtainable from the substitution of one chlorine atom with a hydrogen atom are formed [8]. However, inspection of Fig. 6 shows that the reaction intermediates from BCl_5 to BCl_1 are present in much smaller concentrations than that of both hexachlorobenzene and benzene and that they evolve in the same reaction time range. As a matter of fact, there is no practical interest in studying the kinetics of these intermediates as single compounds. Therefore, in order to analyze the overall kinetics of hexachlorobenzene hydrogenation the concentration data of BCl_5 to BCl_1, were lumped together as $\sum_{i=1}^{5} BCl_i$. After this simplification the data in Fig. 6 are reported in Fig. 7. The continuous curves are the results of the kinetic model to be discussed below.

The network to be analyzed is:

$$BCl_6 \overset{1}{\longrightarrow} \sum_{i=1}^{5} BCl_i \overset{2}{\longrightarrow} B \tag{12}$$

According to the results already obtained for chlorobenzene hydroprocessing, the rates of the two reactions in Eq. (12) were set as:

$$r_1 = -\frac{k_1 c_{BCl_6}}{1 + K_{Cl}\left(\sum_{i=1}^{6} c_{BCl_i}\right) + K_B c_B} \tag{13}$$

$$r_2 = -\frac{k_2 \sum_{i=1}^{5} c_{BCl_i}}{1 + K_{Cl}\left(\sum_{i=1}^{6} c_{BCl_i}\right) + K_B c_B} \tag{14}$$

where r_1 is the reaction rate of hexaclorobenzene $r_1 = (dc_{BCl_6}/dt)\,g_{BCl_6}\,min^{-1}$, r_2 is the reaction rate of intermediate reaction products lumped together $r_2 = d\sum_{i=1}^{5} c_{BCl_i}/dt\,g\,min^{-1}$ and k_1 and k_2 are the kinetic constants (min^{-1}) determined using the HJB [14] algorithm; their values are reported in Table 2. The adsorption constants K_{Cl} and K_B were assumed to be equal to those determined in the analysis of chlorobenzene reaction (i.e. we assume for each chlorobenzene from BCl_6 to BCl_1 the same value
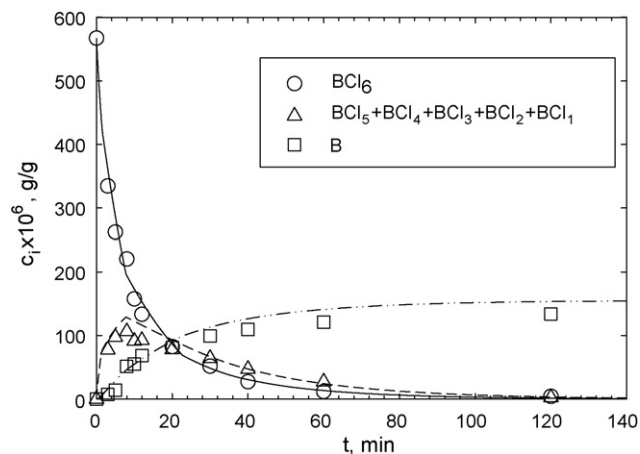

Fig. 7. Distribution of reaction products of HDCl of hexachlorobenzene (BCl_6) as a function of reaction time for run 5. The reaction intermediates (from BCl_5 to $BCl_1 \equiv BCl$) are lumped together. Fitting curves are Eqs. (13) and (14).

Table 2
Parameters of the kinetic equations

Reactant	Eqs.	T (°C)	K_B (g$_{sol}$/g$_B$)	K_{Cl} (g$_{sol}$/g$_i$)	k (min^{-1})	k_1 (min^{-1})	k_2 (min^{-1})
BCl	(11)	20	6.4×10^4	2.7×10^3	4.0	n.a.	n.a.
BCl$_6$	(13) and (14)	30	6.4×10^4	2.7×10^3	n.a.	0.25	0.30
ECl$_6$	(16)	20	n.a.	1.1×10^3	0.42	n.a.	n.a.

of the adsorption constant $K_{BCl_i} = K_{BCl}$). The solid curves through the data in Fig. 7 are Eqs. (13) and (14). Figs. 6 and 7 show that benzene appears in significant amounts even at the initial reaction times. This is an indication of a rapid formation of this compound that can be well modelled by the reaction network in Eq. (12).

3.4. Hydrodechlorination of hexachloroethane

Fig. 8 shows the pattern of hydrodechlorination of hexachloroethane (ECl$_6$) corresponding to run 7. The reaction is quite fast due to the low strength of the C—Cl bond in chlorinated aliphatic molecules. For this reason reaction intermediates of hexachloroethane were detected but only in trace amounts. Therefore, it is not possible to ascertain the network according to which the single chlorine atoms are removed from the host molecule. Thus, the plot in Fig. 8 must be regarded as the result of the overall dechlorination reaction:

$$C_2Cl_6 + 6H_2 \rightarrow C_2H_6 + 6HCl \tag{15}$$

The data of Fig. 8 are well fitted by the reaction rate:

$$r_{ECl_6} = -\frac{kc_{ECl_6}}{1 + K_{ECl_6}c_{ECl_6}} \tag{16}$$

The estimated parameters are: $k = 0.42$ min^{-1} and $K_{ECl_6} = 1.1 \times 10^3$ g$_{sol}$/g$_{ECl_6}$. As a result, the equilibrium constants K evaluated through the best fitting procedure (Table 2) are in the order: $K_{ECl_6} < K_{BCl} < K_B$ with $K_{ECl_6} \cong K_{BCl}$.

Material balances indicate that most benzene is present in the liquid phase, but some minor amounts may remain adsorbed on the catalyst. Indeed, in the case of chlorobenzene HDCl run 4 (Fig. 5) the molar conversion of chlorobenzene to benzene in liquid phase is 94% at $t = 300$ min. In the case of hexachlorobenzene it is 85% at $t = 120$ min.

As shown by Figs. 5, 7 and 8, the kinetic equations hypothesized for chlorobenzene (Eq. (11)), hexachlorobenzene (Eqs. (13) and (14)) and hexachloroethane (Eq. (16)), respectively, together with the kinetic parameters evaluated and reported in Table 2, fit
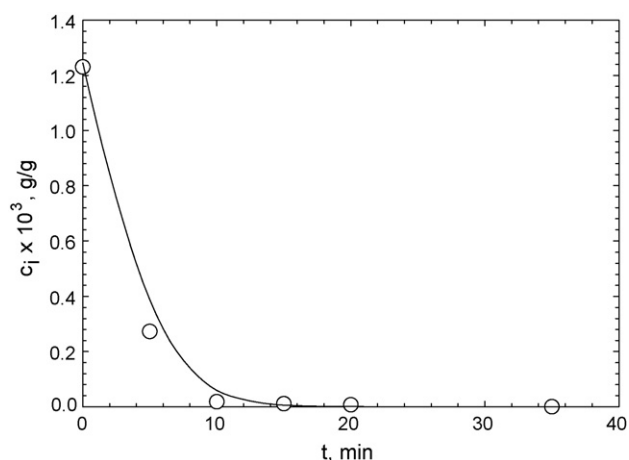

Fig. 8. HDCl of hexachloroethane. Run 7 ($T = 20$ °C, $p_{H_2} = 1$ bar). Fitting curve is Eq. (16).

quite well the rate of reaction of HDCl of each of the three compounds tested. Therefore, it is possible to determine theoretically the destruction efficiency (DE) as a function of reaction time for the HDCl process carried out after the extraction process. DE is defined as the ratio of mass of toxic compound reacted in a defined time to the amount loaded. In a batch and stirred reactor DE% may be expressed as:

$$DE\% = \left(1 - \frac{c_i}{c_i^\circ}\right) \times 100 \tag{17}$$

where c_i° is the concentration of chlorinated compound i (e.g. chlorobenzene, hexachlorobenzene or hexachloroethane) at time $t = 0$ and c_i is the concentration of the same compound at time t. The time required to reach a DE% = 95 (t_{95}) was calculated by integration of the kinetic equations (Eq. (11) for chlorobenzene; Eqs. (13) and (14) for hexachlorobenzene and Eq. (16) for hexachloroethane) and reported in Table 1 for each run. The time depends on the type of C—Cl bond (aromatic compounds need a longer reaction time with respect to the aliphatic ones) and on the initial concentration due to the Langmuir–Hinselwood type kinetics that produces an inhibiting effect of reactants (chlorobenzene, hexachlorobenzene and hexachloroethane) and products (benzene). To compare t_{95} time of different compounds, runs with similar initial molar concentration are considered. They are: run 2 (chlorobenzene), run 6 (hexaclorobenzene) and run 7 (hexachloroethane). It is: $c_i^\circ = 8.32$; 4.10 and 3.58 mM, respectively (see Table 1). The corresponding t_{95} values are 25 min for chlorobenzene; 93 min for hexachlorobenzene and 10 min for hexachloroethane. Another comparison can be carried out at higher initial concentration considering runs 3 (chlorobenzene) and 8 (hexachloroethane) with c_i° equal to 36.4 and 34.1 mM, respectively. In this case t_{95} is 105 min for chlorobenzene and 34 min for hexachloroethane. It was not possible to perform a run for hexachlorobenzene at this concentration level ($c_i^\circ \cong 35$ mM) due its low solubility in the E–A–W solution (Table 1). In conclusion, at the same operating conditions, t_{95} follows this order: hexachloroethane < chlorobenzene < hexachlorobenzene.

Inspection of the chromatograms of liquid samples withdrawn during the HDCl runs of chlorobenzene and hexachlorobenzene showed that no other reaction products besides benzene are formed during the run even for times as long as 300 min. This is a noteworthy result inasmuch as it indicates that the organic compounds forming the solvent (ethylacetate and acetone) are not chemically attacked during hydroprocessing, thus implying that the hydrotreated extract may be recycled and reused in the extraction process. Indeed, it conserves its full extracting capacity towards chlorinated compounds. However, it must be observed that Eqs. (11), (13) and (14) with the relatively high value of the equilibrium constant of benzene ($K_B = 6.4 \times 10^4$ g$_{sol}$/g$_B$) indicate that this compound could have a detrimental effect on the HDCl rate in the case of recycling of the solvent mixture: benzene would accumulate in the liquid phase with an increase in its concentration. The inhibiting effect may be accounted for having determined the adsorption constant of benzene. To determine the inhibiting effect of benzene, we simulated the remediation of a soil contaminated with chlorobenzene at an initial concentration $\omega^\circ = 10^{-3}$ g/g with four extraction stages followed by three hydrotreatments and recycling of the treated extract, to reduce the concentration of chloroben-

Table 3
Simulation of solvent extraction and HDCl of chlorobenzene in the case of recycling of the solvent mixture: results of mass balances

Step	Operation	ω_{BCl} In [g/g]	ω_{BCl} Out [g/g]	c_{BCl} In [g/g]	c_{BCl} Out [g/g]	c_B In [g/g]	c_B Out [g/g]
1	Extraction	10^{-3}	4.0×10^{-4}		0.30×10^{-3}		
	HDCl			0.30×10^{-3}	0	0	0.21×10^{-3}
2	Extraction	4.0×10^{-4}	1.6×10^{-4}		0.12×10^{-3}	0.21×10^{-3}	0.21×10^{-3}
	HDCl			0.12×10^{-3}	0	0.21×10^{-3}	0.29×10^{-3}
3	Extraction	1.6×10^{-4}	6.4×10^{-5}		0.48×10^{-4}	0.29×10^{-3}	0.29×10^{-3}
	HDCl			0.48×10^{-4}	0	0.29×10^{-3}	0.32×10^{-3}
4	Extraction	6.4×10^{-5}	2.56×10^{-5}		0.19×10^{-5}	0.32×10^{-3}	0.32×10^{-3}

Hypothesis: initial concentration of chlorobenzene on soil $w^{\circ}_{BCl} = 10^{-3}$ g/g; extraction efficiency $E\% = 60$; liquid/solid mass ratio $\alpha = m_{\ell}/m_s = 2$; complete conversion of chlorobenzene in HDCl operation, ω_{BCl} = concentration of chlorobenzene on soil; c_{BCl} and c_B are the concentrations in liquid phase of chlorobenzene and benzene, respectively.

zene on soil to a final value below 2.6×10^{-5} g/g (limit value for soils) and calculated the treatment times for a 99% destruction of chlorobenzene in each treatment stage. Input and output concentration at each operation were simply obtained by mass balances, assuming in each extraction step an efficiency $E\% = 60$ (corresponding in Fig. 4 at $\alpha = 2$ for $\omega^{\circ} = 10^{-3}$ g/g) and in each HDCl process a complete conversion of chlorobenzene to benzene. The input and output concentration of chlorobenzene and benzene obtained by mass balances at each step are reported in Table 3. It can be observed that benzene accumulates in liquid phase from 0 to 0.32×10^{-3} g/g. The time required by each HDCl step to obtain a 99% conversion of chlorobenzene (DE% = 99) was calculated by integration of Eq. (11) with the constraint that the initial concentration of benzene would be that reported in Table 3. Thus, in the case of solvent recycling the time required by each HDCl step is: $t_1 = 12$ min, $t_2 = 20$ min and $t_3 = 24$ min. The subscript specifies the treatment stage number. If it were possible to eliminate the benzene from the treated extract phase before its recycling, the corresponding reaction times would be: $t_1 = 12$ min, $t_2 = 6$ min and $t_3 = 3$ min, which means 56 min overall without abatement of benzene, and 21 min if benzene were eliminated from the liquid phase. Finally, it must be observed that removing the benzene from the liquid phase is not only a necessary process to allow recycling of the solvent mixture, but also an environmental requirement since benzene is a toxic compound with carcinogenic effects for human.

4. Conclusions

Organic chlorinated compounds can be removed from contaminated soils by a solvent extraction procedure using the ternary system ethylacetate–acetone–water (E–A–W) as solvent. We proved that the extract phase containing the chlorinated compound can be efficiently hydroprocessed at room temperature with a Pd/C catalyst. This process substitutes a hydrogen atom for each chlorine atom of the host compound. Our experiments showed that hydrotreating of the extract phase completely removes the chlorine atoms from the host molecule and that ethylacetate and acetone do not undergo any reaction. This is a noteworthy result inasmuch as it indicates that the hydrotreated extract may be recycled since it conserves its extracting capacity towards chlorinated compounds. Our experiments also showed that the HDCl process can be completed in reasonably short times. However, benzene produced in the HDCl of chlorinated aromatic compounds has an inhibiting effect on the HDCl reaction rate and limits the possibility of recycling. For this

reason and due to the toxic characteristic of benzene the process should be completed with a complementary operation to remove benzene from the liquid phase after the HDCl unit and before its reuse in the extraction unit. Studies need to be conducted to determine methods for effectively removing benzene from the treated solvent.

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