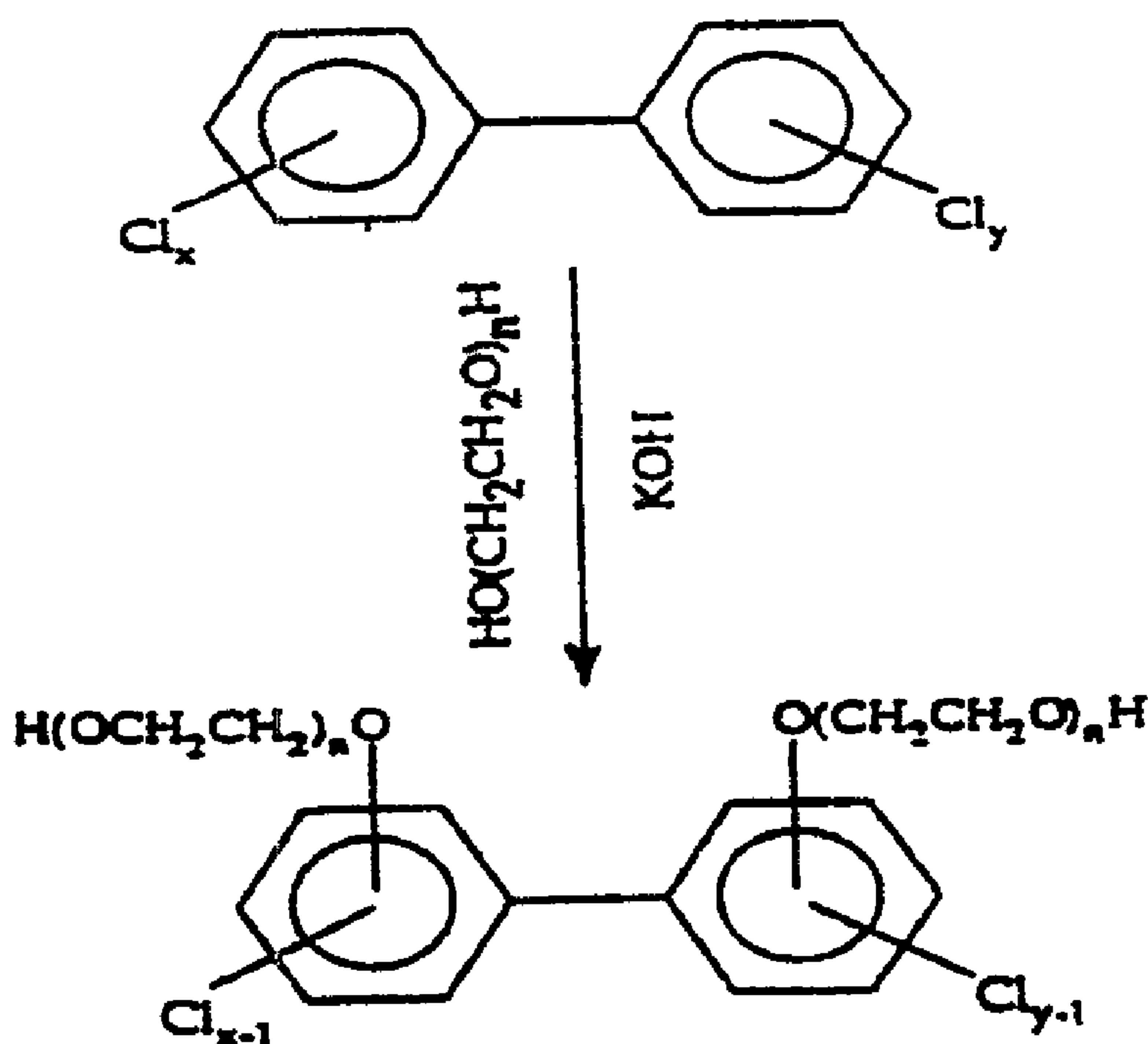




(86) Date de dépôt PCT/PCT Filing Date: 1996/08/21
(87) Date publication PCT/PCT Publication Date: 1997/03/06
(45) Date de délivrance/Issue Date: 2008/03/18
(85) Entrée phase nationale/National Entry: 1998/02/25
(86) N° demande PCT/PCT Application No.: EP 1996/003682
(87) N° publication PCT/PCT Publication No.: 1997/007858
(30) Priorité/Priority: 1995/08/25 (ITTO95A000702)

(51) Cl.Int./Int.Cl. *A62D 3/38* (2007.01)
(72) Inventeurs/Inventors:
TUMIATTI, WANDER, IT;
KAPILA, SHUBHENDER, US
(73) Propriétaire/Owner:
SEA MARCONI TECHNOLOGIES DE WANDER
TUMIATTI S.A.S., IT
(74) Agent: MACRAE & CO.

(54) Titre : PROCEDE DE DECONTAMINATION ET DE TRAITEMENT A CONTRE-COURANT OXYDATIF D'UNE
MATRICE LIQUIDE, GAZEUSE OU SOLIDE
(54) Title: PROCESS FOR THE DECONTAMINATION AND TREATMENT WITH OXIDATIVE COUNTERFLOW OF A
LIQUID, GASEOUS OR SOLID MATRIX



(57) Abrégé/Abstract:

The process includes the phases of filling the first reactor (10) with a particulate support (22), that is a solid matrix to be decontaminated and treated or it is impregnated by a liquid or gaseous matrix to be decontaminated and treated and inlet at one end (23) of the reactor (10) an oxidative flow and trigger at the opposite end (24) a thermoxidation reaction, in such a manner that a mobile flame front (26) is generated in the direction opposite (28) to the oxidative flow having a temperature of at least 1200 °C so to substantially decompose or destroy contaminants, undesired substances and compounds present initially in the matrix. Preferably, prior to triggering the thermoxidation reaction, the particulate support (22) is mixed and/or treated with a decontaminating reagent.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

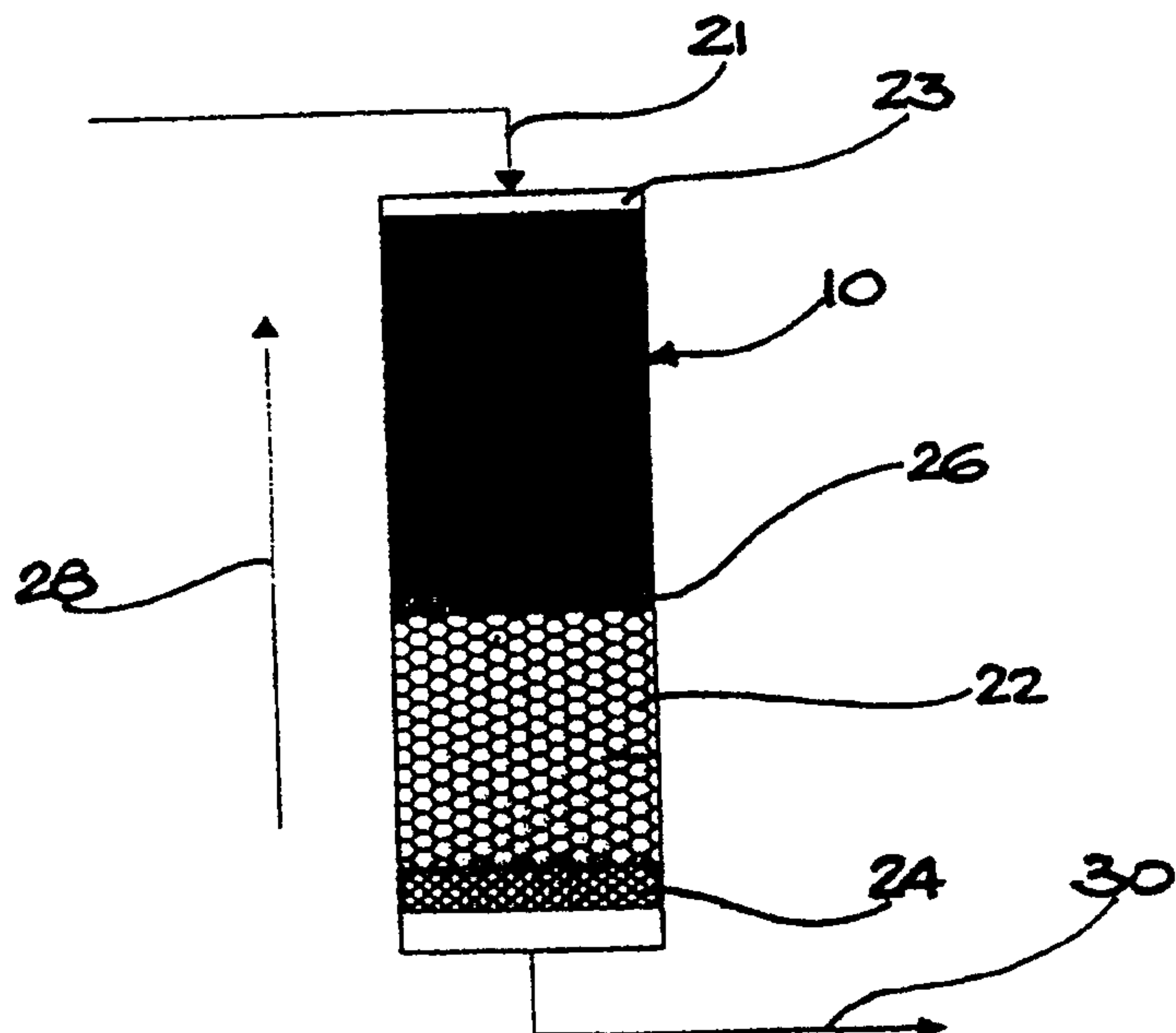
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A62D 3/00	A1	(11) International Publication Number: WO 97/07858 (43) International Publication Date: 6 March 1997 (06.03.97)
(21) International Application Number: PCT/EP96/03682 (22) International Filing Date: 21 August 1996 (21.08.96) (30) Priority Data: TO95A000702 25 August 1995 (25.08.95) IT (71) Applicant (for all designated States except US): SEA MARCONI TECHNOLOGIES DI WANDER TUMIATTI S.A.S. [IT/IT]; Via Principi d'Acaja, 11, I-10143 Torino (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): TUMIATTI, Wander [IT/IT]; Via Bessaneisa, 24/19, I-10098 Rivoli (IT). KAPILA, Shubhender [US/US]; 10576 Greenlefe Drive, Rolla, MO 65401-7799 (US). (74) Agents: GERBINO, Angelo et al.; Jacobacci & Perani S.p.A., Corso Regio Parco, 27, I-10152 Torino (IT).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: PROCESS FOR THE DECONTAMINATION AND TREATMENT WITH OXIDATIVE COUNTERFLOW OF A LIQUID, GASEOUS OR SOLID MATRIX

(57) Abstract

The process includes the phases of filling the first reactor (10) with a particulate support (22), that is a solid matrix to be decontaminated and treated or it is impregnated by a liquid or gaseous matrix to be decontaminated and treated and inlet at one end (23) of the reactor (10) an oxidative flow and trigger at the opposite end (24) a thermoxidation reaction, in such a manner that a mobile flame front (26) is generated in the direction opposite (28) to the oxidative flow having a temperature of at least 1200 °C so to substantially decompose or destroy contaminants, undesired substances and compounds present initially in the matrix. Preferably, prior to triggering the thermoxidation reaction, the particulate support (22) is mixed and/or treated with a decontaminating reagent.



Process for the decontamination and treatment with oxidative counterflow of a liquid, gaseous or solid matrix

This invention refers to a decontamination and treatment process for a liquid, gaseous or solid matrix, containing contaminants, undesired substances or compounds.

Numerous organic contaminants represent, in fact, a danger for the environment and public health. Some classes of them (i.e. halogenated substances) have a high priority, due to their chemical inertia and resistance to natural degradation in the environment. They, in fact, maintain characteristics of persistency, harmfulness and toxicity for a long time (decades), with the possibility of bio-accumulations in the various species, until they determine permanent damages in living organism and in mankind. Some of these halogenated compounds (i.e. PCDDs and PCDFs) present also carcinogen, teratogen and mutagen risks.

In the last decades several methods for the treatment and the disposal of halogenated organic compounds have been proposed, as controlled thermodestruction and the use of "secure" landfills. However, it has been found that, for the disposal of materials contaminated by toxic and halogenated compounds, these methods are not completely satisfactory, especially on large scales, and when the recovery of recyclable materials is desirable. In some instances, the correct disposal of wastes containing these compounds results impossible, since some Countries are totally lacking appropriate disposal systems (i.e. currently in Italy).

Several chemical processes for the decomposition of halogenated organic compounds have been developed. Pytlewski and Smith, in their U.S. patents No. 4 337 368 and No. 4 236 090

demonstrated that polyhalogenated organic compounds were found to be decomposed by the reaction with a pre-formed organo-sodium reagent, such as sodium naphthalenide, NaPEG. In these cases, the use of metallic sodium metal requires special handling procedures and specialized equipment, since even just traces of water in suspension must be eliminated, so as to avoid dangerous side reactions, that could cause explosions and fires.

Later, Brunelle of General Electric, in U.S. Pat. No. 4 351 718 and No. 4 353 793, proposed the removal of polychlorinated aromatic hydrocarbons dissolved in an organic solvent, such as transformer oil, treating the solution with a mixture of polyethylene glycol or monocapped polyalkyleneglycol alkyl ether and an alkali metal hydroxide.

It has been found that such reactions require extended periods of time to reduce the concentration of halogenated contaminants, such as polychlorinated biphenils (PCB's), to a level generally acceptable by the regulations effective in the various Countries.

Also, Peterson of Niagara Mohawk Power Corporation in U.S. Pat. No. 4 532 028 proposed to reduce the level of halogenated aromatics in a hydrocarbon stream by the treatment with an alkaline reactant in a sulfoxide solvent. This process involves a further purification step to remove the sulfoxide solvent, after decontamination, where the resulting decontaminated fluid will be reused.

In U.S. Pat. 4 632 742 and Eur. Pat. No. 0 118 858 in the name of the present Applicant, Tundo disclosed a method for the decomposition of halogenated organic compounds by a reagent which consists of (a) polyethyleneglycol, Nixolens®,

an alcohol or polyhydroxy compounds, (b) a base, such a carbonate or bicarbonate of alkali metal or alkaline earth carbonate and (c) an oxidative agent, such as Na_2O_2 and BaO_2 , or a source of radicals in the absence of oxygen. This method is applicable to the decontamination of mineral oil, soil and various porous surfaces. But the use of sodium peroxide, or other oxidative agents and the source of free radicals pose potential explosion and fire hazards involved in their operation. Also, this method can be prohibitively expensive because of the cost of peroxide.

Further, in U.S. Pat. No. 4 839 042 and Eur Pat No. 0 135 043 in the name of the present Applicant, Tumiatto et al described a continuous decontamination process with a dehalogenation bed, which is composed of a polyethylene glycol or a copolymer of various alkene oxides in a certain proportion and an alkali alcoholate or alkaline earth, which are adsorbed on certain solid carriers. However, this process was found to require a large amount of reagents and extended periods of time to reduce the concentration of halogenated contaminants, such as PCBs, to a generally acceptable level prescribed by current regulations.

In the Application for patent PCT/EP93/03609 dated 20 December 1993, published on July 7, 1994, with No. WO94/14504, in the name of the present Applicant, Tumiatto presented a process for the removal of halogenated organic compounds from fluid and solid contaminated matrices, which allows the functional recovery of such fluids (mainly dielectric mineral oils in operation in electric transformers), after that the dangerous substances are easily decomposed from materials usable according to this dehalogenation process. In the latter, the halogenated organic compounds are rapidly and completely decomposed by a reagent consisting in a non-

alkali metal, a polyalkyleneglycol or a Nixolens® and a hydroxide or a C₁-C₆ alcoholate of alkali metal or alkaline earth. This dehalogenating reagent overcomes the aforementioned deficiencies and gives more effective results than those obtained by using previous art methods with a reagent produced from an oxidative agent or a source of radicals. This reagent can be directly mixed with the fluid or solid matrix, contaminated by halogenated organic compounds, under stirring and at a pre-selected temperature typically from 20°C to 150°C (preferably from 70° to 120°C). The use of ultrasounds and UV sources in the dehalogenation process described above, increases the efficiency of the reaction 10-15% and decreases the duration about 25%.

In particular, this reagent, combined with porous solid supports (i.e. pumice), can become a fixed bed for the continuous removal of halogenated organic compounds in fluids contaminated by PCBs, using a device of appropriate shape and dimension, such as a column and cartridge or a series of cartridges.

With the introduction of the dehalogenation process just described and its subsequent industrialization, it was desirable to find an optimized solution to improve the operating exploitation of the above dehalogenation reagent and for the recovery of the materials eventually used to support it, after the chemical dehalogenation of the PCBs and/or the destruction of the oxidized organic compounds, as alternative to the traditional methods of disposal of the wastes generated.

Moreover, the industrial applications of the decomposition process described above, result to be not conveniently applicable or totally non-applicable in specific situations,

such as, for example, the destruction of ASKAREL (pure PCBs or in mixtures with trichlorinebenzene), oils highly contaminated by PCBs or halogenated substances, other contaminated synthetic fluids (i.e. silicones and esters), solids (soil, recyclable metals from machinery/equipment highly contaminated and destined to disposal by thermodestruction), water based and gaseous matrices.

With the purpose of satisfying the requirements described above and to avoid the inconveniences made evident previously by the known technique, a process as described in claim 1 constitutes a subject of this invention.

The process of the invention can be defined "an oxidative counterflow", including a phase where the front of the flame propagates in the direction opposite to the oxidative flow in the first reactor. Thanks to this, it is possible to pilot accurately the thermoxidation reaction, completely destroying contaminants, undesired substances and compounds and obtaining harmless reaction products.

The above particulate support can be directly the solid matrix to be treated, such as, for example, soil impregnated by hydrocarbons, or an adsorbent support that is impregnated in the mentioned first reactor, by a liquid or gaseous matrix to be decontaminated, prior to starting the thermoxidation reaction. The process of this invention is, therefore, usable for the treatment of liquid, gaseous and solid matrices.

In a process such as the one for this invention, the most important critical factors are: the loss of material being treated, the cost of the energy required, the variation of the adsorbing capability of the supports and the destructive

efficiency of the reacting materials. The process of the invention has surprisingly demonstrated to be intrinsically self-cleaning and practically capable of self-sustaining without the application of energy from outside, requiring only the priming energy necessary to start the thermoxidation reaction. Moreover, it maintains and even improves in time, the physical integrity of the particulate support with a negligible effect on its surface and adsorbent capability.

It was observed that it is possible to apply the process of the invention in an efficient and economically advantageous manner to a large range of highly contaminated matrices that the processes described above of the known technique were not capable to treat properly.

The present invention represents, therefore, an effective and economic alternative to the disposal of matrices contaminated by highly toxic or persistent organic compounds, obtained through controlled thermodestruction, requiring, also, large fixed installations, considerable investments and operational costs, due mostly to high energy consumption, causing a strong environmental impact on the territory with considerable logistic problems, deriving from the transportation and handling of large quantities of wastes, as well as difficult social relations with the population and/or political and administration authorities involved.

In a preferred form of implementation of the process of the invention, prior to the priming of the thermoxidation reaction, the above particulate support is mixed and/or treated with a decontaminating reagent including at least one of the components A), B) and C), representing A) one or more metals or their oxides, B) a polyalkileneglycol or a Nixolens® and C) an hydroxide, a C₁-C₆ alcoholate, a carbonate or bicarbo-

nate of alkali metal or alkaline-earth.

Non-limitative examples of matrices that can be decontaminated and treated with the process of the invention, are:

- water, i.e. drinking, drainage, process or cooling water;
- a liquid, such as solvents, chemical intermediates, process or food fluids, oil or fluids with a dielectric, diathermic, hydraulic, lubricating function, with a mineral, vegetable, animal or synthetic base, or mixtures thereof;
- air, such as coming from working areas, from the environment itself or from a process;
- a technical or process gas;
- a solid, such as an adsorbing or filtering support, a process support, earth, soil, a component or a complete equipment;
- a waste or residue, such as urban, special, toxic, harmful or medical wastes;
- a bio-filter.

Non-limitative examples of contaminants, undesired substances and compounds, that can be treated both in a pure form or diluted with the process of the invention, are:

- halogenated aromatic compounds, such as for example, PCBs, PCDDs, PCDFs, PBBs, DDTs, DDEs;
- dangerous organic compounds, toxic, harmful, cancerogenous, theratogenous, mutagenous compounds and dangerous pollutants, chlorofluorocarbons, sulphur esafluoride or polyaromatic hydrocarbons;
- aggressive chemical agents, bacteriological agents, viruses, retroviruses, fungi and their mixtures, carried on liquid, gaseous, solid or biological matrices;
- derivatives of polar and/or oxidized and/or degraded by-products.

In particular, the process of the invention can be applied to treat a matrix containing exhausted waste reagent used for the decomposition of halogenated components, of the type described in the above mentioned application for a patent WO94/14504 submitted by the present Applicant. In this case, in fact, a surprising synergy is produced between the critical factors of success of the chemical decontamination and thermoxidation and also it is possible to recover materials otherwise destined to be disposed of in appropriate authorized systems.

More in detail, the process of the invention, finalized to the realization of a regeneration and/or recycling of the above reagents - that are used eventually on a support for the industrial dehalogenation with the complete destruction of undesired organic compounds - is based upon the inter-reaction of the reagents, that maintain a sufficient rheologic capability, with the adsorbent supports and with the oxidative counterflow system.

The process of the invention is realized in a reactor where the zone of high temperature thermo-oxidation or flame front is activated and self-maintained by air/oxygen starting from the base of the column of the materials being treated and propagates in the direction opposite to the oxidative flow towards the entrance of the oxidative agent itself. The flame front generated by the process progressively gasifies a fraction of the materials to be treated and produces volatile compounds and a porous residue that is regenerated and can be reused repeatedly. The thermal energy generated during the process is relatively elevated and produces a mixture composed, mainly, by carbon monoxide, carbon dioxide, hydrogen and hydrocarbons. In the thermo-oxidation zone temperatures up to about 1,500 °C are obtained. The residual car-

bon produced by the thermoxidation process can also be used as adsorbent support for the removal of contaminants. The residual carbon residue repeatedly re-used, with a porous surface much higher than carbon at the initial state, becomes extremely more efficient and is also free of tar. The highly reactive ambient in the high temperature thermoxidation zone is capable of virtually destroying all organic compounds. This, together with the adsorbing nature of the carbon support, allows the complete destruction of the residues of organic products left in the supports/reagents treated.

More generally, the process of the invention solves a series of important problems connected with the prevention of environmental damages and the conservation and/or the recovery of vital resources, such as, but not limitatively:

- to detoxify a large variety of halogenated organics, such as polychlorinated bifenils (PCBs) Askarel fluids, polyaromatic hydrocarbons, polychlorinated-dibenzo-p-dioxins (PCDDs), polychlorinated-dibenzo-furans (PCDFs), polybrominated bifenils (PBB's), chlorofluorocarbons (CFCs), dichloro-dyfenil-trichloroetane (DDTs), 2,4,5 trichloro-phenole, polyhalogenated alkilbenzene, sulphur esafluoride and others;
- to eliminate polar and oxidation by-products from oils and fluids (such as in the regeneration of dielectric, diathermic and other oils);
- to regenerate inorganic supports and to recover resources and metals from exhausted reagents and from contaminated equipment destined for disposal (such as electric transformers and capacitors and other machines); and
- to decontaminate soil polluted by hydrocarbons and dangerous organic substances.

The process of the invention is compatible with the environment and offers the unique opportunities of an integrated and flexible system, requiring limited investments for the realization of mobile or fixed operating configurations to be coupled also with other chemical/physical treatment equipment/processes in various operational scenarios with specific contaminants and/or their mixtures.

A regenerated particulate support obtainable at the end of a decontamination and treatment process, as previously described, constitutes a further subject of this invention.

Further advantages and characteristics of this invention will result evident from the detailed description that follows with reference to the drawings enclosed provided purely as a non limiting example, where:

- figure 1 represents a diagram of a system usable for the performance of the process of this invention,
- figure 2 is the more detailed diagram of reactor making part of the system of figure 1,
- figure 3 is a flow diagram, on which a material balance has been based (example 1),
- figure 4 is a dehalogenation reaction diagram (example 1),
- figure 5 is a chromatogram of the residues of PCBs in a typical exhausted waste dehalogenation reagent (example 1),
- figure 6 illustrates chromatograms of residues of PCBs in active carbon impregnated at first - in various proportions - by waste dehalogenation reagent and then subject to the process of the invention (example 1),
- figure 7 is a diagram illustrating the percentage of the loss of mass by the carbon subject to the process of the invention with respect to the substances to be eliminated in function of the load of spent reagent added to the carbon (example 1),

- figure 8 is a diagram illustrating the destructive efficiency of the process of the invention with respect to the substances to be eliminated in function of the load of reagent added to the carbon (example 1),
- figures 9 and 10 represent the chromatograms of the residues of PCBs after the application of the process of the invention to mixtures in different proportions of Askarel and dehalogenation reagent supported by coke (example 2), and
- figure 11 illustrates the variation of the surface area of Darco active carbon with the number of regeneration cycles to which it has been subject (example 3).

A decontamination and treatment system includes (figure 1) a first 10, a second 12 and a third 14 reactor arranged in series and under which a pan 16 is located to contain eventual leakages. Preferably reactors 10, 12, 14 are of the column type and have a length/diameter ratio between 2 and 25. In practical industrial arrangements three reactors 10, 12, 14 can eventually be realized each in a modular form and include several modules to be connected in parallel, as required, to optimize effectiveness and efficiency of the process.

The first reactor 10 is equipped with ducts 18, 20 respectively for the inlet and outlet of a fluid matrix to be decontaminated and a duct 21 for the introduction at one of its ends 23 of an oxidative flow, such as air or oxygen.

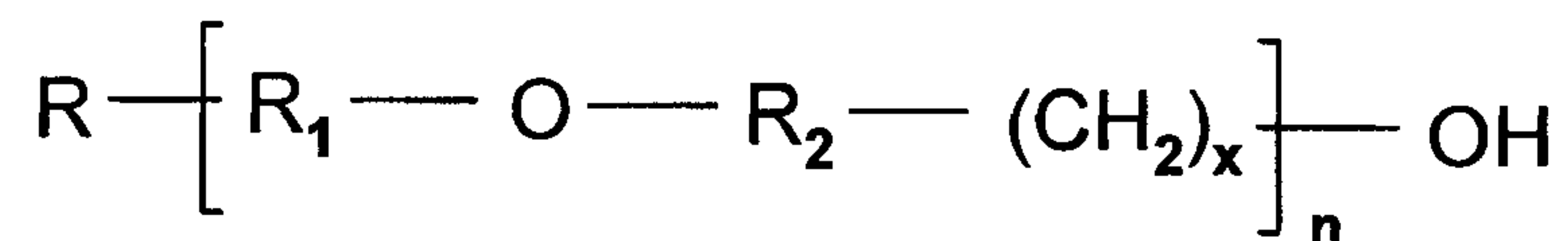
The first reactor 10 is filled (figure 2) of a particulate support 22, preferably of a porous type and chosen, as an example, from the group consisting of coal, coke, active carbon, activated and non alumina, silica gel, fuller earth, diatomee, pumice, zeolite, perlite, molecular sieves, the above dehalogenation reagent, silicates, functionalized and

non ceramic, sand, clay, metal and/or syntherized powders, metal oxides, filtration media, vegetable media and their mixtures. The average granulometry of particulate support 22 is preferably between 0.01 and 250 mm.

In a first phase of the process of the invention the fluid matrix to be treated is flowing, eventually with a recirculation, through reactor 10, passing through ducts 18, 20 in such a manner that support 22 is impregnated, preferably up to saturation, by contaminants, undesired substances and compounds present in the matrix. Depending upon the requirements, the latter can be made flowing from the top to the bottom, as indicated in figure 1, or vice versa.

Should the matrix contain halogenated organic compounds, the impregnated support 22 can also be mixed or treated with a decontaminating reagent as described above, in particular of the dehalogenating type described in previous application for patent WO94/14504.

In synthesis, a polyalkyleneglycol usable in the above dehalogenating reagent has, preferably, the following general formula (I)



wherein x is ≥ 2 ; n is an integer of 1 to 500; R is hydrogen; a straight or branched-chain C_1 - C_{20} alkyl group an aral-

kyl or an acyl group; R_1 and R_2 which can be the same or different, represent a bond, straight or branched-chain C_1 - C_{20} alkyl group, a C_5 - C_8 cycloalkyl or aryl group possibly substituted.

The polyalkyleneglycol is even more preferably Carbowax® 6000.

Nixolens® indicates a series of random copolymers of various alkene oxides in different proportions, which are distributed by the Italian ENICHEM (Milan) Company, usable in the realization of this invention because of its high chemical activities and physical characters. Nixolens®, a common industrial lubricant fluid, includes Nixolens®-NS; Nixolens®-VS and Nixolens®-SL. Of them, the preferred is Nixolens®-VS, such as VS-13, VS-40 and VS-2600, which contains a low percentage of propylene oxide monomers and a relatively high percentage of ethylene oxide monomers.

The hydroxide and alcoholate refer preferably to hydroxides and C_1 - C_6 alcoholate of alkali metals and alkaline-earth metals.

When a polyalkyleneglycol or a copolymer of various alkene oxides, having an average molecular weight more than 6000, is combined with a non-alkali metal and an hydroxide or an alcoholate, a very efficient dehalogenation is obtained, especially for lower halogenated contaminants, such as PCBs in Aroclor® 1242, 1254, mixtures and numerous halogenated alkylbenzenes.

The mole ratio of polyalkyleneglycol or Nixolens® to halogen varies from 1:1 to 30:1 and the mole ratio of hydroxide or alcoholate to halogen ranges from 10:1 to 200:1. At this mo-

le ratio, the concentration of the non-alkali metal in the reaction mixture, which consists of the decomposition reagent and the contaminated matrix, ranges from about 0.02% to 5% by weight, preferably 0.1% to 2% by weight. In particular, when the decontaminating reagent is used to decompose halogenated organic compounds in contaminated solid matrix, such as sludge, a relatively large amount of polyglycol or Nixolens® is employed to serve as both roles of a solvent and the reagent. In general, the amount of the reagent depends upon the type and amount of halogenated contaminants present.

The decontaminating reagent and the particulate support 22 can also be pre-formed on beds functionalized under the form of columns or cartridges of appropriate form and dimension in view of the different matrices, contaminants, undesired substances and compounds to be treated.

Naturally, should it be required to treat a granular solid matrix contaminated by undesired compounds or substances, such as soil impregnated by hydrocarbons or a granular support impregnated by the above exhausted waste decontaminating reagent, the solid is directly loaded into reactor 10 without performing the impregnation. Further, an eventual treatment with fresh decontaminating reagent is performed, with the purpose of causing a removal and/or primary decomposition of the contaminants immobilized and/or adsorbed on the particulate support.

The matrix to be contaminated and treated and the decontaminating reagent can be mixed with the help of mechanical means and eventually ultra-sounds and be irradiated by a source of ultra-violet rays.

The eventual impregnation and treatment phases with decontaminating reagent occur at a temperature preferably included between ambient temperature and about 200°C.

At the end of such phases the oxidative flow coming from duct 21 is activated (figure 2) at the end 23 of the reactor 10 and a thermoxidation reaction is primed at the opposite end 24 - as an example with an electric heater or a propane torch. Thus a mobile flame front 26 is generated in the opposite direction (indicated by arrow 28) to that of the oxidative flow having a temperature of at least 1200°C, with specific thermal parameters depending upon the nature of the eventual decontaminating reagents used and the type and quantity of the undesired compounds to be treated.

In particular, the temperature of the flame front or thermoxidation zone can exceed 1500°C and generate a thermal/oxidative degradation with the mineralization of organic contaminants adsorbed or present in the particulate support 22. The movement of the front 26, as well as the residential time of more traditional thermal degradation processes (such as incineration), is controlled by the oxidative flow and is such to maintain in each section of the first reactor 10 for a time included preferably between 2 and 10 seconds the conditions required by the development of the thermoxidative reaction.

The thermal energy required by this reaction is obtained primarily by the oxidation of the organic contaminants themselves, leaving the particulate support 22 in good measure intact, even if it is made of a carboneous material. This allows the regeneration of carboneous adsorbents such as granulated active carbon, coke or others. The support regenerated in the zone behind the flame front 26 is also cap-

able of removing organic contaminants that escaped the thermodestruction, giving the process of the invention its special and surprising self-cleaning characteristic. Moreover, the process is substantially self-sustained and energetically self-contained, since there is not any energy supply by external sources during the normal operation.

The exhaust gases and the particulate flowing out the first reactor 10 can typically contain acid compounds (chlorinated, sulphured, fluoridated and others) depending upon the type and concentration of the initial contaminants, by-products derived from an incomplete oxidation, especially during the transitional priming phase and eventual micro pollutants.

Consequently, in order to neutralize these compounds, the exhausted gases are bubbled, passing through a duct 30, at the bottom of the second reactor 12, filled with a basified liquid, such as water, a hydrocarbon, polyalkyleneglycol, Nixolens® or mixture thereof.

The basified liquid can also be recirculated (in a manner not illustrated in the figures) through an adsorbing trap made of a particulate support - such as active carbon, activated alumina, pumice or the likes - filtering and/or adsorbing the said decontaminating reagent, and eventually, to recover energy, through a heat exchanger.

Once the activity of the basified liquid contained by the second reactor 12 and by the trap is exhausted, the flow of gas coming from the first reactor 10 is stopped and the content of the trap and the second reactor 12 is transferred into the first reactor 10, where it is subject to an oxidative counterflow treatment. At the same time, the second re-

actor 12 can be loaded with fresh basifying liquid and be supplied again with gas coming from the first reactor 10.

In order to assure the maximum level of protection for the operators and the environment, the gaseous flow getting out the second neutralizing reactor 12 is taken by a line 32 into the third reactor 14 filled preferably by a porous adsorbing support, e.g. active carbon or a mixture formed by active carbon, activated alumina and the likes. This end stage has the purpose of eliminating eventual micro traces of environment unfriendly substances, such as, e.g. sulphured compounds that can generate bad odours, as well as traces of micro pollutants, even if they have already been reduced by the preceding reactors 10, 12 to levels below the thresholds prescribed by current regulations or measurable by instruments. The gas flowing out the third reactor 14 can, finally, be further flowing through a pyrolytic torch 34 prior to its discharge into the atmosphere.

Once the porous support in the third reactor 14 is saturated by the substances adsorbed, the feeding of gases coming from the second reactor 12 is stopped and the third reactor 14 is regenerated, by priming an oxidative counterflow similar to what described with reference to the first reactor 10. As an alternative, the porous support of the third reactor 14 can be loaded into the first reactor 10, where it is subject to the oxidative counterflow process.

As a whole, therefore, the products of the process of the invention obtained are the gaseous effluent getting out of the torch 34, completely free of contaminants and undesired substances or compounds, and the particulate support 22 regenerated, remaining in the first reactor 10, where it can be reused for a new decontamination treatment cycle or from

where it can be removed for further use.

As a result of a variant of realization of the process of the invention, when the flame front reaches the end 23 of the first reactor 10, in which the oxidative flow is supplied, a new priming of the thermoxidation reaction is generated, so that the front of the flame moves now in a downward direction, in conjunction with the oxidative flow, after the first phase as a counterflow.

During this second phase of thermoxidation, the flame consumes all the carbon mass (contaminants, residual reagent and eventual carbaceous material present in the support) obtaining the total destruction of the contaminants adsorbed. The adoption of this variant of the process, not allowing the regeneration of the carbaceous particulate support, depends, obviously, upon the specific requirements of the treatment operation.

Herebelow, a few non-limitative examples of the application of the process of this invention are provided.

Example 1

Regeneration and recovery of supports and exhausted reagents used for chemical dehalogenation

Decontaminating reagents used in particular for chemical dehalogenation, as described in the above mentioned application for patent WO94/14504 submitted by the applicant, have emphasized an exploitation that is typically evaluated around a 10:25% of their effective potential of rheologic capacity. This limitation derives from the necessity of maintaining their level of saturation with residual concentration of halogenated aromatic compounds (i.e. PCBs) within the limits prescribed by current regulations for their clas-

sification as special waste, avoiding that they are subject to the limitations and costs related to the possession, transportation and disposal of toxic/harmful wastes. With the disposal, that includes an intrinsic cost, recyclable materials are also lost, such as particulate solids eventually used to support such reagents.

On the contrary, the coupling of the process following the invention relative to the regeneration and recovery of used reagents in the chemical dehalogenation process already known, especially in mobile units, allows a full exploitation of the reagent and its subsequent on-site treatment, without generating practically any waste. To meet the stated objectives, four sets of experimentals were undertaken, including:

- a) characterization and quantization of exhausted waste reagent to be disposed of, brought to a saturation level about 15 times higher than the current typical value, to determine the level of residues of PCBs, PCDDs, PCDFs, polyethylene-glycols (PEG), chlorine and sodium/potassium;
- b) the examination of the destruction efficiency of the process of the invention on residual PCBs;
- c) determination of the efficiency of the mineralization;
- d) determination of the area of the adsorbing surface of the support of exhausted reagent with an examination with electron microscope.

Analysis of residual PCBs in exhausted reagent sludge

The following experimental procedure has been applied:

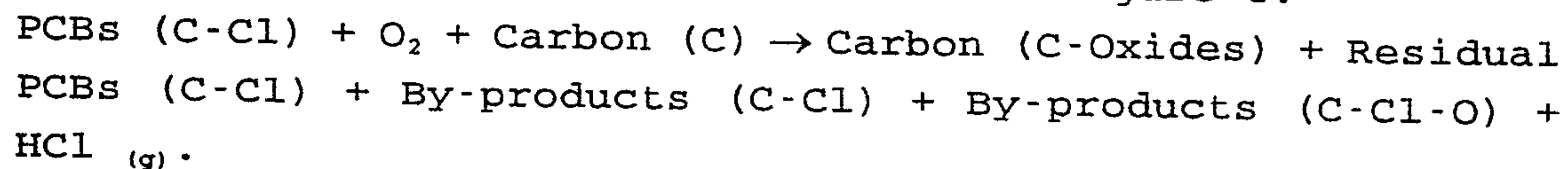
1 gram of exhausted reagent has been dissolved in 100 ml of methanol. A known amount of methanol was introduced into a silica-gel column for a clean up with 40 ml of methylene chloride. The extract was rotavaped and twice solvent exchanged with 20 ml of iso-octane. Final volume was fixed to

2 ml by N₂ stream. The aliquots were analyzed for residual PCBs by high resolution gas chromatography.

A capillary gas chromatography equipped with an electron capture detector was used for this purpose. Separation of PCB congeners was carried out with a 30m x 0.25mm fused silica tubing with 95% methyl + 5 % phenyl polysiloxane stationary phase. A calibration curve for concentration ranges for analysis of PCBs was provided. In addition, a known amount of Aroclor® 1242 was added to the extract in order to identify separate components. Chromatographic peaks were identified by relative retention time matching with pentachlorobenzene. Quantization of PCBs was carried by peak area measurement relative to external calibration standard on the basis of percent contribution of individual chlorobiphenyls to Aroclor® 1242.

Carbon regeneration

A material balance approach (figure 3) was adopted to document the PCBs destruction efficiency and monitor the formation of possible oxygenated by-products, especially PCDDs and PCDFs and evolved hydrochloric acid, during the process of the invention. The likely overall reactions leading to decomposition of PCBs are presented in figure 4:



Gasification and analysis of PCBs and PCDDs/PCDFs on Carbon

An aliquot of activated carbon impregnated by a known amount (respectively 5%, 10%, and 20% w/w) of waste dehalogenation reagent was packed into a reactor and subject to the oxidative counterflow process of this invention. The reactor was made of a column having dimensions 25 mm diameter and 250

mm height, connected by transfer glass lines and a glass bowl having the function of water scrubber and two 25 ml containers used as gas traps. The oxidative flow was 2 l/min of oxygen inlet from the top of the column; pressure 2 bar; temperature 1500°C; time of counterflow cycle 3 min.. The priming was triggered in the low part of the column with a propane torch. After regeneration, a 1 g of aliquot of carbon was Soxhlet extracted with 250ml of benzene for at least 20 hours to remove these strongly adsorbed components on carbon. The extract was cleaned up through a silica-gel column with 40ml of methylene chloride and reduced to approximately 3ml with a rotary evaporator and then concentration down to 2 ml by N₂ stream.

The cleaned extract was analyzed with a gaschromatography and low resolution mass spectrometer interfaced to a high resolution capillary gas chromatography.

Determination of residual PCBs, possible oxygenated products and HCl in traps

The traps and transfer lines were first rinsed with deionized water and rinse was pooled with water from impinger traps. The pooled water was twice extracted with hexane. The traps and transfer lines were also rinsed with hexane. The extracted liquid was used for chloride determination. Hydrochloridric acid was analyzed by an ion chromatography (Model 14, Dionex, Sunnyvale, Ca) equipped with ion resin columns (separator and suppressor column). The samples were quantitated by peak response relative to standard chlorine solution. The hexane extract was dried by passing it over anhydrous sodium sulphate. The dried extract was split into two portions. One portion was used for determination of total residual PCBs. The other was used for determining planar PCBs and PCDDs/PCDFs. For these analysis, the hexane extract was

extracted with DMSO (dimethylsulfoxide). The DMSO extract containing planar PCBs and PCDDs/PCDFs was back extracted with 10% benzene in hexane. The benzene/hexane extract was fractionated with multilayered adsorbent column to remove interferences. The analysis of PCBs and PCDDs/PCDFs was performed with gaschromatography and gaschromatography/mass spectrometer.

Carbon mass loss

The experimental study was accomplished under the optimum temperature (i.e. in the area of 1500°C) to achieve minimal carbon mass loss and to produce regenerated carbon equal in adsorption capacity to that of virgin carbon while maintaining acceptable destruction efficiency for adsorbed waste reagents. For this reason, careful attention was paid to loss of carbon during regeneration process. Mass loss was measured as a function of oxygen flow rate and different loading rate of waste reagent added to carbon.

Surface area determination and scanning microscopic examination

The changes in total surface area of the regenerated carbons were determined with the BET method, that measures the activated carbon's adsorption and desorption of nitrogen under varying conditions. The BET surface area determination was carried out on a Quantasorb QS-10 nitrogen adsorption surface area analyzer (Quantachrome Corp. Syosset N.Y.).

Results and evaluation

The experimental studies were carried out to determine residual PCBs in activated carbon impregnated by waste dehalogenation reagent - i.e. used to treat dielectric oil contaminated by PCBs - and then subject to the process of this invention.

Higher chlorinated PCBs congeners (such as Aroclor 1254 and 1260) are extremely reactive toward nucleophilic aromatic substitution with the above dehalogenation reagent, typically PEG/KOH based. In such a reaction with potassium hydroxide and PEG functioning as a nucleophile, lower chlorinated PCBs are formed, being them more easily biodegradable. As expected, the chromatographic profile (figure 5) of residual PCBs in waste dehalogenation reagent closely resembles that of Aroclor 1242,. For this reason, the quantitative analysis of PCB congeners in dehalogenation reagent residue was identified with Aroclor 1242, based on weight percent contribution of individual chlorobiphenyls. The concentration of each PCB congeners, measured in the dehalogenation reagent residue to be adsorbed on activated carbon and subject to the process of this invention, are demonstrated in table 1. The result indicated that the total concentration of residual PCBs is approximately 774 mg/kg. It was observed that the relative concentration of trichlorobiphenyls, with respect to the total polychlorinated biphenyls, constitutes roughly 30%, tetrachlorobiphenyls about 45%, and pentachlorobiphenyls about 20%.

The development of the oxidative counterflow process included the optimization of variables such as oxygen flow rate, temperature and residue reagent loading rate with respect to activated carbon. It involved, in particular, balancing two parameters: minimization of the carbon mass loss and maximization of the destruction efficiency of residual PCBs in adsorbed waste reagent.

The experiments were carried out over a 5 to 20% of waste loading range of waste dehalogenation reagent with respect to activated carbon, to evaluate the two parameters above mentioned. The gaschromatographic data for destruction effi-

ciency after the oxidative counterflow process are shown in figure 6.

As already mentioned, table 1 demonstrates the concentration of PCBs congeners found in a waste dehalogenation reagent, whereas table 2 shows the concentrations of a few of such congeners in activated carbon impregnated by this reagent and subsequently subject to the oxidative counterflow process of this invention.

The comparison of tables 1 and 2 shows that the PCBs congeners are destroyed with efficiencies of 96% or better, that are progressively increasing when reducing the load of spent reagent from 20% through 5% with respect to the carbon.

It was observed that the highest destruction efficiency occurs at a minimum loading rate with 10% of carbon loss, as shown in figures 7 and 8.

At higher loading level, the destruction efficiency decreases and a lower carbon loss occurs, as shown again by figures 7 and 8.

In addition, no micro contaminants nor toxic oxygenated polychlorinated by-products above the detection limits were detected in the trapped effluents or on the regenerated carbon.

Furthermore, it was obtained that a minor change in the surface area occurred after repeated regeneration cycle, indicating that the adsorptive capacity of the carbon adsorbents remains largely intact, even after being subject to the process of this invention.

TABLE I
Residual PCB congeners & concentration in exhausted
reagent sludge

Chlorobiphenyl No. Structure	Residual PCBs in waste reagent (ppm)	Chlorobiphenyl No. Structure	Residual PCBs in waste reagent (ppm)
4 2,2'-	8.43	48 2,2',4,5-	18.70
10 2,6-	0.56	75 2,4,4',6-	2.51
7 2,4-	0.60	44 2,2',3,5'-	62.72
9 2,5-	0.54	41 2,2',3,4-	15.62
6 2,3'-	3.31	64 2,3,4',6-	13.78
5 2,3-	0.05	40 2,2',3,3'-	17.80
8 2,4'-	6.12	74 2,4,4',5-	17.36
15 4,4'-	1.21	66 2,3',4,4'-	6.64
17 2,2',4-	2.30	95 2,2',3,5',6-	11.48
18 2,2',5-	5.02	91 2,2',3,4',6-	5.58
25 2,3',4-	86.90	56 2,3,3',4'-	17.28
28 2,4,4'-	33.90	60 2,3,4,4'-	14.36
31 2,4',5-	28.55	90 2,2',3,4',5-	4.10
20 2,3,3'-	2.90	101 2,2',4,5,5'-	17.02
33 2',3,4-	34.49	99 2,2',4,4',5-	75.58
53 2,2',4,6'-	4.61	97 2,2',3',4,5-	26.52
22 2,3,4'-	43.65	85 2,2',3,4,4'-	7.21
51 2,2',4,6'-	2.94	77 3,3',4,4'-	2.16
46 2,2',3,6-	13.13	110 2,3,3',4',6-	7.34
52 2,2',5,5'-	45.25	105 2,3,3',4,4'-	5.50
49 2,2',4,5'-	73.44	132 2,2',3,3',4,6-	1.92
47 2,2',4,4'-	21.40	153 2,2',4,4',5,5'-	4.35
		Total	774.83

TABLE II

Residual PCB congeners & concentrations in carbon after treatment

Chlorobiphenyl No. Structure	5% (w/w) waste sludge in carbon	10% (w/w) waste sludge in carbon	20% (w/w) waste sludge in carbon
25 2,3',4-	-	2.4	10.0
28 2,4,4'-	-	1.0	2.9
31 2,4',5-	-	0.5	2.1
20 2,3,3'-	-	0.02	0.3
33 2',3,4-	-	0.4	5.7
53 2,2',5,6'-	-	0.06	0.8
22 2,3,4'-	-	0.6	1.6
51 2,2',4,6'-	-	0.04	0.1
49 2,2',4,5'-	2.0	1.2	3.6
47 2,2',4,4'-	-	-	0.9
48 2,2',4,5-	-	-	0.8
75 2,4,4',6-	-	-	0.1
44 2,2',3,5-	-	-	2.4
41 2,2',3,4-	-	1.2	0.7
64 2,3,4',6-	-	-	0.7
91 2,2',3,4',6-	-	-	0.2
90 2,2',3,4',5-	0.08	0.06	0.1
101 2,2',4,5,5'-	0.36	0.2	0.5
Total	2.44 ppm	7.68 ppm	33.50 ppm

Example 2Degradation of dielectric Askarel - PCB fluids

Askarel, according to the definition of the International Electrotechnical Commission (IEC), refers to synthetic chlorinated aromatic non-flammable hydrocarbons, used as dielec-

tric materials or media in electrical devices (transformers and capacitors). These fluids are commonly composed of mixtures of polychlorinated biphenyls (PCBs) with or without trichlorobenzenes, depending upon the application requirements. Specific combinations of PCBs, commonly referred to by their commercial formulations: Aroclor®, Phenclor® etc. and trichlorobenzenes, were used for particular applications; e.g. a combination of Aroclor 1260 and trichlorobenzene (60% and 40%, respectively). The production, the use and the disposal of these compounds was subject to a large number of international regulations OCSE, USEPA, EEC (Directives 76/769 - 85/467 etc.) and Italian (D.P.R. 216/88 dated 24 May 1988 etc.) for oils/fluids, machinery and equipment containing or contaminated by PCBs beyond the established threshold limits (typically > 50 mg/kg).

Due to their recalcitrant natures, disposal of PCBs, in their pure or highly concentrated form is especially problematic through a thermodestruction process. If the process does not occur at very high temperature (>1200°C) and in rigidly controlled ambient (excess of oxygen; retention time > 2 sec.s), highly toxic, carcinogen, teratogen and mutagen products, such as poly-chlorinated dibenzo furans (PCDFs) and polychlorinated di-benzo-p-dioxin (PCDDs) are formed. While the chemical dehalogenation processes of the known technique are effective and/or economically advantageous on liquid and solid matrices contaminated by PCBs, within certain limits (in typical concentrations up to 2000 mg/kg), the process of this invention was surprisingly found advantageously applicable also for the destruction of pure Askarel-PCBs. For this application, low sulphur coke, with specific dimensions (preferably 0.2 to 5 mm) was used as very low cost particle adsorbent and energy source and was mixed with 10% of dehalogenating reagent in accordance with

the previously mentioned application for patent WO94/14504 of the same applicant, to balance the degradation process. The dehalogenating reagent mixed with coke was packed into a ceramic-lined reactor column and impregnated with Askarel introduced with a shower head sprayer. Destruction efficiencies of the process were evaluated at varied Askarel loadings ranging from 5 to 20 percent (w/w) basis of the total weight support/coke. The process was carried out in single counterflow thermoxidation cycle at the end of which coke was recovered or in two thermoxidation phases (first as a counterflow, then forward flow) in which the coke was consumed during the forward flow phase. A mass balance approach was applied to calculate destruction efficiency. For this purpose, concentrations of residual PCBs, PCDFs, PCDDs and hydrochloric acid (HCl) were determined. Destruction efficiencies in the two-cycle operation were better than 99.999% (figures 9 and 10). In either single and double mode, PCDDs/PCDFs concentrations were found to be below the method detection limit, which was set at 100 part per trillion (ppt), using a gaschromatography with mass spectrometer (GC/MS) in accordance with U.S.E.P.A. protocols and the analytical methodology of example 1. Mineralization efficiency, assessed through conversion of organic chlorine to HCl, was surprisingly found to be nearly complete at 98 percent, which was the limit of analytical methodology.

Example 3

Regeneration of saturated activated carbon

Activated carbon is, as known, one of the most versatile adsorbent of contaminants of various matrices (oils, drinking water, waste waters, air, etc.), but it is very expensive. When this carbon is saturated, it is necessary to provide to its disposal as a special or toxic/harmful waste with subsequent higher costs, or it is possible to decontaminate

and to regenerate it in specialized centers, that are, in any case, not available in every Country. The main limits posed to this regeneration are linked to the remote location of these centers associated with high fixed and variable costs for treatment, transportation and handling. The oxidative counterflow process of this invention surprisingly demonstrated its particular efficiency in pursuing this objective in a mode directly sequential to the adsorbing process, being activated as soon as the saturation of the activated carbon with contaminants, adsorbed substances or compounds, is reached. The results obtained with a variety of granular activated carbons demonstrated that the process of this invention is capable of regenerating efficiently these materials with a minimal total loss of the materials themselves, being this included between 5 and 10 percent for each treatment cycle.

Exhaustive experiment tests relative to surface area and to the adsorbing capacity surprisingly demonstrated that the process enhances effectively both the adsorbing capacity and the active surface area. Results of surface area analysis for a commercially available carbon (Darco Carbon) are shown in figure 11 and were obtained following the methodologies described in example 1 with reference to the adsorption of Nitrogen (BET).

Example 4

Destruction of PCBs and recovery of Aluminum from electrical capacitors impregnated with Askarel

The process of this invention was used to recover high grade electrolytic aluminum (typically > 30% in weight) from capacitors built with Askarel-PCBs impregnated solid insulation. Capacitor packings are shredded to the correct size (0.5÷50 mm) and mixed to 10 percent in weight with low sulphur con-

tent coke. The process, performed in a column type reactor, consumed the paper insulation and destroyed the PCBs, leaving the aluminum largely intact which was recovered through a simple sieving operation. Destruction of PCBs during the process was found to be better than 99.999 percent, measured with GC/MS, in accordance with the U.S.E.P.A. protocol and what explained in the analysis methodology of example 1.

Example 5

Production of activated carbon through the conversion of the carbon of scrap tires

Tens of millions of tires must be scrapped each year. Alternate uses for these materials are being pursued in research and experiments world-wide. Pyrolysis techniques have been utilized to generate useful by-products. One of such by-products is carbon (>30% in weight). The carbon obtained, however, contains typically large amounts of contaminant and dangerous leachable organics released during traditional treatments, thus making it unfit as a carbon adsorbent. Experiments have shown that this mixture of contaminant leachable organics can be conveniently destroyed through the counterflow oxidative process of this invention, with the production of activated carbon from scrap tires. The porous supports, thus obtained, surprisingly showed surface areas up to 400m²/gram and adsorptive capacities comparable to many commercial activated carbons with a very advantageous cost/benefit ratio for decontamination applications considered. The analysis methodologies used are those explained for example 1.

Naturally it is intended that, maintaining the principle of the invention, the details and embodiments thereof can widely change with respect to what was described and illustrated in the drawings, without getting out, for this reason, of the scope of this invention.

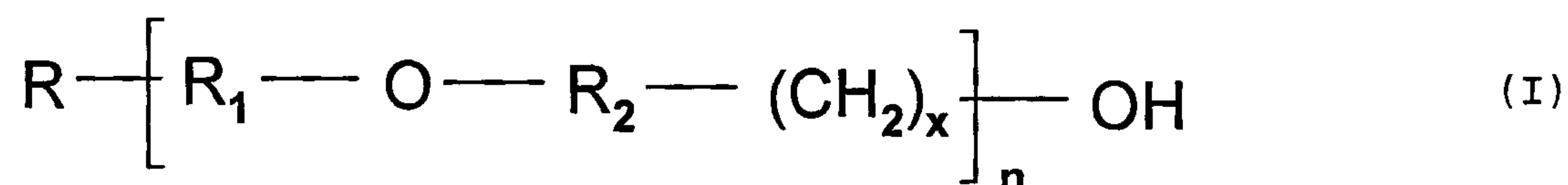
CLAIMS

1. Decontamination and treatment process of a matrix, including the phases of:
 - a) filling a first reactor (10) with a particulate support (22), that is a solid matrix to be decontaminated and treated or it is impregnated by a liquid or gaseous matrix to be decontaminated and treated; and
 - b) introducing at one end (23) of the first reactor (10) an oxidative flow and priming a thermoxidation reaction at the opposite end (24) of the first reactor, so that a flame front (26) is generated moving in an opposite direction (28) with respect to that of the oxidative flow and having a temperature of at least 1200°C, so as to substantially decompose or destroy contaminants, undesired substances and compounds initially present into the matrix, such process being characterised
 - i) in that said matrix contains halogenated aromatic organic compounds;
 - ii) in that gas and the particulate coming out the first reactor (10) at the end of the thermoxidation reaction are scrubbed through the bottom of a second reactor (12) filled with a basified liquid; and
 - iii) in that, prior to the priming of the thermoxidation reaction, said particulate support (22) is mixed and/or treated with a decontaminating reagent including at least one of the components A), B), and C), wherein:
 - A) is one or more metals or their oxides;
 - B) is a polyalkyleneglycol or a random copolymer of various alkene oxides; and
 - C) is a hydroxide, a C₁-C₆ alcoholate, a carbonate of

an alkali metal, a bicarbonate of an alkali metal, a carbonate of an alkaline-earth metal, or a bicarbonate of an alkaline earth metal.

2. The process of claim 1 wherein the basified liquid in the second reactor is selected from the group consisting of water, a hydro-carbon, polyalkyleneglycol, copolymer of alkene oxides and mixtures thereof.

3. Process according to claim 1 or 2, in which the said polyalkyleneglycol has a formula (I)



wherein x is = 2; n is an integer of 1 to 500; R is hydrogen, a straight or branched-chain C₁-C₂₀ alkyl, an aralkyl group or an acyl group; R₁ and R₂ are the same or different and are a bond, a straight or branched-chain C₁-C₂₀ alkyl, unsubstituted or substituted by C₅-C₈ cycloalkyl group or aryl group.

4. A process according to claim 3, wherein the polyalkyleneglycol is Carbowax® 6000.

5. A process according to claim 1 or 2, wherein the mole ratio of polyalkyleneglycol or copolymer of alkene oxides to halogen in the matrix to be decontaminated and treated ranges from 1:1 to 30:1, and the mole ratio of hydroxide or C₁-C₆ alcoholate and said halogen ranges from 10:1 to 200:1.

6. A process according to claim 5 wherein the concentration of the metal ranges from about 0.02% to 5% by weight of the reaction mixture.

7. A process according to any one of claims 1 to 6, wherein the matrix to be decontaminated and treated and the decontaminating reagent are mixed, prior to the beginning of the thermoxidation reaction, with the help of mechanical means and eventually ultrasounds.

8. A process according to any one of claims 1 to 7, wherein the matrix to be decontaminated and treated and the decontaminating reagent are radiated by a source of ultraviolet rays, prior to the beginning of the thermoxidation reactions.

9. A process according to any one of claims 1 to 8, wherein the impregnation of the particulate support (22) and its eventual treatment with said decontaminating reagent occur at a temperature between ambient temperature and about 200°C, said impregnation being performed until the saturation of the particle support (22) is obtained.

10. A process according to any one of claims 1 to 9, wherein the said particulate support (22) is impregnated by the liquid or gaseous matrix to be decontaminated and treated, prior to the beginning of the thermoxidation reaction.

11. A process according to any one of claims 1 to 10, wherein said basified liquid is recirculated through an adsorbing trap made of filtering particulate support and/or adsorbing and/or said decontaminating reagent, and eventually, through a heat exchanger.

12. A process according to any one of claims 1 to 11, wherein the gas coming out the second reactor (12) passes through a third reactor (14) filled with adsorbing porous material.

13. A process according to claim 12, wherein the gas coming out the third reactor (14) passes through a pyrolytic torch (34) prior to being released into the atmosphere.

14. A process according to any one of claims 1 to 13, wherein said reactors (10, 12, 14) are of a column type and have a length/diameter ratio between 2 and 25.

15. A process according to any one of claims 1 to 14, wherein the speed of the displacement of the flame front in the first reactor (10) is such to retain for a time between 2 and 10 seconds in each section of the first reactor (10) the conditions required for the development of the thermoxidation reaction.

16. A process according, to any one of claims 1 to 15, wherein, when the flame front (26) reaches the end (23) of the first reactor (10), in which the oxidative flow is provided, and a new priming of the thermoxidation reaction is generated in this end (23) in such a manner to have the flame front (26) moving forward in the same direction as the oxidative flow.

17. A process according to any one of claims 1 to 16, wherein said particulate support (22) is porous and it is chosen from the group consisting of carbon, coke, activated carbon, activated alumina, non-activated alumina, silica gel, fuller earth, diatomee, pumice, zeolite, perlite, molecular sieves, decontaminating reagent, silicates, functional ceramic,

non-functional ceramic, sand, clay, metallic powders, sintered powders, metal oxides, filtration media, vegetable media and mixtures thereof.

18. A process according to claim 17, wherein the average granulometry of said particulate support (22) is between 0.01 and 250 mm.

19. A process according to any one or claims 1 to 18, wherein said oxidative flow is of air or oxygen.

20. A process according to any one of claims 1 to 19, wherein one or more of the following functions are performed in sequence:

- decontamination of the matrix from contaminants, undesired substances and compounds initially present;
- functional regeneration of the matrix and/or of the particulate support as required by operational necessities;
- recovery of materials and/or resources, such as metals like aluminum, copper and iron from components and equipment; and
- decomposition and/or destruction of contaminants, undesired substances and compounds, initially present in the matrix.

21. A process according to any one of claim 20, wherein the decontamination of the matrix from contaminants, undesired substances and compounds initially present comprises elimination of PCBs from oil.

22. A process according to any one of claim 20, wherein the functional regeneration of the matrix and/or of the particulate support as required by operational necessities

comprises removal of acid, polar and oxidized by products from oils and fluids and elimination of contaminants from saturated adsorbent supports.

23. A process according to any one of claim 20, wherein recovery of materials and/or resources, comprises recovery of aluminum, copper or iron from components and equipment.

24. A process according to claim 23 wherein the components and equipment are capacitors and transformers contaminated by PCBs.

25. A process according to claim 20, wherein the decomposition and/or destruction of contaminants, undesired substances and compounds, initially present in the matrix, comprises decomposition and/or destruction of Askarel based on PCB/TCB or CFC.

26. A process according to any one of claims 1 to 25, in which the matrix to be contaminated and treated is:

- water;
- a liquid, with a dielectric, diathermic or hydraulic function, lubricants with a mineral, vegetable or animal base and mixtures thereof;
- air;
- a technical or process gas;
- a solid;
- a waste or residue; or
- a bio-filter.

27. A process according to any one of claim 26, in which the matrix to be contaminated and treated is drinking water, effluent water, process water or cooling water.

28. A process according to any one of claim 26, in which the matrix to be contaminated and treated is a liquid with a dielectric, diathermic or hydraulic function, selected from solvents, chemical intermediates, fluids from processes or foodstuff, oils, lubricants with a mineral, vegetable or animal base and mixtures thereof.

29. A process according to any one of claim 26, in which the matrix to be contaminated and treated is air coming from work ambients, from the environment or a process.

30. A process according to any one of claim 26, in which the matrix to be contaminated and treated is a solid which is an adsorbing or filtering support, a process support, earth, soil, a component or an integral equipment.

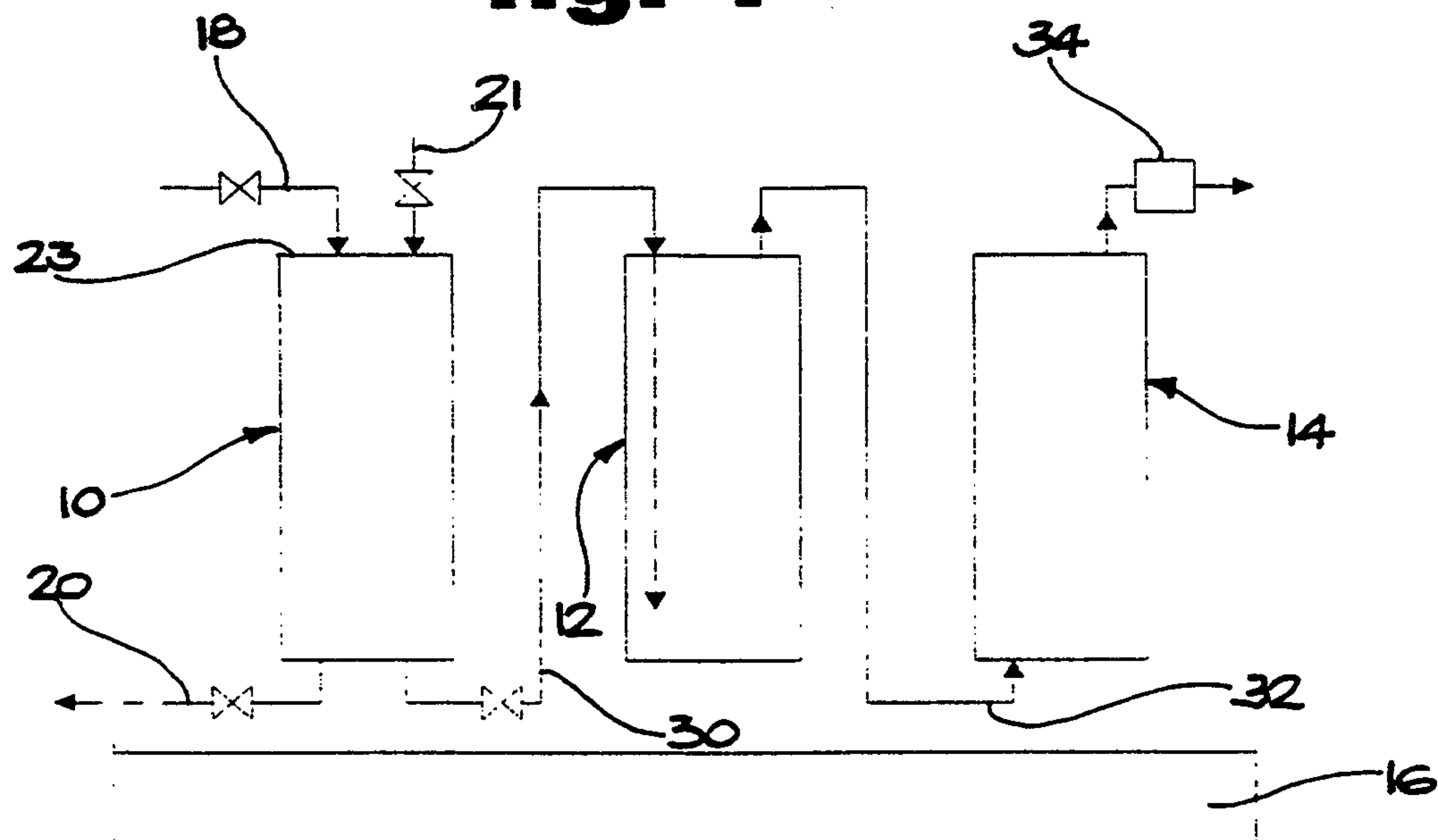
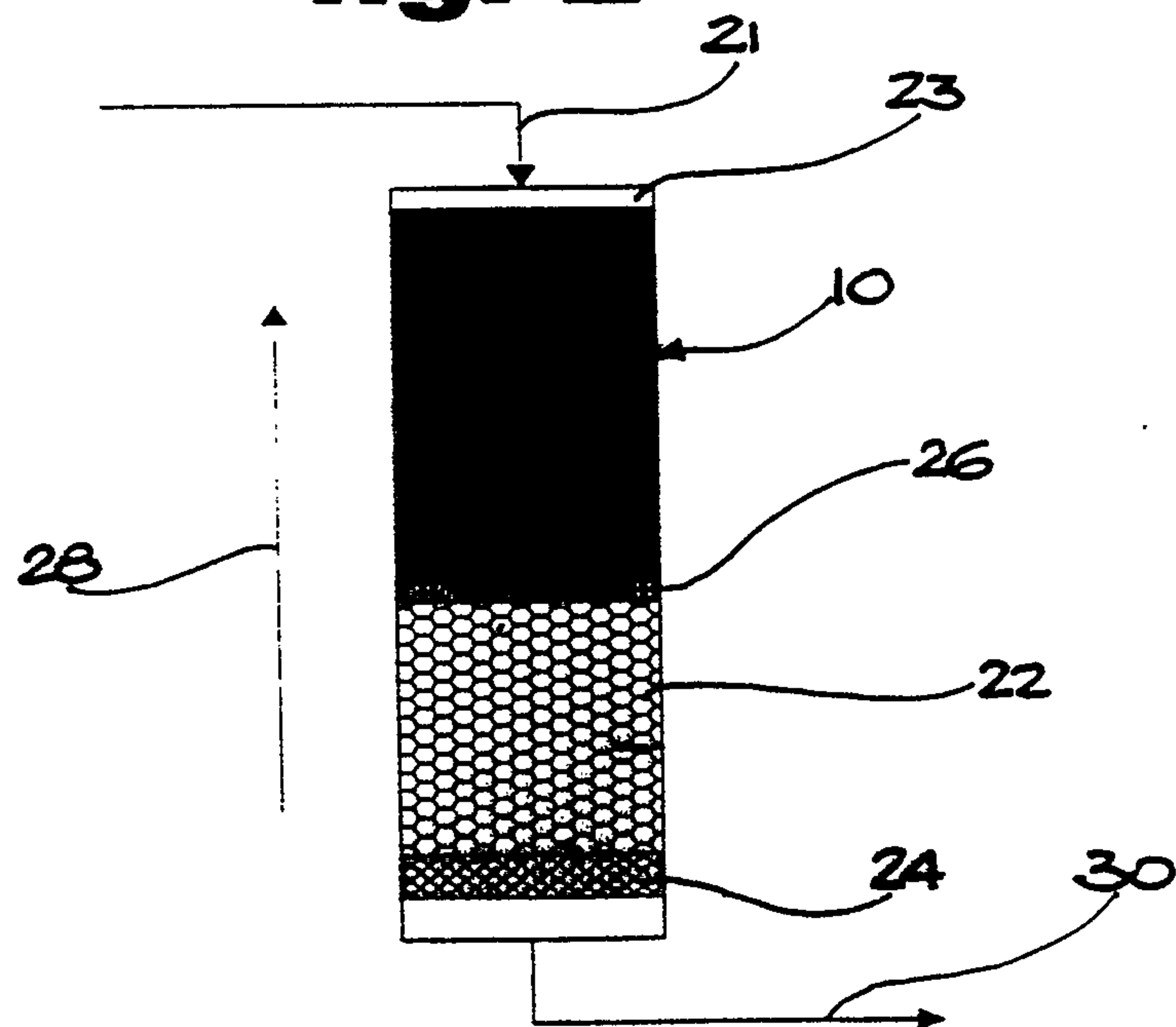
31. A process according to any one of claim 26, in which the matrix to be contaminated and treated is domestic, special, toxic, harmful or medical wastes.

32. A process according to any one of claims 1 to 31, in which said contaminants, undesired substances and compounds, present in a pure or diluted form are halogenated aromatic compounds.

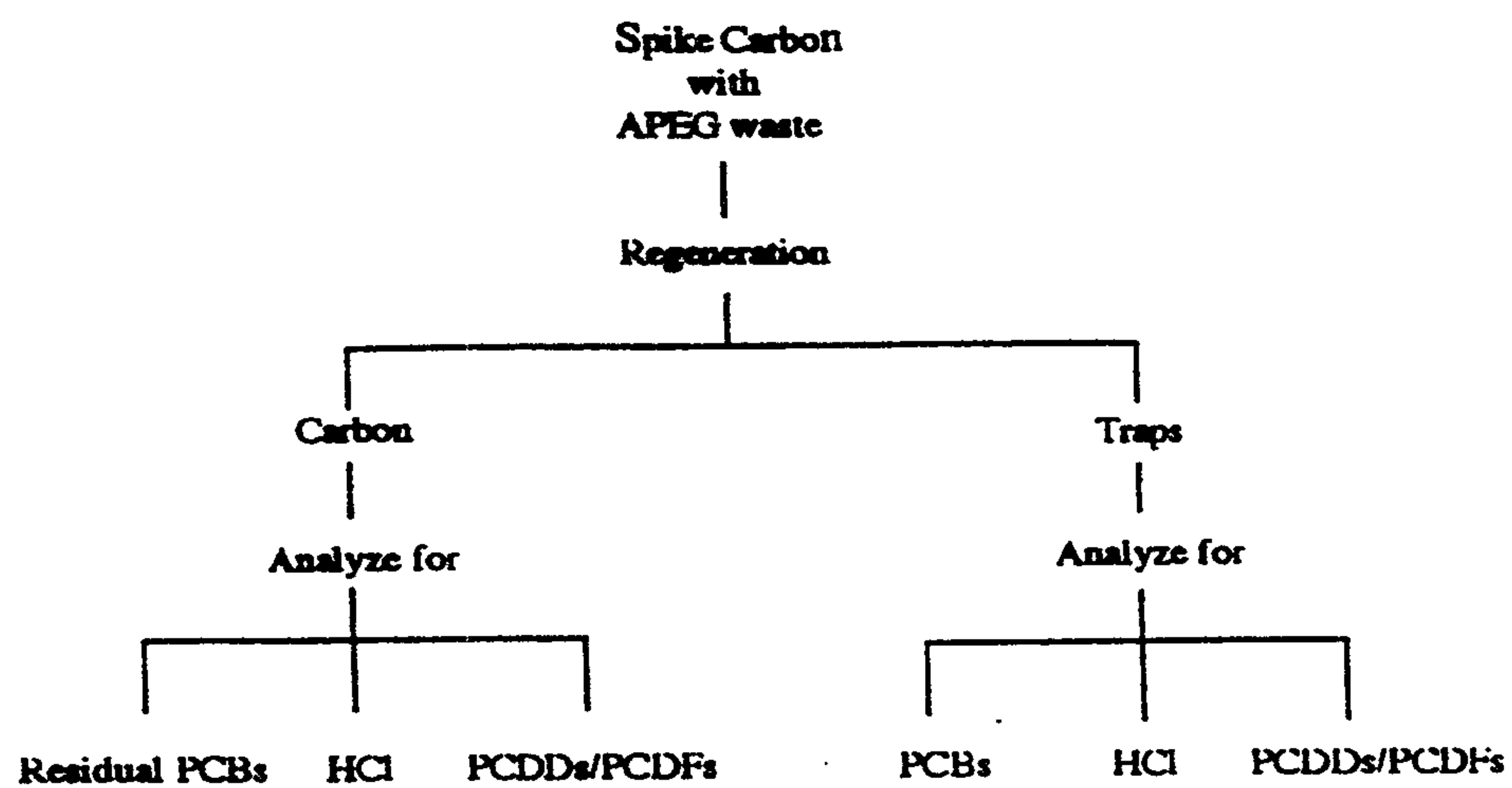
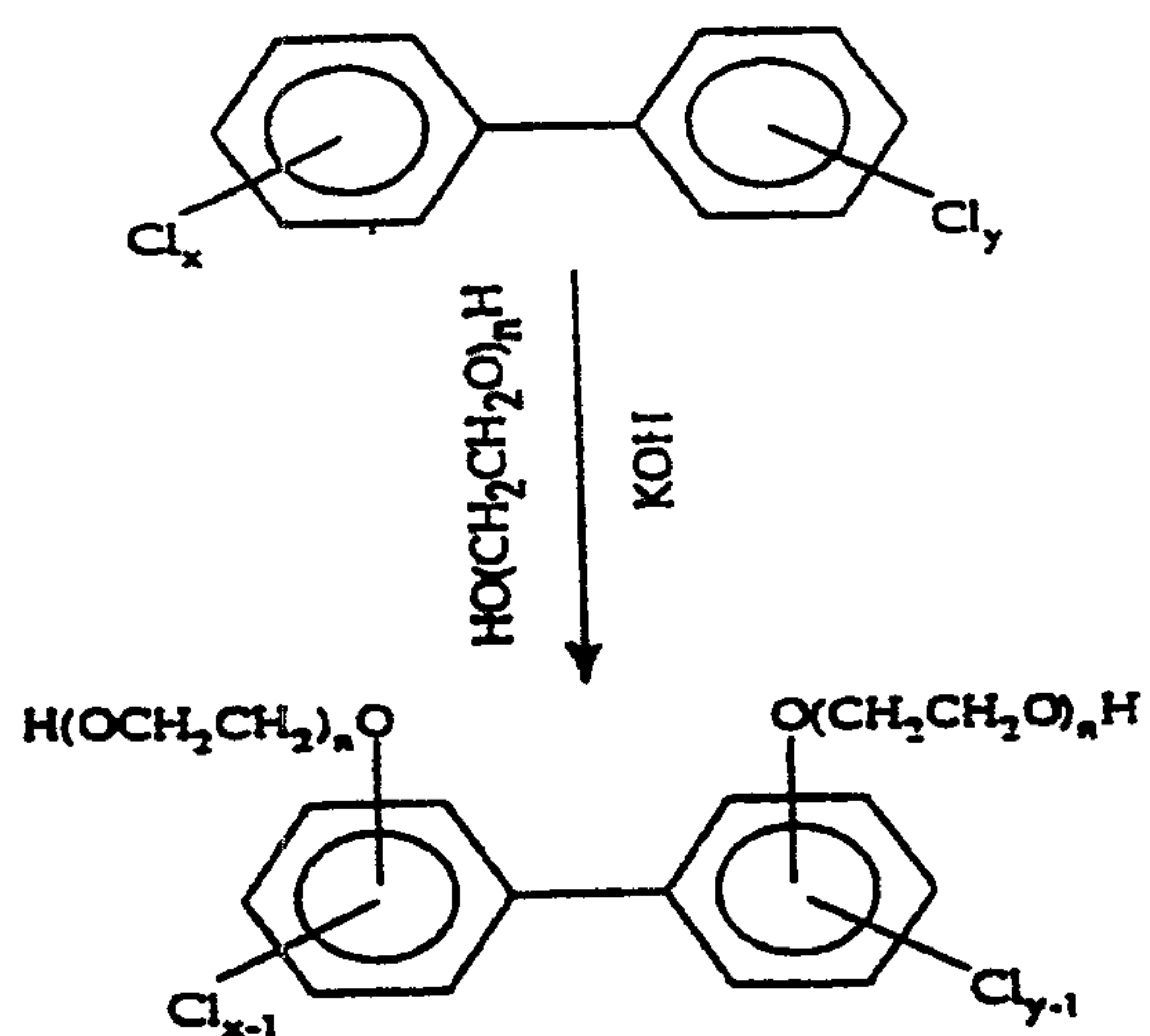
33. A process according to claim 32 wherein the halogenated aromatic compounds are selected from PCBs, PCDDs, PCDFs, PBBs, DDTs, and DDEs.

34. A process according to any one of claims 1 to 33, in which said particulate support (22) and/or decontaminating reagent are pre-formed on functional beds under the form of columns or cartridges.

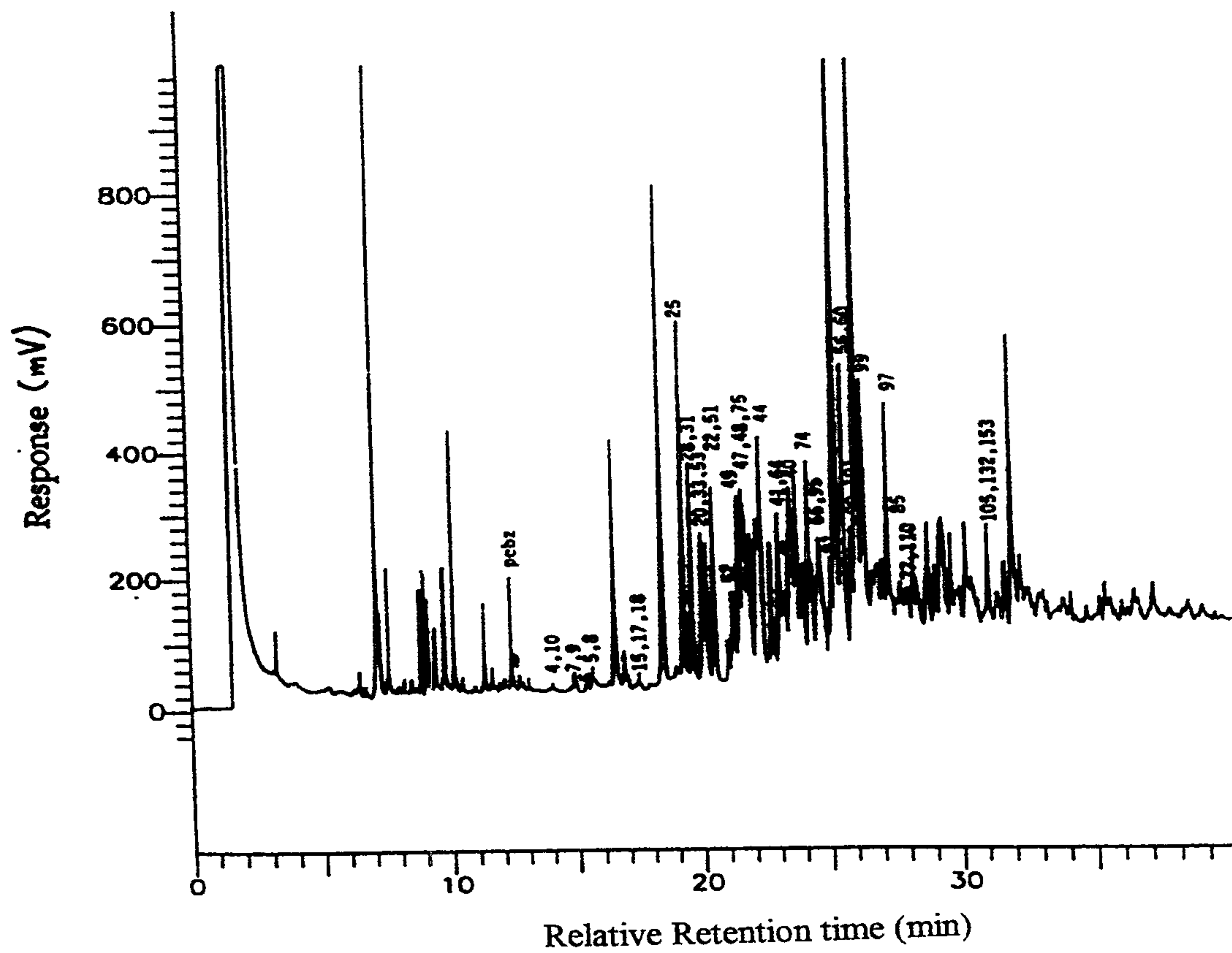
1/8

fig. 1**fig. 2**

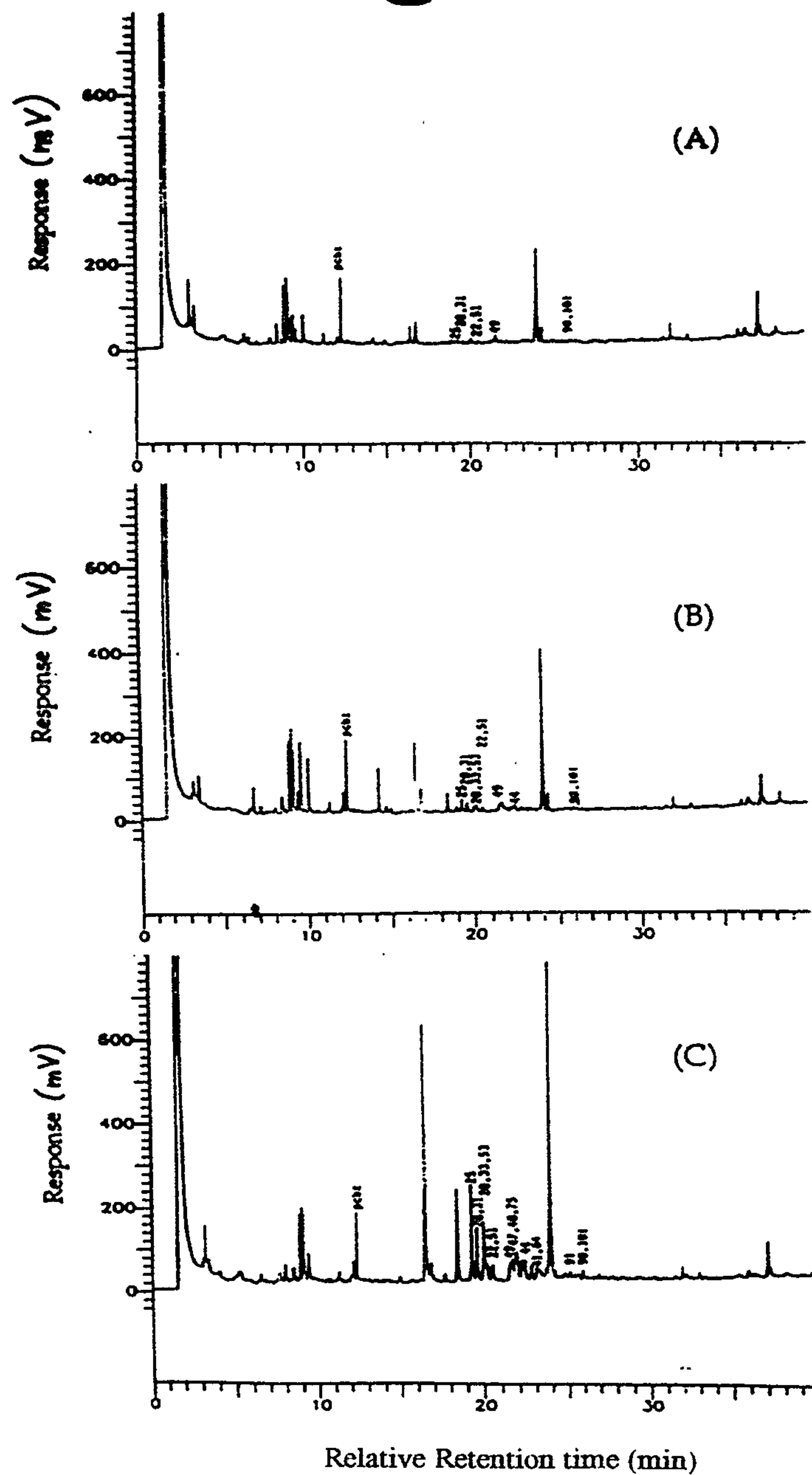
2/8

fig. 3**fig. 4**

3/8

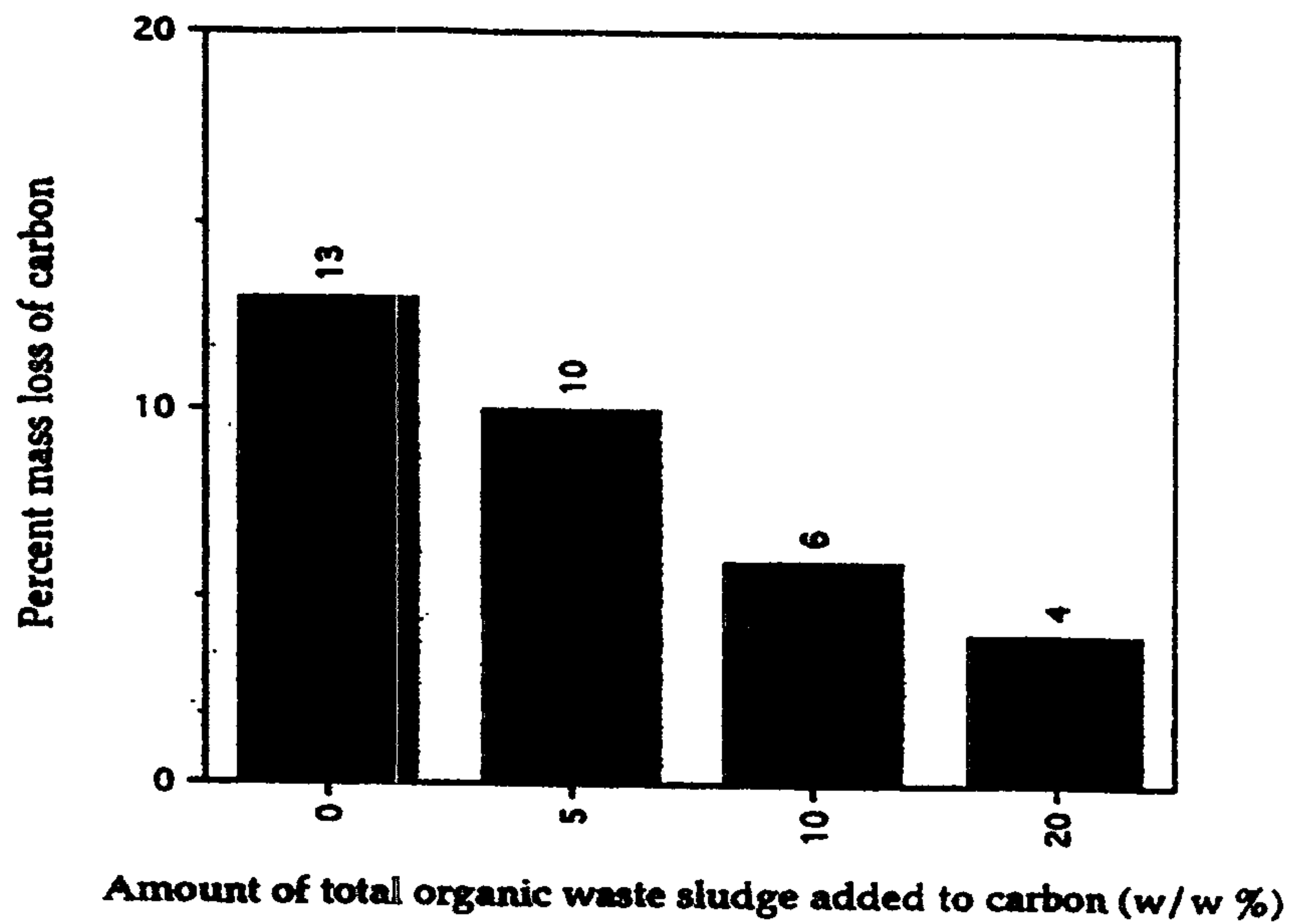
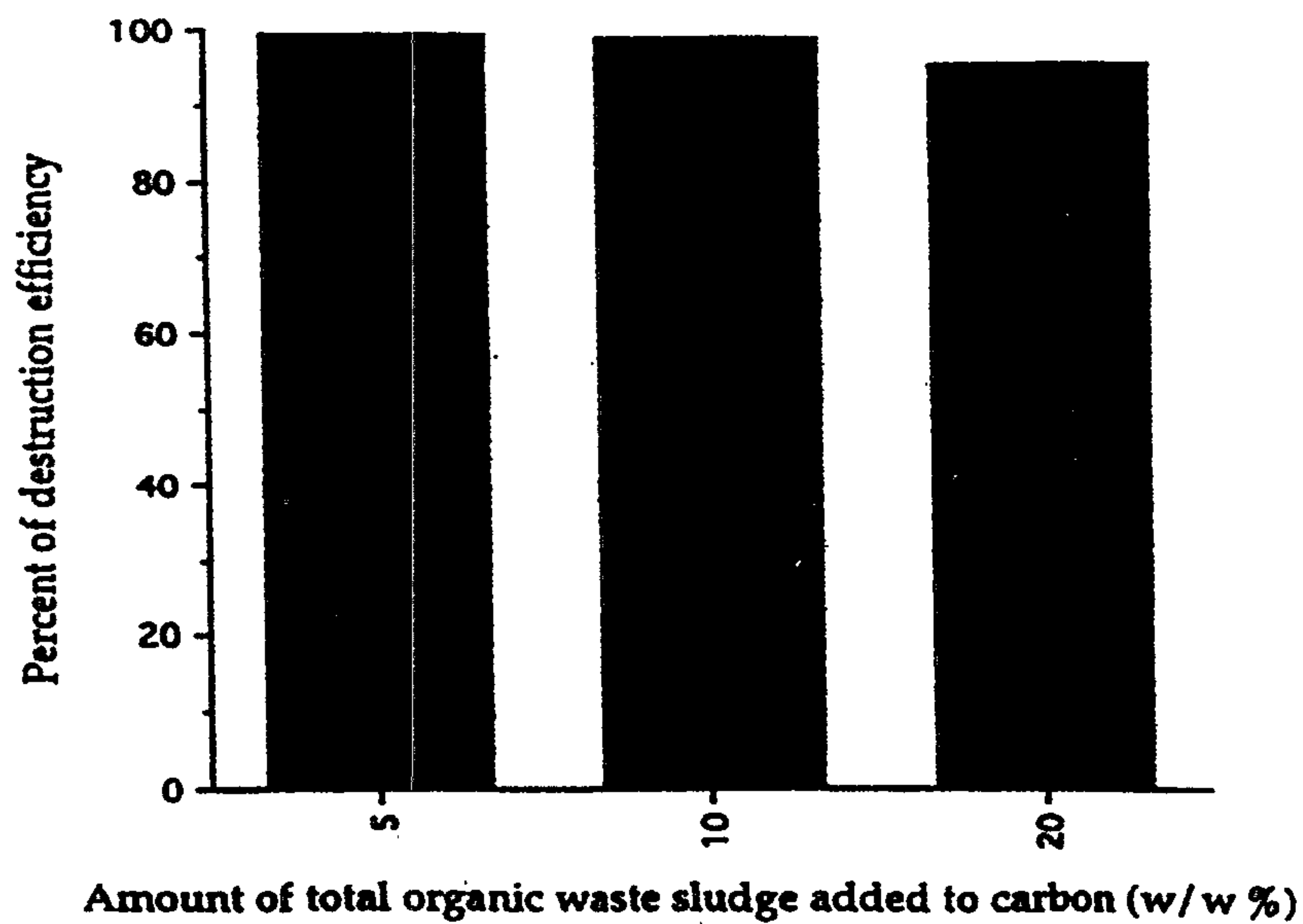
fig. 5

4/8

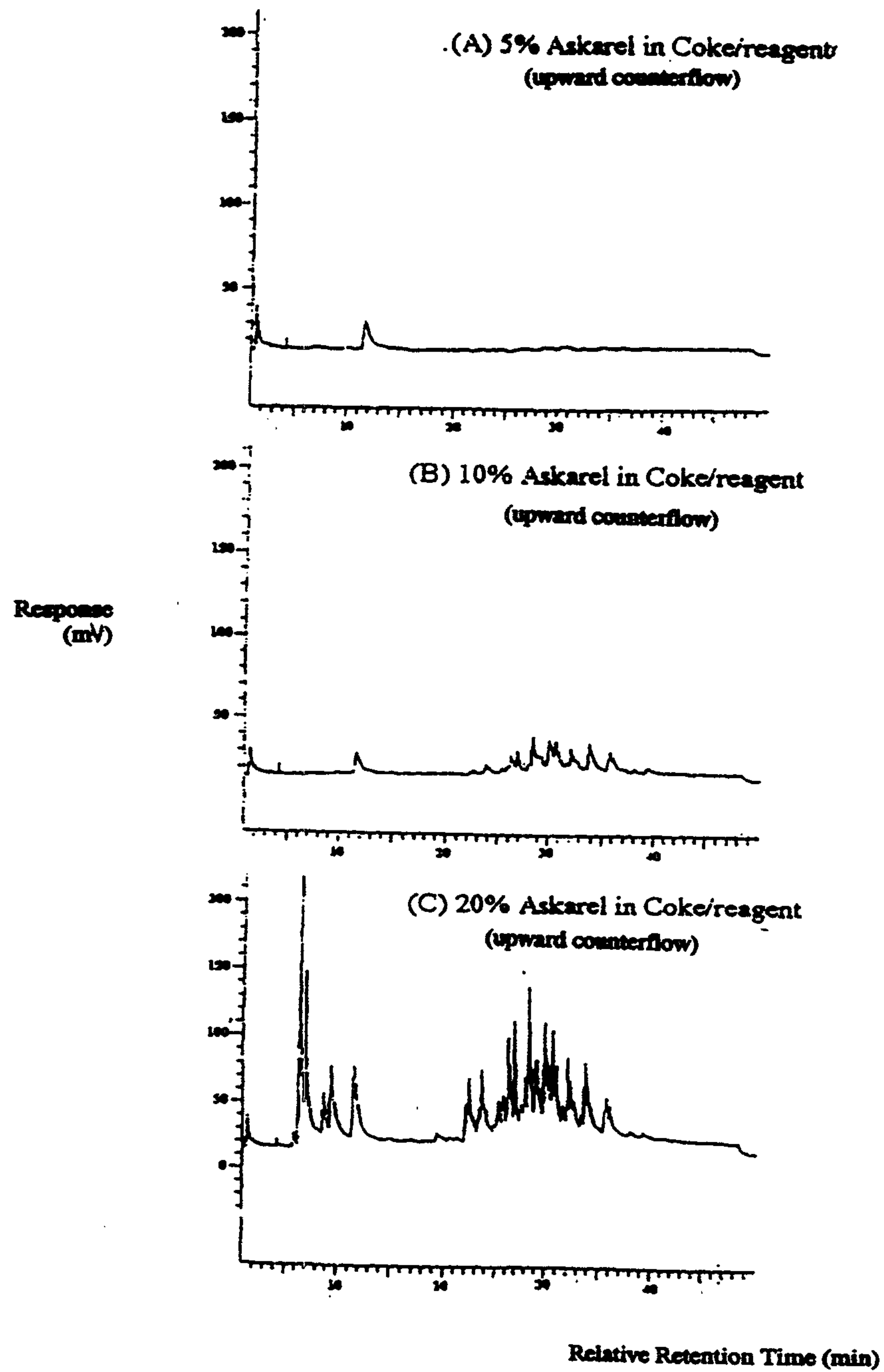
fig. 6

Chromatograms of Residual PCBs after COR Treatment
(A) 5% (B) 10% (C) 20% Waste dehalogenation reagent added
to Activated Carbon (w/w %)

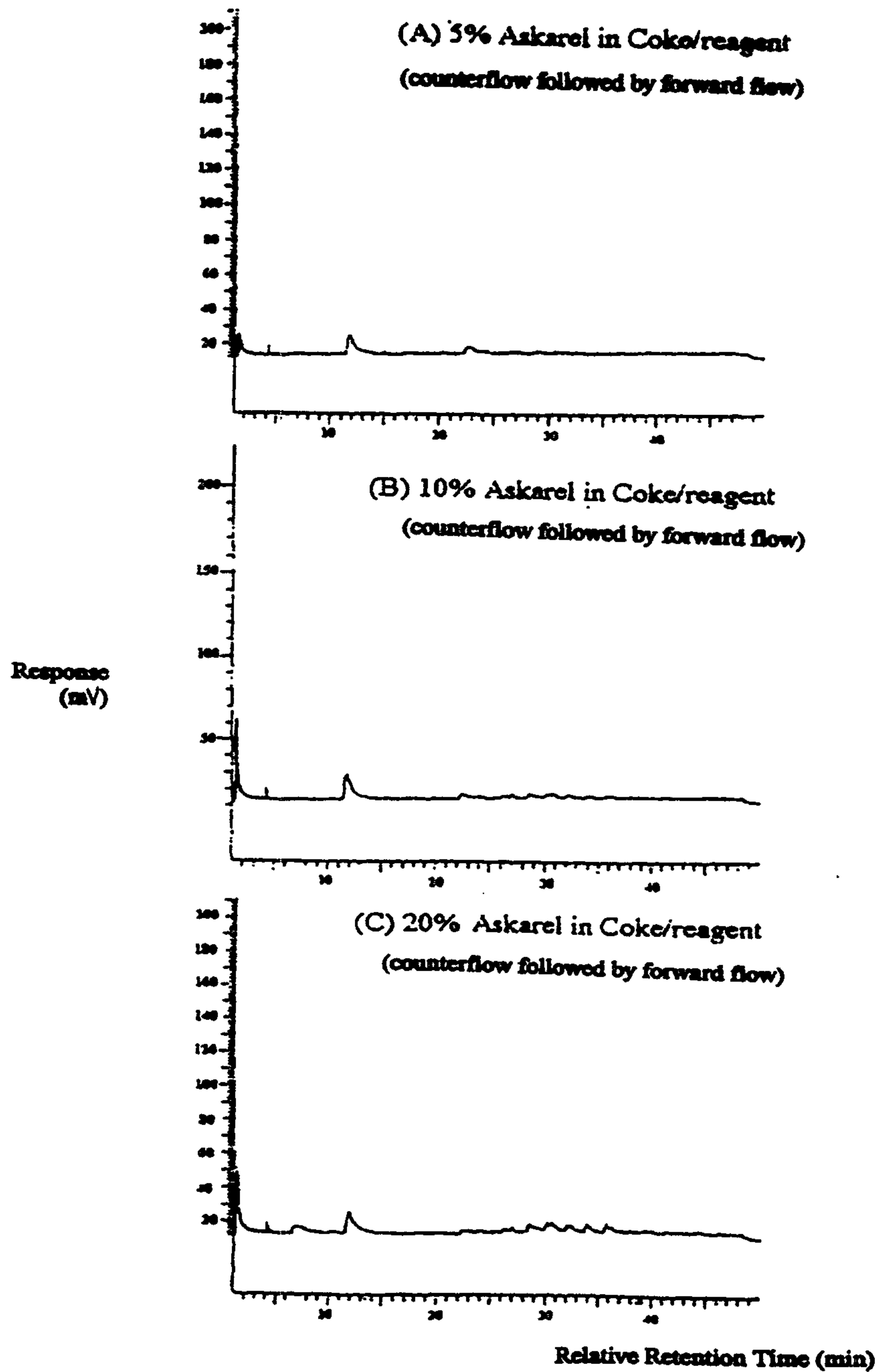
5/8

fig. 7**fig. 8**

6/8

fig. 9

7/8

fig. 10

WO 97/07858

PCT/EP96/03682

8/8

fig. 11