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(54) Title: MODIFIED ACTIVATED CARBON AS ADSORBENT FOR ANIONIC AND CATIONIC INORGANIC POLLUTANTS

(57) Abstract: Activated carbon modified by a cationic or anionic modifier or by a chelant is used as sorbent for removing heavy metal complexes and anionic and/or cationic inorganic contaminants and optionally organic contaminants from a fluid.

MODIFIED ACTIVATED CARBON AS ADSORBENT FOR ANIONIC AND CATIONIC INORGANIC POLLUTANTS

FIELD AND BACKGROUND OF THE INVENTION

The present invention is in the field of water treatment and purification and, more particularly, relates to modified activated carbon sorbents and to an adsorption method for removal of heavy metal complexes and anionic and cationic inorganic pollutants from water sources by the modified activated carbon sorbents.

In arid and semi-arid zones the amount of water is limited. In addition, in many developed as well as developing and underdeveloped countries, sewage and industrial waste have contaminated water reservoirs with organic and inorganic pollutants, thus threatening health and environment. Water reuse and purification of polluted water reservoirs could be the key for increased development, but it should be ensured that quality of the reused water and the purified water does not impose environmental hazards.

Industrial and household sewage might contain several chemicals that must be removed. This is especially important in the case of chemicals defined by the US Federal Clean Water Act as "priority pollutants", which might be hazardous to human health and the environment (EPA, 1999).

Carbon has been used as an adsorbent for water treatment for hundreds of years. The first documented use of carbon for water treatment was in 200 B. C. "to remove tastes." In 1785, experimental chemists learned that carbon could accumulate unwanted disagreeable contaminants from water. Carbon in the activated form was first used as a filter medium in the late 1800s. The use of carbon for adsorption progressed in the late 19^{th} and early 20^{th} centuries, when vapor phase organic carbon was developed and given its first widespread use as a defense against gas warfare during the First World War.

Activated carbon (AC) is a natural material derived from bituminous coal, lignite, wood, coconut shell, etc., activated by several means. Carbon particles are "activated" by exposing them to an activating agent, such as steam at high

temperature. This process develops a porous, three- dimensional graphite lattice structure. The size of the pores depends on the exact treatment. Longer exposure times result in larger pore sizes.

Granular activated carbon (GAC) filters used for water treatment were first installed in Europe in 1929. In the 1940s, GAC was found to be an efficient purification and separation technology for the chemical industry. By the late 1960s and early 1970s, GAC was found to be very effective for removing a broad spectrum of synthetic chemicals from water and gases (i. e., from the vapor phase).

Powdered Activated Carbon (PAC) is made up of crushed or ground carbon particles, 95– 100% of which will pass through a designated mesh sieve or sieves. There are several definitions for the differences between GACs and PACs based on the sieve used to separate. PAC is not commonly used in filtering devices due to low hydraulic conductivity that causes high head loss. PAC is generally added directly to other process units, such as raw water intakes, rapid mix basins, clarifiers, and gravity filters. GAC, in granular form, is designated by sizes for liquid phase extruded or vapor phase applications. The most popular aqueous phase carbons are the 12X40 and 8X30 sizes because they have a good balance of size, surface area, and head loss characteristics (USEPA, 2001).

Activated carbon in general is considered an effective adsorbent for organic molecules but not for metals and inorganic compounds (Monser and Adhum, 2002). Several works have suggested different modifications for activated carbon by various chemical treatments, and a list of such modifications is reviewed by Yin et al. (2005). Such modifications might result in different physical and chemical properties and therefore different sorption characteristics (Julien et al., 1998; Cañizares et al., 2006; Monser and Adhum, 2002; Başar et al., 2003). Acid treated activated carbon (Calgon F400, Calgon Carbon Corp., USA) was shown to have different sorption characteristics for phenol due to changes in the functional groups on the AC surface (Cañizares et al., 2006). Başar et al. (2003) studied the effect of modification of AC by surfactants on the electrostatic properties of the surface (zeta

potential) and concluded that adsorption of ionic surfactants by hydrophobic interactions might lead to charged AC surface.

Monser and Adhoum (2002) studied the removal of heavy metals by AC treated with cationic (tetrabutyl ammonium) or anionic (diethyldithiocarbamate) modifiers and found that the modification with tetrabutyl ammonium led to a better sorption capacity for Cr(VI). However, the cations used in this study did not adsorb completely to the AC and, therefore, there is a high probability that it might leak from the AC to the treated effluent, becoming a pollutant by itself, and even releasing the chromate previously adsorbed.

Garcia-Martin et al. (2005) described the adsorption of two pyrimidine-containing compounds on the surface of activated carbon and the removal of chromate ions from aqueous solutions. A recent review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions (Yin et al., 2007) discloses a wide spectrum of activated carbon modification techniques along with their advantages and disadvantages.

Methods for removal of perchlorate have been described. US 6,881,348 describes a method for removing perchlorate or other anionic contaminants from a fluid which comprises the step of passing the fluid over activated carbon, wherein the activated carbon has been either preloaded with an organic cation functional group or organic cation polymer or cationic monomer, or tailored with ammonium or other reduced nitrogen-containing compound. US 7,157,006 discloses such a method wherein the activated carbon material has been loaded with an organic cation polymer or cationic monomer having thereon functional groups; and regenerating said cation-loaded activated carbon material via thermal treatment, wherein said cation-loaded activated carbon material has a bed volume life of at least about 10% of initially treated cation-loaded activated carbon material. US 2006/102562 and WO 2006/047613 describe a method for removing at least one oxyanion from a fluid comprising passing said fluid over a carbonaceous material that has been loaded with or preconditioned with at least one ionic organic species or hydroxide species and at least one metal or alkaline earth metal or halide.

US 5,705,269 discloses modified activated carbon material for removing bacteria from a liquid, comprising activated carbon fiber having an organic bactericidal compound selected from the group consisting of brilliant green, rivanol, benzyl alcohol and zephiran containing active bactericidal groups physically adsorbed thereon, said modified carbon material being capable of binding undesirable bacteria and thus removing same from said liquid.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a modified activated carbon sorbent for removing a heavy metal complex and anionic and/or cationic inorganic contaminants from a fluid, said sorbent comprising activated carbon modified by an agent selected from:

(i) a cationic modifier or a salt thereof selected from crystal violet, berberine, methylene blue, benzalkonium, tetraphenylphosphonium, malachite green or methyl green;

(ii) an anionic modifier or a salt thereof selected from fast green, erythrosine B, acid yellow or amaranth;and/or

(i) a chelant selected from phenanthroline, 2,2′-bipyridyl, a free-base porphyrin, histidine, malic acid, a glutathione-derived metal binding peptide (phytochelatin), EDTA (ethylenediaminetetraacetic acid) or NTA (nitrilotriacetic acid).

The activated carbon for use as a sorbent according to the invention may be powdered activated carbon (PAC) or granular activated carbon (GAC), and it may be virgin or regenerated.

In one embodiment, the activated carbon is modified by a cationic modifier as defined above and is useful for removing, for example, oxyanions such as, but not limited to, chromate, perchlorate, arsenate, phosphate, nitrate, borate or selenate. In preferred embodiments, the oxyanion is chromate, perchlorate or arsenate.

In another embodiment, the activated carbon is modified by an anionic modifier as defined above and is useful for removing, for example, cationic

inorganic pollutant such as heavy metal Cd, Pb, Hg, Cu, Ni, Co, Mn, Fe, Ag or Au, or NH_4^+ compounds, or mixtures thereof, preferably Cu or Ni compounds.

In a further embodiment, the activated carbon is modified by a chelant as defined above and is useful for removing, for example, heavy metal complexes, e.g., $CdCl_2^0$, $Hg(OH)_3^-$, and the like, and/or heavy metal cationic inorganic pollutants as defined above.

In another aspect, the present invention relates to a method for treating a fluid containing heavy metal complexes, anionic and/or cationic inorganic pollutants and optionally organic compounds, or mixtures thereof, comprising treating said contaminated fluid with a modified activated carbon sorbent as defined above.

In a further aspect, the invention provides a method for recovery and regeneration for further use of an exhausted column comprising a modified activated carbon sorbent of the invention saturated with the adsorbed pollutant, for further use of the modified sorbent and, if desired, recovery of the pollutant, e.g., chromate from the effluent of electroplating industry, for further use.

In yet another aspect, the present invention provides an additional method for recovery and regeneration for extended use of a sorbing column comprising a modified activated carbon sorbent of the invention with enhanced reduction of specific pollutants on the sorbent, leading to decomposition of the hazardous pollutant to non-hazardous species, e.g., perchlorate to chlorine or nitrate to nitrogen, enabling extended use without accumulation of the pollutant

BRIEF DESCRIPTION OF THE DRAWINGS

Fig 1 shows adsorption isotherms of chromate to unmodified PAC (triangles), PAC modified by crystal violet (PAC-CV-03, squares) and PAC modified by berberine (PAC-BER-04, circles).

Fig. 2 shows adsorption isotherms of 2,4,5-trichlorophenol to PAC (rhombus), PAC-CV-03 (squares) and PAC-CV-03 previously saturated with Cr (triangles).

Fig. 3 shows chromate adsorption versus time on PAC-CV-03 (open symbols) and PAC-BER-04 (full symbols) with initial Cr concentrations of 100 μM (triangles) and 50 μM (squares).

Fig. 4 shows a breakthrough diagram of chromate solution to GAC1 (squares) and GAC1-BER-03 (rhombus). Initial chromate concentration=500 μM.

Fig. 5 shows adsorption isotherm of As to GAC1 (open squares), GAC1-BER-025 (full squares), GAC4-BER-033 (asterisks) and GAC4-MG-020 (triangles). Error bars represent triplicate standard deviations.

Fig. 6 shows breakthrough diagram of a 100 μM As solution on a GAC-BER-03 column with retention time of 18 seconds.

Fig. 7 shows breakthrough diagram of a 100 μM chromate solution on a GAC1-BER-025 column with retention time of 18 seconds showing adsorption on a new column (rhombus) and in a regenerated column (squares) after 7 cycles of regeneration.

Figs. 8A-8B show removal of Cu (8A) and Ni (8B) from initial concentrations of 6750 ppb and 11400 ppb, using 10g/L or 20g/L sorbent, respectively. At such conditions, treatment with non-modified AC leaves ~20% - 30% of the added pollutant in solution, whereas treatment with several activated carbons (based on GAC3) modified by a chelant achieves total removal.

DETAILED DESCRIPTION OF THE INVENTION

Activated carbon (AC) in general is considered an effective adsorbent for organic molecules but not for metals and inorganic molecules. According to the present invention, a modification is performed on either powdered (PAC) or granular activated carbon (GAC) aiming to add to the sorbents the ability of removing inorganic pollutants.

The modification of AC according to the invention is performed by the binding of an ionic or polar aromatic molecule to the activated carbon matrix. This organic modifier should consist of a hydrophobic part based on one or several separated or fused aromatic rings, which anchors the modifier to the AC, and an

ionic or polar part, which interacts with the pollutant. For this purpose, several compounds including organic dyes have been selected as detailed below, but similar compounds with such characteristics would also be suitable and are encompassed by the present invention.

In one embodiment, the modification is performed by using a cationic modifier, for example, a salt of an organic dye such as berberine chloride, crystal violet chloride, malachite green oxalate, methylene blue chloride or methyl green chloride, or another cationic compound such as tetraphenylphosphonium chloride or benzalkonium chloride, in order to remove anionic pollutants such as chromate, arsenate, perchlorate, phosphate, nitrate, borate, selenate, and the like.

Crystal violet or CV is a triphenylmethane dye found in gentian violet and is also called hexamethyl pararosaniline chloride. Berberine, a yellow dye, is an isoquinoline alkaloid found in some medicinal plants. Malachite green is a synthetic dye also called aniline green, basic green 4, diamond green B, or victoria green B. Benzalkonium chloride is a mixture of alkylbenzyl dimethylammonium chlorides of various alkyl chain lengths, commonly used as an antiseptic and spermicide. Methylene blue is a bright greenish blue organic dye belonging to the phenothiazine family and used in biology in staining procedures. Tetraphenylphosphonium can be abbreviated Ph_4P+ or PPh_4+.

In another embodiment, the modification is performed by using an anionic modifier, for example, a salt, e.g. sodium salt, of anionic dyes such as fast green, acid yellow, or amaranth in order to remove cationic pollutants such as mercury, lead, nickel, cupper, cadmium, and the like.

Fast green is an acid arylmethane dye. Erythrosine B or tetraiodofluorescein is a fluorescent red acid dye. The Acid Yellow dye is preferably Acid Yellow 14. Amaranth or 2-hydroxy-1,1'-azonaphthalene-3,6,4'-trisulfonic acid trisodium salt, is also called Acid Red 27.

In an additional embodiment, the modification is performed by using a chelant. As known in the art, chelation refers to the binding or complexation of a bi- or multidentate ligand to metals by bonds that might be coordination bonds, ionic

bonds or a combination thereof. These ligands, usually multifunctional organic compounds, are called chelants, chelators, chelating agents, or sequestering agent and these terms may be used interchangeable herein.

In accordance with the invention, the chelating agent is selected from phenanthroline, 2,2'-bipyridyl, free-base porphyrin, histidine, malic acid, a glutathione-derived metal binding peptide (phytochelatins), EDTA or NTA, in order to remove heavy metal pollutants such as mercury, lead, nickel, cadmium, copper and the like, either in cationic form or as complexes based on such metals.

Phenanthroline, particularly 1,10-phenanthroline, acts as a bidentate ligand in coordination chemistry and forms strong complexes with most metal ions. It is used in metallocene industry in several applications including coordination of organometallic-complexes, redox mediators in biosensors, catalysts for the oxidative organic synthesis, water treatment, photolysis chemistry, etc.

2,2'-Bipyridine or bipyridyl is a bidentate chelating ligand that forms complexes with many transition metals.

Free-base porphyrins are known chelating agents forming complexes with transition and heavy metals. The term "free base" is used for porphyrin in which no metal is inserted in its cavity. Examples of free base porphyrins that can be used according to the invention include, but are not limited to, corphine, corroles, porphine, coproporphyrins, etc.

Phytochelatins are oligopeptides of glutathione found in plants, fungi, nematodes and all groups of algae including cyanobacteria. Phytochelatins act as chelators, and are important for heavy metal detoxification.

As shown in the Examples hereinafter, several results are presented based on PAC and GAC modified by the organic molecules defined above. The modified sorbents exhibit impressive improved sorption characteristics for the pollutants above. In the case of Cr oxyanions, for example, complete removal was observed at the low concentration range, with very high selectivity for Cr. The modification did not hinder the original excellent adsorption properties AC poses for phenol and several other organic pollutants.

According to the present invention, the modification of GAC and PAC makes them suitable for removal of metal and other inorganic molecules, without hindering the capabilities of sorption of organic pollutants. The modification is based on the adsorption of an organic molecule that has strong and almost irreversible interaction and that its addition to the AC at low concentration leaves no organic molecule remaining in solution at equilibrium. Such organic molecules are also not released from the AC upon washing; thus, the modifier adsorbed concentration is not depleted. Such organic compounds used as modifiers are either based on an aromatic cation and a non hazardous inorganic anion (as Cl^-), or on an aromatic anion and a non hazardous inorganic cation (as Na^+), or on industrially used chelants. The organic molecules comprising an aromatic cation might be used for the removal of anionic inorganic pollutants as oxyanions, by exchanging them with the Cl^-, and the anionic modifiers might be used for the removal of cationic inorganic pollutants such as heavy metals or ammonium, by exchanging them with the Na^+. Chelant modifiers might be very effective for the removal of heavy metals. The modified platforms proposed were tested for chromate, arsenate, phosphate, perchlorate, nitrate, nickel, copper, etc. presenting good to excellent capabilities as for the amount of inorganic pollutant removal, and in several cases complete removal of the pollutant was observed at least at the low concentration range.

In some preferred embodiments of the invention, the modified sorbent consists of PAC and is suitable for use in batch systems. The PAC is preferably modified by about 0.1–0.6 mmole modifier per g PAC.

In preferred embodiments, the PAC is modified by crystal violet (CV) chloride or berberine (BER) chloride. More preferably, the PAC comprises 0.3 mmole CV per g PAC (herein PAC-CV-03) or 0.4 mmole BER per g PAC (herein PAC-BER-04). These sorbents are very suitable for removal of chromate (Cr(VI)) and perchlorate while maintaining its capability of sorption of organic pollutants as shown herein in the examples.

In some preferred embodiments of the invention, the modified sorbent consists of GAC and is suitable for use in both batch systems and column filters. The GAC is preferably modified by about 0.2–0.6 mmole modifier per g GAC.

In preferred embodiments, the GAC is modified by crystal violet (CV) chloride or berberine (BER) chloride, more preferably the GAC comprises 0.2 mmole CV per g GAC (herein GAC1-CV-02), 0.25 mmole BER per g GAC (herein GAC1-BER-025) or 0.33 mmole BER per g GAC (herein GAC1-BER-033). These sorbents are very suitable for removal of chromate (Cr(VI)), perchlorate and arsenate while maintaining its capability of sorption of organic pollutants as shown herein in the examples.

In other preferred embodiments, the GAC is modified by methyl green (MG) chloride or benzalkonium (Benz) chloride, more preferably the GAC comprises 0.2 mmole MG per g GAC (herein GAC2-MG-02) or 0.3 mmole Benz per g GAC (herein GAC2-Benz-03). These sorbents are suitable for removal of arsenate both in batch and in column systems as shown herein in the examples.

In most preferred embodiments, after removing the pollutant from the polluted effluent, the AC may be regenerated from the cationic-modified sorbent by elution with high NaCl concentration brine. Even though the sorbent has high affinity to the pollutant, at large chloride concentrations the Cl^- anions exchange the pollutant anions, which might be the treated or precipitated in high pollutant concentration brine, by usual methods (generally redox treatment). A similar procedure of elution may be used in cationic polluted sorbents. Simultaneous organic/inorganic pollutant experiments demonstrate that the modified PAC and GAC retain their ability to adsorb non-ionic organic compounds and both pollutants were adsorbed non-competitively (see Fig. 2).

In other preferred embodiments, the GAC is modified by phenantroline (Phen) or 2,2'-bipyridine (Bipy), more preferably the GAC comprises 0.6 mmole phenantroline per g GAC (herein GAC3-Phen-06) or 0.4 mmole 2,2'-bipyridine per g GAC (herein GAC3-Bipy-04). These sorbents are suitable for removal of nickel

and copper both in batch and in column systems as shown hereinafter in the examples.

Regeneration of chelant-based modified GAC is performed by means of a solution of other chelant, usually one with lower adsorption affinity to the activated carbon such as NTA or EDTA, but high affinity to the metal in case. The solution is passed or circulated through the column until the majority of the pollutant is desorbed from the modified AC (concentrations and contact times may vary according to operating conditions). After regeneration, the filter is washed with clean water in order to remove any remaining free chelant. The column is then ready for reuse, whereas the regeneration solution might be treated by redox or acidification procedures, to release the metal from the eluting chelant (which might be reused), and induce precipitation.

Regeneration of the exhausted modified activated carbon may be done with GAC or PAC, with different conditions for each.

In another aspect, the present invention provides a method for removing contaminants selected from heavy metal complexes, anionic or cationic inorganic contaminants or mixtures thereof and optionally organic contaminants from a fluid, comprising treating said contaminated fluid with at least one modified activated carbon of the present invention.

The anionic and cationic inorganic contaminants are, for example, oxyanions selected from chromate, perchlorate, arsenate, phosphate, borate and the like or cationic compounds including heavy metal (Cd, Pb, Hg, Ni, Co, Mn, Fe, Ag, Au) and NH_4^+ compounds, or mixtures thereof, and the heavy metal complexes are from metals such as Cd, Pb, Hg, Ni, Co, Mn, Fe, Ag, Au. The modified activated carbon may be modified virgin or regenerated powdered or granular activated carbon.

In one embodiment, the present invention comprises a method for treating a fluid for removal of anionic as well as cationic inorganic pollutants possibly along with heavy metal complexes comprising treating the fluid with a combination of several modified activated carbons in order to maximize removal of all pollutants

present. It should be noted that one platform does not hinder the activity of the other(s), such that they can be combined in the same filtering device

The fluid to be treated according to the invention may be any contaminated water such as, but not limited to, potable water, tap water, bottled water, groundwater, surface water, industrial effluent, and agricultural or municipal wastewater and reservoirs. The fluid may contain also organic compound contaminants besides the inorganic contaminants. When the modifier is a dye having biocidal activities such as crystal violet, berberine or methylene blue, the method of the invention will also be useful for removal of microorganisms, e.g., viruses, bacteria and fungi, from the fluid, and particularly to hinder or to overcome problems caused by biofouling of the sorbent.

The present invention also provides a method for regeneration of exhausted modified activated granular carbon saturated with a pollutant selected from chromate, arsenate, perchlorate or Ni, or a mixture thereof, comprising eluting a column of the modified GAC with a solution of a salt, preferably NaCl, KCl, or $CaCl_2$ recovering the pollutant from the collected effluent, and washing the excess of NaCl, KCl or $CaCl_2$ from the column, thus recovering the modified GAC column substantially free from adsorbed pollutants for further use. The regeneration of the sorbent by washing with a salt solution can also be done with PAC in batch procedures. In some cases, regeneration of the sorbent may be performed by enhanced reduction of the pollutants to non-hazardous species such as the reduction of perchlorate to chlorine.

The modified activated carbon of the present invention has many uses and applications, including:

(i) adsorption and complete removal of high amounts of oxyanions such as chromate, arsenate, perchlorate, nitrate, borate, selenate, and phosphate, as shown herein in the examples, while even high quality non-modified activated carbon is almost ineffective for the adsorption of those oxyanions that are severe pollutants;

(ii) adsorption of cationic compounds including heavy metals such as Cd, Pb, Hg, Ni, Co, Mn, Fe, Ag, Cu and Au or other cationic environmentally

problematic species such as NH_4^+, are removed efficiently by GAC or PAC modified with a suitable organic anionic salt or a suitable chelant;

(iii) adsorption of heavy metal complexes such as complexes of the metals mentioned above in (ii), that are removed efficiently by GAC or PAC modified with a suitable chelant; and

(iv) regeneration of polluted modified AC platforms. In the organic anionic or cationic modified AC platforms, the inorganic pollutants may be leached by eluting with a high concentration brine of a non-hazardous salt as NaCl, whereas in chelant based AC platforms the inorganic pollutants might be leached by eluting with a suitable free chelant. The brine can be treated for the precipitation or removal of the inorganic pollutants, and in some cases, as with chromium, the recovered metal might be used as a resource. In cases of combination with organic pollutants, those might be removed by the usual heating procedures of regeneration of PAC or GAC. If the modifying molecule is removed by heating, the remaining PAC or GAC might be re-modified and re-used. Such procedures make the sorbent more cost effective. Regeneration of the sorbent may also be performed by enhanced reduction of the pollutants to non-hazardous species.

The invention will now be illustrated by the following non-limiting Examples.

EXAMPLES

In order to keep coherent nomenclature, each sorbent will be identified in the Examples herein by a XXX-YYY-000 notation. The first group of letters (XXX) indicates the type of activated carbon used, the second group of letters (YYY) indicates the modifier molecule, and the third group of algarisms (000) indicates the amount of modifier in units of mmole attached to the activated carbon in g. For example, PAC-CV-045, indicates powdered activated carbon with crystal violet adsorbed at 0.45 mmole CV per g PAC.

Five different types of activated carbon were used in the following examples: PAC (Sigma C4386); GAC1 (Chemviron R 9107); GAC2 (Sigma C3014); GAC3

(Reactive Ltd., Israel, NT 12*40) and GAC4 (Norit PK 0.25-1). The modifiers are denoted by the following abbreviations: crystal violet (CV), berberine (Ber), methylene blue (MB), benzalkonium (Benz), tetraphenylphosphonium (TPP), malachite green (ML) and methyl green (MG), fast green (FG), Erythrosine B (EB), acid yellow (AY), amaranth (AM), phenantroline (Phen) and 2,2'-bipyridine (Bipy) (all modifiers were purchased from Sigma).

Example 1. Modified activated carbon – preparation protocol

All the descriptions that refer to "granular activated carbon" (GAC) were performed with several types and brands of granular activated carbons. A similar modification procedure is used for several types and brands of powdered activated carbon (PAC). Use of PAC is not recommended for filtering columns due to low hydraulic conductivity, but it might be applied in batch experiments or sequential batch devices.

Modification of GAC was performed as follows:

The optimum loading of modifier is deduced from preliminary experiments (adsorption isotherms) of the modifier on the raw GAC as the maximum loading that did not yield "free" modifier in the equilibrium solution. Exact amounts of loadings depend on brand and type of AC and may change according to AC type, origin and particle size distribution. In addition, the influence of other parameters should be considered such as temperature, pH, ionic strength, ratio sorbent to liquid, etc. In types of AC and modifiers tested it ranged between 0.05 to 0.35 mmole modifier g^{-1} AC. The cationic modifiers tested (all in the chloride salt form) were: crystal violet (CV), berberine (Ber), methylene blue (MB), benzalkonium (Benz), tetraphenylphosphonium (TPP), malachite green (ML) and methyl green (MG). The anionic modifiers tested (all in the sodium salt form) were: fast green (FG), Erythrosine B (EB), acid yellow (AY), and amaranth (AM).The chelant modifiers tested were phenantroline (Phen) and 2,2'-bipyridine (Bipy).

GAC was weighed into a glass bottle to the desirable amount, the appropriate amount of modifier was added as powder, and distilled water, tap water or

controlled ionic strength water was added. In our experiments we added 1 l of water per 200 g AC, however the water to solid ratio is not critical. On the other hand, the ionic strength of the water used is an important parameter for optimization of the process. For example, tap water (EC≈500 μSi/cm) instead of distilled water (DW<10 μSi/cm) yielded higher amounts of modifier sorbed.

The bottle was placed on an orbital shaker and stirred until no free modifier was detected in the solution. The concentration of modifier is monitored by UV-visible spectroscopy or any method that can detect the relevant molecules in solution. In our experiments the process took 12-48 h, depending on the modifier and the AC concentration.

In the next step, the modified GAC that sorbed modifier molecules is separated from the solution. The separation might be easily carried out by filtration. Afterwards the modified GAC is left to air dry. The granules obtained are used to fill columns for use as filtering devices.

The above procedure yielded sorbent columns that were proved as very effective for adsorption of chromate, arsenate, and phosphate, and preliminary encouraging results for adsorption of iodine and nickel. Further optimization of the process might be achieved by changing temperature and or/pH conditions, increasing the salt concentration of the water to simulate different water profiles (ionic strength/EC), changing the ratio GAC/water.

The optimum loading is not always the maximum loading. Steric considerations of the modifier adsorbed on the granular AC may lead to a better performance at lower loadings. In the case of modification by means of benzalkonium, for example, better pollutant (chromate and phosphate) removal was obtained at 67% of the maximum loading at the relevant conditions.

Example 2. Pechlorate removal by modified AC in batch experiments.

Perchlorate is an endocrine-disrupting compound (EDC) (Wolff, 1998) that is difficult to remove from water by standard water treatment practices (Urbansky, 1998). Most of the perchlorate manufactured in the United States is used as the

primary ingredient of solid rocket propellant. Wastes from the manufacture of perchlorate-containing chemicals are increasingly being discovered in soil and water. Treatment systems designed to reduce perchlorate concentrations below the recommended 4 ppb quantitation level are based on biological treatment and ion (anion) exchange systems, with additional treatment technologies under development (EPA, 2007).

Table 1 shows results of a preliminary experiment performed in order to test the ability of three types of modified powdered ACs (PAC-CV-03, PAC-BER-04 and PAC-BER-05) and one granular AC (GAC1-BER-025) in perchlorate removal in double-distilled water (DDW) containing 1000 ppb perchlorate or tap water containing 500 ppb perchlorate, as tested at the Israel Water Commission laboratory by the ion chromatography method. Perchlorate concentration was measured by ion chromatography with a limit of detection of 4 ppb.

Table 1. Removal of perchlorate by PAC, GAC and several modified ACs.

	Sorbent	added concentration	Matrix	Sorbent Concentration	equilibrium concentration
		Ppb		%	Ppb
1	unmodified PAC	1000	DDW	0.2	207.9
2	PAC-CV-03	1000	DDW	0.2	bLOD
3	PAC-BER-04	1000	DDW	0.2	bLOD
4	polluted water sample (internal standard)	500	DDW	-	501
5	unmodified GAC1	500	Tap water	1	33
6	GAC1-BER-025	500	Tap water	1	bLOD
7	PAC-BER-05	500	Tap water	0.1	bLOD

bLOD -below limit of detection of the pollutant

As it can be seen from Table 1, non modified PAC is not suitable for perchlorate adsorption even in batch experiments, whereas three different modified AC were very effective, lowering the amounts on solution below the limit of detection (LOD) of the instrument. Additional experiments with modified AC using tap water as a matrix (rows 6-7) demonstrate that the previous results obtained for modified PAC were achieved again, even when the ionic strength is higher than for

distilled water. Removal of perchlorate in tap water demonstrates the feasibility of the process even when other ions are present in the water (rows 6-7). Unmodified GAC1 removes relatively large amounts of perchlorate, but it should be considered that at this experiment sorbent concentration was relatively high. At the same conditions, modified GAC1 removes perchlorate below LOD.

It should be emphasized that the ability/efficiency of the modified AC in removing organic pollutants was not hindered by the modification.

Table 2 shows the results of an experiment where several volatile pollutants, at concentrations of 100 ppb each, were equilibrated in batch experiments with unmodified AC (PAC or GAC1) or with modified AC (PAC-BER-04, GAC1-CV-025 or GAC1-BER-03). Powder sorbents (columns 2,3) were added at concentrations of 1 g/l whereas all granular sorbents (columns 4-6) were added at concentration of 5 g/l. The table presents the amounts of pollutant remaining after adsorption, as measured by purge and trap gas chromatography.

Table 2. Removal of volatile pollutants by different sorbents.

Pollutant	PAC	PAC-BER-04	GAC1	GAC1-CV-025	GAC1-BER-03
1,2,3-trichlorobenzene	0.0	0.0	0.0	0.0	0.0
naphthalene	0.0	0.0	0.0	0.0	0.0
n-butylbenzene	0.0	0.0	0.0	0.0	0.0
1-chloro-4-methylbenzene	0.0	0.0	0.0	0.0	0.0
1,2,4_trichlorobenzene	0.0	0.0	0.0	2.3	0.0
1,4-p-dichlorobenzene	0.0	0.0	0.0	2.7	0.0
1,3-m-dichlorobenzene	0.0	0.0	0.0	3.1	0.0
1,3,5-trimethylbenzene	0.0	0.0	0.0	3.7	0.0
sec-butylbenzene	0.0	0.0	0.0	3.9	0.0
hexachlorobutadiene	0.0	0.0	0.0	4.1	3.0
p-isopropyltoluene	0.0	0.0	0.0	4.1	0.0
styrene	0.0	0.0	0.0	4.5	2.5
1,2-dichlorobenzene	0.0	0.0	2.7	4.7	3.3
propylbenzene	0.0	0.0	0.0	5.0	2.6
1,2,4-trimethylbenzene	0.0	0.0	0.0	5.0	2.7
1-chloro-2-methylbenzene	0.0	0.0	0.0	5.1	2.9
bromobenzene	0.0	0.0	0.0	5.5	3.8
p-xylene	0.0	0.0	0.0	6.0	4.0
monochlorobenzene	0.0	0.0	0.0	6.5	4.5
o-xylene	0.0	0.0	0.0	7.0	3.8

isopropylbenzene	0.0	0.0	0.0	7.1	3.8
m-xylene	0.0	0.0	2.3	7.3	4.8
tertbutyl-benzene	0.0	0.0	2.3	7.6	4.3
1,2,3-trichloropropane	0.0	2.6	0.0	8.2	5.4
1,1,2,2-tetrachloroethane	0.0	4.9	0.0	8.2	0.0
toluene	0.0	0.0	0.0	8.5	6.0

It can be seen that original high quality activated carbons (PAC and GAC) are very effective on all pollutants in the table. It is interesting to notice that the modifications performed on both granular and powdered activated carbon did not hindered sorption and, in all cases, more than 90% of the organic pollutant was removed. Thus, the modification performed to the activated carbons in order to functionalize them for the adsorption of oxyanions as perchlorate almost does not hinder their ability to sorb volatile pollutants.

Example 3. Removal of chromate by modified AC

Adsorption isotherms of Cr(VI) were prepared in 10 ml glass tubes with plastic screw caps by adding 1 ml of continuously stirred sorbent: unmodified PAC, PAC-CV-03 or PAC-BER-04 (10 g/L), and the appropriate amount of chromate (added as dissolved K_2CrO_4 salt). Distilled water was added to achieve a final volume of 10 ml, thus the sorbent final concentration was 1 g/L. The tubes were agitated on an orbital shaker for 24 h and then centrifuged (2000 RPM for 30 min). Following centrifugation the supernatant was measured for Cr(VI).

Fig. 1 presents the adsorption isotherms of chromate to the sorbents. All adsorption experiments were conducted in triplicates at room temperature and the sorbed concentration was calculated by a mass balance. As shown in Fig. 1, whilst Cr adsorption to the unmodified PAC is weak and does not present any range of complete removal, both modified adsorbents exhibit H-type isotherms indicating strong affinity of Cr to the modified adsorbents (Sparks, 1995). The Cr(VI) removal is complete up to adsorbed amounts of 0.1 and 0.13 mmole g^{-1} for PAC-CV-03 and PAC-BER-04, respectively, with a saturation value for the latter somewhat higher (0.19 mmole/gr) than for PAC-CV-03(0.155 mmole/gr).

In order to demonstrate that the modification of the PAC does not hinder its ability of sorption of organic pollutants, besides the series of experiments presented already in Table 2, we tested the adsorption of Cr(VI) and 2,4,5-trichlorophenol (TCP) added simultaneously. **Fig. 2** shows that adsorption of TCP by PAC-CV-03 is almost the same as for the original PAC, and adsorption of chromate by the modified AC still allows very high efficacy for TCP adsorption. No release of preadsorbed Cr was measured.

Kinetics of Cr adsorption to the modified platforms was also tested. **Fig. 3** shows Cr adsorption versus time on PAC-CV-03 (open symbols) and PAC-BER-04 (full symbols) with initial Cr concentrations of 0.1 mM (triangles) and 0.05 mM (squares). At such concentrations, unmodified PAC leaves 60% of the added chromate (C/C_0=0.6) in tens of minutes time, whereas the modified PAC show almost complete removal ($C/C_0 \approx 0$) in a 1 minute period.

Similar results were obtained by comparing granular AC (GAC1) with modified GAC1s. Adsorption capacities for chromate to GAC1-CV-02 and GAC1-BER-03 are three times higher than those on GAC1, exhibiting total removal at low amounts, whereas GAC1 does not present total removal of chromate at all. **Fig. 4** shows breakthrough diagram of a column prepared with GAC1-BER-03 compared with a column prepared with GAC1. It can be seen clearly that GAC1-BER-03 presents more than 120 pore volumes with complete removal of chromate, whereas non-modified GAC1 shows breakthrough of the pollutant after 3 pore volumes.

An experiment was performed with a very high chromate initial concentration (500 μM=58 ppm), whereas the LOD is 0.1 ppm. Thus, 4.3 g of adsorbent (GAC1-BER-03) sorbed 225 mmole chromate. Extrapolating from these results and assuming water polluted with 0.2 ppm (200 ppb), removal might be obtained for tens of thousands of pore volumes. Similar results were obtained for other modified GACs, e.g., GAC2-BER-033, GAC1-BER-025, and GAC2-Benz-0235. Due to the high hydraulic conductivity of the GAC1 and GAC1-BER-03, the experiment presented in Fig. 4 was performed even without the need of a pump, while the retention time at the filter was less than 90 seconds.

Example 4: Arsenate removal with modified GAC in batch and column systems

The adsorption isotherm of arsenate (As) to unmodified GAC1 and modified GAC1-BER-025, GAC4-BER-033, and GAC4-MG-020 is presented in **Fig. 5**. As can be seen, the As adsorption increases substantially following modification. The adsorption experiments were conducted using tap water, therefore we can deduce that the As uptake is feasible even when other anions (mostly chloride) are present in solution.

Modified GAC4s were proven to have even very strong affinity to As: a 10 gr/L of GAC4-MG-020 or GAC2-Benz-03 removed 85% and 78%, respectively, of a 0.1 mM As solution (in tap water matrix). Complete removal of As from the effluent was observed for GAC4-MG-02 up to 10 mmole As gr^{-1} sorbent.

The breakthrough curve of As from a column filter filled with GAC1-BER-03 is presented in **Fig. 6**. The column retained As completely for approximately 120 pore volumes before breakthrough occurred. The influent solution was tap water spiked with As to a concentration of 0.1 mM and the retention time 18 seconds. In similar experimental conditions, a column filter filled with GAC4-MG-02 achieved complete removal of more than 250 pore volumes.

The adsorbent shown in Fig. 6 is the same as in Figs. 4 and 7, thus the same adsorbent may be useful for the removal of several oxyanions.

Example 5. Batch Ni and Cu removal with anionic modifier or chelant

5.1 In order to remove cationic heavy metals from water, AC treated with an anionic modifier was used. For example, a 10 g/L GAC2-AY-03 removed 88% of an initial concentration of 0.2 mM Ni in tap water matrix, whilst the unmodified GAC2 did not remove Ni at all at pH values lower than 8.5.

5.2 An even more effective heavy metal removal is achieved by chelant modifiers such as phenantroline (Phen) and 2,2'-bipyridine (Bipy). **Figs. 8A-B** show almost complete to complete removal of very high concentration solutions of Cu

and Ni, respectively, by several chelant-based modified activated carbon: AC-Phen-03, AC-Phen-05, AC-Phen-08, AC-Bipy-02, AC-Bipy-04 and AC-Bipy-06 (Fig. 8A) and AC-Phen-03, AC-Phen-05, AC-Phen-08, AC-Phen-09, AC-Bipy-02 and AC-Bipy-04 (Fig. 8B). All ACs used here were prepared based on GAC3. Treatment with non-modified activated carbon at the same conditions left about 20-30% of the heavy metals in solution.

Example 6. Modified activated carbon – Regeneration protocol

In this example, the experiments were performed with filtering columns packed with modified granular activated carbons (GACs) of several types and brands. Regeneration of powdered activated carbon (PAC) was similarly tested in a batch system.

The regeneration process of an exhausted modified GAC column after use and saturated with pollutant depends on the type of modification. In cases where modification was performed with cationic or anionic compounds as CV, BER, Benz, Amaranth, etc., for example, and the GAC was saturated with chromate, the regeneration was performed as follows:

(i) Elution - a 200 g/L NaCl (commercial table salt) solution was pumped through a column of modified GAC, e.g. GAC1-BER-025, GAC2-BER-033, or GAC2-Benz-0235 that previously sorbed chromate, at a flow rate equivalent approximately to 25% of the volume of the filter per minute (for example, if the volume of the filter was 1000 ml, it was washed at flow rates of 250 ml per minute). It should be mentioned that considering that about 60% of the volume of the GAC in use is pores, the flow rate was about 0.4 pore volumes per minute. A total of 2.5 filter volumes (about 4 pore volumes) were used to wash the filter.

(ii) Washing - after elution, the column was washed at a flow rate of about 2 filter volumes per minute (3 pore volumes per minute) with tap water, for a total of 5-6 filter volumes (10 pore volumes) in order to wash out the accumulated NaCl salt.

(iv) Reuse - the column was then recovered and ready to be used again.

It should be noted that the salt concentration, flow rates, and the number of filter volumes or pore volumes mentioned for the elution washing might depend on the exact type and brand of AC, the specific modifier, the specific pollutant, pH and temperature conditions, etc. The values given here are only a framework of reference that actually were used and worked effectively in several cases. Furthermore, in several cases, the elution stage could be stopped after the third pore volume and the washing stage could also be shortened to 3 pore volumes as well.

Reuse of the pollutant is possible according to usual recycling processes. For example, recycle of chromate from the eluted solution was made by reducing it in an alkaline environment and collecting the $Cr(OH)_3$ precipitate. Experiments show that the procedure leads to a precipitate that might be easily separated from the NaCl washing solution and reused. For example, the electroplating industry generates effluent with high chromate concentrations from the process, and the Cr in this case is both a pollutant and a needed product. Thus, the washing solution might be reused several times and the separated metal, in this case chromium, is thus reintroduced to the process.

Regenerated columns of this type were used in our laboratory at least for seven cycles, with a small decrease in performance between the first two cycles (see **Fig. 7**) and no further decrease afterwards. The method was tested also for different pollutants (first cycle chromate, second arsenate, etc.).

Regeneration of chelant-based GAC or PAC was performed by a similar process, but the eluent was a solution of a chelant with relatively low adsorption affinity to the activated carbon such as NTA or EDTA. The solution was circulated through the column for three to five pore volumes, until the majority of the pollutant was desorbed from the modified AC (concentrations and contact times vary according to operating conditions). After regeneration, the filter was washed with clean water in order to remove any remaining of free chelant. The column was then ready for the next cycle. The chelant may be reclaimed from the regeneration solution by changing redox or acidity conditions of the regeneration solution. For example, in the case of NTA-based regeneration solution, lowering the pH by

concentrated HCl releases the bound metal, leading to precipitation of NTA, which might be recollected. Suitable redox process might lead to precipitation of the metal, and removal by appropriate means.

Example 7. Regeneration of the modified AC columns and of the pollutant

Very promising preliminary results were obtained for the regeneration of modified activated carbon by ion exchange. Modified GAC (GAC1-BER-03) that was previously saturated with chromate was regenerated easily by the simple and inexpensive chemical procedure described in Example 6 above and 96% of the preadsorbed chromate was recovered. Following the elution of Cr(VI) from the column it might be reduced to the insoluble Cr(III) and the precipitate can be separated by filtration (Korngold et al 2003). The Cr recovered from the column might then be recycled as raw material (Lin & Kiang 2003). In an additional experiment presented in **Fig. 7**, and based on the functionalized GAC mentioned above (GAC1-BER-03), the breakthrough of chromate can be observed in the original column after 320 pore volumes. The same column after the regeneration process had a somehow reduced performance, but it was still able to remove chromate for more than 250 pore volumes. Similar results were measured for arsenate (not shown).

Fig. 7 shows a breakthrough diagram of a 100 μM chromate solution on a GAC1-BER-03 column with retention time of 18 seconds, showing adsorption on a new column (rhombus) and in a regenerated column (squares) after 7 cycles of regeneration.

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CLAIMS:

1. A modified activated carbon sorbent for removing heavy metal complexes, anionic and/or cationic inorganic contaminants from a fluid, said sorbent comprising activated carbon modified by:

(i) a cationic modifier selected from crystal violet, berberine, methylene blue, benzalkonium, tetraphenyl-phosphonium, malachite green or methyl green, or a salt thereof;

(ii) an anionic modifier selected from fast green, erythrosine B, acid yellow or amaranth, or a salt thereof; and/or

(iii) a chelant selected from phenanthroline, 2,2′-bipyridine, a free-base porphyrin, histidine, malic acid, a glutathione-derived metal binding peptide (phytochelatin), EDTA or NTA.

2. The modified activated carbon sorbent according to claim 1, for removing anionic inorganic contaminants from a fluid, said sorbent comprising activated carbon modified by a cationic modifier or a salt thereof selected from crystal violet, berberine, methylene blue, benzalkonium, tetraphenylphosphonium, malachite green or methyl green.

3. The modified activated carbon sorbent according to claim 2, wherein said anionic inorganic contaminant is an oxyanion selected from chromate, perchlorate, arsenate, phosphate, nitrate, borate, and selenate.

4. The modified activated carbon according to any one of claims 1 to 3, wherein said activated carbon is powdered activated carbon (PAC) and the PAC is modified by about 0.1–0.6 mmole modifier per g PAC, preferably 0.3 mmole crystal violet, 0.4 or 0.5 mmole berberine per g PAC.

5. The modified activated carbon according to any one of claims 1 to 3, wherein said activated carbon is granular activated carbon (GAC) and the GAC is modified by about 0.2–0.6 mmole modifier per g GAC, preferably 0.2 mmole crystal violet, 0.25 mmole berberine, 0.3 mmole berberine, 0.3 mmole benzalkonium chloride or 0.2 mmole methyl green chloride, per g GAC.

6. The modified activated carbon sorbent according to claim 1, for removing cationic inorganic contaminants from a fluid, said sorbent comprising activated carbon modified by an anionic modifier or a salt thereof selected from fast green, erythrosine B, acid yellow or amaranth.

7. The modified activated carbon sorbent according to claim 6, wherein said cationic inorganic contaminants are selected from Cd, Pb, Hg, Ni, Cu, Co, Mn, Fe, Ag, Au and NH_4^+ compounds, or mixtures thereof.

8. The modified activated carbon sorbent according to claim 7, wherein said cationic inorganic contaminant is Ni.

9. The modified activated carbon sorbent according to claim 1, for removing heavy metal complexes and/or heavy metal cationic inorganic contaminants from a fluid, said sorbent comprising activated carbon modified by a chelant selected from phenanthroline, 2,2′-bipyridine, a free-base porphyrin, histidine, malic acid, a glutathione-derived metal binding peptide (phytochelatin), EDTA or NTA.

10. The modified activated carbon sorbent according to claim 9, wherein said heavy metal complexes and/or heavy metal cationic inorganic contaminants are selected from complexes and/or cationic Cd, Pb, Hg, Ni, Cu, Co, Mn, Fe, Ag, and Au compounds, or mixtures thereof.

11. The modified activated carbon sorbent according to claim 10, wherein said activated carbon is granular activated carbon (GAC) and the GAC is modified by phenanthroline or 2,2′-bipyridine, preferably 0.6 mmole phenantroline or 0.4 mmole 2,2'-bipyridine per g GAC.

12. The modified activated carbon sorbent according to claim 10, wherein said heavy metal cationic inorganic contaminants are selected from Ni and Cu compounds and said heavy metal complexes are selected from Cd and Hg complexes, or mixtures thereof.

13. The modified activated carbon according to claim 1, wherein the modification does not significantly hinder sorption of organic pollutants.

14. A method for removing contaminants selected from heavy metal complexes, anionic or cationic inorganic contaminants or mixtures thereof and optionally organic contaminants from a fluid, comprising treating said contaminated fluid with at least one modified activated carbon of claim 1.

15. The method according to any claim 14, wherein said fluid is contaminated water selected from potable water, tap water, bottled water, groundwater, surface water, industrial effluent, and agricultural or municipal wastewater and reservoirs.

16. A method for regeneration of exhausted modified granular activated carbon as defined in claim 1 saturated with a pollutant selected from chromate, perchlorate, arsenate, phosphate, borate, nitrate or selenate, Cd, Pb, Hg, Ni, Cu, Co, Mn, Fe, Ag, Au cationic compounds or metal complexes or NH_4^+ compounds, or mixtures thereof, comprising eluting a column of the modified GAC with a solution of NaCl or KCl, recovering the pollutant from the collected effluent, and washing the accumulated NaCl from the column, thus recovering the modified activated carbon column substantially free from adsorbed pollutants for further use, and optionally further enhancing reduction of the pollutant to non-hazardous species..

17. A method for regeneration of exhausted modified activated carbon wherein said activated carbon is modified by a chelant and said modified activated carbon is saturated with a pollutant selected from Cd, Pb, Hg, Ni, Cu, Co, Mn, Fe, Ag, Au

cationic compounds or metal complexes by means of another chelant, particularly NTA or EDTA.

18. The modified activated carbon of any one of claims 1 to 13 or the method of any one of claims 14 to 17, wherein said modified activated carbon is virgin or regenerated modified GAC or PAC.

Fig. 1

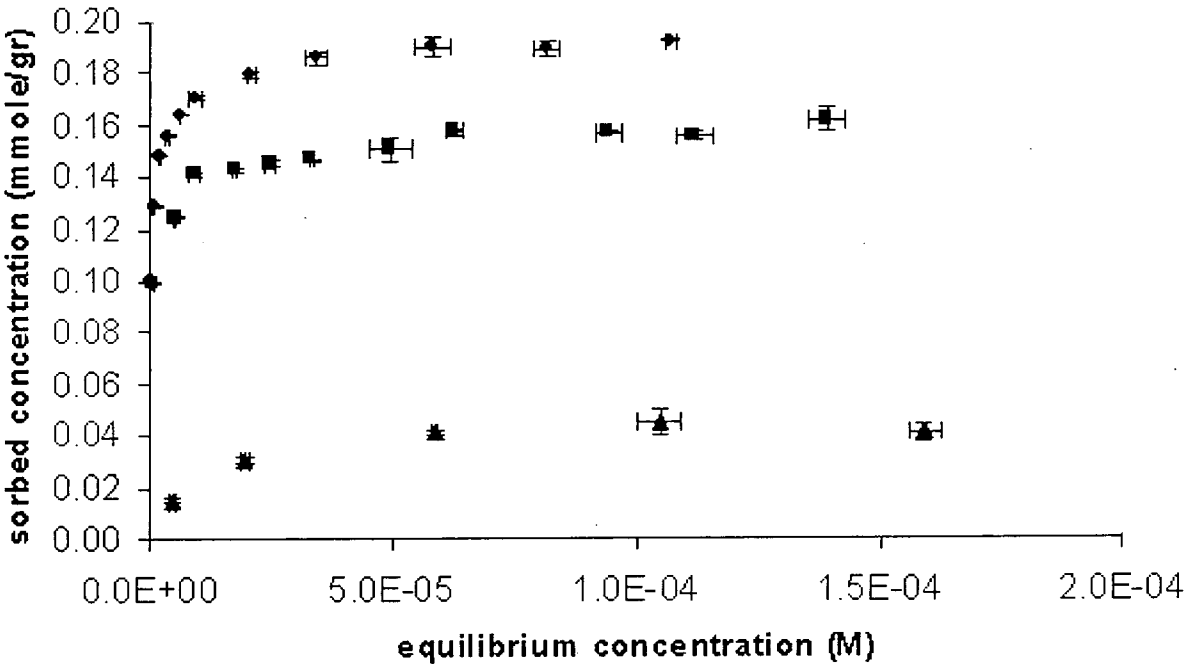

sorbed concentration (mmole/gr)
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.0E+00
5.0E-05
1.0E-04
1.5E-04
2.0E-04
equilibrium concentration (M)

Fig. 2

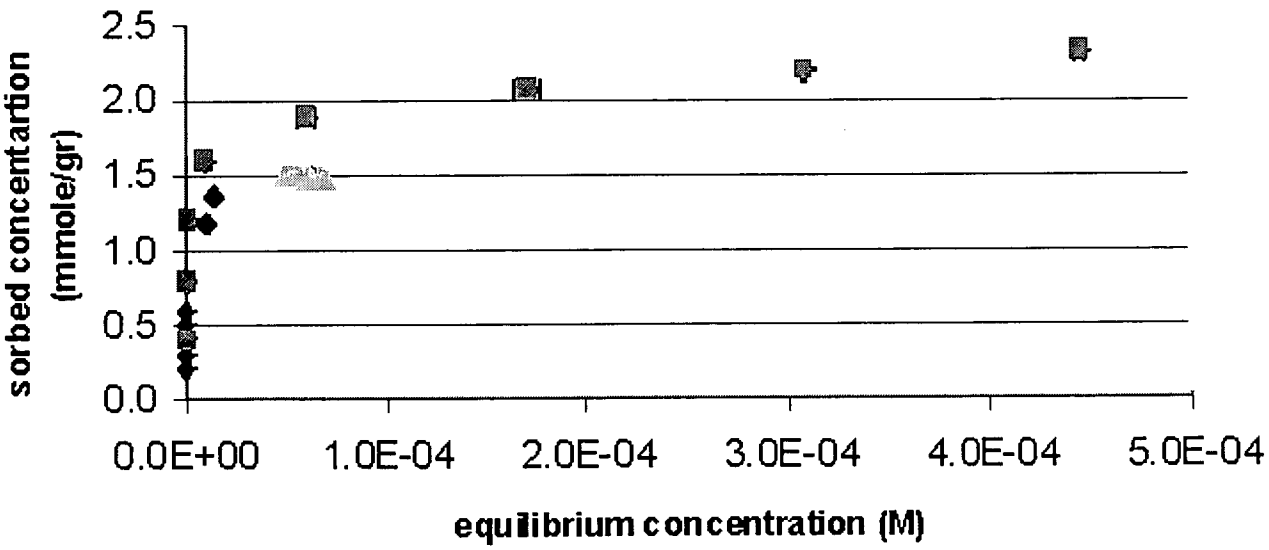

sorbed concentartion (mmole/gr)
2.5
2.0
1.5
1.0
0.5
0.0
0.0E+00
1.0E-04
2.0E-04
3.0E-04
4.0E-04
5.0E-04
equilibrium concentration (M)

Fig. 3

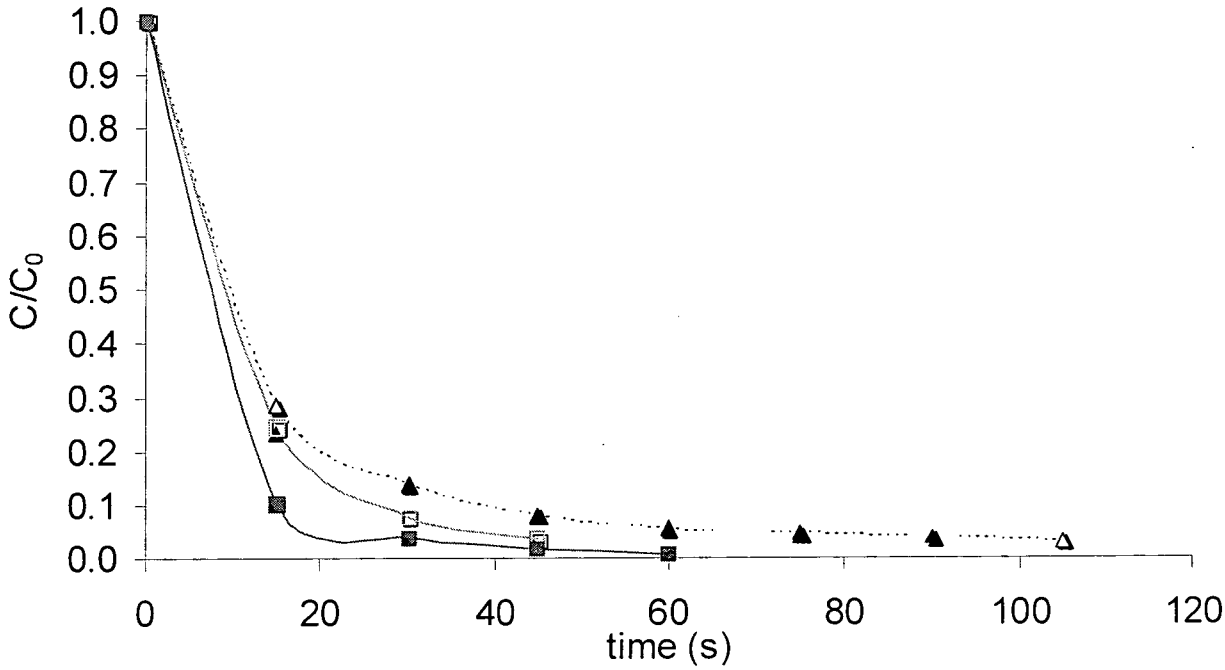

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
C/C0
0
20
40
60
80
100
120
time (s)

Fig. 4

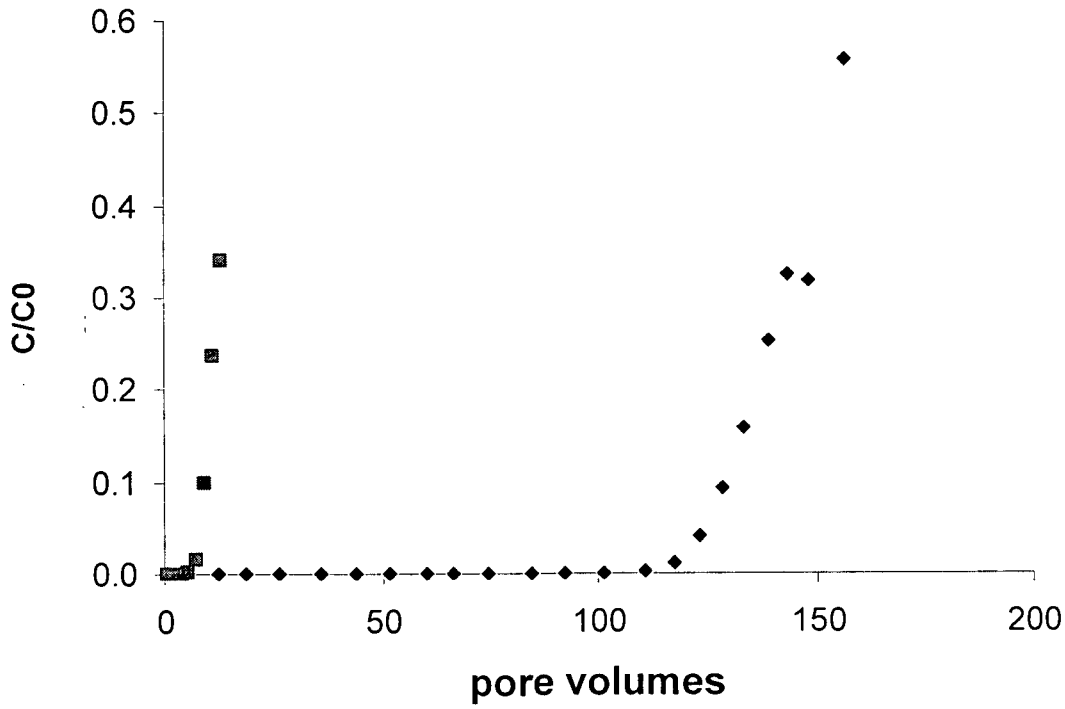

0.6
0.5
0.4
0.3
0.2
0.1
0.0
C/C0
0
50
100
150
200
pore volumes

Fig. 5

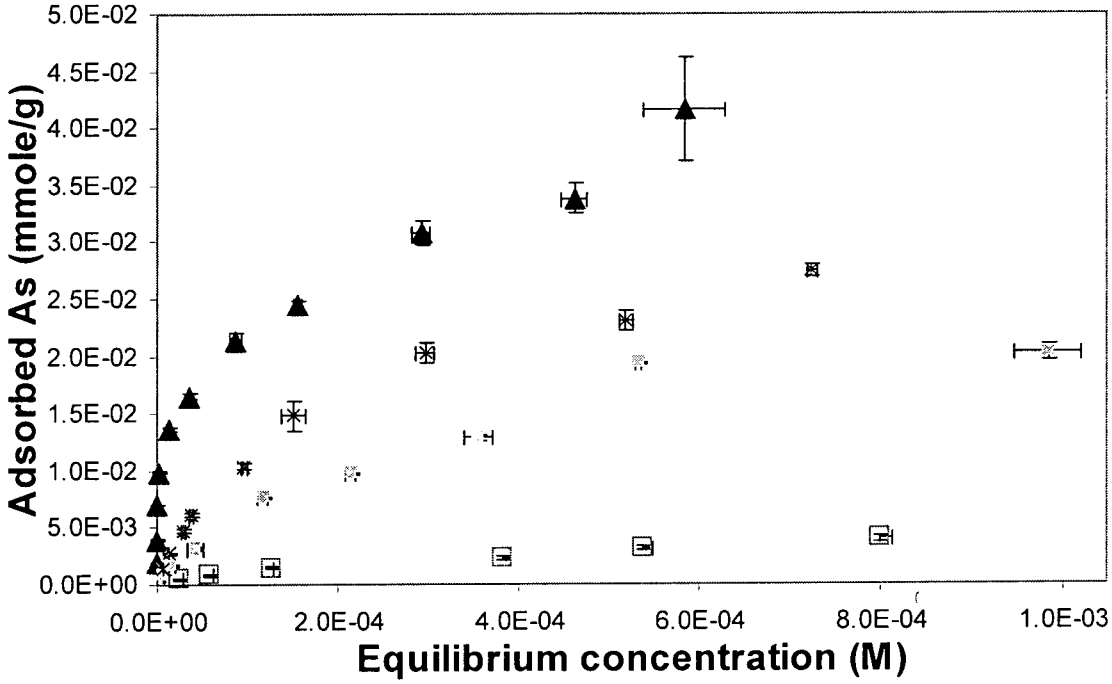

5.0E-02
4.5E-02
4.0E-02
3.5E-02
3.0E-02
2.5E-02
2.0E-02
1.5E-02
1.0E-02
5.0E-03
0.0E+00
Adsorbed As (mmole/g)
0.0E+00
2.0E-04
4.0E-04
6.0E-04
8.0E-04
1.0E-03
Equilibrium concentration (M)

Fig. 6

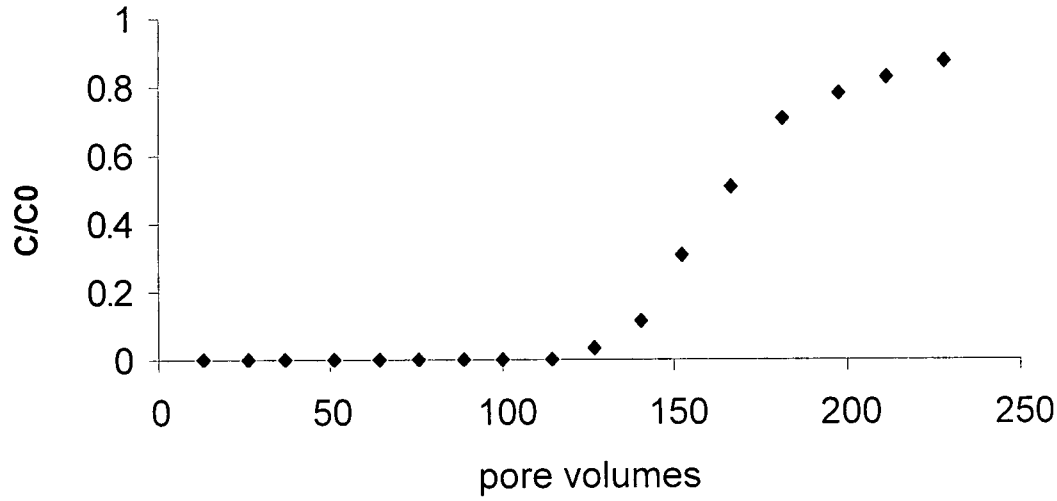

1
0.8
0.6
0.4
0.2
0
C/C0
0
50
100
150
200
250
pore volumes

Fig. 7

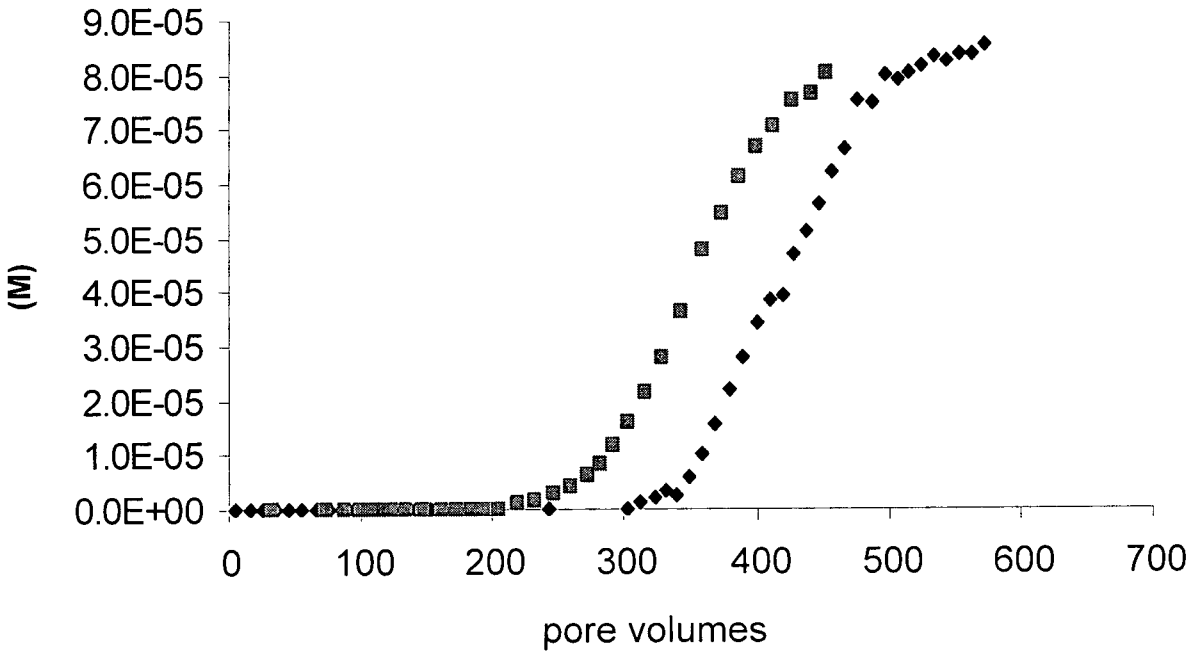

9.0E-05
8.0E-05
7.0E-05
6.0E-05
5.0E-05
4.0E-05
3.0E-05
2.0E-05
1.0E-05
0.0E+00
(M)
0
100
200
300
400
500
600
700
pore volumes

Fig. 8A

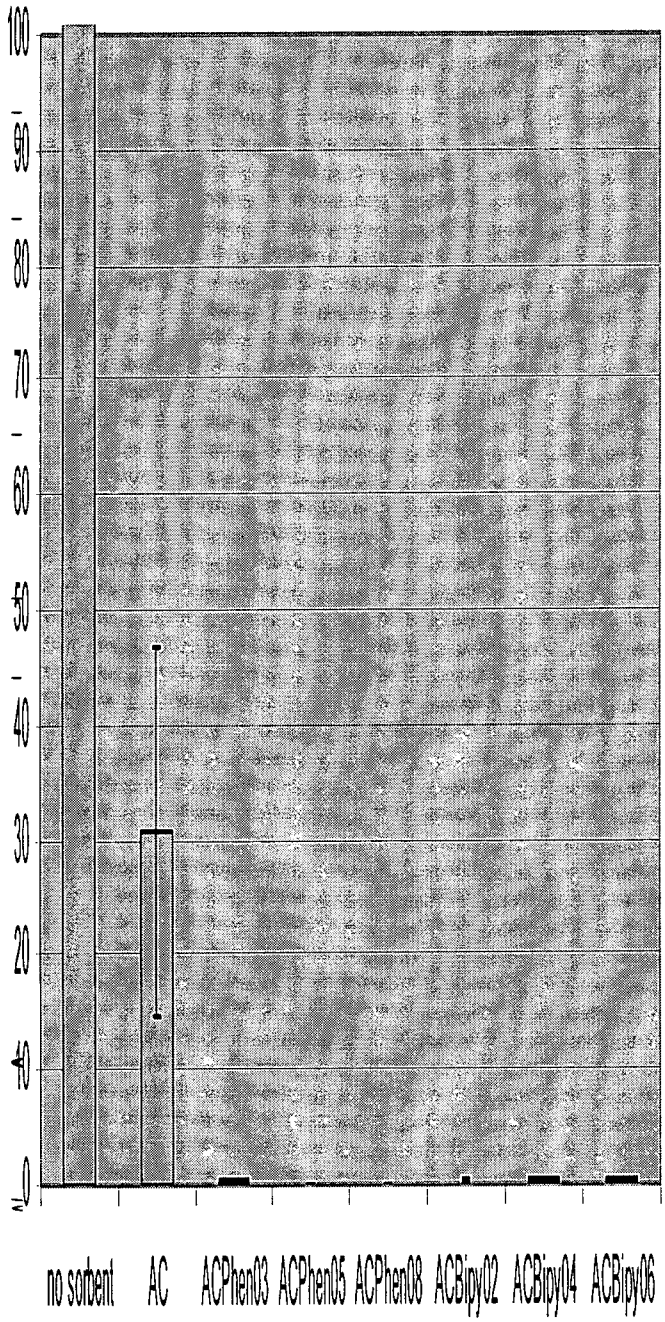
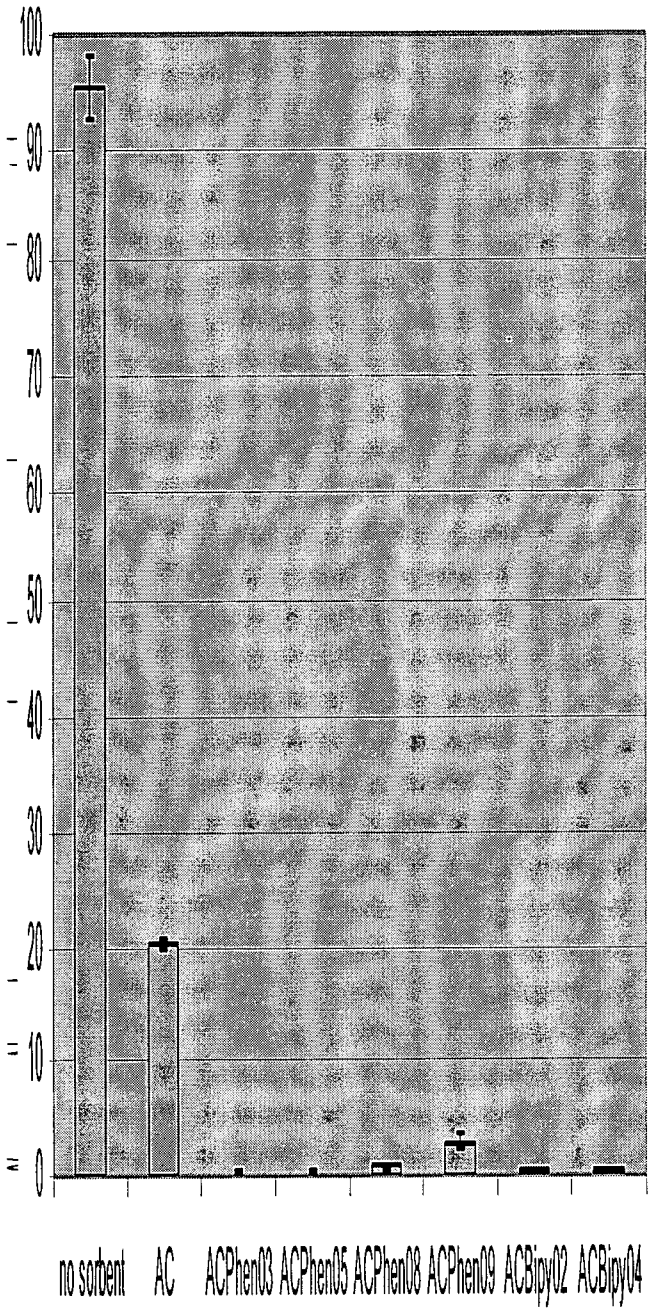

100
90
80
70
60
50
40
30
20
10
0
no sorbent
AC
ACPhen03
ACPhen05
ACPhen08
ACBipy02
ACBipy04
ACBipy06

Fig. 8B


100
90
80
70
60
50
40
30
20
10
0
no sorbent
AC
ACPhen03
ACPhen05
ACPhen08
ACPhen09
ACBipy02
ACBipy04

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2008/001370

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J20/20 B01J20/32 B01J39/24 B01J41/18 B01J20/34
C02F1/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 876 232 A (BARKATT AARON [US]) 24 October 1989 (1989-10-24) column 8, line 41 - line 42; claim 1 column 8, line 29 - line 30 column 8, line 66 - column 9, line 3	1,9-15, 18

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 2009	23/03/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Hilgenga, Klaas

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2008/001370

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International application No
PCT/IL2008/001370

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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International application No
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