



**EVALUATION OF THE RISKS ASSOCIATED WITH USE OF FILTRATION
SUPPORTS COATED WITH METALLIC OXIDES AS SELECTIVE ADSORBENTS
FOR THE TREATMENT OF WATER DESTINED FOR HUMAN CONSUMPTION**

**“WATERS” SPECIALIST EXPERT COMMITTEE REPORT
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EVALUATION OF THE RISKS ASSOCIATED WITH USE OF FILTRATION SUPPORTS COATED WITH METALLIC OXIDES AS SELECTIVE ADSORBENTS FOR THE TREATMENT OF WATER DESTINED FOR HUMAN CONSUMPTION

Following the appearance of new water treatment supports, the French Food Safety Agency (Afssa) has been approached on several occasions with requests relating to the use of filtration supports coated with metallic oxides as selective adsorbents to remove particularly arsenic, selenium and antimony in the treatment of waters destined for human consumption.

Three opinions have already been published on this type of support.

Considering the increase in requests and the permanent concern for equitable treatment of requests, the Afssa "Waters" SEC made a self-referral of the problem on 4 May 2004.

In addition, the Director general for health in a letter dated 4 September 2004, asked Afssa to describe to him/her:

- the general conditions under which water treatment by adsorption onto oxides or oxyhydroxides of iron could be authorised for the removal of arsenic, antimony and selenium in water destined for human consumption,
- the general conditions for use of the treatment processes for arsenic, antimony and selenium on activated alumina and manganese dioxide (not stated in the circular of 28 March 2000).
- the nature of the supports which may be used and any purity criteria to be observed;
- the conditions of use to be recommended to ensure effective treatment of sufficient water (in terms of pH, filtration speed, support regeneration etc.)

This report is designed to provide a general evaluation of the safety and efficacy of these supports from a literature review of these processes (attached in the annex) and to define their conditions for use in order to guarantee the health safety of water destined for human consumption.

This evaluation should enable the Ministry responsible for health to have access to the necessary information to revise circular DGS/VS4/2000 no. 166 dated 28 March 2000 relating to products and processes for the treatment of waters designed for human consumption.

This overall evaluation of the selective adsorption processes using metallic oxides will allow closure of the specific ongoing cases based on the same subject:

- 2004-SA-0024: request for opinion relating to the use of the substance "GEH" containing ferric oxyhydroxide with a view to removal of selenium from water designed for human consumption,
- 2004-SA-0326: opinion relating to the authorisation for use of the substance "GEH" in a procedure for removing antimony from water designed for human consumption,
- 2004-SA-0398: request for opinion relating to certification of the "Infiltraflo As" arsenic removal process for water destined for human consumption by filtration through iron hydroxide (following the Afssa opinion dated 11 September 2003),
- 2005-SA-0020: request for opinion relating to authorisation for use of a process for removal of arsenic from water destined for human consumption by filtration through the product "Bayoxide E33".

I. Regulatory and health setting

A. Regulatory setting

Products and processes for the treatment of water destined for human consumption are subject to authorisation by the minister responsible for health on opinion of Afssa (article R. 1321-48 of the Code of Public Health legislation) which stipulates that:

"No treatment product used in the preparation of water designed for human consumption must be found in the water made available to the user in concentrations above the quality limits set in 1 of annex 13-1, nor carry a potential danger to public health. [...]"

More restrictive arrangements concerning toxic chemical impurities which may be present in treatment products used in the preparation of water destined for human consumption may be imposed by the minister when he/she approves the correction methods. [...] At the end of the treatment the water must not be aggressive, corrosive nor hinder disinfection”.

The aforementioned circular DGS/VS4/2000 no. 166 dated 28 March 2000 states in annex I BIS that for refining (modifying mineralisation) the following treatment stages are approved for the production of water destined for human consumption:

- Adsorption on activated alumina;
- Filtration through manganese dioxide or sand, coated with manganese dioxide;
- Water defluorination on activated alumina or apatite;
- Removal of arsenic, selenium and antimony on activated alumina or on manganese dioxide;

It its annex, this circular also provides lists of substances and treatment processes which may be used for the production of water destined for human consumption.

B. Health setting

Certain treatments for water destined for human consumption are more potent than others and have the disadvantage of leading to the formation of sub-products which may adversely affect human health. This applies, for example, to ozone which in the presence of bromides may lead to the formation of bromates, carcinogenic compounds.

Amongst the less powerful processes used are precipitation-coprecipitation and adsorption on filtering supports.

In terms of the treatment of water destined for human consumption, the filtration supports coated with metallic oxides may be used as selective adsorbents, particularly for arsenic, selenium and antimony. This type of treatment allows the toxic minerals to be adsorbed specifically, although it cannot replace a disinfection stage by a biocide, in partly reducing microbiological water pollution. It also has the advantage of being able to be used in low volume installations supplying a limited population with limited resources, to improve the health safety of the water which is distributed.

In addition, the quality limits relating to the content of mineral micropollutants in drinking water are becoming increasingly lower and in order to meet these limits treatments involving increasingly effective processes are being used.

Recent studies have shown that sands coated with iron oxyhydroxides or aluminium or manganese dioxide are very good selective adsorbents, which are inexpensive and in some cases more effective than the normally used techniques such as precipitation, co-precipitation or adsorption onto activated charcoal granules. In addition, selective adsorption also allows chemical groups to be retained which conventional methods do not remove.

II. Nature and safety of the supports and their oxide deposits

A. Supports

The supports can be those which are resistant to alkalinity if the water to be treated is aggressive, as authorised by circular DGS/VS4/2000 no. 166 of 28 March 2000.

"LIST A2 : mineral supports:

Mineral treatment supports:

- Sands and gravel made of silica (NF EN 12904) (If the filtration involves direct filtration of a non-aggressive water, the sand may also be made of calcium carbonate. In this case the weight loss test does not apply).
- Clays (NF EN 12905).
- Active charcoal granules (NF EN 12915) (The weight loss test proposed in annex III of circular dated 7 May 1990 does not apply to active charcoal granules. [Certain] activated carbon tissues [...] and [certain] adsorbent sheets [...] are approved for the treatment of water destined for human consumption as a charcoal filter).
- Calcium carbonate if the water is not aggressive (NF EN 1018).
- Mixed calcium and magnesium carbonate and oxides (NF EN 1017).
- Mixed calcium and magnesium carbonates.
- Sulphur granules (autotrophic denitration process– Circular dated 24 July 1985).
- Baked clays.
- Anthracite – Hydroanthracite (NF EN 12909).
- Pumice stone (NF EN 12906).
- Pozzolana.
- Garnate (NF EN 12910).
- Rashig rings in baked earth.
- Manganese dioxide sand (pr NF EN 13752) ".

These products must observe the purity norms listed for each, or failing this, the purity criteria defined in annex II of the circular dated 7 May 1990.

Natural sands associated with glauconite (a clay mineral), also called "Albien or Eocène green sands" are used for the treatment of water and may be coated with magnesium oxide.

B. Oxide depositions

Substances authorised in annex 1 of the circular dated 28 March 2000, the major coagulation function of coagulation are as follows:

Aluminium sulphate (NF EN 878) (pH coagulation-flocculation between 6.0 and 7.5)

Aluminium chloride (NF EN 881) (pH coagulation-flocculation between 6.0 and 7.5)

Sodium aluminate (NF EN 882) (pH coagulation-flocculation between 6.0 and 7.5)

Ferric chloride (NF EN 888)

Iron chlorosulphate (NF EN 891).

Other substances, however, such as potassium permanganate which is authorised by this circular but which has a different principal function, may be used to form the oxide deposit on the filtration support.

Oxides deposited from these substances, identified in the literature are:

- Manganese oxides MnO_2 ,
- Iron oxyhydroxides $FeOOH$,
- Aluminium oxyhydroxides $Al(OH)_3$.

Sands coated with these oxides have the advantage of offering improved mechanical performances. Several methods of preparation and metallic oxide deposition onto the filtrating supports are possible. These deposits may be created:

- either naturally when the water is manganese-rich (in this case a black layer of MnO_2 forms on the surface of the sand granules), or when the water is rich in iron or coagulated with an iron or aluminium salt.

- or by specific deposition methods but under conditions which may have an impact on adsorption capacities.

These substances must always meet the accompanying purity norm. For activated aluminium granules, for example, the norm which applies is norm NF EN 13753 (classification index: T94-431) – Products used for the treatment of water destined for human consumption.

In general terms, the treatment supports (the metallic oxides) and the products used in their manufacture must observe the purity norms for products destined for treatment of water destined for human consumption.

Nature of deposit	Important parameters to take into account in the preparation of the supports
Iron oxyhydroxide deposits	<ol style="list-style-type: none"> 1. water pH and iron concentration are very important parameters 2. the distribution between the two chemical forms – amorphous ferric hydroxide and crystallised ferrihydrite – depends on the preparation conditions and particularly on the temperature and iron concentrations 3. the iron oxyhydroxides formed under different conditions have different adsorption properties 4. the oxide deposit may slightly increase the diameter of the sand grains and reduce their density 5. the iron oxyhydroxides change depending on the age of the deposit 6. the characteristics of the deposit are the density of the iron oxide layer, resistance of the deposit to abrasion and specific surface area 7. drying temperature plays a very important role in the adsorbent properties of the iron oxide deposited.
Aluminium oxyhydroxide deposits	<ol style="list-style-type: none"> 1. adsorption increases with decreasing pH of the deposit (pH approximately 6) 2. as for iron, the preparation is started from an aluminium solution, gradually adding caustic soda solution and drying at 70 °C
Manganese oxide deposits	The deposit is obtained from $KMnO_4$ in a hot alkaline medium for 48 hours in a solution of $MnCl_2$
Mixed deposits	Mixed aluminium-iron with iron-manganese deposits may be formed.

III. Efficacy

A. Principle and advantages of treatment with supports coated with metallic oxides

Supports coated with metallic oxides fulfil several functions:

1. They improve the water clarification in the filtration stages through a retention effect.

Sand is a naturally negatively charged support and when the coagulation treatment is insufficient, colloids which are also negatively charged are poorly retained by filtration. Conversely, retention may be improved by using neutral or positively charged filtration supports. In this case the amount of coagulant product required is reduced.

Sands coated with a metallic oxide deposit may be positively charged and as a result improve filtration.

2. They have Re-dox properties.

3. They enable selected adsorption of positive mineral groups, organic compounds and complex toxic minerals.

Depending on pH, the charges on the oxide deposits may change and the coated sands may retain either cationic or anionic chemical groups.

Compared to conventional methods used to reduce heavy metal concentrations in water destined for human consumption (precipitation of hydroxides, carbonates or sulphides in a very narrow pH range followed by separation by filtration), the use of adsorption has the advantage of broadening the pH range and, in particular, allowing retention of CrO_4^{2-} , SeO_2^{2-} and AsO_3^{3-} for which conventional methods are ineffective.

B. Effectiveness conditions

Adsorption and the adsorption yields depend on:

- the water pH: if the pH of the filtered water is less than 5, H^+ ions compete with cationic chemical groups and complex groups may be formed from the mineral ligands,
- the concentration of the chemical groups to be removed,
- the presence of interferents (competitive ions),
- the sand particle size.

The same applies to anionic groups when the pH is over 8.

As a general rule, adsorption occurs very rapidly and over the first 12 centimetres of the filter although slow adsorption has been reported when multi-adsorption or high adsorbate/adsorbent ratios are present.

The quality of the raw water and its pH directly influences the effectiveness of adsorption: it is preferable that slightly acid or neutral water be used for ammoniacal groups in the same way as it is preferable to use slightly alkaline or neutral waters for cationic groups.

C. Reduction levels for specific mineral pollutants

Effectiveness varies depending on the oxides fixed to the filter. The following table shows the cationic and anionic groups adsorbed by supports coated with iron oxyhydroxides, magnesium oxide and aluminium oxyhydroxides.

SUPPORTS COATED WITH IRON OXYHYDROXIDES

Cationic groups Classification of groups by decreasing affinity: Pb > Hg = Cu > Zn = Fe > Cd > Co = Ni > Mn	
Fe²⁺	<ul style="list-style-type: none"> - Removal increases with the extent of the iron oxide layer - Production of sludge is reduced - Adsorption is 20 to 25 times greater on a coated sand than on a conventional sand - Adsorbed iron is oxidised on the support, producing very good results - Iron adsorption depends on pH and the concentration of the oxidation agent - Adsorption is accompanied by release of H⁺ ions, although if the pH of the water falls the amount of adsorbed iron also falls - Water alkalinity plays a very major role - The amount of oxygen required are in the region of 2 mg/ml - Adsorption and biological iron removal are produced at the same time and in the support
Pb²⁺	<ul style="list-style-type: none"> - Iron oxyhydroxides produce better results than aluminium oxyhydroxides for adsorption - Adsorption depends water pH and falls greatly with an acid pH
Cu²⁺ Zn²⁺ Cd²⁺ Co²⁺ Ni²⁺ Hg²⁺	<ul style="list-style-type: none"> - Two stage retention: rapid surface adsorption followed by distribution into the oxide particles - Manganese oxides are more effective than iron oxyhydroxides - Iron oxyhydroxides are more effective than aluminium oxyhydroxides
UO₂²⁺	<ul style="list-style-type: none"> - The pH must be between 4 and 10 - At a pH of less than 4, H⁺ ions compete and adsorption does not occur. - At pH over 10, uranium is in a form which is not retained and is returned into solution
PuO²⁺	<ul style="list-style-type: none"> - Identical adsorption to that of uranium

Anionic groups Classification of groups by decreasing affinity: OH⁻ > H₂AsO₄⁻ > H₂PO₄²⁻ > H₂SiO₄⁻ > F⁻	
As(III) As(V)	<ul style="list-style-type: none"> - Important role of pH : Adsorption of trivalent or pentavalent arsenic depends on the water pH. If this is close to neutrality both forms are adsorbed simultaneously. - Retention of tri and pentavalent groups - Competition with fluoride and phosphate ions - Greater adsorption capacity than aluminium oxyhydroxides but less than manganese oxides - Adsorption produces content less than 10 µg/L. If interfering ions are present or if the content in the raw water is greater than 100 µg/L, 2 serial adsorption stages must be planned.
Se(IV) Se(VI)	<ul style="list-style-type: none"> - Adsorption onto iron oxides of Se(IV) and Se(VI) groups - Important role of pH - The system achieves a concentration of 10 µg/L
Sb(III) Sb(V)	<ul style="list-style-type: none"> - The action is the same as for arsenic, with the same yields
Cr(III) Cr(VI)	<ul style="list-style-type: none"> - Only selective adsorption allows retention of hexavalent chromium - Iron oxyhydroxides can retain up to 99% of hexavalent chromium - The presence of pentavalent arsenic reduces chromium adsorption. In this case serial adsorbents must be planned
PO₄³⁻	<ul style="list-style-type: none"> - Analogous behaviour to that of arsenic

SUPPORTS COATED WITH MANGANESE DIOXIDE

Cationic groups Classification of groups by decreasing affinity: Pb > Hg = Cu > Zn > Cd > Co > Mn	
Fe²⁺	<ul style="list-style-type: none"> - Same action as iron oxyhydroxides: the iron is adsorbed and then oxidised - Manganese oxides are more effective than iron oxyhydroxides - Production of sludge is reduced - Adsorption is reduced if the pH falls
Mn²⁺	<ul style="list-style-type: none"> - Adsorption kinetics are dependent on water pH (80% loss of adsorption between pH 6 and 8) and the amount of MnO₂ deposited on the support - Auto-oxidation of Mn²⁺ by MnO₂ requires alkaline pH - Oxidation of Mn²⁺ requires either chemical or biological oxidation - Two stages: selective adsorption followed in some cases by oxidation - The adsorbed manganese is rapidly oxidised by chloride at pH up to 6.1 - Efficacy does not depend on the amount of MnO₂ deposited but above all on the number of exchange sites
Pb²⁺	<ul style="list-style-type: none"> - Same action as iron oxyhydroxides - Importance of pH: acid pH greatly reduces adsorption
Cu²⁺ Zn²⁺ Cd²⁺ Co²⁺ Ni²⁺ Hg²⁺	<ul style="list-style-type: none"> - Same action as iron oxyhydroxides - Manganese oxides are more effective than iron oxyhydroxides and aluminium oxyhydroxides
UO₂²⁺	<ul style="list-style-type: none"> - Same action as iron oxyhydroxides
PuO²⁺	<ul style="list-style-type: none"> - Identical behaviour to uranium

Anionic groups Classification of groups by decreasing affinity: OH⁻ > H₂AsO₄⁻ > H₂PO₄²⁻ > H₂SiO₄⁻ > F⁻	
As(III) As(V)	<ul style="list-style-type: none"> - Adsorption capacity of manganese oxides greater than that of iron oxyhydroxides and, for the trivalent form, greater than that of aluminium oxyhydroxides - Adsorption of trivalent arsenic followed by oxidation into pentavalent arsenic - Quality limit in water: 10 µg/L - Retention of tri and pentavalent forms - Important role of pH: alkaline pH (> 8) greatly reduces adsorption - Competition with fluoride and phosphate ions - Adsorption produces content less than 10 µg/L. If interfering ions are present or if the content in the raw water is greater than 100 µg/L, 2 serial adsorption stages must be planned.
Se(IV) Se(VI)	<ul style="list-style-type: none"> - Identical to arsenic
Sb(III) Sb(V)	<ul style="list-style-type: none"> - Same action as arsenic - Adsorption produces content less than 10 µg/L. If interfering ions are present or if the content in the raw water is greater than 100 µg/L, 2 serial adsorption stages must be planned.
Cr(III) Cr(VI)	<ul style="list-style-type: none"> - At pH between 4 and 7 trivalent chromium is oxidised into hexavalent chromium and the hexavalent chromium is adsorbed selectively onto the manganese oxides
PO₄³⁻	<ul style="list-style-type: none"> - Analogous behaviour to arsenic

SUPPORTS COATED WITH ALUMINIUM OXYHYDROXIDES¹ AND ACTIVATED ALUMINA

¹ No classification of chemical groups by decreasing affinity can be given because of a lack of data

Cationic forms	
Pb²⁺	- Same action as iron oxyhydroxides - Importance of u pH: pH must be greater than 6
Cu²⁺ Zn²⁺ Cd²⁺ Co²⁺ Ni²⁺ Hg²⁺	Same action as iron oxyhydroxides

Anionic forms	
As (V)	- Same action as iron oxyhydroxides
Se (IV) Se (VI)	- Quality limit in water: 10 µg/L - Adsorption of the Se (IV) group is better the Se (VI) group
Sb (V)	- Same action as arsenic
PO₄³⁻	- Analogous behaviour to arsenic
F⁻	- Adsorption is possible onto aluminium oxyhydroxides as for iron oxyhydroxides although better results are obtained with heat activated alumina

D. Effectiveness on organic materials and micro-organisms

Organic oxides, particularly organic acids are adsorbed onto all three oxides. Manganese oxides are more effective than iron oxyhydroxides, which in turn are more effective than aluminium oxyhydroxides.

In terms of adsorption of micro-organisms, data show that whilst filtration through supports coated with metallic oxides reduces micro-organism content in water, this must also be followed by or incorporated into a treatment system including disinfection with a biocidal product for the treatment of waters destined for human consumption.

Negatively charged micro-organisms are adsorbed onto positive iron oxyhydroxides to form a bio-film but when the positive charges are saturated the micro-organisms have no more attachment sites and remain suspended in the water.

Selective adsorption of micro-organisms	
Iron oxyhydroxides, Manganese oxides	Reduction in bacteria by 1 to 2 log units Reduction in viruses by 1 to 2 log units Moderate reduction in Cryptosporidium oocystes,
Aluminium oxy- hydroxides, Activated alumina	Reduction in bacteria by 1 to 2 log units Reduction in viruses by 1 to 2 log units, iron oxyhydroxides are more effective than aluminium hydroxides More effective reduction in Cryptosporidium oocystes; iron oxyhydroxides are more effective than aluminium hydroxides.

IV. Life cycle of a sand – waste to be treated

A. Application

These processes do not require specific precautions to be taken for the transport, installation or handling of the sands.

Cleaning is achieved by rinsing with water.

Final disinfection may be performed with chlorinated water

B. Production of treatment sub-products

As for conventional filtration, nitrification from bacteria fixed in the filter may occur if the water contains ammonium ions and if the pH is neutral or alkaline.

If the pH is less than 6, this effect cannot take place.

C. Regeneration treatment following clogging or saturation effect (products to be processed and disposal of regeneration and cleaning products)

Retention of elements depends on the level of saturation of adsorption sites. The support is very effective initially and becomes less so as the sites are saturated, at which point the filter must be regenerated and cleaned. The term yield is therefore not used. The saturation life of a filter depends on the concentration of the group to be adsorbed and the filtration rate.

Several treatment stages with metallic oxides may be used in series.

Supports can be regenerated either by acid-base treatment or by Redox reaction. The supports can also be regenerated several tens of times without losing their properties.

The waste obtained during the regeneration must not be disposed of in the natural environment, but treated appropriately in accordance with regulations.

Following a regeneration stage, the filter must be washed and it must then be ensured that no residue of the product used at this stage is present in the treated water

The filters may be cleaned by counter-current washing; in this case the wash water flow rates must be controlled to avoid loss of sand, as the oxide deposits on the surface of the granules may reduce the density of the sand.

For supports coated with manganese oxides, addition of air into the counter-current wash improves in better deposit regeneration. The same applies if chlorinated water is used.

The wash waters must not be disposed of in the natural environment, but must be treated specifically.

D. End of life

Normally the material lasts for a very long time (approximately 10 years). Granule size changes through loss of the smallest particles. The supports must be disposed of in accordance with current rules.

V. Specific on-site monitoring

When a filter using a material coated with metallic oxides is installed on a site the saturation of the material must be monitored.

When pilot tests are performed on the water to be treated and the adsorption capacity is known, information must be available about the volume of water filtered.

TRANSLATOR NOTE

Element is translated as group or chemical group in the context as it refers to both elements eg Pb^{++}
but also groups eg SO_4^-