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(54) Title: ELECTRODE FOR ELECTROCHEMICAL ABATEMENT OF CHEMICAL OXYGEN DEMAND OF INDUSTRIAL WASTES

(57) Abstract: The invention relates to an electrode suitable for decreasing the chemical oxygen demand of waste-water comprising: a) a permanent component; and b) a sacrificial component arranged face-to-face and releasably attached to the permanent component and in electrical contact therewith, said permanent component consisting of a Substrate of a valve metal equipped with a catalytic coating containing noble metals or oxides thereof, said sacrificial component containing elemental iron. Further the invention relates to a method for abatement of the chemical oxygen demand in an aqueous waste containing oily compounds, glycols or waxes, optionally consisting of a foundry waste, by an electrolytic process involving anodic chlorine evolution in the presence of trivalent iron. Chlorine evolution may be carried out on the surface of an anode consisting of a catalytically activated-valve metal permanent component coupled to an iron-containing sacrificial component.

ELECTRODE FOR ELECTROCHEMICAL ABATEMENT OF CHEMICAL OXYGEN DEMAND OF INDUSTRIAL WASTES

FIELD OF THE INVENTION

The invention relates to an electrochemical method of abatement of chemical oxygen demand of an aqueous waste and to an electrode suitable therefor.

BACKGROUND OF THE INVENTION

The invention relates to an electrochemical method of abatement of chemical oxygen demand in foundry residues or other industrial wastes containing non aqueous components such as oily compounds, glycols or waxes, which make the relevant treatment difficult and expensive. Foundry waste-waters require treatments aimed at abating a remarkable amount of organic substances accumulated during the various process steps in order to allow their reuse or disposal.

The typical waste of an aluminium foundry, which represents one of the most complex and common industrial cases, consists of tap or well-water polluted by release agents (such as alkylaryl siloxanes and ethoxylated polyethylene waxes), hydraulic fluid normally consisting of glycol mixtures (for instance ethylene-propylene glycol), emulsifying agents, paraffin mineral oils, synthetic oils (for instance carboxylic ester-based oils), antifoams (for instance silicone-type ones), oxidation inhibitors (such as boric amide), biocides, complexing agents (such as EDTA) besides dust particles and fat residues. The chemical oxygen demand (COD) of a foundry residue is therefore not only very high (with typical values of 40,000 mg/l) but also deriving from a very complex mixture of components. In order to reduce COD to values allowing the reuse of such waste stream as process water (i.e. values not higher than 1,000 and preferably lower than 500 mg/l of oxygen) a combination of treatments of various kinds can be used, with a series of associated drawbacks. As it could be verified, the treatment by thermocompression in suitable concentrators, which has the advantage of not requiring the employment of particularly qualified staff for its operation, is not sufficient to bring COD below the required threshold and is inevitably affected by a drag of components such as hydrocarbons, glycols and surfactants in the condensate, requiring a post-treatment. In addition or as an alternative, it is possible to carry out a combined treatment of deoiling, ultrafiltration and reverse osmosis, which conversely has to be managed by dedicated personnel especially in the extremely delicate stage of rinsing of the relevant membranes. A combination of chemico-physical and biological processes often lends good results but is made difficult by the variability in the concentration of pollutant species

to be treated, besides entailing a heavy handling of chemical reactants and the need for specialised staff. All of these problems finally apply to chemical oxidation treatments with Fenton's reagent followed by ultrafiltration and reverse osmosis which nevertheless, if accurately managed, can provide a high quality water.

For some specific applications it is known that electrochemical waste-water treatments, sometimes attractive for the simplicity of the process and for the very competitive costs, may be taken into consideration; most of COD components in a foundry waste could for instance be abated by oxidation on the surface of an anodically-polarised electrode, after a possible addition of salts to the waste for the sake of imparting a sufficient electrical conductivity. On the other hand, the untreated waste contains pollutant species liable to form pitches and oligomers which would lead to the quick fouling of the electrode surface and its consequent deactivation. Wishing to make an attempt at an electrochemical treatment on a foundry waste, a preliminary deoiling step would at least be required, sensibly decreasing the overall process competitiveness.

It has thus been identified the need of providing a method of treatment of aqueous wastes containing oily compounds, glycols or waxes, in particular of wastes coming from foundry processing, overcoming the inconveniences of the prior art.

SUMMARY OF THE INVENTION

Various aspects of the invention are set out in the accompanying claims.
Under one aspect, the invention relates to a method for decreasing the chemical oxygen demand of a waste-water containing oily compounds, glycols or waxes, comprising a step of electrolysis of the waste-water with anodic evolution of chlorine in the presence of trivalent iron. The inventors surprisingly noticed that it is possible to carry out the electrochemical oxidation of wastes typical of foundry operations or similar with no fouling of electrodes and cells employed by adding, if necessary, an appropriate amount of chloride ions to the waste to be treated – indicatively 1 to 10 g/l, for instance 3 to 5 g/l – and by means of a Fe (III) ion addition, so as to combine the oxidising action of nascent chlorine on an anode surface with the flocculating action of trivalent iron. The presence of iron was found to be fundamental in particular in a primary step of the electrolysis, when it is necessary to prevent the degeneration of polymerisable substances, such as siloxanes, to a rubbery deposit; in a subsequent secondary step, the electrolysis may be advantageously carried out in the absence of iron. In this case, it may be advisable to carry out a waste settling and/or filtration step between the two electrolysis steps in a suitable unit outside the electrolytic cell. In one embodiment, after the secondary

electrolysis of the waste a final purification step may be carried out by reverse osmosis, whenever it is desirable to reduce the outlet COD value to an extreme extent and to abate the salt concentration, favouring the recycling of the depurated water to the original process. The disclosed method provided excellent experimental results with various types of foundry wastes and in general with waste-waters containing siloxanes, polyethylene waxes, glycols, mineral oils, synthetic oils, silicone antifoams, non-silicone antifoams, surfactants, EDTA or boric amide.

Under another aspect, the invention relates to an electrode particularly suitable as anode for electrochemical oxidation of organic compounds in waste-waters aimed at decreasing the chemical oxygen demand thereof, consisting of a permanent component and a sacrificial component releasably attached thereto and in electrical contact therewith, wherein the permanent component comprises a substrate of a valve metal, for instance titanium optionally alloyed, and a catalytic coating containing noble metals or oxides thereof, for instance oxides of ruthenium and/or iridium optionally in admixture with oxides of titanium and/or tantalum and the sacrificial component contains elemental iron. This has the advantage of allowing carrying out the electrolysis with no external addition of trivalent iron salts, obtaining the required amount of iron by the electrolytic dissolution of the sacrificial component, which is released into solution in trivalent form in the presence of nascent chlorine. The releasable sacrificial component further allows easily carrying out the electrolysis in two stages, with an optional step of filtration and/or settling of flocculated oily or waxy components in-between, providing for its removal before the secondary electrolysis step. The term “releasably attached” is used herein to indicate that the sacrificial component is a separate piece coupled to the permanent component by mechanical fastening and configured to be intentionally detached by a simple manual operation; in one embodiment, the sacrificial component consists of a metal mesh or wire hooked to the permanent component, e.g. hanged to the top side thereof.

In one embodiment, the sacrificial component is substantially coextensive with the permanent component and releasably attached thereto in a face-to-face configuration.

Under another aspect, the invention relates to an electrochemical system for decreasing the chemical oxygen demand of industrial waste-waters comprising an electrolytic cell, either unseparated or subdivided into two compartments by means of a separator, containing an electrode as hereinbefore described operating as anode and a valve metal or steel electrode operating as cathode. In one alternative embodiment, the invention relates to an electrochemical system for decreasing the chemical oxygen demand of industrial waste-waters comprising an electrolytic cell, either unseparated or subdivided into two compartments by means of a separator containing two electrodes as hereinbefore described, each of them being

alternatingly polarised as anode and as cathode at periodic time intervals. This can have the advantage of eliminating or strongly reducing the possible fouling by lime-scales of the electrode during the cathodic cycle, allowing its dissolution during the following cycle of anodic operation. In one embodiment, the electrochemical system comprises a settling and/or filtration unit hydraulically connected to the electrochemical cell. In one embodiment, the electrochemical system comprises a reverse osmosis unit downstream the electrochemical cell.

Some of the most significant results obtained by the inventors are illustrated in the following examples, which are not intended to limit the extent of the invention.

EXAMPLE 1

4 litres of a foundry waste with a COD of 38,700 mg/l of oxygen (detected by spectrophotometry with a suitable kit), consisting of slightly more than 90% by volume of tap water with average total hardness of 32°F and containing 0.15% by volume of alkyl aril siloxanes, 0.06% by volume of ethoxylated polyethylene waxes and minor amounts of the following contaminants:

- non ionic and anionic emulsifying agents
- ethylene/propylene glycol
- high viscosity (ISO VG 460) paraffinic mineral oil
- carboxyl ester-based synthetic oil
- silicone antifoam
- boric amide
- bacterial inhibitors
- EDTA
- typical foundry dirt (aluminium alloy dust, fats, environmental dust)

were added with 4 g/l of NaCl and 1 g/l of $Fe_2(SO_4)_3$ and fed to an electrochemical cell comprising an anode consisting of a 114 cm² titanium plate activated with a mixture of oxides of ruthenium, iridium and titanium, a cathode consisting of a non-activated titanium mesh of the same size and a separator consisting of a 0.2 mm thick polypropylene mesh, with an anode-to-cathode gap of 1 mm. The cell was operated at a current density of 500 A/m², recycling the electrolyte at a constant flow-rate of 400 l/h. The treatment was carried out monitoring the COD and chloride levels, the latter being constantly kept above 1 g/l by subsequent additions of salt (every 20 hours approximately). The test was discontinued after 130 hours, when the COD value attained, of about 900 mg/l of oxygen, showed no tendency to decrease any further while the cell voltage, until then stable around a value of 7.4 V, started increasing slightly.

After disassembling, the cell presented a consistent fouling of the cathodic surface and a partial clogging of the separator.

EXAMPLE 2

The test of example 1 was repeated with the same waste, added with sodium chloride and ferric sulphate as above, in an equivalent electrochemical cell except that it comprised two identical electrodes, both consisting of a 114 cm² titanium plate activated with a mixture of ruthenium, iridium and titanium oxides, one acting as the anode and one as the cathode. The electrode polarity was reversed every 60 minutes. The test was discontinued after 150 hours when the COD value attained, of about 700 mg/l of oxygen, showed no tendency to decrease any further. The cell voltage remained stable at 7.4 V during the whole test.

After disassembling, the cell presented a slight fouling of the electrodes and a partial clogging of the separator.

EXAMPLE 3

The test of example 2 was repeated with the same waste but with no external addition of ferric sulphate, in an equivalent electrochemical cell except that the two electrodes, both obtained from a 114 cm² titanium plate activated with a mixture of ruthenium, iridium and titanium oxides, had a wide mesh soft iron net secured thereto by mechanical hooking to the top edge of the plate. The electrode polarity was reversed every 60 minutes. The test was discontinued after 4 hours, after which the iron nets were detached from the activated titanium plates and the waste was subjected to filtration. The electrochemical treatment was then resumed and protracted for 63 hours more, with a cell voltage of 7.3 V, detecting a residual COD of 140 mg/l of oxygen, further decreased to 21 mg/l of oxygen upon reaching 200 hours of overall treatment.

After disassembling, the cell presented a slight fouling of the electrodes and a negligible clogging of the separator.

COUNTEREXAMPLE 1

The test of example 1 was repeated with the same waste in an equivalent electrochemical cell, with no external addition of ferric sulphate. The test was discontinued after 110 hours when the cell voltage attained a value of 8 V from the initial 7.35 V, with a residual COD slightly above 900 mg/l of oxygen.

After disassembling, the cell presented a grey-coloured rubbery coating on the anodic surface, impossible to remove mechanically without damaging the catalytic activation, besides a consistent fouling of the cathodic surface and of the separator. Also the cell walls, which remained clean after the previous tests, showed evidence of a grey-coloured rubbery and sticky coating.

The previous description shall not be intended as limiting the invention, which may be used according to different embodiments without departing from the scopes thereof, and whose extent is solely defined by the appended claims.

Throughout the description and claims of the present application, the term "comprise" and variations thereof such as "comprising" and "comprises" are not intended to exclude the presence of other elements, components or additional process steps.

The discussion of documents, acts, materials, devices, articles and the like is included in this specification solely for the purpose of providing a context for the present invention. It is not suggested or represented that any or all of these matters formed part of the prior art base or were common general knowledge in the field relevant to the present invention before the priority date of each claim of this application.

CLAIMS

1. Electrode suitable for decreasing the chemical oxygen demand of waste-water comprising:
   a) a permanent component; and
   b) a sacrificial component arranged face-to-face and releasably attached to the permanent component and in electrical contact therewith,
   said permanent component consisting of a substrate of a valve metal equipped with a catalytic coating containing noble metals or oxides thereof, said sacrificial component containing elemental iron.

2. The electrode according to claim 1 wherein said sacrificial component consists of a metal mesh or wire hooked to said permanent component.

3. The electrode according to claim 1 or 2 wherein said sacrificial component is coextensive with said sacrificial component.

4. The electrode according to any one of the preceding claims wherein said catalytic coating contains oxides of ruthenium and/or iridium in admixture with oxides of titanium and/or tantalum.

5. Electrochemical system for decreasing the chemical oxygen demand of industrial waste-water comprising an electrolytic cell containing an electrode according to any one of the preceding claims operating as the anode and an electrode of a valve metal or steel operating as the cathode.

6. Electrochemical system for decreasing the chemical oxygen demand of industrial waste-water comprising an electrolytic cell containing a pair of electrodes according to any one of claims 1 to 4, each of them alternatingly polarised as anode and as cathode.

7. The system according to claim 5 or 6 comprising a settling and/or filtration unit hydraulically connected to said electrolytic cell.

8. The system according to any one of claims 5 to 7 comprising a reverse osmosis unit downstream said electrolytic cell.

9. Method for decreasing the chemical oxygen demand of a waste-water containing oily compounds, glycols or waxes, comprising a step of electrolysis of the waste-water with anodic evolution of chlorine in the presence of trivalent iron.

10. The method according to claim 9 comprising the following sequential steps:
    a) optional addition of salts to the waste-water up to reaching a chloride ion concentration of 1-10 g/l;
    b) primary electrolysis of the waste-water in said electrolytic cell of the electrochemical system according to claim 5 or 6 with evolution of chlorine on the surface of said permanent component and partial dissolution of said sacrificial component;
    c) secondary electrolysis of the waste-water in said electrolytic cell of the electrochemical system after releasing said sacrificial component of said electrode.

11. The method according to claim 9 comprising the following sequential steps:
    a) optional addition of salts to the waste-water up to reaching a chloride ion concentration of 1-10 g/l;
    b) primary electrolysis of the waste-water in said electrolytic cell of the electrochemical system according to claim 7 with evolution of chlorine on the surface of said permanent component and partial dissolution of said sacrificial component;
    c) primary purification of the waste-water exiting said primary electrolysis in said settling and/or filtration unit;

d) secondary electrolysis of the waste-water in said electrolytic cell of the electrochemical system after releasing said sacrificial component of said electrode.

12. The method according to claim 9 comprising the following sequential steps:
a) optional addition of salts to the waste-water up to reaching a chloride ion concentration of 1-10 g/l;
b) primary electrolysis of the waste-water in said electrolytic cell of the electrochemical system according to claim 8 with evolution of chlorine on the surface of said permanent component and partial dissolution of said sacrificial component;
c) primary purification of the waste-water exiting said primary electrolysis in said settling and/or filtration unit;
d) secondary electrolysis of the waste-water in said electrolytic cell of the electrochemical system after releasing said sacrificial component of said electrode;
e) final purification of the waste-water exiting said secondary electrolysis in said reverse osmosis unit.

13. The method according to any one of claims 9 to 12 wherein said waste-water is a foundry residue.

14. The method according to any one of claims 9 to 13 wherein said waste-water contains one or more components selected from the group consisting of siloxanes, polyethylene waxes, glycols, mineral oils, synthetic oils, silicone antifoams, non-silicone antifoams, surfactants, EDTA and boric amides.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/052403

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/461 C25B11/04 C02F1/467
ADD.

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)
C25B 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 practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 225 061 A (WESTERLUND GOETHE O [CA]) 6 July 1993 (1993-07-06) column 7, line 24 - column 8, line 14	1-8
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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 application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
2 July 2013	12/07/2013

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/052403

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 995 550 A (APPL HERBERT [DE] ET AL) 26 February 1991 (1991-02-26) column 4, line 16 - column 7, line 10	1-8
A	US 4 070 504 A (BIANCHI GIUSEPPE ET AL) 24 January 1978 (1978-01-24) column 1, line 25 - column 4, line 51	1-8
X	WO 2004/002900 A1 (HITACHI LTD [JP]; SAHO NORIHIDE [JP]; ISOGAMI HISASHI [JP]; ASANO KATS) 8 January 2004 (2004-01-08)	6
A	page 5, line 22 - page 7, line 2; figures 1-7 page 12, line 8 - page 33, line 17	10-14
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Y	paragraph [0014]; examples 1,2,3	10-14
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Y	paragraphs [0006] - [0016], [0021] - [0028]	10-14
A	US 2003/098247 A1 (NAKAMURA SHINICHI [US] ET AL NAKAMURA SHINICHI [JP] ET AL) 29 May 2003 (2003-05-29) paragraphs [0020] - [0032]; example 1	9-14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2013/052403

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-8

Electrode consisting of permanent component comprising a substrate of a valve metal and a catalytic coating containing noble metal or oxides thereof and releasable attached a sacrificial component containing elemental iron.
Claims 2 - 4 concern specification of the electrode defined in claim 1 and claims 5-8 concern a method of using the electrode defined in claims 1-4.

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2. claims: 9-14

Method for decreasing the chemical oxygen demand of waste water containing oily compounds, glycols or waxes, comprising o step of electrolysis of waste water in the presence of trivalent iron.
Claims 10 -14 concern specification of the method defined in claim 9.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/052403

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