

(19) AUSTRALIAN PATENT OFFICE

(54) Title
Improved COD abatement process for electrochemical oxidation

(51)⁶ International Patent Classification(s)
C02F 1/467 (2006.01) 20060101AFI2006042
C02F 1/467 7BHEP
PCT/EP2005/011197

(21) Application No: 2005296759 (22) Application Date: 2005 .10 .18

(87) WIPO No: W006/042741

(30) Priority Data

| (31) Number | (32) Date | (33) Country |
|---------------|--------------|--------------|
| MI2004A001974 | 2004 .10 .18 | IT |

(43) Publication Date : 2006 .04 .27

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(56) Related Art
US 2001/040102 A1
US 5833831 A

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 April 2006 (27.04.2006)

PCT

(10) International Publication Number
WO 2006/042741 A1

(51) International Patent Classification:
C02F 1/467 (2006.01)

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(21) International Application Number:
PCT/EP2005/011197

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SI, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 18 October 2005 (18.10.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI2004A001974 18 October 2004 (18.10.2004) IT

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2006/042741 A1

(54) Title: IMPROVED COD ABATEMENT PROCESS FOR ELECTROCHEMICAL OXIDATION

(57) Abstract: The invention relates to an effluent COD treatment procedure by anodic oxidation combining the use of two different types of anode with a suitable apportionment of current. The first type of anode is preferably based on diamond doped-synthetic diamond, the second is an anode with high oxygen overvoltage preferably containing tin and antimony oxides.

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IMPROVED COD ABATEMENT PROCESS FOR ELECTROCHEMICAL OXIDATION

5 The treatment of effluents very rich in COD (Chemical Oxygen Demand) upstream the biologic purification units is quite challenging. For this reason, a few electrochemical techniques of COD pre-treatment have been explored. COD oxidation may be carried out by electrolysis on anodes characterised by high oxygen evolution overvoltage or with similar specific electrocatalytic properties.

10 The tin and antimony oxide-coated electrodes are included among those, and reference will be made in the following as a non-limiting example of high oxygen overvoltage anodes. Such electrodes have been used in plain electrolyzers known in the art, for instance in perpendicular flow-type electrolyzers. In such electrolyzers the solution to be treated passes alternatively through anodes and cathodes consisting of meshes or sponges. The COD reduction of several effluents by this technique was
15 actually observed, nevertheless a very low faradic yield is associated to such system, even though the COD reduction is as low as about 50%.

Another kind of electrode having a higher oxygen overvoltage than the tin and antimony oxide-coated anodes is known, namely the boron-doped diamond electrode (BDD), which consists of a layer of boron-doped diamond deposited on a conductive
20 support. The drawbacks of this type of electrode are twofold, namely its cost and its relative brittleness requiring special and expensive electrolyzers for its utilisation; on the other hand, its much higher potential under oxygen evolution leads to much bigger COD reduction rates with better faradic yields. It can be supposed that, due to the higher potential, a number of molecules contributing to the COD are degraded by the
25 dissociation of their backbones.

A reference herein to a patent document or other matter which is given as prior art is not to be taken as an admission or a suggestion that that document or matter was known or that the information it contains was part of the common general knowledge as at the priority date of any of the claims.

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According to one aspect, the present invention provides a device for COD treatment of effluents by anodic oxidation, comprising a first electrolyser equipped with a first type of anode for oxygen evolution connected in series or in parallel to at least one second electrolyser equipped with a second type of anode for oxygen evolution, said second type of anode having higher overvoltage for oxygen evolution than said first type of anode, wherein the first type of an anode and second type of anode are made of different materials.

The invention consists of the simultaneous use in series or in parallel of at least two types of electrode. The rationale is to utilise to a highest degree the handier and less expensive elements, that is the tin and antimony oxide-based anodes or other equivalent electrodes, installed in a conventional electrochemical plate or tube reactor, and to a lesser extent the BDD electrode installed in its own

appropriate electrolyser to accomplish the part of reaction which cannot be carried out on the tin and antimony oxide-based anodes or equivalent thereof. Being the molecules making up the COD partially degraded by the BDD anode, it becomes easier to complete their oxidation on the tin and antimony oxide-based anode, as confirmed by the experimental observations. For each type of effluent, it will be necessary to determine the most convenient apportionment of electrical current between the two processes of oxidation on BDD and on the tin and antimony oxide-based electrode. The ideal current apportionment is usually comprised between 55:45 and 95:5, depending on the effluent type; such apportionment may be obtained in a very simple manner by acting on the overall anodic surface of each electrolyser (for instance by fixing the ratio between overall anodic surface of tin and antimony oxide-based anode to BDD at a value comprised between 55:45 and 95:5), but other solutions are also possible. For plants having to treat several kinds of effluent, it is advisable that such current apportionment be adjustable by means of systems known in the art.

The tin and antimony oxide-based electrode may be constructed according to various typologies, for example it may be obtained as a ceramic electrode, for instance sintered from powders of two oxides optionally mixed to other components, or it may consist of a metallic base, for instance of titanium or other valve metal, coated with tin and antimony oxides optionally mixed to small amounts of conductive elements (for example copper) or elements with desirable electrochemical properties (for example iridium) in order to adjust its potential. In principle, also anodes of titanium coated with oxygen-evolution catalysts (for example iridium and tantalum oxide mixtures) might be used, nevertheless the oxygen overvoltage turns out to be too low in this case and the electrolyser coupling of the invention leads to less favourable results.

The results relative to the COD treatment of a typical degreasing bath are reported hereafter. With electrodes coated with tin and antimony oxides installed in a RETEC[®]-type electrolyser, the COD decreased by one half in the course of 100 hours with an average faradic yield of about 7%. Once coupled the previous electrolyser with a second electrolyser containing the BDD electrode, setting 90%

of the current on the RETEC[®]-electrolyser and 10% on the BDD-equipped electrolyser, the destruction of 80% of the COD was achieved in the course of about 100 hours with an average faradic yield higher than 24%. This method thus permits a strong improvement in the rate of destroyed COD, with a better faradic yield (lower electric energy costs), simultaneously limiting the capital investment deriving from the use of BDDs restricting the application thereof to a small percentage of the treatment.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

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- 5 1. Device for COD treatment of effluents by anodic oxidation, comprising a first electrolyser equipped with a first type of anode for oxygen evolution connected in series or in parallel to at least one second electrolyser equipped with a second type of anode for oxygen evolution, said second type of anode having higher overvoltage for oxygen evolution than said first type of anode, wherein the first type of anode and second type of anode are made of different materials.
- 10 2. The device of claim 1 wherein said at least one second electrolyser has an overall anodic surface lower than said first electrolyser.
- 15 3. The device of claim 1 or 2 wherein said second type of anode for oxygen evolution of said at least one second electrolyser is a boron-doped diamond anode.
4. The device of any one of the previous claims wherein said first type of anode for oxygen evolution of said first electrolyser comprises tin and antimony oxides.
- 20 5. The device of claim 2 wherein the ratio between the active surface of said first electrolyser and the active surface of said at least one second electrolyser is comprised between 55:45 and 95:5.
- 25 6. The device of any one of the previous claims wherein the ratio between the electrical current supplied to a said first and to said at least one second electrolyser is adjustable.
7. An effluent COD treatment process comprising carrying out an anodic oxidation process in the device of any one of the previous claims.
- 30 8. The process of claim 7 wherein the ratio between the electrical current supplied to a said first and to said at least one second electrolyser is comprised between 55:45 and 95:5.