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(54) Title: A METHOD FOR WATER DISINFECTION USING CA2FE2O5 IN ABSENCE OF LIGHT

(57) Abstract: Invention relates to a water treatment technology, especially to the disinfection of water from gram-positive and a gram-negative bacteria using a formulation comprising Ca2Fe2O5. Invention is a method for water disinfection, wherein the method consists of following steps: a) providing a formulation comprising Ca2Fe2O5; b) applying said formulation to a water to disinfect thereof and this step is performed without presence of light. The invention provides environmentally friendly catalytic material that performs physical disinfection of waterborne pathogens.

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A METHOD FOR WATER DISINFECTION USING CA2FE2O5 IN ABSENCE OF LIGHT

DESCRIPTION

[001] Invention relates to a water treatment technology, especially to the disinfection of water from gram-positive and a gram-negative bacteria using a formulation comprising Ca2Fe2O5.

[002] International patent application publication No. WO2019/003079 discloses a water remediation technology used for photocatalysis in visible light, for example, water purification reactors. It discloses a narrow n- and p-type semiconductor system with high oxidation-reduction potential and low photoinduced charge carrier recombination, which is provided by Z-scheme charge transfer mechanism. System contains photocatalysts from earth abundant chemical elements. Photocatalyst system Fe2O3/Ca2Fe2O5 can be used in visible light photocatalysis: (i) water purification; (ii) disinfection; (iii) air purification; (iv) sterile surfaces; (v) water splitting; (vi) synthesis of chemical compounds from ambient CO2. Chinese patent application publication No. CN108726626 discloses a method for treating water comprising CaFeO4 under visible light conditions.

[003] The present invention is a method for disinfection of liquid substances in dark, preferably a water from a gram-positive and a gram-negative bacteria using a formulation comprising Ca2Fe2O5.

[004] The catalytic material Ca2Fe2O5 employed in the invention has the following physical characteristics: particle size is less than 100 nm, material purity is 99.9%, density is about 100gr/litre, specific surface area is 13.55 m2/gr. Ca2Fe2O5 concentration in the formulation is 1.0g/L to 5.0g/L, for example Ca2Fe2O5 in water suspension. Ca2Fe2O5 in water suspension has pH in the range of 8.2 to 8.8, preferably 8.5. Ca2Fe2O5 has a light yellowish colour.

[005] Brownmillerites are oxygen deficient compounds with general formulation A2B2O5. The B are octahedral and tetrahedral site cations arranged in layers and A is a large cation occupying space between layers. Srebrodolskite is member of Brownmillerite subgroup with general formulation Ca2Fe2O5. It is non-stoichiometric perovskite group material with

orthorhombic crystal system. Mineral is named in honour of Boris Ivanovich Srebrodolsky and approved in 1984.

[006] The invention includes a method for water disinfection. The method consists of following steps: a) providing a formulation comprising Ca2Fe2O5; and b) applying said formulation comprising Ca2Fe2O5 to a water to disinfect thereof. The step b) is performed without presence of light allowing to perform disinfection in enclosed volumes or spaces significantly improving disinfection capabilities. Without presence of any light includes no use of visible light, ultraviolet radiation and infrared light. The prior art discloses other catalysts disinfectants that work only in visible light decreasing its application in water systems as most water systems are enclosed and are not designed to be subject to visible light.

[007] The method further comprises a step of applying an effective amount of the formulation comprising CaFeO, preferably Ca2Fe2O5, to the water to be disinfected. The effective amount of the formulation to the water is in the range of 0.2 to 0.7 weight%.

[008] In one embodiment of the invention, the formulation comprising Ca2Fe2O5 (5 g/L) in water has demonstrated a 7.5 log decrease in cultivable E. coli and 6.5 log decrease in cultivable S. aureus within 30 minutes. The test was performed in the dark environment – without a presence of any light, ultraviolet radiation and infrared light. The observed antimicrobial activity is due to hydroxyl radical generation as indicated by electron paramagnetic resonance measurements.

[009] In another embodiment of the invention the method further comprising the step of applying the formulation comprising Ca2Fe2O5 to the water for coagulation of bacteria and other solids. Accordingly, the disinfection of water may be made without additional coagulants.

[010] The key of the invention is a use of the environmentally friendly catalytic material (inorganic antimicrobial agent), that performs physical disinfection of waterborne pathogens. Disinfection technology can be described as an aqueous synthase obtained catalytic material, with high disinfection efficacy on a broad spectrum of pathogens in suspended system.

Catalytic material has been synthesized from non-toxic earth abundant Ca and Fe elements as Ca(NO3)2, Fe(NO3)3, NH4OH and citric acid.

[011] The formulation comprising Ca2Fe2O5 may be prepared in a slurry including a dispersion of the formulation comprising Ca2Fe2O5 in water with an ultrasonic homogenizer.

[012] Preparation of a powder of Ca2Fe2O5 for use in a disinfection of the water from gram-negative and gram-positive bacteria may be performed in the following manner:
a) obtaining a precursor solution in water containing the same number of moles of calcium nitrate and iron nitrate and twice the number of moles of citric acid as the number of moles of a single nitrate;
b) adjusting the pH of the solution by adding NH4OH dropwise;
c) evaporation the water from the solution under constant stirring at 80 °C;
d) the resulting mass after evaporation of water is dried at 80 °C till no mass changes can be observed;
e) combustion reaction initiation at 300°C to obtain as-prepared $Ca_2Fe_2O_5$ powder;
f) grinding the as-prepared Ca2Fe2O5 powder; and
g) annealing at 800°C for 20 minutes to obtain monophasic Ca2Fe2O5.

[013] Disinfection occurs due to radical generation and mechanical impact on bacteria membrane. The radical generation is a result of structural transformations of Ca-Fe oxide in water and formation of ionised point defects that are splitting the water and generating the radicals. The structural transformations also lead to the formation of flake like particles with the 2D morphology that are interacting and disrupting the bacteria membrane.

[014] The results of method for preparation of Ca2Fe2O5 are illustrated in Fig. 1. Fig. 1 illustrates a XRD pattern for compound Ca2Fe2O5. The crystalline phases for as-prepared and annealed nanopowders from sol-gel auto-combustion were studied by XRD. The XRD studies reveal a phase pure brownmillerite Ca2Fe2O5 (ICDD 00-047-1744) formation after annealing at 800 °C.

[015] Ca2Fe2O5 effect on disinfection of liquid substances, preferably a water from a gram-positive and a gram-negative bacteria excluding any light, ultraviolet radiation and infrared

light, is illustrated in Fig. 2. Disinfection test with Ca2Fe2O5 catalyst was performed in filtered tap water contaminated with specific species of bacteria. The catalyst suspension was added to the contaminated water so that the catalyst concentration in the final sample was 5 g/l. In control samples, filtered tap water was used instead of the catalyst suspension. Changes in colony-forming unit (CFU) over time for E-coli and S-aureus bacteria are shown in Fig. 2. Immediately after adding the catalyst suspension to the contaminated water, a sample was taken. The inoculation of the sample on the medium took about 10 minutes, so the time scale starts from negative 10 minutes. CFU decreases from $1.17 * 10^7$ to 0.37 CFU/ml for E-coli and from $2.12 * 10^6$ to 0.73 CFU/ml for S-aureus within 30 minutes. This is a seven-fold reduction for both species counting from control sample.

[016] Fig. 3 illustrates a degradation of *S. aureus* bacteria during the time at different powder or catalyst concentrations.

[017] Pre-filtered tap water (0.2 µm pore size filters, pH range of ≥ 6.5 and ≤ 9.5) complying to EU Directive 2020/2184 on the quality of water intended for human consumption was used in all microbial activity tests.

[018] While the invention may be susceptible to various modifications and alternative forms, specific embodiments of which have been shown by way of example in the figures and have been described in detail herein, it should be understood that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention includes all modifications, equivalents, and alternatives falling within the scope of the invention as defined by the following claims.

CLAIMS

1. A method for water disinfection, wherein the method consists of following steps:

   a) providing a formulation comprising Ca2Fe2O5, wherein the particle size of Ca2Fe2O5 is less than 100 nm, specific surface area of Ca2Fe2O5 is 13.55 m2/gr, wherein pH of the formulation is 8.2 to 8.8, preferably about 8.5, and Ca2Fe2O5 concentration in the formulation is 1.0g/L to 5.0g/L;

   b) applying said formulation comprising Ca2Fe2O5 to a water having pH in a range of $\geq$ 6.5 and $\leq$ 9.5 to disinfect thereof;

   wherein the step b) is performed without presence of any light, infrared light and ultraviolet radiation.

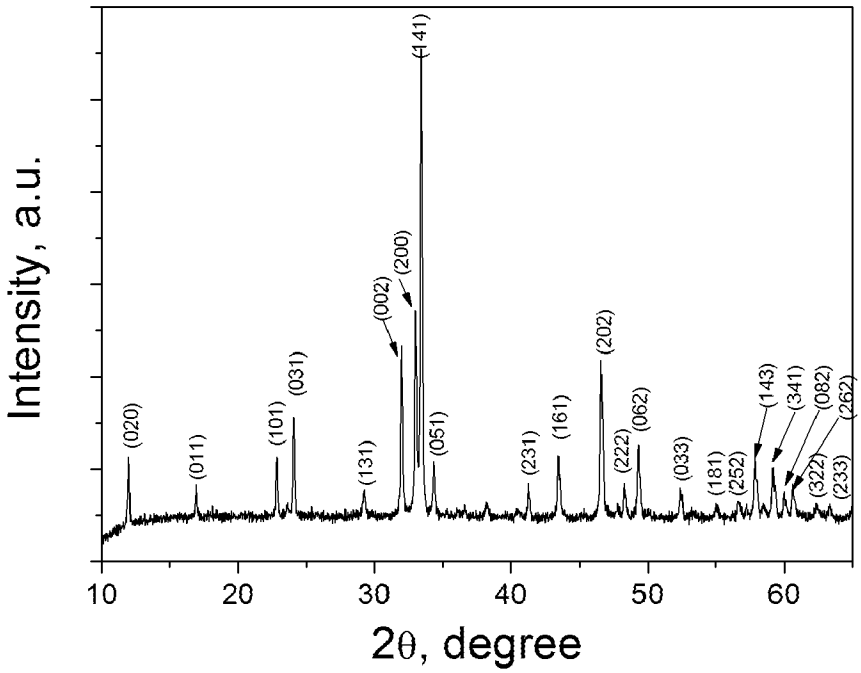
2. The method for water disinfection according to Claim 1, further comprising the step of applying the formulation comprising Ca2Fe2O5 into to the water to be disinfected, wherein the content of applied formulation in the water is 0.2 to 0.7 weight%.

3. A method for water coagulation, wherein the method consists of following steps:

   a) providing a formulation comprising Ca2Fe2O5;

   b) applying said formulation comprising Ca2Fe2O5 to a water for coagulation of bacteria and other solids.

4. A use of Ca2Fe2O5 in disinfection of liquid substances, preferably a water from a gram-positive and a gram-negative bacteria, characterized in that the disinfection is performed without presence of any light, infrared light and ultraviolet radiation.


Intensity, a.u.
2θ, degree
10
20
30
40
50
60
(020)
(011)
(101)
(031)
(131)
(002)
(200)
(141)
(051)
(231)
(161)
(202)
(222)
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(033)
(181)
(252)
(143)
(341)
(082)
(322)
(233)
(262)

Fig. 1

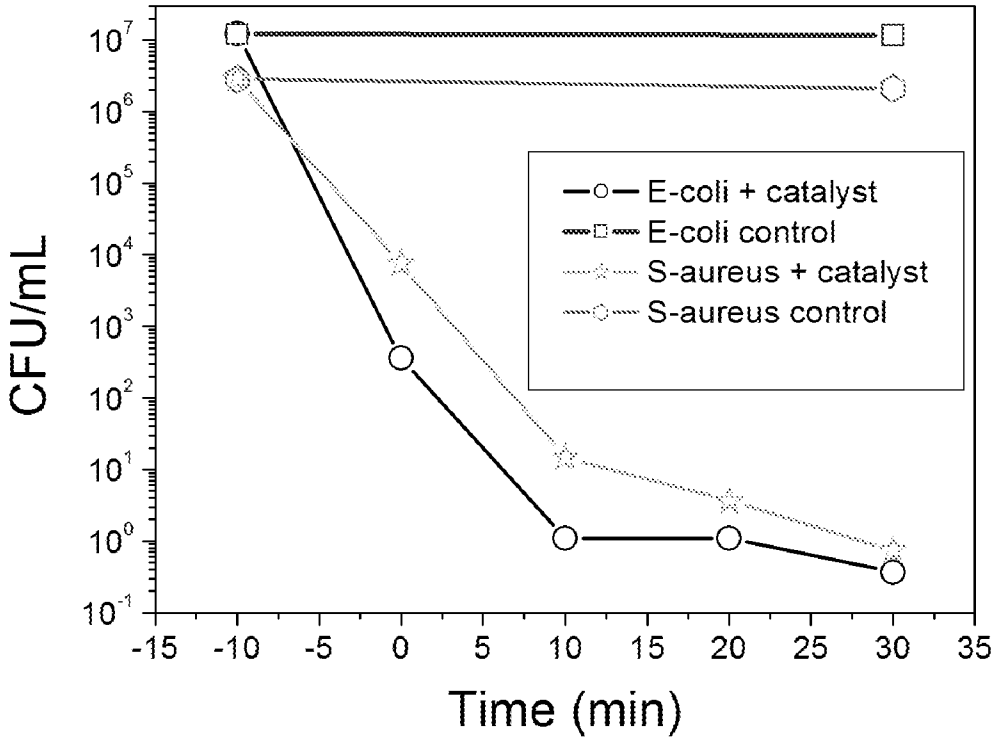
CFU/mL
Time (min)
E-coli + catalyst
E-coli control
S-aureus + catalyst
S-aureus control

Fig. 2

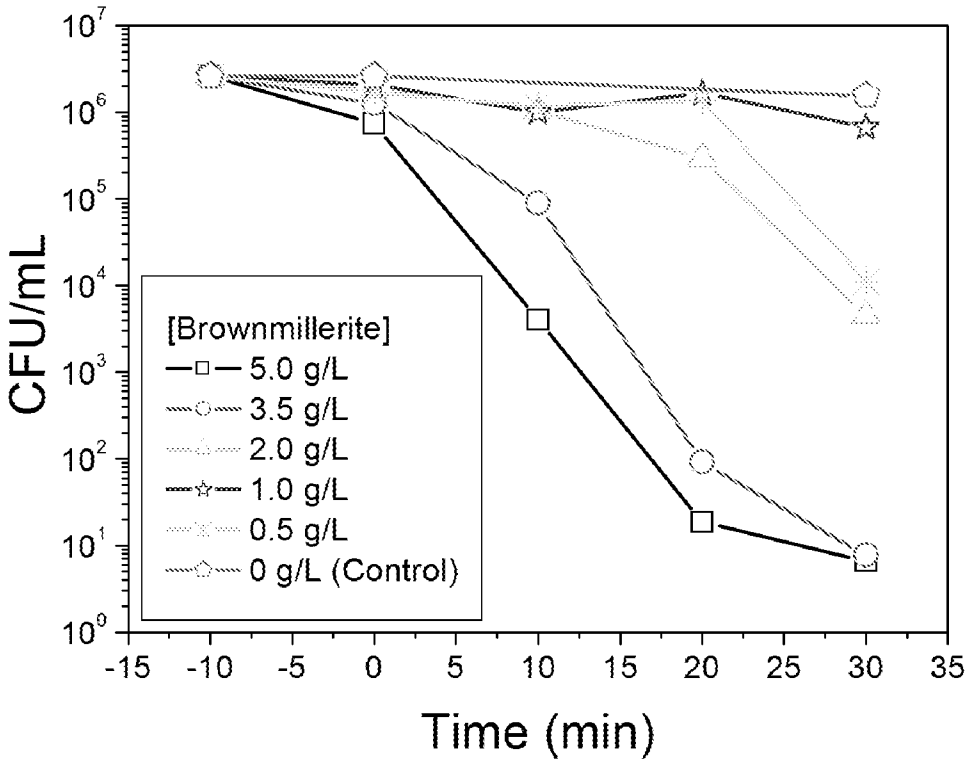
CFU/mL
Time (min)
[Brownmillerite]
5.0 g/L
3.5 g/L
2.0 g/L
1.0 g/L
0.5 g/L
0 g/L (Control)

Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2021/052390

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61L2/23
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)
A61L

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2019/003079 A1 (RIGAS TEHNISKA UNIVERSITATE [LV]) 3 January 2019 (2019-01-03)	3
Y	see, in particular, claim 1 as well as page 1, lines 1-3 and page 3, lines 19-26	1-4

X	GB 427 199 A (ATILIO ANTONIO MANUEL BADO) 17 April 1935 (1935-04-17)	4
Y	see, in particular, page 1, lines 10-20	1-4

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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

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"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
12 June 2021	24/06/2021

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	Rumbo, Angel

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	VANAGS MARTINS ET AL: "Sol-gel auto-combustion synthesis of Ca2Fe2O5 brownmillerite nanopowders and thin films for advanced oxidation photoelectrochemical water treatment in visible light", JOURNAL OF ENVIRONMENTAL CHEMICAL ENGINEERING, vol. 7, no. 4, 1 August 2019 (2019-08-01), page 103224, XP055813228, NL ISSN: 2213-3437, DOI: 10.1016/j.jece.2019.103224	3,4
Y	see , in particular, Abstracts lines 1-5; point 2.3 "Photocatalysis tests"; point 2.4" PEC and PECWT tests"; page 3, left column, lines 5-6	1-4

A	GANGULY PRIYANKA ET AL: "Antimicrobial activity of photocatalysts: Fundamentals, mechanisms, kinetics and recent advances", APPLIED CATALYSIS B. ENVIRONMENTAL, vol. 225, 1 June 2018 (2018-06-01), pages 51-75, XP055812761, AMSTERDAM, NL ISSN: 0926-3373, DOI: 10.1016/j.apcatb.2017.11.018 see, in particular, point 6.2 "Irradiation length and intensity" terms" the inactivation was effective and remained constan even in the dark"	1-4

A	EL-RAFEI A M ET AL: "Electrospun magnetically separable calcium ferrite nanofibers for photocatalytic water purification", JOURNAL OF MAGNETISM AND MAGNETIC MATERIALS, ELSEVIER, AMSTERDAM, NL, vol. 428, 11 December 2016 (2016-12-11), pages 92-98, XP029927903, ISSN: 0304-8853, DOI: 10.1016/J.JMMM.2016.12.020 see, in particular, abstracts point 3.4 "MIcrostructure of NFs calcined at differen tempertures" and page 95 right column	1-4

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WHEELER GARRETT P. ET AL: "Investigation of p-type Ca 2 Fe 2 O 5 as a Photocathode for Use in a Water Splitting Photoelectrochemical Cell", ACS APPLIED ENERGY MATERIALS, vol. 1, no. 9, 24 September 2018 (2018-09-24), pages 4917-4923, XP055812765, ISSN: 2574-0962, DOI: 10.1021/acsaem.8b00934 Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/acsaem.8b00934> see, in particular figures 1, 2 and page 4919 lerf col. -----	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2021/052390

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2019003079 A1	03-01-2019	LV 15381 B	20-10-2019
		WO 2019003079 A1	03-01-2019
GB 427199 A	17-04-1935	NONE	