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TQ Fondo

MINISTERIO DE COMERCIO INDUSTRIA Y TURISMO
SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES

E.

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D.

SUPERINDUSTRIA Y COMERCIO
Radicacion : 00098551 00000004
Fecha (AMD): 2004-10-27 16:15:28
Tramite : 002 PATENTES D 1 REGISTRO/ 993 IMPULSO F
Dependencia: 2020 DIVISION DE NUEVAS CREACIONES
Folios: 2

REFERENCIA : SOLICITUD DE REGISTRO DE LA PATENTE METODOS
DE PURIFICACIÓN DE AGUA CON GENERACIÓN DE
FLOCULANTE DE HIDRÓXIDO DE METAL
EXPEDIENTE No. 00098551
CODIGO : 001 - 002 - 181

Yo, **FERNANDO TRIANA SOTO**, mayor de edad, domiciliado en la ciudad de Bogotá, D.C., Republica de Colombia, abogado titulado e identificado como aparece al pie de mi firma, en mi calidad de apoderado de la sociedad **POTABLE WATER SYSTEMS LTD.**, existente y organizada conforme a las leyes del Estado de Texas, Estados Unidos de América, con domicilio en la ciudad de Houston, Estado de Texas, Estados Unidos de América, atentamente me permito manifestar al Despacho lo siguiente:

1. El veintinueve (29) de diciembre de dos mil (2000), la sociedad **POTABLE WATER SYSTEMS LTD.**, solicitó ante la División de nuevas Creaciones la solicitud de patente de la referencia.
2. La solicitud de registro de la patente **METODOS DE PURIFICACIÓN DE AGUA CON GENERACIÓN DE FLOCULANTE DE HIDROXIDO DE METAL**, fue publicada en la Gaceta de Propiedad Industrial No. 520 del veintisiete (27) de septiembre de dos mil dos (2002), sin que contra la misma se hubieren presentado oposiciones.
3. El trece (13) de febrero de dos mil tres (2003), la sociedad **POTABLE WATER SYSTEMS LTD.**, por intermedio de su apoderado presentó un memorial en el cual solicitó el examen de patentabilidad de la patente de la referencia.
4. En vista de lo anterior y teniendo en cuenta que han transcurrido más de veinte (20) meses sin que la División de Nuevas Creaciones de la Superintendencia de Industria y Comercio se haya pronunciado acerca del presente trámite, solicito a ustedes dar un **IMPULSO PROCESAL** a este trámite ya que no existe razón legal que justifique dicho retraso.



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De la Señora Jefe,


FERNANDO TRIANA SOTO
C.C. No. 79.154.036 de Usaquén
T.P.A. No. 45.265 del C.S. de la J.

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES**

2020

Bogotá D.C., Septiembre 26 de 2005

Doctor

FERNANDO TRIANA SOTO

Apoderado **POTABLE WATER SYSTEMS LTD.**

ASUNTO	Radicación	00-98551	
	Trámite	002	
	Evento	001	
	Actuación	430	9191
	Oficio		
	Folios	017	

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados:

- A. Para el presente estudio se tuvo en cuenta el capítulo descriptivo, comprendido en los folios 10 a 35 del expediente correspondiente a la solicitud en estudio, tal como fue radicado al inicio del trámite.
- B. El capítulo reivindicatorio tomado en cuenta para el presente estudio comprende 19 reivindicaciones y se encuentra en los folios 36 a 43, tal como fue radicado al inicio del trámite.
- C. Conforme lo establecen los artículos 9, 10 y 11 de la Decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 29 de diciembre de 2000, en el momento de la radicación no se reclamó prioridad.

2. Objeto de la invención:

- A. Las reivindicaciones 1 a 19 de la solicitud en estudio se refieren a: un método para purificar agua contaminada que comprende: suministrar una cámara para la generación in situ de hidróxido de metal insoluble en agua; suministrar un lecho fluidizable de partículas de dicho metal en dicha cámara; hacer fluir el agua contaminada por dicha cámara fluidizando así el lecho; hacer fluir un gas que comprende oxígeno por dicha cámara y en contacto con dichas partículas fluidizando así adicionalmente el dicho lecho; en un ambiente libre de corriente eléctrica generada y aplicada, mantener la superficie de dichas partículas libres de óxido y de otros contaminantes. Se obtiene un hidróxido de metal insoluble en agua y formar jabones de metal insolubles en agua con cualquier ácido graso presente en dicha agua contaminada; aglomerar y separar los contaminantes del agua.
- B. El objeto de la solicitud se puede clasificar según la clasificación internacional como C 02 F 7/00.

3. Claridad de la Solicitud:

- A. El artículo 28 de la Decisión 486 de la Comisión de la Comunidad Andina establece

"la descripción deberá divulgar la invención de una manera suficientemente clara y completa para su comprensión y para que una persona capacitada en la materia técnica correspondiente pueda ejecutarla"

En la descripción se encuentran unas expresiones que carecen de claridad. En el folio 23, página 14 de la descripción se puede leer: "los métodos de la presente invención un hidróxido de metal insoluble en agua..." Es obvio que hay un error de transcripción. En la página 16, folio 25 del expediente, se puede leer: "los métodos de la presente invención además métodos de remoción..." En esta expresión parece faltar un verbo porque carece de claridad. En la página 18, folio 27 del expediente, se puede leer: "el lecho es fluidizado por el flujo tanto de gas pro la cámara" Esto carece de claridad.

En general, a lo largo de toda la descripción aparecen varios errores de transcripción que restan claridad al texto. Se requiere una revisión y una corrección de los errores en un nuevo texto del capítulo descriptivo.

En la página 15 de la descripción, folio 24 del expediente, se puede leer: "En razón a que los métodos de la presente invención requieren una entrada de energía eléctrica para activar la disolución y oxidación, ellos pueden ser conducidos en un ambiente libre de cualquier corriente eléctrica aplicada o generada". En un mismo párrafo parece haber una contradicción: al principio se afirma que los métodos de la invención requieren entrada de energía eléctrica y que en razón a eso los métodos pueden ser conducidos en un ambiente libre de corriente eléctrica. Se requiere una explicación o una corrección.

De acuerdo con lo anterior, la descripción no cumple con el requisito de claridad según lo establecido en el artículo 28 de la Decisión 486.

- B. En el artículo 30 de la decisión 486 de la Comisión de la Comunidad Andina se establece: "Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará una reivindicación dependiente múltiple." En el artículo 51 se establece además: "El alcance de la protección conferida por la patente estará determinado por el tenor de las reivindicaciones."
- i. El capítulo reivindicatorio no se encuentra correctamente redactado. Por su estructura todas las reivindicaciones deben constar de dos partes. Una primera parte, el preámbulo, sirve para situar el objeto de la invención dentro de un contexto técnico; es lo que se conoce y sobre lo cual no se reclama ningún privilegio. La segunda parte o parte característica, define lo que se considera novedoso y se desea proteger. Estas dos partes están separadas por expresiones como "caracterizado por" o similares. Las reivindicaciones independientes no establecen claramente cuál o cuáles pasos del método es o son novedosos e inventivos. Dichas reivindicaciones carecen de concisión porque enumeran todos los pasos del método y no identifican el aporte del inventor sobre el estado previo de la técnica. Debe corregirse el capítulo, en especial las reivindicaciones

independientes.

- ii. Además de la falta de concisión individual de las reivindicaciones, el capítulo reivindicatorio presenta una falta general de concisión al presentar cuatro reivindicaciones independientes para un método. El solicitante debe hacer uso de reivindicaciones dependientes para especificar las distintas modalidades del objeto de su solicitud y no emplear más de una reivindicación independiente, lo cual genera falta de concisión e incluso falta de unidad de invención.
- iii. El capítulo reivindicatorio no está enteramente sustentado en la descripción. En las reivindicaciones 6 y 12, por ejemplo, se menciona un "aceite oxidante" que no había sido mencionado en la descripción.
- iv. En algunas partes de las reivindicaciones el solicitante caracteriza el método objeto de su solicitud por el resultado. En la primera reivindicación se puede leer: "en un ambiente libre de corriente eléctrica... mantener la superficie de dichas partículas libres (sic) de óxido... facilitando así la introducción gradual dentro de dicha agua de cationes..., dichas porciones son oxidados (sic) por..." etc. Se requiere que se especifique cómo se mantiene la superficie de las partículas libre de óxido y no que se mencione el resultado de mantenerlas libres de óxido. Además, en dicho fragmento se presentan errores de redacción o transcripción que no permiten entender qué se encuentra libre de óxido: ¿las partículas o su superficie? Tampoco es posible entender a qué porciones oxidados (sic) se refiere el solicitante.
- v. En general, el método no se debe caracterizar por resultados sino por la forma en que llegó a ese resultado. Proteger un resultado provocaría que el alcance de la reivindicación incluyera no sólo la solución propuesta por el solicitante, sino todas las alternativas presentes o futuras que lleguen a ese resultado.
- vi. La reivindicación 10 parece no tener sentido. Allí se afirma que el gas oxidante se selecciona de oxígeno y agua. En la descripción no se menciona que el agua sea gaseosa ni que pueda servir como agente oxidante.

De acuerdo con lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad según lo establecido en el artículo 30 de la Decisión 486. El solicitante deberá anexar un nuevo capítulo reivindicatorio con todas las correcciones aquí requeridas.

4. Evaluación de la unidad de invención

El artículo 25 de la decisión 486 de la Comisión de la Comunidad Andina establece: "La solicitud de patente sólo podrá comprender una invención o un grupo de invenciones relacionadas entre sí, de manera que conformen un único concepto inventivo."

La presente solicitud carece de unidad de invención toda vez que configura cuatro métodos diferentes. Aunque aparentemente se dirigen a un mismo método de purificación de agua, el solicitante ha redactado de tal manera el capítulo reivindicatorio que no es posible detectar el concepto común inventivo entre esos cuatro métodos diferentes. Lo común entre dichas reivindicaciones 1, 3, 6 y 12 son el suministro de la cámara, del lecho fluidizable, de hacer fluir el agua contaminada y

el agente oxidante, de aglomerar y de separar los contaminantes. Estos elementos comunes ya pertenecían al estado previo de la técnica. Luego, no parece haber un concepto común inventivo entre los métodos de las reivindicaciones mencionadas.

El solicitante debe establecer una sola reivindicación independiente dirigida al método en su forma más general posible. Partiendo de allí, establecer reivindicaciones dependientes que especifiquen esa forma simple hasta su forma más preferida.

De acuerdo con lo anterior, la presente solicitud no cumple con el requisito de unidad de invención según el artículo 25 de la Decisión 486.

5. Determinación del estado de la técnica:

El artículo 16 de la Decisión 486 de la Comisión establece que: "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Solo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40"

La fecha para determinar el estado de la técnica es el 29 de diciembre de 2000.

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 02 F 7/00, se encontró que antes del 29 de diciembre de 2000 habían sido publicados los documentos enumerados en la siguiente tabla. No obstante, tan pronto se reciban las aclaraciones sobre claridad por parte del solicitante se realizará una búsqueda más exhaustiva.

No.	Documento	Título	Fecha de publicación
D1	US 5.558.755	Method for removing contaminants from an aqueous medium	1996-09-24
D2	US 5,879,555	Electrochemical treatment of materials	1999-03-09
D3	US 4,802,991	Method and apparatus for water purification	1989-02-07

6. Evaluación de los requisitos de patentabilidad:

El artículo 14 de la Decisión 486 de la Comunidad Andina establece que: "Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial".

En cumplimiento del artículo 14 de la Decisión 486, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad del objeto de la solicitud reivindicado en la solicitud en estudio.

A. Evaluación de la Novedad:

El artículo 16 de la decisión 486 de la Comisión de la Comunidad Andina establece:

"Una invención se considerará nueva cuando no esté comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

1. El documento D1 trata de un método para remover contaminantes de un medio acuoso. Se tiene un aparato con un lecho fluidizado de partículas a través del cual se hace fluir ese medio acuoso y una corriente eléctrica. De esa manera se generan hidróxidos de metal no solubles en agua. También se hace fluir aire a través de la cámara del aparato para ayudar a la fluidización de las partículas. El método descrito en D1 comprende también aglomerar y separar los contaminantes del agua. Luego, el documento D1 afecta la novedad de las reivindicaciones 12 a 19.
2. El documento D2 también trata de un método de tratamiento de agua que comprende suministrar una cámara con un lecho de partículas metálicas fluidizables. A través de ese lecho se hace pasar el agua que va a ser tratada. El proceso de tratamiento se induce en la superficie de las partículas formándose productos de oxidación – reducción que se encargan de aglomerar y separar los contaminantes del agua. Luego, esta divulgación afecta la novedad de todas las reivindicaciones porque este proceso se lleva a cabo en ausencia de corriente eléctrica generada o aplicada.

B. Evaluación del nivel Inventivo:

El artículo 18 de la Decisión 486 de la Comisión de la Comunidad Andina dispone que: "Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

El documento D3 afecta el nivel inventivo del método reivindicado porque, en combinación con lo enseñado en D1 o D2, un técnico medio en la materia habría derivado de manera evidente el uso de las partículas fluidizables para el tratamiento del agua aglomerando y retirando contaminantes en forma de jabones metálicos del agua.

Por lo tanto, la solicitud en estudio no cumple con el requisito de nivel inventivo establecido por el artículo 18 de la Decisión 486.

C. Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud podrían encontrarse afectados así:

No.	Documento	Reivindicaciones afectadas	Requisito afectado
D1	US 5.558.755	12 a 19	Novedad y nivel inventivo
D2	US 5,879,555	1 a 19	Novedad y nivel inventivo
D3	US 4,802,991	1 a 19	Nivel inventivo

Se anexa copia de las anterioridades mencionadas.

7. Notificación

En cumplimiento del artículo 45 de la decisión 486 de la Comisión de la comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e) del capítulo quinto del título primero de la circular única No. 10 de 2001.

ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 06 OCT 2005

CONCEPTO TÉCNICO Número: 1523	EXAMINADOR TÉCNICO Código: 202043
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United States Patent [19]
Gardner-Clayson et al.

[11] Patent Number: 5,558,755
[45] Date of Patent: Sep. 24, 1996

[54] METHOD FOR REMOVING
CONTAMINANTS FROM AN AQUEOUS
MEDIUM
[75] Inventors: Thomas Gardner-Clayson, Buffalo;
Patrick J. Flley, Amherst, both of N.Y.
[73] Assignee: Recra Environmental, Inc., Amherst,
N.Y.
[21] Appl. No.: 219,701
[22] Filed: Mar. 28, 1994

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3723745	9/1988	Germany

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"Electro-Coagulation—Some Basic and Operating Charac-
teristics", Donini et al. 11th International Coal Preparation
Congress, Toyko, 1990, pp. 253-256.
"Alternating Current Electrocoagulation for Superfund Site
Remediation", C. F. Farrell, presented at U.S. Environmen-
tal Protection Agency Seventeenth Annual RREL Hazardous
Waste Research Symposium, Cincinnati, Ohio, Apr. 1991.

Primary Examiner—John Niebling
Assistant Examiner—William T. Leader
Attorney, Agent, or Firm—Hodgson, Russ, Andrews, Woods
& Goodyear, LLP

Related U.S. Application Data
[62] Division of Ser. No. 882,341, May 13, 1992, Pat. No.
5,372,690.
[51] Int. Cl.⁶ C02F 1/46
[52] U.S. Cl. 205/753; 204/571; 205/754
[58] Field of Search 204/149, 186,
204/150, 151, 152, 571; 205/753, 754

[56] References Cited

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3,766,034	10/1973	Veltman	204/149
3,919,062	11/1975	Lundquist, Jr. et al.	204/149
3,988,221	10/1976	Garrett et al.	204/105 R
4,004,994	1/1977	Andrus	205/753
4,014,766	3/1977	Watanabe et al.	205/754 X
4,048,030	9/1977	Miller	204/149
4,053,378	10/1977	Moeglich et al.	204/149
4,072,596	2/1978	Moeglich	204/241
4,094,755	6/1978	Moeglich	204/149
4,123,345	10/1978	Shetel	204/275
4,131,526	12/1978	Moeglich	204/149
4,176,038	11/1979	Moeglich	204/277
4,240,886	12/1980	Hodges et al.	204/112

[57] ABSTRACT
Apparatus and method for removing contaminants from an
aqueous medium. The apparatus includes a fluidized bed of
metallic particles through which the medium is flowed and
through which an electric current is applied by electrodes for
agglomerating contaminants in the medium. In order to
allow the electrodes to be non-consumable so that they do
not require frequent replacement, the particles are consum-
able.

7 Claims, 2 Drawing Sheets

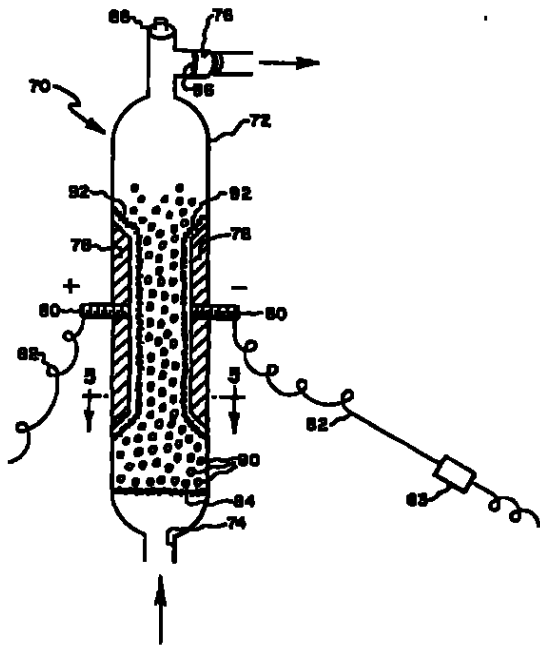


Fig. 1.

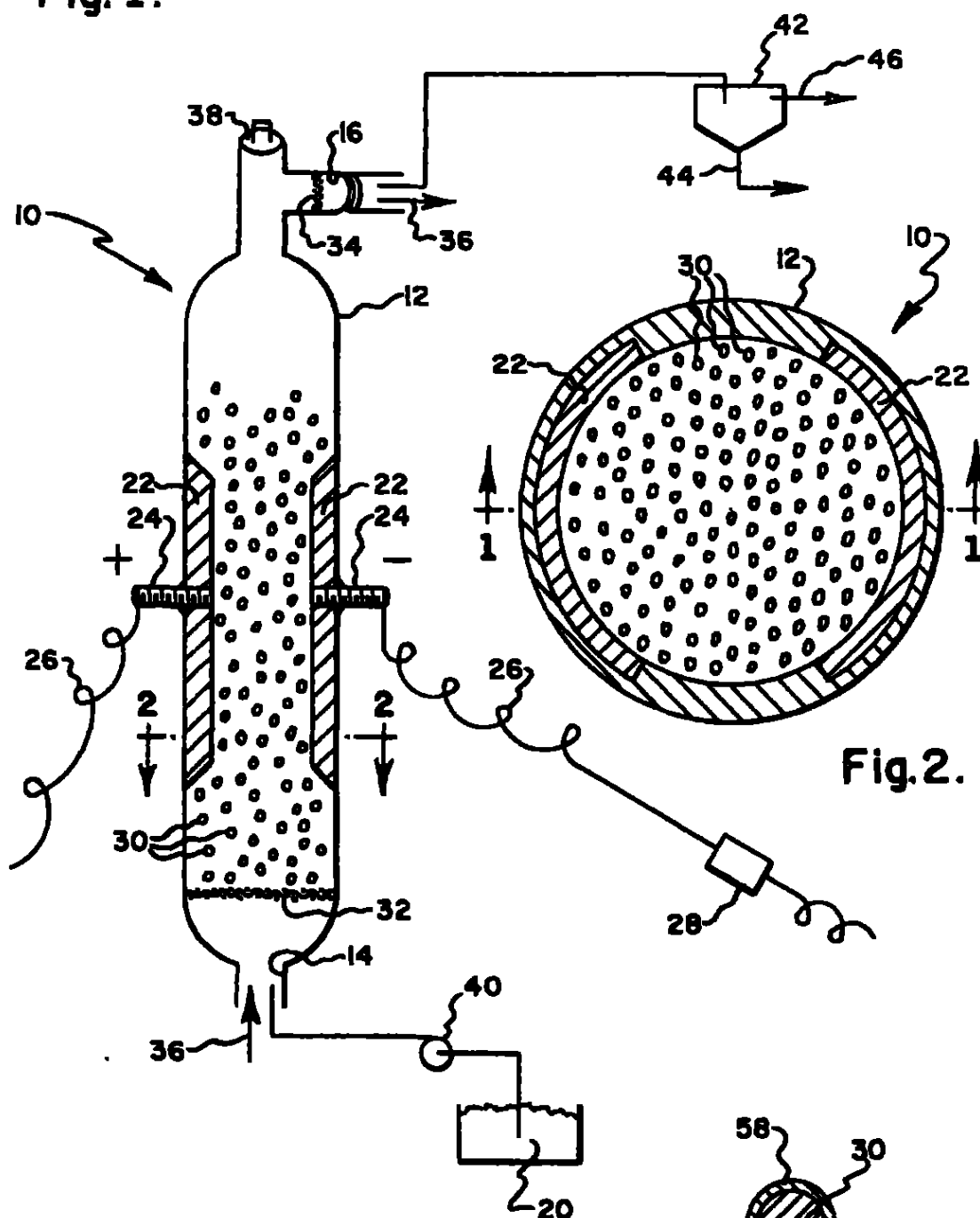


Fig. 2.

Fig. 3.

METHOD FOR REMOVING CONTAMINANTS FROM AN AQUEOUS MEDIUM

This is a divisional of application Ser. No. 07/882,341 filed May 13, 1992, now U.S. Pat. No. 5,372,690.

The present invention relates generally to the removal of contaminants from an aqueous medium. More particularly, the present invention relates to electrochemical apparatus and method for agglomerating contaminants in an aqueous medium to effect their separation therefrom. This is meant to include co-precipitating soluble contaminants and oil-in-water emulsion breakage as well as solid-liquid separation.

Contaminants have been removed from wastewater or the like by flowing the water between a pair of sacrificial consumable electrodes such as aluminum electrodes in the presence of a fluidized bed of conductive attrition-resistant particles such as graphite, and passing an alternating current therethrough. Aluminum would be dissolved from the electrodes into the solution where it would affect the solids to cause coagulation thereof so that they could then be removed such as by skimming or settling. It is stated that the turbulence of the particles improves conductivity and current efficiency, minimizes electrode erosion, and provides a scrubbing action to minimize fouling or scaling of the electrodes. See, for example, U.S. Pat. No. 4,053,387 to Mocqlich et al. Also see U.S. Pat. Nos. 4,072,596; 4,094,755; 4,176,038; 4,131,526 to Mocqlich and 4,329,211 to Plantec et al. In addition, see U.S. Pat. Nos. 4,123,345 to Shettel; 2,130,789 to Campbell; 3,919,062 to Lundquist, Jr. et al.; and 4,048,030 to Miller; European patent document 341,614; and German patent document 3,723,745. Also see "An Electrochemical Way of Stripping Waste from Water" Chemical Engineering, December, 1990, at page 15, and "Electro-Coagulation - Some Basic and Operating Characteristics", by Donini et al. 11th International Coal Preparation Congress, Tokyo, 1990, at pages 253 to 256.

Consumable electrodes, which are expensive, require frequent labor-intensive replacement periodically, perhaps as often as every 3 months.

It is accordingly an object of the present invention to eliminate the requirement of frequent periodic replacement of the electrodes.

It is a further object of the present invention to provide increased aluminum or metallic dissolution into a solution so that heavy suspensions and emulsions may be effectively treated.

It is yet another object of the present invention to provide an apparatus for agglomerating solids in an aqueous medium which is low-maintenance, efficient, rugged, easy to use, and inexpensive.

In order to allow the electrodes to be non-consumable so that they do not require such frequent replacement, in accordance with the present invention an apparatus for removing contaminants in an aqueous medium includes a fluidized bed of consumable metallic particles through which the medium is flowed and through which an electric current is applied between the electrodes.

The above and other objects, features, and advantages of the present invention will be apparent in the following detailed description of the preferred embodiments when read in conjunction with the accompanying drawings wherein the same reference numeral denotes same or similar parts throughout the several views.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a vertical sectional view, partly schematic, taken along lines 1—1 of FIG. 2, of apparatus which embodies the present invention.

FIG. 2 is a sectional view, taken along lines 2—2 of FIG. 1, of the apparatus.

FIG. 3 is a sectional view of a fluidized bed particle for the apparatus of FIGS. 1 and 2.

FIG. 4 is a view similar to that of FIG. 1 and taken along lines 4—4 of FIG. 5, of an alternate embodiment of the present invention.

FIG. 5 is a sectional view of the apparatus of FIG. 4 taken along lines 5—5 thereof.

FIG. 6 is a schematic view illustrating an alternate arrangement of electrodes in the apparatus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIGS. 1 and 2, there is shown generally at 10 apparatus for agglomerating solids suspended, and soluble pollutants entrained, in an aqueous medium, illustrated at 20. The apparatus 10 comprises a generally cylindrical elongate casing 12 composed of a suitable non-conductive material such as, for example, a 6 inch diameter schedule 80 PVC pipe or composed of fiberglass. The cell casing 12 can however be of any material or design that will contain aqueous solutions and of any geometric shape that will allow and contain upflow solution and bed fluidization between charged electrodes, as discussed hereinafter. The material should be chemically inert or corrosion-resistant, preferably non-conductive, although the casing may be composed of metal if proper insulation is applied. The casing 12 has an inlet 14 at one end and an outlet 16 at the other end for receiving the aqueous medium 20 to be treated and to discharge the medium. The aqueous medium 20 is flowed through the casing 12, as illustrated at 36, by means of a suitable pump 40 for treatment, as described hereinafter, and discharged to a suitable vented vessel, tank, or other apparatus such as vented clarifier 42 the purpose of which will be described hereinafter. It should be understood that more than one cell 12 may be connected in parallel or series.

A pair of spaced electrodes 22 are provided on opposite sides of the casing 12 so that the medium 20 may be flowed therebetween. The electrodes 22 are connected to the casing by suitable means such as, for example, threaded rods 24 which are installed to sealingly penetrate the casing wall and to which may be connected electrical wires 26 which are connected to an electrical power source, illustrated at 28, so that a circuit is completed by the discharge of electrical energy between the electrodes 22. A quantity of metallic particles 30 is maintained within the casing by a grating or screen 32 across the inlet 14 and another grating or screen 34 across the outlet 16. The screen size should be sufficient to contain the particles 30 but not so small that clogging is induced or fluid flow is otherwise unnecessarily impeded. A plug 38 is provided at the outlet to allow access to the casing 12 for maintenance thereof and for replenishment of the metallic particles 30, as discussed hereinafter. The screens should be installed to allow convenient access for removal or addition of bed material. Thus, as shown in FIG. 1, the screen 34 is installed in one fork of the outlet, and the plug 38 is installed in another fork which is closed by the plug.

As the fluid 20 is flowed through the casing 12, highly charged polymeric aluminum hydroxide species or other

metallic hydroxide species are introduced into the fluid, as hereinafter discussed, to neutralize electrostatic charges on suspended solid and/or oil droplets to facilitate their agglomeration (or coagulation) and resultant separation from the aqueous phase. They will also prompt the co-precipitation of certain soluble ionic species such as metals and alkaline earths. Phase separation occurs at the clarifier 42 with the agglomerated solids falling to the bottom and being removed through an underflow line 44 to a filter press incinerator or other means for disposal thereof. The clarified liquid phase is removed through an overflow line 46 for use of the liquid or for its delivery to a sewer. Thus, apparatus 10 may have application in the fields of effluent remediation (removal of soluble and suspended pollutants), and in product recovery (capture for reuse of fine-grained product).

Metal hydroxide species for neutralizing electrostatic charges on suspended particles in a fluid have conventionally been provided by consumable metal electrodes wherein the metal is gradually dissolved into the fluid under the influence of an electric charge as the fluid is flowed thereby. Not only do the expensive consumable electrodes require close spacing of perhaps $\frac{1}{2}$ inch so that more of them are required for a particular volume flow rate, but they must be replaced frequently, perhaps about every 3 months, which is a labor-intensive process. Furthermore, an oxide coating tends to build up on the electrodes resulting in reduced operating efficiency. This coating commonly originates from coagulated material which adheres to the electrodes or is baked on the electrode as a result of heat generated during electrocoagulation. In order to eliminate such frequent replacement of the electrodes, in accordance with the present invention particles 30 are consumable metallic particles such as, for example, aluminum pellets, which will dissolve under the influence of an electrical field between the electrodes 22 to produce charged metal ionic and hydroxyl species that act to treat wastewater or the like by destabilizing emulsions and suspensions, co-precipitating various ions, and increasing the mean size of the particle aggregate. The particles 30 are of a suitable density that, in combination with the flow rate of the medium 20 through the casing 12, a fluidized bed of the particles is provided allowing electrical discharge throughout the volume of fluid between the electrodes and with dispersal of the metal ionic and hydroxyl species throughout the fluid for effective agglomeration. If desired, compressed air may be introduced into the casing 12 to assist in maintaining the turbulent fluidized bed and enhancing the aluminum dissolution efficiency by increasing the anodic surface area. Charge neutralization is initiated within the electrocoagulation cell 12 and continues following discharge of the aqueous medium 20 from the apparatus.

The use of the consumable particles 30 allows the electrodes 22 to be non-consumable so that frequent periodic replacement thereof is advantageously not required and efficiency reducing oxide build-up on the electrodes may advantageously be reduced. Instead of perhaps every 3 months continuous use for replacement of consumable electrodes in conventional apparatus, the non-consumable electrodes allowed by the present invention may be permanently installed, i.e., for a period of perhaps 5 years or more of continuous use without replacement. The cost of the pellets, i.e., recycled beads or metal turnings or the like (perhaps \$0.75 per pound of high purity aluminum) may generally be less than the cost of manufactured electrodes (perhaps \$2.00 per pound), and the pellets are merely added whereas the electrodes require labor intensive replacement. Thus, the use of consumable pellets allows lower operating and maintenance cost.

The electrodes may be composed of any suitable electrically conductive substance, preferably a non-consumable metal, and more preferably corrosion-resistant alloys or noble metals. As used herein and in the claims, the term "non-consumable" refers to a chemically inactive material which, under the influence of an electric charge, remains chemically stable so as to be resistant to dissolution. Examples of non-consumable materials include, but are not limited to, stainless steel (even though some iron may leach out), tantalum, tungsten, titanium, carbon, graphite, copper, silver, platinum, and other noble metals. The term "non-consumable" also includes a layer of such a material over a consumable material whereby the consumable material is not exposed and therefore not consumed during the process. Non-consumable materials may be in a matrix form. Non-consumable electrodes do not provide the metal ionic and hydroxyl species in sufficient quantities for effective agglomeration. When non-consumable electrodes are used, the species must be provided by the pellets 30.

The electrodes 22 are shown in FIG. 2 to be hemispherical so as to maximize the surface area thereof, and are disposed in recesses in the wall of the casing 12. However, the electrodes may be otherwise suitably shaped. For example, the electrodes may be rectilinear, have the shape of rods or screening, or have any other suitable shape or geometry including concentric that will allow a fluidized bed between alternately charged electrodes. Referring to FIG. 6, there is shown an alternate embodiment of the present invention wherein an apparatus 50 is similar to apparatus 10 except that it has a plurality of alternately charged electrodes 52 connected in series across the casing 54 thereof with the fluidized bed of particles 56 between and among the electrodes 52. The electrodes 52 may be said to be in a "plate pack" wherein the side-by-side electrodes allow an increased cross-sectional area for use with a low conductivity medium 20. For another example, the electrodes may comprise rods which are adjustably inserted into the medium 20 within a casing so that the electrode surface area presented to the medium can be varied depending upon the conductivity thereof.

The fluidized bed particles 30 may be any consumable metallic pieces, turnings, particles, or shot of any suitable size or geometry, which is consumable, preferably spherical shot, more preferably an aluminum or ferrous alloy. As used herein and in the claims, the term "consumable" refers to a chemically active metal which, under the influence of an electric charge through an aqueous solution, oxidizes and introduces ions which form charged species such as ionic and hydroxyl species which are provided at a sufficient rate to effectively destabilize suspensions or emulsions to cause phase separation. The consumable metal is not chemically stable but is instead used up in the process. Examples of consumable metals include, but are not limited to, steel, aluminum, and magnesium. This is in contrast to materials such as charcoal, alumina (a crystalline form of aluminum oxide or hydroxide) perlitic, and ceramic material which are not consumable.

Typically, consumable electrodes may require replacement after about every 3 months of continuous use whereas stainless steel or other suitable non-consumable electrodes of the present invention may not require replacement for at least about 5 years continuous use with alternating current. The electric source 83 is preferably a source of alternating current so as to allow the constantly changing polarities to provide a "scrubbing" action for cleaning thereof and so as to prevent a build-up of rust which might necessitate more frequent electrode replacement if direct current is used.

pellets. When the level falls below a certain level, all that would be required is to merely unscrew the top plug 38, pour in the pellets to the desired level (by looking through the appropriate sight port), and secure the plug. This is an advantageously simpler and less expensive procedure than disassembling a cell to replace expensive consumable electrodes.

Electrocoagulation operating conditions are dependent upon the chemistry of the aqueous medium 20 and the conductivity, pH, and chloride ion concentration therein. The treatment rate of the aqueous medium 20 through the electrocoagulation cell 12 is dependent both on the solution chemistry (conductivity), the nature of the entrained suspension or emulsion, and the extent of electrocoagulation required to achieve the treatment. The following is an example of apparatus which may be provided in accordance with the present invention, the example being provided for purposes of illustration and not for purposes of limitation. Alternating current electrocoagulation may be used to treat a pigment-bearing overflow stream from a clarifier to recover the fine-grained (0.3 micron diameter) TiO_2 that is being lost to a disposal lagoon. The clarifier may receive filtrate from the final rotary vacuum drum filter stage of production of high-purity TiO_2 ; the clarifier is used to recover as much as possible of the fine-grained TiO_2 that passes through the filters (<0.5 microns) through gravity settling over a 12 hour residence time. A portable skid-mounted alternating current electrocoagulation unit with a nominal throughput capacity of 70 gpm may be used. The apparatus may contain 4 electrocoagulation cells manufactured from 4-inch diameter 36-inch high Schedule 80 PVC pipes, a self-priming, close-coupled centrifugal pump, supporting piping and valving, a 24 KVA transformer, and an electrical control panel. Within each electrocoagulation cell may be installed two electrodes (316 stainless steel which may be silver electroplated), each 2 inches in width and 14 inches in length, installed on diametrically opposed sides of the cell. Two threaded 0.5-inch diameter stainless steel bolts may be welded to the back of each electrode and extend through the PVC wall of the electrocoagulation cell to enable electrical connections to be made. The 4 PVC pipes may be oriented vertically and the clarifier overflow stream to be electrocoagulated may be pumped in an upflow manner through the cells. At the base and top of each cell may be installed perforated plastic screens (nominal openings 0.05 inches) to contain the fluidized bed aluminum pellets within the electrocoagulation cells. At the top of each electrocoagulation cell may be installed a 6.5-inch segment of clear PVC to enable fluidization of the aluminum bed to be viewed when the electrocoagulation cell is in operation and to determine when replenishment of the aluminum pellets is required. PVC valving enables from 1 to 4 electrocoagulation cells to be used; although the centrifugal pump may have but one pumping rate (99 gpm at 10-feet Total Head), use of a by-pass line to divert a portion of the pump discharge back to the untreated overflow reservoir enables the solution throughput rate to be reduced and any number of electrocoagulation cells to be operated. Compressed air can be injected into the effluent feed line at the base of each electrocoagulation cell (immediately below the basal perforated plastic screen) to assist in creating turbulence within the cell or in improving the pellet dissolution rate. Switching within the electrical control panel permits electrical power to be applied to the electrocoagulation cells at 5 distinct potentials: 60 VAC, 90 VAC, 120 VAC, 135 VAC, and 160 VAC. The maximum current that can be driven in each electrocoagulation cell is limited to 90 amperes. The influent

overflow stream from the clarifier may have the following characteristics: approximately 20–28 mg/l aluminum, a conductivity of 1,650 S/cm, an initial temperature of 25° C., a TiO_2 content of 850 mg/l, and a turbidity in excess of 1,000 NTU. Electrocoagulation of this stream through 4 electrocoagulation cells at a rate of 55 gpm with 160 VAC applied to each cell enables from 11 to 13 amperes electrical current to be passed through each cell. Approximately 8 to 10 psig of compressed air may be introduced into the base of each electrocoagulation cell. The electrocoagulated stream may be discharged to a settling tank to provide the necessary residence time to permit separation of the coagulated TiO_2 from the aqueous medium. After 10 minutes of settling, for example, the total suspended solids content of the supernate phase may be reduced from 850 mg/l to 2 to 3.5 mg/l and the turbidity to 50 to 65 NTU. Treatment may entail addition of approximately 100 to 150 mg/l aluminum. The settled, coagulated TiO_2 could be collected for reuse and the clarified supernate phase could be discharged to the municipal sewer system generally without imposition of discharge penalties. For typical commercial applications the capacity would of course have to be increased.

It is to be understood that the invention is by no means limited to the specific embodiments which have been illustrated and described herein, and that various modifications thereof may indeed be made which come within the scope of the present invention as defined by the appended claims.

What is claimed is:

1. A method for removing contaminants from an aqueous medium comprising the steps of:

- providing a chamber having at least one pair of electrodes;
- providing a fluidizable bed of metallic particles in the chamber between the electrodes;
- flowing the medium through the bed thereby fluidizing the bed;
- applying an electric current between the electrodes to effect dissolution of the metallic particles thereby introducing ions which effect agglomeration of the contaminants; and
- removing the agglomerated contaminants from the medium after the medium has flowed out of the chamber.

2. A method according to claim 1 further comprising providing a barrier between the electrodes and metallic particles to prevent contact between the electrodes and metallic particles thereby to prevent electrical shorting between the electrodes and metallic particles and to allow ionic mobility and charge transfer and further comprising selecting the barrier to be a screen.

3. A method according to claim 1 further comprising selecting the metallic particles to have an insulative coating.

4. A method according to claim 1 further comprising selecting the electrodes to be composed of a material selected from the group consisting of stainless steel, tantalum, tungsten, titanium, carbon, graphite, copper, and the noble metals.

5. A method according to claim 1 further comprising applying an alternating current between the electrodes.

6. A method according to claim 1 further comprising selecting the metallic particles to be composed of a material selected from the group consisting of steel, magnesium, and aluminum.

7. A method for agglomerating contaminants in an aqueous medium comprising the steps of:

- providing at least one pair of electrodes;



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[54] ELECTROCHEMICAL TREATMENT OF MATERIALS

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[58] Field of Search 210/615, 631,
210/719, 748, 722, 743, 742, 746, 663,
747, 717, 757

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Primary Examiner—Neil McCarthy

[57] ABSTRACT

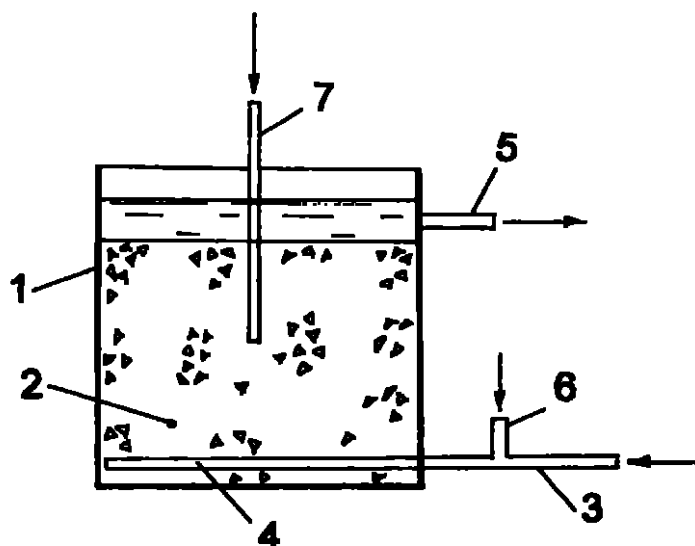
This is a method of treatment of materials with the use of a sacrificial metal and reducible ions which comprises steps of

a) contacting the material to be treated with the surface of the said sacrificial metal, wherein the said material to be treated is included in an aqueous solution or emulsion or suspension; and

b) inducing treatment processes at the surface of the said sacrificial metal by providing said reducible ions included in an electrolyte, wherein the said reducible ions react with the said sacrificial metal to form oxidation-reduction products comprising dissolved or suspended reduced species and dissolved or suspended species from oxidizing the said sacrificial metal.

The method can be used for treatment of water, groundwater, including in-situ, wastewater, polluted gases, solid waste, and other materials.

24 Claims, 3 Drawing Sheets



ELECTROCHEMICAL TREATMENT OF MATERIALS

FIELD OF THE INVENTION

The present method belongs to electrochemical treatment of materials found in gaseous emissions, wastewater, water, groundwater, solid waste, and other media containing organics, especially recalcitrant and toxic organics, heavy metals, and other constituents, the said method makes use of elemental metals as reagents.

PRIOR ART

Here, the following reactions and physical chemical processes involving elemental metals are of concern: reduction of organics by a single metal, transformations of organics by a metallic couple, cementation (metal displacement), and processes with migrational species transport at the sacrificial metal surface.

Reduction of organics by metals was described in 1913 by Clemmensen (R. T. Morrison and R. N. Boyd, "Organic Chemistry", Allyn and Bacon, Inc., Boston, 1973), many such reactions are described by J. March in "Advanced Organic Chemistry", McGraw-Hill Book Co., 1968. Sweeny (U.S. Pat. No. 3,640,821) teaches to use zinc in acidic media for partial decomposition of DDT. Gillham (U.S. Pat. No. 5,266,213) teaches to use metals placed underground for cleaning halogenated contaminants from groundwater. The Gillham process is also limited by anaerobic conditions in the treated water (Eh=-100 to -200 mV, absence of oxygen and other oxidants). S. M. Shifrin, O. M. Spivakova, and I. G. Krasnoborod'ko ("On Color Removal from Textile Wastewater", Selected Papers of the Leningrad Civil Engineering Institute, Issue No. 69, 1971) demonstrated an aerated filter with a scrap steel for destruction of dyes. Contrary to Gillham, organics (COD) and color removals in this process improved with aeration. However, large quantity of sludge was generated. All elemental metal processes require the finely divided metals, preferably, metal dusts or submillimeter size particles. Metal reduction of organics is driven by the potential difference between grains in the metal lattice. The magnitude of such difference is small (about 0.1 V). Accordingly, the organics transformation is very slow (hours to days) and incomplete (low removal of original compounds and high content of toxic residual products).

Metallic couples such as Ni—Al, Ni—Ag, etc. (Renay catalysts) are used in organic reduction and hydration processes, and for catalyzing oxidation-reduction in fuel cells (K. R. Williams, "Introduction to Fuel Cells", Elsevier, Amsterdam, 1966; B. V. Nekrasov, "General Chemistry", Moscow, Khimia, 1973). Sweeny (U.S. Pat. Nos. 3,773,384 and 4,382,865) teaches to use metallic couples for reductions and transformations of various organics. He prepares the bi-metal couples by grinding metal alloys into fine particles or by depositing the "second" metal on the "first", where the first metal is the expendable metal (hereinafter, it is called the sacrificial metal). R. D. Vidic and E. G. Pohlman ("Remediation Technology Status Report: Treatment Walls", prepared for Ground-water Remediation Technologies Analysis Center, 615 William Pitt Way, Pittsburgh, Pa., October 1996) reviewed recent studies on and applications of the single metal and bi-metal (metal couples) processes for remediation of groundwater polluted with organics and heavy metals. The driving force in the metallic couple processes is the potential difference between two metals in an electrolyte (water being treated), which magnitude is 1 V.

Accordingly, the organics transformation is faster and more complete than in processes with the single sacrificial metal. Nonetheless, the use of finely divided sacrificial metals (powders, ground particles, or sponge and wool) does not insure sufficient organics transformation in these systems. Additionally, there is always a concern that the second metal in a couple can solubilize and pollute the treated effluent with a toxic heavy metal.

Cementation (metal displacement) is also a process involving reductions of a second (noble) metal in solutions contacting a sacrificial elemental metal. Complex and contradictory behavior of cementation processes was described in many sources. B. M. Khudenko ("Mathematical Models of Cementation Processes", Journal of Environmental Engineering, ASCE, Vol. 113, No. 4, 1987, and U.S. Pat. No. 5,348,629), B. M. Khudenko and J. P. Gould ("Specifics of Cementation Processes", Water Science and Technology, IAWPRC, Vol. 24, No. 7, 1991), and J. P. Gould, I. B. Escovar, and B. M. Khudenko ("Examination of Zinc Cementation of Cadmium in Aqueous Solutions", Water Science and Technology, Vol. 19, 1987) have reexamined this process. All Khudenko publications and the patent given herein are incorporated into this invention by reference. In the new models cathodic and anodic sites are spontaneously induced at the sacrificial metal surface. In addition to the noble species, reacting species include hydrogen and hydride ions. At anodic sites, the sacrificial metal is dissolved thus freeing electrons which flow to the cathodic sites. At cathodic sites, hydrogen ions are adsorbed accept one electron, become monoatomic hydrogen which dissolves in the sacrificial metal, wherein it accepts one more electron and becomes hydride ion. This hydride ions react and reduce the noble species. The process rate, yield, and efficiency depend on the transportation regime of the reacting species in the system. At certain conditions (a given sacrificial metal, type and concentrations of noble species, pH, temperature, mixing rate, concentrations of indifferent ions, Li^+ , K^+ , or Na^+ , concentration of anions, Cl^- , SO_4^{2-} , presence and concentration of promoters, etc.) the noble species are transported from the bulk (solution) to the cathodic sites by diffusion. For example, low or high concentrations of noble species and low or high mixing rates favor diffusional regime. At cathodic sites, they are reduced on the metal surface by hydrides and form considerably smooth deposits. Hydride ions revert to hydrogen ions which can take part in the next rotation at and in the metal. At intermediate conditions, the diffusional transport of noble species is replaced with migration (electric current) of hydrogen ions to the metal surface and hydride ions from the metal surface across a microscopic boundary layer at cathodic sites. Accordingly, hydride ions react with noble species at the outer side of the boundary layer. The solid products formed from the noble ions are solid primary particles. Such particles will travel across the boundary layer to the metal surface under the effect of electrophoresis and form powdery and rough deposits. Spontaneous processes at the metal surface occur in pulses. Certain amount of hydride is accumulated over time and then reacts with noble species. In migrational regimes, the accumulated charge of hydrides crosses the migration boundary layer as a microscopic plasma streamer. Diffusional cementation regimes have a slow to moderate process rate as for previously described metal and bi-metal organics reductions. Migrational regimes are very fast.

The advantages of the migrational regime for treatment of organics in electrolytes are described in our previous invention (U.S. Pat. No. 5,348,629). Additionally, methods of

wool, and similar materials. Medium size pieces would be particles of one to few millimeter size, including metal cuttings and shavings. Larger pieces can be from one centimeter to a meter size, or whatever is convenient to handle. Various scrap materials can be used. Sometimes, scrap needs additional shredding and cleaning. Preferably, the bulk of the said metal pieces are in electrical contact with each other so that the microscopic electrical circuits between anodic and cathodic sites on the sacrificial metal surface amplify each other and propagate through the most of the metal used in a treatment apparatus. Accordingly, the reducible ions can be provided only to a portion of the said metal pieces. Other pieces will be activated through the electrical contact with each other. Moreover, such propagation of electrical circuits throughout the entire electrically connected body of the sacrificial metal pieces can be provided across an electroconducting partition. For example, a reaction between Fe(III) and Fe^{0} can be conducted in a metal container electrically connected to the said sacrificial metal pieces. The container will be filled with the electrolyte containing Fe(III) , and the sacrificial metal pieces will be in contact with the aqueous solution containing materials to be treated, but the said electrolyte and the said aqueous solution are isolated hydraulically. Electrical circuits induced in the said container will transmit to the body of the sacrificial metal used for the said treatment of materials. The electroconducting container can be made from the same metal as the sacrificial metal. Such a container will corrode. It can also be made of a metal more noble than the sacrificial metal and the reducible species. Such container will not corrode, but a corrodible sacrificial metal needs to be placed inside of such container.

The metal pieces can be placed in a reactor, or other containing means, for example, underground well, a trench, or other structure. These pieces can form a continuous bed of sacrificial metal pieces, or smaller size pieces can be fluidized. Further, the continuous bed with the bulk of the particles in electrical contact can be placed in a bed of a filtration medium. For example, nonfluidizable (massive) metal pieces can be placed in a fluidized bed of a granular media (sand, granular activated carbon-GAC). Or such pieces can be placed in a filter of a dense granular media (such as water treatment filter with sand, or sand and gravel). During the operation of the granular bed in the fluidization regime or during the filter backwash, the metal pieces will sink in the fluidized or expanded bed of the granular media, form a self-supporting skeleton, and electrically contact each other. Voids between these pieces will be filled with the granular media. Gradually, metal pieces will be spent. They can be replaced by loading new metal pieces on the top of the combined granular media/metal bed. These new pieces will eventually sink in the granular media bed. The combined granular media/metal bed is a simple means for controlling the turbulence of flows around the metal pieces thus increasing the process rate and efficiency. Additionally, fluidizing the granular media within the metal bed will provide cleaning of the bed from any chemical deposits. The granular filtration medium can be gravel, sand, glass beads, coal, green sand, ceramsite (baked clay), ilmenite, garnet, plastic beads, granular activated carbon, synthetic adsorption media, zeolite, ion exchange resins, and combinations thereof. The granular bed can be used for filtration as in water filter. It can be an adsorption device for the original constituents in the aqueous solution and/or intermediate products of treatment of materials with the said sacrificial metal submerged in the granular bed. It can also be an ion exchange apparatus or a reactor for conducting chemical

reactions, or other processes involving granular media-metal bed. Biological treatment of organics, particularly, anaerobic, is especially advantageous. It can be carried out with different granular media. For example, groundwater with biodegradable organics and biodegradable products from the metal treatment processes can be treated with GAC seeded with anaerobic, anoxic, aerobic, methanotrophic and other bacteria. Compounds for supporting biological processes, additional carbon sources, nutrients (N and P), and various micronutrients can be added to the filtration medium. The reducing conditions in anaerobic processes will additionally increase the rate and efficiency of the metal treatment processes.

Reduced ions, for example Fe(II) or Ni(II) , and ions formed by dissolving the sacrificial metal, for example Fe(II) or Al(III) , can be used for the further treatment. At approximately neutral pH, they form hydroxides, which can be used as coagulants for particles flocculation and sedimentation, or for direct coagulation/filtration in apparatus with granular media. In anaerobic processes, these ions will immobilize sulfides. They also will precipitate phosphorus.

The aqueous solution or emulsion or suspension which can be treated in the present process can be surface water, groundwater, drinking water, process water, wastewater, aqueous media from intermediate steps of water and wastewater treatment, aqueous based absorption media derived from gas treatment processes, aqueous based leachates separated from solid materials or solid waste, aqueous based leachates within solid materials or solid waste.

DESCRIPTION OF DRAWINGS

FIG. 1 is a reactor with the sacrificial metal bed.

FIG. 2 is a filter with the sacrificial metal bed submerged in a bed of a granular filtration medium.

FIG. 3 is an alternative design of the reactor of FIG. 1.

FIG. 4 is a system for treatment of gaseous streams.

FIG. 5 is a system for in-situ treatment of groundwater.

PREFERRED EMBODIMENTS

Referring now to FIG. 1, there is shown a reactor comprising a reactor vessel 1, a bed 2 of the sacrificial metal pieces, an influent line 3 for feeding the aqueous solution of materials to be treated in the vessel 1, line 3 attached to a distribution manifold or other distribution means 4 in the vessel 1, an effluent line 5, a line 6 attached to the line 3 for feeding the electrolyte and other reagents for conducting and optimizing the treatment of materials, an alternative line 7 for feeding the electrolyte and other reagents for conducting and optimizing the treatment of materials.

The apparatus of FIG. 1 is operated as follows. The aqueous solution containing the materials to be treated is fed in the reactor 1 via line 3 and is distributed under the sacrificial metal bed 2 by using the distribution means 4, flows through and becomes treated by the bed 2, the treated effluent is collected at the top of the bed 2 and is discharged via line 5. The bed 2 can be made of fine, medium or large sacrificial metal pieces. Most practicable metals are Al and Fe, although many other metals can be used. The electrolyte containing the reducible ions and, optionally, reagents for optimization of the process rate and efficiency as previously described are fed in the line 6 and mixed with the aqueous solution in the line 3. This would result in a single mixed stream of the aqueous solution and the electrolyte contacting the said metal bed 2. Alternatively, the electrolyte can be fed

via line 7. It can be either distributed in the volume of the entire bed 2, or it can be applied to a portion of the bed 2 at any location in the bed. In FIG. 1, line 7 ends at about the center of the bed 2, but it can be at any other location, provided that most of the metal pieces in the bed are electrically connected. Some other reagents for optimizing the process rate can also be fed through line 7, for example, reagents for pH adjustments, such as acids. Other reagents can be provided through line 6 and applied uniformly to the entire bed. Most preferably Fe(III) should be used as reducible ions, but other ions satisfying the requirements stated above, nontoxic and soluble or flocculent after reduction, can also be used. The added reducible ions induce the treatment processes to rapidly convert the materials to be treated. Particularly, various organics can be treated as previously described, some mineral materials can also be treated, for example, many heavy metals can be removed, nitrates and nitrites can be reduced to nitrogen, suspensions and emulsions can be collected and their constituents electrochemically converted. This apparatus can be used for treatment of water, groundwater (in pump-and-treat systems), industrial and other wastewater, and other waste and non-waste materials. Unlike the prior art, this is a very simple apparatus and operation which is free from toxicity associated with the bi-metal or other systems.

Referring now to FIG. 2, there is shown a reactor or a filter as described in FIG. 1 and further provided with a bed of a granular material 8 into which the bed of the sacrificial metal pieces is submerged. This embodiment is operated similarly to the one presented by FIG. 1, however, with additional advantages afforded by the use of the granular bed 8. For example, if the sand is used in the bed 8, in addition to the sacrificial metal treatment as previously described, the apparatus can be operated as a contact filter for water purification. The Fe(II) and possibly Al(III) ions would hydrolyze, if needed with pH correction, flocculate and trap the suspended and some dissolved solids in the water stream being treated, the said flocculated material is deposited on the sand grains and retained in the filter till the backwash operation. The filter can be backwashed with water, or with air and water. The deposited flocculated solids will be dislodged and carried away. It should be noted that the sand/metal filter can be operated in either upflow mode as illustrated in FIG. 2, or in a downflow mode as known in the art. The filter can be further improved by using bed 8 made of GAC. Particularly, the biodegradable products of the metal treatment and some constituents in the stream being treated will be adsorbed and, at least partially, biologically decomposed. Biological processes in the GAC can be further improved by seeding appropriate microorganisms. For example, anaerobic microorganisms, denitrifiers, and aerobic organisms can be used. Several zones holding and propagating these groups of organisms can be developed in the bed 8. There is an unexpected feedback in such a system: anaerobic microorganisms can lower oxidation reduction potential in beds 2 and 8 and further increase the metal treatment rate and efficiency. Another unexpected effect is that the turbulence can be increased in the apparatus with the metal/granular bed design as compared to metal bed, thus further increasing the process rate and efficiency. At optimal conditions, the electromagnetic fields in the metal filter are sufficiently strong for disinfection, including kill and deactivation of pathogenic bacteria, viruses, and cysts. The apparatus of FIG. 2 can be operated with some expansion of the granular bed or as a fluidized bed, or the motion of the granular bed particles can be produced during the backwash. In either case, the surface of the sacrificial metal pieces will be

cleaned, thus further increasing the process rate and efficiency. Metal pieces are spent during the operation of the system. Spent metal can be replaced by adding new pieces at the top of the reactor 1 and by allowing them to sink under the force of gravity during expansion, or fluidization, or backwashing of the bed. This is another improvement in the present method because it allows to maintain the tight contact between the metal and the granular material and between the metal pieces simultaneously. An unexpected advantage of combining the sacrificial metal bed and the GAC bed is that GAC to metal contact promotes corrosion and can increase the rate and the efficiency of treatment of materials. Similar effect can be produced by adding powdered activated carbon to the treatment system.

Referring now to FIG. 3, there is shown a reactor as described in FIG. 1 and further provided with a means for striking the said metal pieces across a partition, comprising a container 9 with an electrolyte feed line 10, a line 11 for the evacuation of the spent electrolyte, and an optional sacrificial metal pieces 12 inside the said container 9, the said container 9 is in the electrical contact with the said metal bed 2. The container 9 can be made from a noble metal or from a sacrificial metal. The noble metal container will not corrode. For example, copper container will not corrode in a system with the sacrificial iron. The iron container will corrode and therefore is expendable with the sacrificial iron. The system is operated similarly to that shown in FIG. 1, but the induction step is carried out by conducting a cementation reaction in the container 9 by feeding electrolyte with reducible ions and reacting it either with the walls of the container 9 made of the sacrificial metal, or with sacrificial metal pieces placed in the container 9 made of noncorroding metal. Electromagnetic fields and microscopic electrical circuits induced inside the container 9 will be transmitted to the sacrificial metal bed 2 due to the contact between the bed 2 and the container 9. The spent electrolyte is not toxic and can be either discharged, or used for other purposes, or treated without generating hazardous streams.

Referring now to FIG. 4, there is shown a system for treatment of gaseous streams comprising a reactor 1 with the sacrificial metal bed (not shown), and an absorber 13 for transferring in the aqueous solution the constituents of the gas to be treated by the sacrificial metal, the said absorber is optionally provided with a contact bed 14, influent and effluent lines 15 and 16, a distributor for the aqueous solution 17, and lines 5 and 3 with a pump 18 for circulating the aqueous solution between the reactor 1 and the absorber 13. Reactor 1 can be a design as depicted in FIGS. 1, or 2, or 3, or an alternative design. Various modifications of the absorber 13 can also be used. For particular conditions, one skillful in art can design a single apparatus for combining the functions of the reactor 1 and the absorber 13. The materials to be treated enter the absorber 13 with a gaseous stream, such as polluted air, or a vent gas in the chemical storage tank, or in a chemical reactor or other process, or other gaseous stream, via line 15, pass through the contact bed 14 irrigated with the aqueous solution using the distribution means 17, become absorbed by the aqueous solution, and conveyed via line 3 by the pump 18 to the apparatus 1 such as described in FIGS. 1 to 3, or modifications thereof. This solution is treated in the apparatus 1 and recycled to the absorber 13. The treated gas is evacuated from the absorber 13 via line 16.

Referring now to FIG. 5, there is shown a cross-section of a permeable underground structure 1 which can be a circular well, or a rectangular cavity in the ground layer 21 having a water bearing stratum 19 with a flowing stream of polluted

84 7

water 20. The structure 1 is filled with the sacrificial metal bed 2 spanning the thickness of the groundwater stratum (or its polluted portion). The portion of the structure above the groundwater level and above the bed 2 is supported by a casing 22. It can alternatively be filled with a soil or other material. The bed 2 is provided with the line 7 for feeding the previously described electrolyte and additional reagents, and/or by means 9 for striking the bed 2 across the partition as described above. Granular material, preferably GAC, can be provided to form the bed 8 (not shown) within the voids between the metal pieces in the bed 2. The structure 1 is similar to the reactors and filters described in FIGS. 1, 2, and 3. The groundwater filtering through the bed 2 is treated as previously described. The induction of the treatment is provided by the electrolyte and the additional reagents via line 7 and/or by using means 9. The GAC is used to adsorb the constituents not treatable by the metal and the products of the metal treatment. The biodegradable fraction of these constituents will be further treated. As in previous embodiments, microorganisms can be added to the GAC bed 8.

While the invention has been described in detail with particular reference to preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as previously described and as defined by the claims. For example, various combinations of the described embodiments can be used, reactors can be operated under elevated pressure and/or temperature, and various external electrical circuits can be used to induce the treatment processes.

I claim:

1. A method of treatment of materials with the use of a sacrificial metal and reducible metal ions which comprises the steps of

- a) contacting the material to be treated with a surface of the said sacrificial metal, wherein the said material to be treated is included in a medium selected from the group consisting of an aqueous solution, an aqueous emulsion, an aqueous suspension and combinations thereof; and
- b) inducing treatment processes at the surface of the said sacrificial metal by providing said reducible metal ions included in an electrolyte, wherein the said reducible metal ions react with the said sacrificial metal to form reduced metal ion species in dissolved or suspended form and said sacrificial metal is oxidized to form oxidized metal ion species in dissolved or suspended form.

2. The method of claim 1, wherein the said materials to be treated are selected from the group consisting of organic compounds, suspended or emulsified particles, metal containing species, microorganisms, and combinations thereof.

3. The method of claim 1, wherein the said sacrificial metal is selected from the group consisting of Zn, Al, Fe, and Ni.

4. The method of claim 1, wherein the said reducible metal ions are selected from the group consisting of Ni and Fe ions, or combinations thereof.

5. The method of claim 1, wherein the said reducible metal ions are produced by a process selected from the group consisting of a dissolution of a dry salt, and an anodic dissolution of a metal, or a combination thereof.

6. The method of claim 1, wherein the said reducible metal ions are provided continuously.

7. The method of claim 1, wherein the said reducible metal ions are provided periodically.

8. The method of claim 1, wherein electric current from an outside source is applied to the said sacrificial metal.

9. The method of claim 1, wherein the rate and the efficiency of the said treatment processes are increased by steps selected from the group consisting the addition of at least one indifferent ion to said electrolyte, the addition of at least one anion to said electrolyte, the addition of at least one complexing agent to said electrolyte, the addition of at least one hydride compound to said electrolyte, optimizing pH of the said electrolyte, increasing temperature of the said electrolyte, optimizing the mixing rate of the said electrolyte, optimizing oxidation-reduction potentials in the said electrolyte, or a combination thereof.

10. The method of claim 1, wherein the rate and the efficiency of the said treatment processes are increased by steps selected from the group consisting of the addition of at least one indifferent ion to said aqueous solution, the addition of at least one anion to said aqueous solution, the addition of at least one complexing agent to said aqueous solution, the addition of at least one hydride compound to said aqueous solution, optimizing pH of the said aqueous solution, increasing temperature of the said aqueous solution, optimizing the mixing rate of the said aqueous solution, optimizing oxidation-reduction potentials in the said aqueous solution, or a combination thereof.

11. The method of claim 1, wherein the said electrolyte and the said aqueous solution containing material to be treated is the same solution.

12. The method of claim 1, wherein the said sacrificial metal is selected from the group consisting of finely divided metal pieces, medium size metal pieces, large size metal pieces, or combinations thereof.

13. The method of claim 12, wherein at least some of the said metal pieces are in electrical contact with each other.

14. The method of claim 12, wherein the said reducible metal ions are provided to a portion of the said metal pieces.

15. The method of claim 12, wherein the said reducible metal ions are provided to the said metal pieces across an electroconducting partition.

16. The method of claim 12, wherein the said sacrificial metal pieces are placed in a sacrificial bed submerged in a bed of a filtration medium.

17. The method of claim 16, wherein the said sacrificial bed sinks into the said bed of a filtration medium.

18. The method of claim 16, wherein the said filtration medium is selected from the group consisting of gravel, sand, glass beads, coal, green sand, vermiculite, ilmenite, garnet, plastic beads, granular activated carbon, synthetic adsorption media, zeolite, ion exchange resins, and combinations thereof.

19. The method of claim 16, wherein microorganisms are added to the said filtration medium.

20. The method of claim 16, wherein compounds for supporting biological processes are added to the said filtration medium.

21. The method of claim 1, wherein the said aqueous solution or emulsion or suspension is selected from the group consisting of surface water, groundwater, drinking water, process water, wastewater, aqueous media from intermediate steps of water and wastewater treatment, aqueous based absorption media derived from gas treatment processes, aqueous based leachates separated from solid materials or solid waste, aqueous based leachates within solid materials or solid waste.

22. The method of claim 1, wherein the said reduced metal ion species and/or oxidized metal ion species are used as coagulants.

23. The method of claim 1, wherein the said reduced metal ion species and/or oxidized metal ion species are used as reagents.

24. The method of claim 1, wherein the said process steps (a) and (b) are applied to in-situ groundwater treatment.

* * * * *

United States Patent [19]
Miller

[11] Patent Number: 4,802,991
[45] Date of Patent: Feb. 7, 1989

- [54] METHOD AND APPARATUS FOR WATER PURIFICATION
- [75] Inventor: George Miller, Bogota, Colombia
- [73] Assignee: Hidrotronic Watercleaning Systems, Ltd., Switzerland
- [21] Appl. No.: 656,866
- [22] Filed: Oct. 2, 1984
- [30] Foreign Application Priority Data
- Oct. 6, 1983 [DE] Fed. Rep. of Germany 3336460
- [51] Int. Cl.⁴ C02F 1/46; C02F 1/52
- [52] U.S. Cl. 210/708; 204/149; 204/273; 204/275; 210/709; 210/717; 210/748; 210/96.1; 210/192; 210/221.2
- [58] Field of Search 210/661-663, 210/665, 667-669, 673, 703, 709, 743, 748, 799, 800, 804, 806, 807, 94, 95, 96.1, 243, 259, 262, 265, 266, 274, 299, 703, 717, 192, 221.2; 204/149, 273, 275
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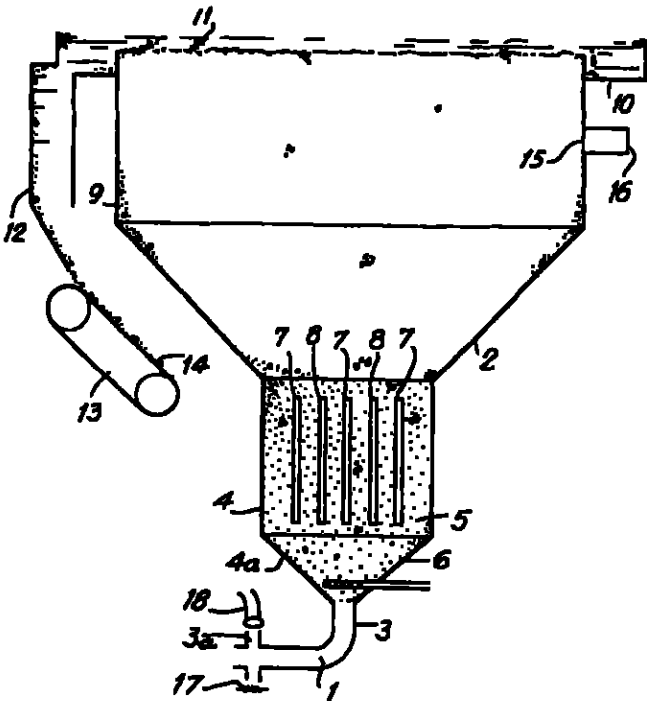
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Attorney, Agent, or Firm—Cohen, Pontani & Lieberman

[57] ABSTRACT

A method and apparatus for water purification, wherein ions are released from electrodes during electrolysis and combine with impurities to form a floc which, in turn, absorbs other impurities. A moving bed of solid, non-conductive particles surrounding the electrodes is also provided to insure self-cleaning of the electrodes. The apparatus for carrying out the process comprises an electrolysis chamber containing a moving bed of solid particles surrounding the electrodes, an inlet conduit for contaminated water at one end of the chamber, and a conically extending flocculation basin at the opposite end of the chamber. The invention simplifies water purification processes and apparatus.

21 Claims, 1 Drawing Sheet



86

SUPERINTENDENCIA DE INDUSTRIA Y C MERCI

RADICACIÓN: 0-88551

EDICTO No. 3713

LA SECRETARÍA GENERAL AD-HOC HACE SABER:

Que esta Superintendencia profirió Resolución No. 2018 de 31-ENE-2006. Que el contenido de la parte resolutive es como sigue: El Superintendente de Industria y Comercio.

RESUELVE

ARTICULO PRIMERO: Negar el privilegio de patente de invención para la solicitud correspondiente a "METODOS DE PURIFICACION DE AGUA CON GENERACION DE FLOCULANTE DE HIDROXIDO DE METAL".

ARTICULO SEGUNDO: Notificar personalmente el contenido de la presente resolución al doctor Fernando Triana Soto, o a quien haga sus veces, en su calidad de apoderado de Potable Water Systems Ltd., entregándole copia de la misma, advirtiéndole que contra ella procede el recurso de reposición interpuesto ante el Superintendente de Industria y Comercio, al momento de la notificación o dentro de los 5 días hábiles siguientes a ella.

NOTIFÍQUESE Y CUMPLASE

Dada en Bogotá, D.C., a los **31 ENE 2006**

EL SUPERINTENDENTE DE INDUSTRIA Y COMERCIO,


JAIRO FÚLIO ESCOBAR

Para notificar a los interesados, se fija el presente EDICTO en lugar visible al público en la SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO, por el término de (10) diez días hábiles contados a partir de las 8:30 a.m. de hoy.

Secretaría General Ad-Hoc 06-MAR-2006 Este edicto se desflja hoy 17-MAR-2006 a las cinco (5:00 p.m.)
Secretaría General Ad-Hoc
EDICTO No. 3713