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(54) METHOD AND APPARATUS FOR REMOVAL OF IMPURITIES FROM LIQUIDS

(71) I, GARMT JOHAN NIEUWENHUIS, a citizen of the United States of America, of 3611 East Lake Sammanish Shore Lane South-East, Issaquah, 98027 Washington, United States of America, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by he following statement:—

This invention relates to apparatus for the removal of heavy metals from aqueous liquids and to a method for doing so.

Removal of heavy metals from aqueous liquids such as aqueous solutions, particularly when the heavy metals are present in small quantities in waste water effluent, is an acute problem due to the toxicity of the heavy metals and the increasingly stringent water quality regulations regulating discharge of such materials into water bodies. In many areas, water containing small quantities of heavy metals such as chromium, lead, mercury, cadmium, beryllium, etc. cannot be discharged into municipal sewage systems without removal of the heavy metals to an extremely low level.

The removal and recovery of hexavalent chromium from aqueous metal treating baths by contact of the hexavalent chromium with a lead compound to form a water-insoluble lead chromate is disclosed in United States Patent No. 3,493,328. US Patent No 3,791,520 also discloses a system for removing chromium anions present in small quantities from waste waters by contacting the waste water stream with a particulate carrier having a water-insoluble lead compound adsorbed thereon, the lead compound reacting with the chromium in the waste water stream to form a water-insoluble lead chromate. The system for chromium removal disclosed in US Patent No 3,791,520 provides an effective method of chromium removal; however, the flow rate through the system must be closely controlled to prevent "channeling" which results in adequate removal of the chromium anions from the incoming waste water stream. In an effort to overcome the problems encountered with the unit described in US Patent No 3,791,520, the unit disclosed and claimed herein was designed.

The use of chitin and chitosan to remove metal ions from aqueous solutions is known from US Patent Nos 3,533,940 and 3,635,818.

According to one aspect of the present invention there is provided a method for the removal of heavy metals from aqueous liquids containing the same, the method comprising:

passing the liquid containing the heavy metals successively into contact with loosely compacted, particulate, treating material containing chitin or chitosan, said material being contained in a vessel and then passing said liquid through an inert, packed layer of particulate, finely-divided filter material retained in small openings in the vessel wall immediately adjacent the treating material, the filter material having a particle size sufficient to prevent passage therethrough of any particulate solids contained in the liquid, and

repeatedly sweeping the inner surface of the vessel wall over the openings in which the filter material is retained to prevent blinding of the filter material.

The preferred filter material is diatomaceous earth, while the treating material is conveniently selected from the particulate shells of lobster, crab and shrimp previously treated with a solution containing an aldehyde, preferably formaldehyde.

According to a further aspect of the present invention, there is provided apparatus for removing heavy metals from aqueous

liquids containing the same, the system comprising:

a vessel holding a quantity of a loosely compacted, particulate treating material containing chitin or chitosan, the vessel having multiple small openings in a wall thereof,

a packed layer of particulate, finely-divided filter material in each of the openings in the vessel wall, means for retaining the layer of filter material in each of the openings, and

means for repeatedly sweeping over the openings in which the filter material is retained to prevent blinding of the filter material.

Said apparatus preferably further comprises means for maintaining a pressure differential between the inside and outside of the vessel to aid in passage of the liquid through the filter material retatined in the openings.

A preferred apparatus according to the invention comprises:

an outer housing having a discharge opening therein;

a cylindrical vessel mounted with its longitudinal axis horizontally oriented in the housing, the vessel having spaced end walls connected by a cylindrical wall with a thickness of from $\frac{1}{4}$ to $\frac{1}{2}$ inches, the cylindrical wall having multiple openings therein around its entire circumferential surface ranging in size from $\frac{1}{8}$ to $\frac{1}{2}$ inches in diameter;

a quantity of a loosely compacted, particulate, treating material in the vessel, said material containing chitin or chitosan;

a packed, finely-divided, particulate filter material embedded in the multiple openings of the cylindrical wall of the vessel;

a woven material covering the outer surface of the cylindrical wall of the vessel and the openings therein and having a mesh size sufficient to prevent passage therethrough of the finely-divided filter material embedded in the openings of the cylindrical shell.

a series of blades extending substantially the length of the vessel mounted on a rotatable shaft axially positioned within the vessel, for repeatedly sweeping across the inner surface of the cylindrical wall of the vessel and over the openings therein to premix the quantity of treating material withvent blinding of the filter material and to in the vessel;

means for feeding an aqueous solution containing the impurities into the cylindrical vessel; and

power means connected to the shaft for rotation thereof.

By way of examples only, the aspects of the invention will now be described in greater detail with reference to the accompanying drawings of which:

Fig. 1 is a cross-sectional view of apparatus for carrying out the invention disclosed;

Fig. 2 is a cross-sectional view along line 2—2 of Fig. 1; and

Fig. 3 is an enlarged cross-sectional view of a portion of the cylindrical vessel wall of Fig. 1 illustrating the location of the finely divided particulate material and the woven mesh material which retains the particulate material in the small openings of the cylindrical vessel.

Aqueous streams containing heavy metal ions such as chromium, cadmium, lead, zinc found in waters in the plating industry can be treated with the apparatus disclosed to remove the metal ions to such a low level that there is no problem in discharging the resultant effluent into water bodies.

Fig. 1 illustrates one system for removing heavy metals from aqueous liquids. An outer cylindrical housing 10 having end walls 16 and 18 is provided with a discharge port 12 for discharge of treated aqueous liquid after it passes into and through the openings in the wall of an inner cylindrical vessel 14. End walls 16 and 18 include shoulder portions 17 and 19 of substantially the same diameter as the inner diameter of shell 20 of the inner cylindrical vessel. The end walls 16 and 18 cap the open ends of vessel 14. O-ring 21 provides an effective seal between wall 20 and the shoulder portion 17, of end wall 16. End wall 18 includes a flange portion 11 which is secured to an integral flange portion 13 of housing 10 by suitable fastening means 15. O-ring 23 provides an effective seal between portion 13 and housing 10. Cylindrical wall 20 is secured by suitable means over the flange portion 19 of end wall 18.

End wall 19 has an inlet port 25 therein for introducing the liquid to be treated into the interior of vessel 14. The inlet port may be fitted with a pressure meter 27 and/or flow meter if desired.

Cylindrical wall 20 has multiple small openings 22 therein (see Fig. 3). The size of the openings may vary but preferably range from $\frac{1}{8}$ to $\frac{1}{2}$ inch in diameter. The outer housing 10, cylindrical vessel 20 and end walls 16 and 18 are preferably manufactured from a synthetic plastic material which can withstand highly acidic materials without damage thereto. The units may also be manufactured from stainless steel or other suitable metals if desired, depending on the water to be treated.

Embedded in each of the openings 22 is a finely-divided, particulate, inert, filter material 24, such as diatomaceous earth. The particle size of the filter material is chosen

depending on the solids to be retained. The particle size of the filter material 24 should be sufficiently small to prevent passage therethrough of particulate solids in the waste water. A preferred particle size is on the order of 2 to 5 microns, on average. Too small a particle size of filter material results in too slow filter rate while too large a particle size does not effectively remove the impurities sought to be removed.

To retain the filter material within the openings 22, a woven fabric 33 or other suitable material having a mesh size small enough to prevent passage of the particulate filter material therethrough is placed over the outer surface of the cylindrical shell 20 and over the openings 22. For example, a woven nylon or polyester knit cloth adhesively bonded to the outer surface of the cylindrical shell has been found to work adequately.

Mounted within the vessel are a series of blades 26 which extend substantially the length of the vessel. Each blade is secured by suitable struts 28 to a rotatable shaft 30 axially mounted in the vessel. The outer periphery of each of the blades is designed to pass over the inner openings as close as possible to the inner surface of the wall 20 without affecting the filter material 24 contained in the opening 2. The clearance between the blades and the inner surface of wall 20 is preferably about 1/64 inch. Shaft 30 extends through an opening in wall 18 and is connected to suitable power means 32, such as a hydraulic motor by a connector 29 for rotation thereof. A standard shaft packing gland 31 surrounds shaft 30 to prevent leakage through end wall 18.

The smaller the particle size of filter material used, the lower the rate of filtration. A pressure differential between the interior and exterior of vessel 14 of 3 to 6 psi is maintained for adequate filtration. It has also been found that a wall thickness of the cylindrical shell 20 should be from $\frac{1}{4}$ to $\frac{1}{2}$ inches and preferably $\frac{3}{8}$ inches for optimum results. The depth of the diatomaceous earth 24 filling the openings 22 in the cylindrical shell is equal to the wall thickness.

The system disclosed is useful for removal of heavy metals, such as nickel, cadmium, mercury and lead present in small quantities in water streams, using a particulate treating material containing chitin or chitosan as disclosed in US Patent No 3,533,940 and 3,635,818.

Chitin is the main structural component of lobster, shrimp and crab shells as well as the exterior skeletons of other crustaceans, insects and spiders. Chitin is composed of chains of glucose units in which one hydroxyl in every glocose fragment is replaced by acetamido group.

Chitosan, a deacylated form of chitin produced by heating chitin in aqueous acid, has similar properties to chitin. Both chitin and chitosan act as ion exchange materials for the removal of heavy metals such as chromium, lead, mercury, zinc and cadmium in water soluble form in water streams.

The cylindrical vessel 14 is filled with particulate shrimp, lobster or crab shells or other source of chitin or chitosan, the chitin or chitosan acting as an ion exchange material to remove the solubilized heavy metals in the water stream fed into the vessel. The pH of the entering stream to be treated is preferably adjusted to less than about 7, such as 6.5. The particle size of the chitin or chitosan should range between 6 and 60 mesh (US Sieve Series).

The small openings in the vessel wall are filled with a compact, finely-divided, particulate filter material such as diatomaceous earth. Blades within the vessel are used to uniformly mix the particulate treating material contained therein to prevent channeling and to assure uniform action of the heavy metals contained in the water stream with the treating material.

The water discharged from the unit can be continuously monitored to determine the effective removal of the heavy metals contained therein. When the ion exchange properties of the chitin or chitosan have been substantially spent, the incoming water to be treated can be transferred to a second unit. The heavy metals sequestered by the treating material in the cylindrical vessel can be recovered by pyrolysis of the material. Pyrolysis is a known technique involving the heating of the bed of treating material in a closed vessel in the absence of oxygen sufficient to decompose the treating material and recover the metal.

One of the problems associated with the use of shrimp or crab shells is that they begin to smell very quickly after the meat is removed from the shells due to decay. This makes them almost impossible to use because of the odour associated therewith. It has been found that soaking the shells in a solution of 0.5 to 4 percent by weight formaldehyde prevents their decay. After soaking in formaldehyde the shells can be dried and used without any odour associated therewith.

The addititon of formaldehyde or other aldehyde to the treating material also has the advantage of destroying free and/or chemically combined cyanide present in the aqueous solution to be treated, as described in US Patent No 3,505,217.

If the aqueous stream to be treated contains large amounts of heavy metals it is

preferable to subject it to a pretreatment to reduce the level of the heavy metals. For example, acid solutions such as pickle liquor solutions may be pretreated by adjusting the pH of the solution with caustic or other suitable base, preferably to around pH 6.5, and then adding sodium sulphide to precipitate out the heavy metal.

The unit may also be used in conjunction with chitin or chitosan to remove cyanide present in aqueous streams. For example, in a solution containing caustic and nickel cyanide, an aldehyde such as formaldehyde or acetaldehyde is added which reacts with and breaks down the cyanide. The pH of the solution is then preferably adjusted to around pH 6.5 and sodium sulphide added to precipitate out the heavy metal which is retained within the filter unit by the filter material 24.

WHAT I CLAIM IS:—

1. A method for the removal of heavy metals from aqueous liquids containing the same, the method comprising:

passing the liquid containing the heavy metals successively into contact with loosely compacted, particulate, treating material containing chitin or chitosan, said material being contained in a vessel and then passing said liquid through an inert, packed layer of particulate, finely-divided filter material retained in small openings in the vessel wall immediately adjacent the treating material, the filter material having a particle size sufficient to prevent passage therethrough of any particulate solids contained in the liquid, and

repeatedly sweeping the inner surface of the vessel wall over the openings in which the filter material is retained to prevent blinding of the filter material.

2. The method of claim 1 wherein the filter material retained in the openings is diatomaceous earth.

3. The method of claim 1 or claim 2 wherein the treating material containing chitin or chitosan is one selected from the particulate shells of lobster, crab and shrimp previously treated with a solutiton containing an aldehyde.

4. The method of claim 2 or claim 3 when dependent from claim 2 wherein the average particle size of the diatomaceous earth is from 2 to 5 microns.

5. Apparatus for removing heavy metals from aqueous liquids containing the same, the apparatus comprising:

a vessel holding a quantity of a loosely compacted, particulate treating material containing chitin or chitosan, the vessel having multiple small openings in a wall thereof,

a packed layer of particulate, finely-divided filter material in each of the openings in the vessel wall, means for retaining the layer of filter material in each of the openings, and

means for repeatedly sweeping over the openings in which the filter material is retained to prevent blinding of the filter material.

6. The apparatus of claim 5 and further comprising means for maintaining a pressure differential between the inside and outside of the vessel to aid in passage of the liquid through the filter material retained in the openings.

7. The apparatus of claim 5 or claim 6 wherein the filter material is diatomaceous earth.

8. The apparatus of any one of claims 5 to 7 wherein the vessel has a cylindrical wall with closed end walls, the cylindrical wall containing multiple small openings therein in which the particulate filter material is embedded, wherein the means for retaining the particulate filter material in the openings is a woven material covering the outer surface of the cylindrical wall of the vessel and openings therein, the woven material being bonded to said outer surface of the cylindrical wall and having a mesh size sufficiently small to prevent the particulate filter material from passing therethrough, and wherein the means for repeatedly sweeping across the inner cylindrical wall is a series of blades extending substantially the length of the vessel mounted on a rotatable shaft axially positioned within the vessel.

9. The apparatus of any one of claims 5 to 8 wherein the thickness of the wall and filter material is from $\frac{1}{4}$" to $\frac{1}{2}$" and the size of the multiple openings in the wall is from $\frac{1}{8}$" to $\frac{1}{2}$" in diameter.

10. The apparatus of claim 8 or claim 9 when dependent from claim 8 wherein the longitudinal axis of the cylindrical vessel is horizontally oriented.

11. Apparatus for removing heavy metals from aqueous solution comprising:

an outer housing having a discharge opening therein;

a cylindrical vessel mounted with its longitudinal axis horizontally oriented in the housing, the vessel having spaced end walls connected by a cylindrical wall with a thickness of from $\frac{1}{4}$ to $\frac{1}{2}$ inches, the cylindrical wall having multiple openings therein around its entire circumferential surface ranging in size from $\frac{1}{8}$ to $\frac{1}{2}$ inches in diameter;

a quantity of a loosely compacted, particulate, treating material in the vessel, said material containing chitin or chitosan;

a packed, finely-divided, particulate filter material embedded in the multiple openings of the cylindrical wall of the vessel;

a woven material covering the outer sur-

face of the cylindrical wall of the vessel and the openings therein and having a mesh size sufficient to prevent passage therethrough of the finely-divided filter material embedded in the openings of the cylindrical shell,

a series of blades extending substantially the length of the vessel mounted on a rotatable shaft axially positioned within the vessel, for repeatedly sweeping across the inner surface of the cylindrical wall of the vessel and over the openings therein to prevent blinding of the filter material and to mix the quantity of treating material within the vessel;

means for feeding an aqueous solution containing the impurities into the cylindrical vessel; and

power means connected to the shaft for rotation thereof.

12. The apparatus of claim 11 wherein the filter material is diatomaceous earth.

13. A method of purifying liquid substantially as herein described with reference to the accompanying drawings.

14. Apparatus for purifying liquid substantially as herein described with reference to and as shown in the accompanying drawings.

MEWBURN ELLIS & CO.,
Chartered Patent Agents,
70 & 72 Chancery Lane,
London WC2A 1AD.
Agents for the Applicant.

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1563537 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

fig-1

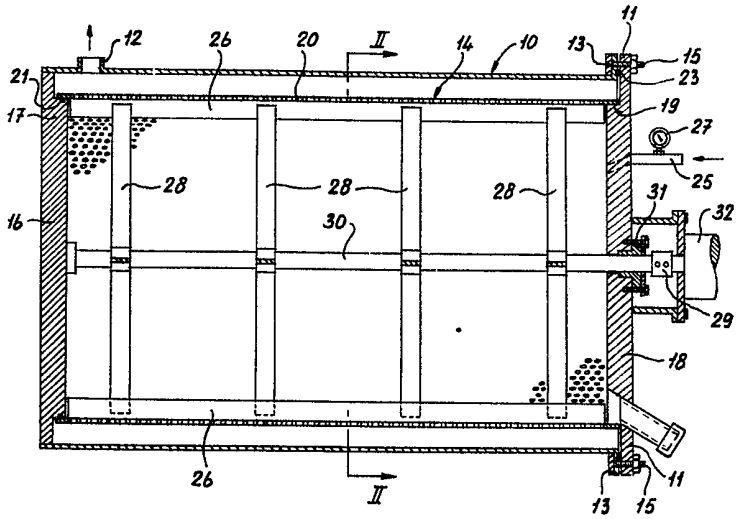

fig-2

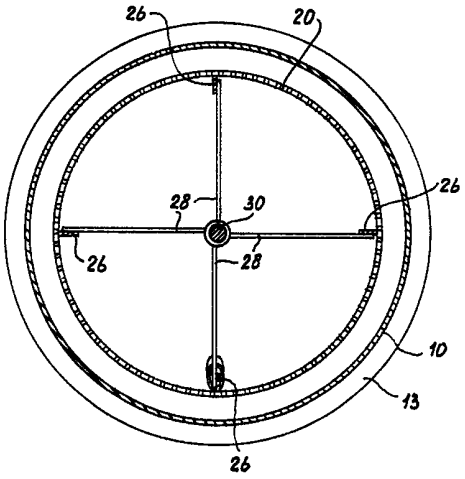

fig-3