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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 May 2007 (24.05.2007)

PCT

(10) International Publication Number
WO 2007/057521 A1

(51) **International Patent Classification:**
C02F 1/52 (2006.01) *C02F 101/30* (2006.01)
C02F 1/66 (2006.01) *C02F 101/20* (2006.01)

(21) **International Application Number:** **PCT/FI2006/050503**

(22) International Filing Date: 20 November 2006 (20.11.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20055615 18 November 2005 (18.11.2005) FI

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

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

Published:
— *with international search report*

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

WO 2007/057521 A1

(54) Title: METHOD FOR REMOVING SUBSTANCES FROM AQUEOUS SOLUTION

(57) Abstract: The present invention provides methods and the use of compositions for removing substances from aqueous solutions wherein the pH of said solution is raised from acidic to basic. In these methods a composition containing Fe3+ and Mg2+ as sulfates is added to said solutions before raising the pH to settle said substances. The substances to be removed may be metals or heavy metals, such as complexed Cu-ions.

Method for removing substances from aqueous solution

Field of the invention

The present invention relates to methods and the use of compositions for removing substances from aqueous solution wherein the pH of said solution is raised from acidic to basic. More particularly the present invention relates to removal of metals and heavy metals from waste waters.

Background of the invention

The contamination of water, such as waste waters or natural waters (groundwater or surface water) has become a major concern in many countries. Several water treatment processes and methods are employed to remove certain types of substances contaminating the water. Generally water treatment is important in several industrial processes where water contaminating substances, such as metals or heavy metals, are produced. One example of such contaminant is copper which is produced e.g. in processes of preparing printed circuit boards. In such process complex waste containing complex forming agents and other organic compounds, such as solvents, inks, developing solutions, amines, surfactants etc. together with heavy metals, such as copper or lead, are produced. Such waste is toxic and difficult to process.

Several methods for treating water to remove contaminants are known, such as treatment with coagulants or flocculants.

Certain methods comprise steps of adjusting the pH of the water or the solution to be treated. In the first step the pH of the solution is acidic (or it is adjusted to be acidic) and in the subsequent step the pH is raised to basic area. If there are complexed substances to be removed, they are displaced in the acidic solution by added ferric ions and precipitated in the step of raising the pH. Generally in these methods ferric ions are used to aid the removal of desired substances from the solution.

GB 2 292 378 A discloses a method for treating an effluent containing both complexing agents and potentially toxic heavy metals, said method comprising the steps of adjusting the pH of the effluent to below 4, and adding ferric ions to a molar concentration greater than that of all other heavy metals present in the effluent;

then leaving the effluent for a period long enough for displacement by ferric ions of other heavy metals from complexes to occur; then raising the pH to at least 10; and then separating any precipitates from the treated effluent. In the examples the method is used for removing copper and nickel.

US 4 802 993 discloses a method of treating liquid wastes containing heavy metal chelate compounds. The pH of liquid waste is adjusted to 4 or less, adding at least one heavy metal ion, such as Fe^{3+} or Fe^{2+}, adjusting pH to 9 or more with base containing Ca^{2+} and flocculating to precipitate the resulting heavy metal hydroxides by using flocculant and then separating them. It is specifically stated that if the pH value is less than 9, chelates of heavy metals other than copper may remain or copper chelate is formed again to reduce the heavy metal and COD removal rates.

US 6 238 571 discloses a similar method wherein a source of ferric ions and a source of ferrous ions is introduced into the solution and the pH is adjusted to a value greater than about 10. In said reaction wide range of ferrites with varied properties are formed, such as $(FeCu)O \cdot Fe_2O_3$ when copper is treated.

There is still need for simple, economical and efficient methods and materials for water treatment to remove or recover substances from aqueous solutions. Further, the corrosion problems related to the use of certain compounds should be avoided. Also the recovery of the precipitate formed should be easy.

It is an object of the present invention to provide methods which are efficient when compared to methods using compositions containing only Fe^{3+} or Fe^{3+} and Fe^{2+} to remove substances from solutions by methods where the pH of the solution is raised from acidic to basic as described herein. It is also an object of the present invention to provide such methods which are substantially non-corrosive and which do not necessarily require such high pH's as generally are used.

Summary of the invention

The present invention is based on the discovery that a composition containing Fe^{3+} and Mg^{2+} as sulfates is efficient for removing substances, such as metals or heavy metals, from aqueous solution by methods where the pH of the solution is raised from acidic to basic.

Such compositions and methods for preparing thereof by mixing Fe^{3+} with Mg^{2+} in an aqueous solution are described herein.

One aspect of the present invention provides a method for removing substances from aqueous solution having pH below 3 comprising raising the pH to range of 5.5-12. Composition described above is added to the solution to settle said substances. Generally pH's as high as 12 or even over 10 are not required when Mg^{2+} is used together with Fe^{3+}. pH of 9 or less is enough and this saves chemicals needed for the adjustment of the pH.

Another aspect of the present invention provides the use of said composition for removing substances from aqueous solution with said method.

The solution to be treated with the composition or by the method of the invention comprises substances, such as heavy metals or other contaminants or impurities. The substances may be in the form of a complex with any complex forming agent. Preferably said substances are 2-valent metal ions. Examples of said substances are Cu, Ni, Zn, Co and Pb.

Detailed description of the invention

The present invention provides a method for removing substances from aqueous solution having low pH, preferably below 3, said method comprising raising the pH to the range of 5.5-12, wherein the composition described herein containing Fe^{3+} and Mg^{2+} as sulfates is added to the solution before raising the pH, to settle said substances. Generally the pH is raised to pH 9 at maximum, the range of 5.5-9 being preferred and range of 7.5-9 is more preferred.

Said Fe^{3+} and Mg^{2+} are substantially present as sulfates. The benefit of the sulfate-based coagulant solution is that it causes significantly less corrosion problems compared to e.g. chloride-based solution. It was also surprisingly discovered that the removal of the insoluble precipitate is also faster and easier when sulfate-based composition is used. As the precipitate is usually separated mechanically, for example by filtering, the precipitate formed when using sulfate-based composition is more dry after the separation and therefore less waste will be formed.

"Aqueous solution" as used herein refers to any solution containing water. Preferably said aqueous solution is any solution containing sufficient amount of water phase to be used in the current invention. Said aqueous solution may be for example water, groundwater, waste water, industrial water, sludge or solids suspension, pulp suspension or any other suitable aqueous solution. One specific non-limiting example of said solution is a waste water from electronics industry containing complexed copper, such as the waste water from processes of preparing printed circuit boards.

In the beginning the pH of the solution must be low. In one embodiment of the method the pH of the aqueous solution has been adjusted to below 3. In still another embodiment said composition is added to adjust the pH to below 3. Since the composition itself is acidic it may be sufficient to add the composition to the aqueous solution to adjust the pH. In this case the step of separately adjusting the pH can be omitted. If this is not sufficient, the pH may be adjusted using any suitable acidic agent, such as sulfuric acid. The pH used in the beginning is generally in the range of 0.8-2.2.

In still another embodiment said composition is added before the pH is adjusted to below 3. In still another embodiment said composition is added after the pH is adjusted to below 3. It is preferred to add the composition to solution already having the pH below 3 to ensure the most efficient function of the composition. Subsequent raising of the pH then leads to the precipitation of iron and impurities. The pH may be raised using any suitable basic agent, such as NaOH, sodium carbonate or sodium aluminate.

The residence times generally used are in the range of 5-60 minutes at the pH below 3 and 5-60 minutes at the higher pH.

In one embodiment said method further comprises the step of adding flocculating polymer to the solution having the pH in the range of 5.5-12. In industrial scale the use of flocculating polymer may be especially advantageous to speed up the precipitation in large tanks used. Said flocculating polymer may be anionic polyacrylamide, cationic polyacrylamide, non-ionic polyacrylamide or combinations thereof or any other suitable polymer. A person skilled in the art can define the amounts of flocculants to be used. Generally flocculating polymer may be added e.g. in amounts ranging from 0.4 to 5 ml/l of 0.2% polymer solution.

The substances to be removed or recovered from the aqueous solution refer to any suitable substances present in said solution. Such substances may be harmful or beneficial substances, for example contaminants, reaction products or by-products. Non-limiting examples of said substances are elements and compounds thereof, such as inorganic compounds, organometallic compounds, organic compounds, metals and heavy metals in their different oxidation states and the like. In one embodiment of the present invention said substances comprise Cu, Ni, Zn, Co or Pb or combinations thereof.

Said substances may have been complexed with a complex forming agent, such as monoethanolamine, ethylenediamine, diethylenetriamine, or any other complexing agent capable of complexing 2-valent metal ions, such as EDTA. Said complexes may have been formed e.g. in industrial processes or the like as described above.

Coagulation is the destabilization of colloidal particles brought about by the addition of a chemical reagent known as a coagulant. Fine particles in a suspension collide with each other and stick together. Usually the particles are brought near to each other by Brownian motion or by flow (Water Treatment Handbook, Vol 1 and Vol 2, 1991, Degremont). Generally coagulant is an inorganic (anion/cation) or organic (polyelectrolyte) chemical, which neutralizes the negative or positive surface charge (destabilization) of the impurities, such as colloidal particles. As used herein "coagulant" refers to the composition containing Fe^{3+} and Mg^{2+} as described below.

The molar ratio of Fe^{3+} to Mg^{2+} may be in the range of 0.5-4.0. In one embodiment said ratio is in the range of 0.5-2. In still one embodiment said ratio is in the range of 0.5-1.2. Generally the composition is acidic in aqueous solution and it has less than 2% (w/w) of free H_2SO_4. Also, the molar ratio of OH to Fe in aqueous solution is generally less than 0.15. To keep the composition stabile this ratio should be close to zero. The composition may be provided for use as solid or as aqueous solution.

The amount of composition to be used may vary depending on the concentrations of the substances to be removed. For example to water containing 10-30 mg/l of copper and 2-5 mg of nickel about 1-5 kg/m^3 of the composition of the invention may be used. A person skilled in the art can define the suitable amounts and concentrations of the compositions.

Generally the composition to be used may contain Fe^{3+} in the range of 1-7% (w/w), preferably 3-7% (w/w) and more preferably 5-7% (w/w). The concentration of Mg^{2+} may be in the range of 1-3% (w/w), preferably 2-3% (w/w) and more preferably 2-2.5 % (w/w). Said ranges are examples of economically reasonable concentrations, but technically e.g. more dilute concentrations may work as well. Preferably the ratio of said Fe^{3+} and Mg^{2+} concentrations is within the range of 0.5-4 as defined above.

One embodiment of the present invention provides the composition described above, said composition being obtainable by one of the following reactions:

(1) $Fe_2(SO_4)_3 + MgO + H_2SO_4 + H_2O$,

(2) $Fe_2(SO_4)_3 + Mg(OH)_2 + H_2SO_4 + H_2O_1$

(3) $Fe_2(SO_4)_3 + MgCO_3 + H_2SO_4 + H_2O$, or

(4) $Fe_2(SO_4)_S + MgSO_4 + H_2O$

One embodiment of the present invention provides a method for preparing said composition for removal of substances from aqueous solution by mixing Fe^{3+} with Mg^{2+} in an aqueous solution. This may be carried out by any of the reactions (1) to (4) described above and the components of said reactions may be added in any possible order. Non-limiting examples of magnesium salts useful in said reaction (4) are anhydrous $MgSO_4$, $MgSO_4$-H_2O (Kieserite) and $MgSO_4$-$7H_2O$ (Epson salt). When using said reactions Mg^{2+} bases, such as MgO, are used for preparing the coagulant. In the final composition the magnesium is substantially present as sulfate but not as a base, such as MgO.

One embodiment of the present invention provides the use of the composition described for removing substances from aqueous solution. This may be carried out by any of the methods described herein wherein the pH of an acidic solution is raised and the composition of the present invention is added. The embodiments described above are all applicable to the use of said composition.

Examples

The following examples are provided to show some non-limiting methods for preparing the compositions of the present invention. It should be noted that in industrial scale production some steps, such as the step of adding magnesium oxide, may take longer time than described in the examples, such as 1-2 hours more.

Example 1. The preparation of the composition of the invention

21.4 g of magnesium sulfate ($MgSO_4$-$7H_2O$) was added by stirring to 46.4 g of aqueous ferric sulfate solution containing 11.0% of Fe^{3+}. 32.2 g of 20^{0}C water was added and stirred for 2 hours. The mixture was filtrated through MN 640 filter paper and the solution was stored in room temperature. The composition contained 5.1% (w/w) of Fe^{3+} and 2.1 % (w/w) of Mg^{2+}. The Fe^{3+}: Mg^{2+} molar ratio was 1.06.

Example 2. The preparation of the composition of the invention

25.5 g of magnesium sulfate ($MgSO_4$-$7H_2O$) was added by stirring to 36.4 g of aqueous ferric sulfate solution containing 11.0% of Fe^{3+}. 38.1 g of 20^0C water was added and stirred for 2 hours. The mixture was filtrated through MN 640 filter paper and the solution was stored in room temperature. The composition contained 4.0% (w/w) of Fe^{3+} and 2.5 % (w/w) of Mg^{2+}. The Fe^{3+}: Mg^{2+} molar ratio was 0.7.

Example 3. The preparation of the composition of the invention

27.6 g of magnesium sulfate ($MgSO_4$-$7H_2O$) was added by stirring to 30.0 g of aqueous ferric sulfate solution containing 11.0% of Fe^{3+}. 42.4 g of 20^0C water was added and stirred for 2 hours. The mixture was filtrated through MN 640 filter paper and the solution was stored in room temperature. The composition contained 3.3% (w/w) of Fe^{3+} and 2.7% (w/w) of Mg^{2+}. The Fe^{3+}: Mg^{2+} molar ratio was 0.54.

Example 4. The preparation of the composition of the invention

54.7 g of 93% sulfuric acid was added to 300 g of aqueous ferric sulfate solution containing 10.5% of Fe^{3+}. The temperature of the solution increased to 47°C. 20.75 g of magnesium oxide was added to the solution during 10 minutes and the temperature further increased to 81^0C. Finally 168 g of water was added quickly and the temperature decreased to 64^0C. The mixture was filtrated through MN 640 filter paper and the solution was stored in room temperature. The composition contained 5.8% (w/w) of Fe^{3+} and 2.3% (w/w) of Mg^{2+}. The Fe^{3+}: Mg^{2+} molar ratio was 1.10.

Comparative example 1. The preparation of a composition containing Fe^{3+} and Fe^{2+}

9.5 g of ferrosulfate ($FeSO_4$-$7H_2O$) was added by stirring to 51.8 g of aqueous ferric sulfate solution containing 11.0% of Fe^{3+}. 38.7 g of 20^0C water was added and stirred for 2 hours. The mixture was filtrated through MN 640 filter paper and the solution was stored in room temperature. The composition contained 5.7% (w/w) of Fe^{3+} and 1.9% (w/w) of Fe^{2+}. The Fe^{3+}: Fe^{2+} molar ratio was 3.0.

Example 5: Comparison of different compositions

Waste water containing heavy metals and complex forming agents having the copper content of 140 mg/l was treated with the compositions described in the previous examples. Dosages of different compositions containing certain concentrations (w/w %) of Fe^{3+}, Mg^{2+} and Fe^{2+} as shown in table 1 were added to 500 ml portions of solutions having pH of about 0.8, stirred for 30 minutes and the pH of the solution was raised to about 9 with solution of NaOH. Each solution was further stirred for 5 minutes and the precipitate was left to settle for 10 minutes. Almost clear liquid phase was filtered through 1.2 µm membrane. Copper concentrations and pH were determined as shown in table 1. The rise of pH only and rise of pH combined with addition of ferric sulfate only as well as composition containing both Fe^{3+} and Fe^{2+} were used as references. As seen in the table 1 all three compositions according to the present invention yielded significantly better results than the rise of the pH alone or the use of coagulants containing only iron.

Table 1. Comparison of removal methods

Experiment	Fe^{3+} w/w %	Mg^{2+} w/w %	Fe^{2+} w/w %	Fe^{3+}/Me^{2+} molar ratio	dosage of composition g/l	final pH	Cu mg/l
rise of pH						8.75	2.1
ferric sulfate solution	11.8				0.93	8.60	2.2
Comparative example 1	5.7		1.9	3.0	1.51	8.77	1.6
Example 1	5.1	2.1		1.06	1.89	9.00	1.0
Example 2	4.0	2.5		0.70	1.18	8.75	1.1
Example 3	3.3	2.7		0.54	1.41	8.88	1.1

Example 6: Flocculant

Contaminated water having pH of 2.2 contained 26 mg/l of complexed copper and 2.9 mg/l of nickel. 2.5 g/l of composition containing 5.8% (w/w) of Fe^{3+} and 2.3% (w/w) of Mg^{2+} was added to the water and mixed 10 minutes. After this the pH was raised to 8.2 with sodium hydroxide and mixed 10 minutes. Then 0.4 ml/l of Fennopol A305 flocculating polymer solution was added (concentration 0.17% w/w) and mixed 10 minutes, floe was let to settle to the bottom and Cu and Ni were analyzed from the liquid phase. Both were below the detection limit 0.1 mg/l.

Claims

1. A method for removing substances from aqueous solution having pH below 3 wherein the pH is raised to the range of 5.5-12, **characterized** by adding composition containing Fe^{3+} and Mg^{2+} as sulfates to the solution before raising the pH, to settle said substances.

2. The method of claim 1, **characterized** in that the molar ratio of Fe^{3+} to Mg^{2+} is in the range of 0.5-4.0.

3. The method of claim 2, **characterized** in that the molar ratio of Fe^{3+} to Mg^{2+} is in the range of 0.5-1 .2.

4. The method of any of the preceding claims, **characterized** in that said composition is obtainable by one of the following reactions: $Fe_2(SO_4)_3 + MgO + H_2SO_4 + H_2O$, $Fe_2(SO_4)_3 + Mg(OH)_2 + H_2SO_4 + H_2O$, $Fe_2(SO_4)_3 + MgCO_3 + H_2SO_4 + H_2O$ or $Fe_2(SO_4)_3 + MgSO_4 + H_2O$.

5. The method of any of the preceding claims, **characterized** in that the pH is raised to the range of 5.5-9.

6. The method of any of the preceding claims, **characterized** in that the pH is raised to the range of 7.5-9.

7. The method of any of the preceding claims, **characterized** in that the pH of the aqueous solution has been adjusted to below 3.

8. The method of any of the claims 1-7, **characterized** in that said composition is added after the pH is adjusted to below 3.

9. The method of any of the claims 1-7, **characterized** in that said composition is added before the pH is adjusted to below 3.

10. The method of any of the claims 1-7, **characterized** in that said composition is added to adjust the pH to below 3.

11. The method of any of the preceding claims, **characterized** by further comprising the step of adding flocculating polymer to the solution having the pH in the range of 5.5-12.

12. The method of claim 11, **characterized** in that said flocculating polymer is anionic polyacrylamide, cationic polyacrylamide, non-ionic polyacrylamide or combinations thereof.

13. The method of any of the preceding claims, **characterized** in that said substances to be removed comprise Cu, Ni, Zn, Co or Pb or combinations thereof.

14. The method of any of the preceding claims, **characterized** in that said substances have been complexed with complex forming agent.

15. The method of claim 14, **characterized** in that said complex forming agent is monoethanolamine, ethylenediamine, diethyienetriamine, EDTA or any other complexing agent capable of complexing 2-valent metal ions.

16. Use of composition containing Fe^{3+} and Mg^{2+} for removal of substances from aqueous solution with the method of any of the preceding claims.

INTERNATIONAL SEARCH REPORT

International application No
PCT/FI2006/050503

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F1/52
ADD. C02F1/66 C02F101/30 CO2F101/20

According to International Patent Classification (IPC) orto both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 2002/158023 Al (WURZBURGER STEPHEN RAY [US]) 31 October 2002 (2002-10-31) paragraph [0044]; claims -----	1-16
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☒ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search 21 February 2007	Date of mailing of the international search report 01/03/2007
Name and mailing address of the ISA/ European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040, Tx 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Serra, Renato

INTERNATIONAL SE=ARCH REPORT

International application No
PCT/FI2006/050503

C(Contlnuatlon). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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