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**WO 01/64006 A2**

(54) Title: TREATMENT OF SCALE

(57) **Abstract:** A method for reducing/preventing the formation of scale or removal of scale in a municipal or industrial waste water treatment facility comprising introducing an antiscalent composition which comprises: A) A water soluble polymer of molecular weight below 20,000 and containing anionic groups, and B) A sequesterant compound containing at least one phosphonate group and salts thereof, characterised in that component (A) is formed from a monomer or monomer blend consisting of one or more ethylenically unsaturated carboxylic acid monomer(s) and optionally not more than 50 % by weight of an ethylenically unsaturated water-soluble nonionic monomer. Preferred antiscalent compositions include a blend of A) a polymer of acrylic acid and/or maleic acid and B) diethylentriamine penta (methyleneephosphonic acid) or salts thereof. Also claimed is the use of the above composition for the treatment of struvite scale.

### Treatment of Scale

The present invention relates to a novel method of treatment for the prevention, reduction or removal of scale in municipal and industrial waste water treatment facilities. The invention employs a new anti-scaling or de-scaling composition which is especially useful for the treatment of waste treatment plants prone to struvite scaling.

The precipitation of struvite is a problem that frequently occurs in sewage treatment plants, especially in anaerobic sludge digestion systems. Soluble magnesium combines with ammonia and phosphate, released during the aerobic digestion to form magnesium ammonium phosphate ( $MgNH_4PO_4 \cdot 6H_2O$ ) which is frequently referred to as struvite. Struvite is a hard, tenacious solid that is extremely difficult to remove from equipment surfaces and pipelines. It is generally encountered in sludge lines and downstream processes following biological phosphate removal and subsequent anaerobic digestion, although it can form wherever the solubility limit is exceeded. This can also be related to pH changes caused by sludge degassing. Deposits tend to form in pipes where waste waters stand between intermittent flows, but also in areas where there is turbulent flow, pressure change or where cavitation occurs. Thus struvite deposition occurs most frequently in pipes, pipe elbows, valves, centrifuge weir overflows, pumps etc.

Struvite deposition is becoming an increasingly widespread problem for a great many waste water treatment plants, since it reduces throughputs, which could adversely affect subsequent sludge processing. In extreme cases the struvite can reduce the throughput so significantly that the plant operation has to be stopped and then the blocked pipework and other equipment must be cleaned. Generally struvite deposits can only be removed completely by treatment with acid. This can be expensive and involve potentially dangerous handling and disposal of cleaning products (acidic solutions) which can also cause excessive wear to the equipment. In addition the plant closure time during the cleaning operation can also be costly.

Various proposals have been made in order to deal with this problem, many with some degree of success, but none of them have successfully overcome this problem completely.

For instance it is known to attempt to control the release of phosphate biologically. In an article by Nic Booker CSIRO, Molecular Science, entitled, "Struvite formation in wastewater treatments plants: an accident waiting to happen?", the issue of nutrient removal from wastewater discharges is discussed. The study claims that Biological phosphorus removal plants can reduce phosphorus concentrations to less than 1mg/L. However there is a tendency for some plants with insufficient ready assimilable carbon in the feedwater to have difficulty in consistently achieving this level. In addition the biological phosphorus plants involve a number of different stages of treatment, including anaerobic, aerobic and anoxic zones and require long liquid residence times of around 24 hours.

In US 5,352,365 the use of an aqueous solution, comprising a terpolymer of acrylic acid, 2-acrylamido-2-methylpropane sulphonic acid and specific non-ionic monomer in combination with a phosphonic acid or phosphonate, to remove or reduce scale, including calcium carbonate, vivianite and stuvite. The solution is at a pH between 2 and 9 and preferably includes hydrochloric acid. The preference to using aqueous solutions at acidic pH is also apparent from the illustration of a scale treatment at a sewage treatment plant, where removal of scale is accompanied by effervescence. Such acidic treatment would have the disadvantage of being expensive and involve potentially dangerous handling and disposal of cleaning products (acidic solutions) which can also cause excessive wear to the equipment. By contrast this reference teaches that a combination of phosphonhydroxyacetic acid and acrylate copolymers merely disperse and suspends rather than actually dissolve calcium carbonate in cooling tower descaling experiments. Furthermore the use of terpolymers alone are said not to be capable of dissolving iron oxides and calcium phosphates and silicates.

There have also been suggestions to prevent struvite formation by removing ammonia and phosphate chemically by the addition of magnesium to raise the pH. However, in practice this was found to be unsuccessful on the whole.

Another proposal has been to add 20mg/L ferric salts and 0.25mg/L anionic polymer. However, the addition of such large amounts of ferric salt could have a detrimental effect on the plant equipment.

In JP-A-08-099091 it is proposed to prevent the generation of struvite scale in piping by chemical reaction/crystallisation employing special separation equipment to recover the crystals of struvite. However, installing such struvite precipitating equipment adds an additional burden to the operation of the waste water treatment plant.

Thus there exists a need to simply and conveniently removal or prevent or significantly reduce the formation of struvite in waste water treatment facilities. Furthermore there is also a need to find a simple and convenient treatment of aqueous systems containing struvite deposits.

Thus according the present invention we provide a method of preventing/reducing the formation of scale or removal of scale in a municipal or industrial waste water treatment facility comprising introducing an antiscalent composition which comprises:

- A) A water soluble polymer of molecular weight below 20,000 and containing anionic groups, and
- B) A sequesterant compound containing at least one phosphonate group and salts thereof,  
characterised in that component (A) is formed from a monomer or monomer blend consisting of one or more ethylenically unsaturated carboxylic acid monomer(s) and optionally an ethylenically unsaturated water-soluble nonionic monomer.

We have found that the special combination of low molecular weight carboxylic anionic water soluble polymer and phosphonate sequesterant give surprisingly effective results in reducing or preventing scale, especially struvite in waste water treatment systems. Thus it is essential to the present invention that the sequesterant comprised in the antiscalent composition of the present invention is a compound containing at least one phosphonate group.

The antiscalent composition may be used for the treatment of any scale deposits in a water treatment facility. The method is of particular relevance when the scale deposits comprise crystalline precipitate formed by the combination of phosphate, ammonia and magnesium, which may exist as magnesium ammonium phosphate ( $MgNH_4PO_4 \cdot 6H_2O$ ) which is generally referred to as struvite.

The method may be applied to any waste water treatment facility in which scale deposits are a particular problem, especially where the scale deposit is struvite. We have found the method is especially valuable in removing, reducing or preventing scale deposition in sewage treatment plants. Hence in a particularly preferred form of the invention we provide a method in which struvite deposition is removed, reduced or prevented in a sewage treatment plant employing as a treatment aid the aforementioned antiscalent composition.

A further aspect of the invention relates to the treatment of any aqueous system containing struvite deposits. Thus we provide the use of a composition comprising,

A) A water soluble polymer of molecular weight below 20,000 and containing anionic groups, and

B) A sequesterant compound containing at least one phosphonate group and salts thereof,

for the treatment of aqueous systems containing struvite, characterised in that component (A) is formed from a monomer or monomer blend consisting of one or more ethylenically unsaturated carboxylic acid monomer(s) and optionally an ethylenically unsaturated water-soluble nonionic monomer.

The antiscalent composition employed in the present invention preferably comprises 25 to 75% by weight of the water soluble polymer (component A) and 25 to 75% by weight of the sequesterant (component B). Generally we have found that for many treatments it is preferred that the antiscalining composition comprises 30 to 70% by weight, most preferably 40 to 60%, of the water soluble polymer and between 30 and 70% by weight, most preferably 40 to 60%, of the sequesterant.

The water soluble polymer component of the antiscalent composition is formed from a monomer or monomer blend consisting of one or more ethylenically unsaturated carboxylic acid monomer(s) and preferably not more than 50% by weight of an ethylenically unsaturated water-soluble nonionic monomer.

The polymer is desirably formed from ethylenically unsaturated anionic monomer or anionic monomer blend in which the monomer blend comprises at least one ethylenically unsaturated carboxylic acid. The anionic carboxylic monomers may include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid and crotonic acid. When more than one monomer is employed in a blend, the monomer blend may comprise any of the aforementioned anionic monomers and up to 50% by weight of an ethylenically unsaturated nonionic monomer, for instance acrylamide or methacrylamide. The polymers may exist in the free acid form or more preferably they are partially or fully neutralised. A particularly preferred water soluble polymer is the homopolymer of acrylic acid, homopolymer of maleic acid, homopolymer maleic anhydride or a copolymer of acrylic acid with either maleic acid or maleic anhydride. Especially preferred is the homopolymer of acrylic acid (or salt) or a copolymer of acrylic acid (or salt) with either maleic acid (or salt or anhydride) or itaconic acid (or salt or anhydride).

Typically the water soluble polymer is polymerised to a relatively low molecular weight. By low molecular weight we mean that the polymer will have a molecular weight as determined by GPC of below 20,000. However, the molecular weight of the polymer may desirably be in the range 1,500 to 10,000, preferably 2,000 to

5,000.

One way of preparing the water soluble polymer is by solution polymerisation of an aqueous solution of the monomers. Generally the aqueous monomer solution should be between 20 and 40% concentration, preferably around 30 to 35%. The monomer solution may also include a chain transfer agent, for instance sodium hypophosphite, 2-mercaptoethanol or isopropanol. If sodium hypophosphite is used as the chain transfer agent, the amount can be as much as 2000 ppm by weight, but is preferably in the range 10 to 500 ppm by weight, particularly 10 to 50 ppm. Where isopropanol is used as the chain transfer agent it is usual to use this as a part of the solvent system. Thus the monomers would be mixed with an isopropanol/water mixture and then polymerised.

A suitable initiator system, for instance aqueous ammonium persulphate, sodium metabisulphite or tertiary butyl hydroperoxide, optionally with other initiators is introduced. When preparing gel polymers by solution polymerisation the initiators are generally introduced into the monomer solution. Optionally a thermal initiator system may be included. Typically a thermal initiator would include any suitable initiator compound that releases radicals at an elevated temperature, for instance azo compounds, such as azobisisobutyronitrile. The temperature during polymerisation should rise to at least 70°C but preferably below 95°C.

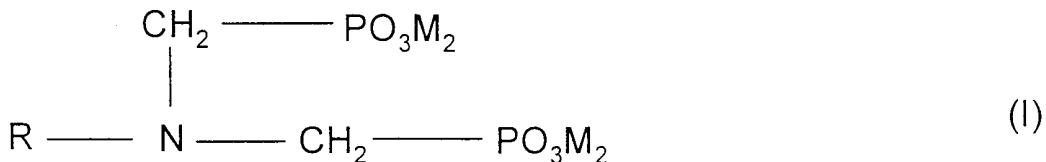
Depending upon the molecular weight and the concentration of polymer in solution the formed polymer may be a slightly viscous but pourable aqueous solution or could be a rigid gel. Polymer gels may be further processed in a standard way by first comminuting the gel into smaller pieces, drying to the substantially dehydrated polymer followed by grinding to a powder. Pourable solutions of the polymer do not need further processing and would normally be supplied in this form where they may be further diluted on application.

Alternatively the polymers are produced as beads by suspension polymerisation or as a water-in-oil emulsion or dispersion by water-in-oil emulsion polymerisation,

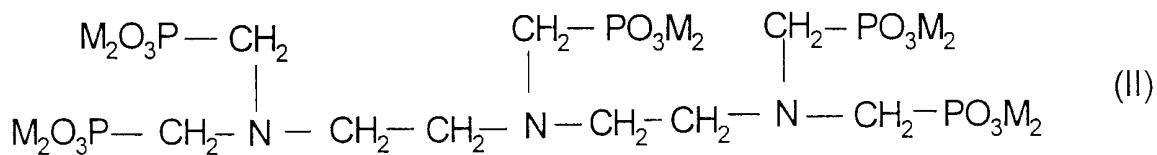
for example according to a process defined by EP-A-150933, EP-A-102760 or EP-A-126528.

Although to the invention in some instances beneficial results may be obtained when the polymer has a narrow polydispersity. Thus such polymers would contain a narrow molecular weight distribution. Typically such polymers may have a polydispersity of below 1.5. They may be prepared in accordance with the teachings of EP-A-127388, EP-A-129329 and EP-A-185458.

According to the invention the antiscalent composition comprises as component B a sequesterant compound containing at least one phosphonate group and salts thereof. The invention embraces any phosphonate sequesterant compound that in combination with the water soluble anionic polymer of component A produces a beneficial effect in the removal, reduction and prevention of scale deposits, especially struvite. Preferably the phosphonate sequesterant comprises at least two phosphonate groups which at least one nitrogen atom. Desirably the phosphonate sequesterant can be desirably a compound of the formula I



wherein M is hydrogen, alkali metal or ammonium and R is selected from the group consisting of -H, -CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub>, -N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub> and -(CH<sub>2</sub>)<sub>6</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub>. A particularly preferred sequesterant is the compound of formula II,



known as diethylenetriamine penta (methylene phosphonic acid) and including the corresponding alkali metal or ammonium salts, most preferred are the sodium salts.

The phosphonate sequesterant may be any one of a number of commercially available sequesterant products, for example Dequest<sup>TM</sup> 2066 which is a post acidified sodium salt of diethylenetriamine penta (methylene phosphonic acid) available from Solutia.

The antiscalent composition is generally prepared by mixing an aqueous solution of the anionic water soluble polymer component with an aqueous solution of the phosphonate sequesterant. Generally the composition does not require any added mineral acid, such as hydrochloric acid or sulphuric acid. In fact effective antiscalining and scale prevention are achieved by a composition which contains substantially no substantial amount of any other ingredients. Thus preferably the antiscalent composition consisting essentially of component (A) and component (B).

The antiscalent composition may be applied at any point in the waste water treatment process. Desirably though it may be applied more effectively shortly before where the scale or struvite deposits have formed or are prone to form. Struvite tends to form in pipes where waste waters stand between intermittent flows, or in areas of turbulent flow, for instance where a pressure change or cavitation occurs. Thus since struvite deposition occurs most frequently in pipes, pipe elbows, valves, centrifuge weir overflows, pumps etc., it may be desirable to dose at or prior to these points. For instance it may be preferred to apply the antiscalent composition up to 200 metres prior to the area where scaling occurs. Thus it may be preferred to add the antiscalent such that it will thoroughly mix into the substrate before reaching the point where scaling occurs.

The antiscalent composition may be added in any effective amount, for instance up to 100 ppm This dose is based on active sequesterant/polymer content per

volume of waste water/substrate to be treated i.e. mg active antiscalent composition per litre of waste water. Generally though effective scale prevention/reduction may be achieved with much smaller doses, for instance 5 or 10 ppm, but may be as low as 2 or 3 ppm. We have found that scale/struvite can be effectively reduced or removed by an initial treatment of the antiscalent composition, for instance in the range 10 to 60 ppm, more preferably in the range 20 to 40 ppm. Following this initial treatment we have surprisingly found that sustained scale/struvite prevention can be achieved using reduced doses of the antiscalent composition, for instance between 5 or 10 ppm lower than the initial dose.

The following examples illustrate the invention.

#### Example 1

A plant trial was carried out at a waste water treatment plant which had been suffering from struvite deposition. The sewage treatment plant has a primary treatment stage which comprises a moving bed biofilm process biological reactors. In addition there is a pre-screening and pumping of the primary sewage. The secondary treatment stage includes intermediate contact/settlement and fine bubble aeration (conventional activated sludge). The primary sewage sludge and secondary activated sludge are anaerobically digested prior to centrifuge dewatering and pelletising in a drier. The plant was experiencing struvite build-up in the centrate discharge lines.

An antiscalent composition comprising A) 48% w/w sodium salt of a sodium polyacrylate of molecular weight 4,500 to 5,000 (measured by GPC) aqueous solution as a 40 weight % active polymer content and B) 52% sodium salt of diethylenetriaminpenta (methylenephosphonic acid) provided as a 45 to 49% post acidified aqueous solution.

The antiscalent composition is dosed at 30 mg/l (based on active antiscalent per litre of substrate) after the common sludge feed approximately 100 metres before

the centrifuge.

The treatment showed that struvite deposition was reduced from about 330 mg/m<sup>3</sup> to 160 mg/m<sup>3</sup> sludge flow.

### Example 2

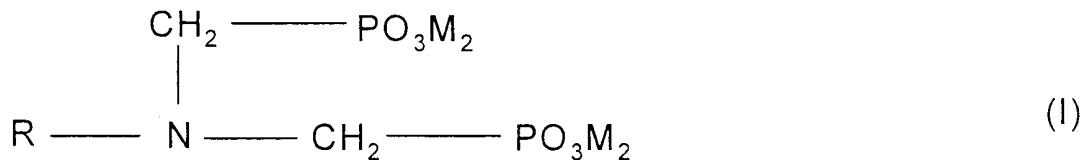
A plant trial was carried out at a waste water treatment plant which had been suffering from struvite deposition. The preliminary and primary treatment of the wastewater is treated in non-nitrifying activated sludge plant then in nitrifying trickling filters. The secondary activated sludge is co-settled in primary tanks then anaerobically digested and dewatered in a centrifuge.

A Bardenpho plant is installed to treat part of the flow with an anaerobic/aerobic sequence to facilitate phosphorus uptake and an anoxic/aerobic recycle sequence to remove ammonical nitrogen and prevent struvite precipitation. However, the plant does experience struvite precipitation in the digested sludge pipelines.

The antiscalent composition of Example 1 is dosed to the digested sludge pipelines at a dose of 50mg/l, with the result of preventing struvite precipitation.

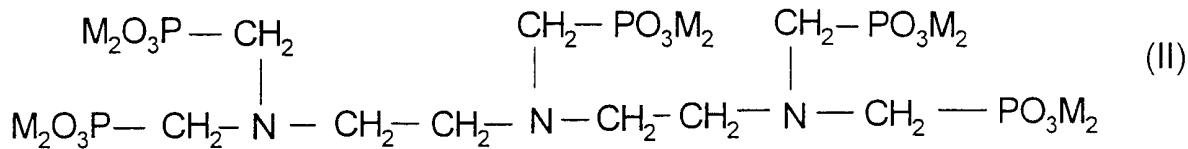
Claims

1. A method for reducing/preventing the formation of scale or removal of scale in a municipal or industrial waste water treatment facility comprising introducing an antiscalent composition which comprises:
  - A) A water soluble polymer of molecular weight below 20,000 and containing anionic groups, and
  - B) A sequesterant compound containing at least one phosphonate group and salts thereof,
 characterised in that component (A) is formed from a monomer or monomer blend consisting of one or more ethylenically unsaturated carboxylic acid monomer(s) and optionally an ethylenically unsaturated water-soluble nonionic monomer.
2. A method according to claim 1 in which the scale is struvite.
3. A method according to claim 1 or claim 2 in which the waste water treatment facility is a sewage treatment plant.
4. A method according to any one of claims 1 to 3 in which the antiscalent composition comprises 25 to 75% by weight of component A and 25 to 75% by weight of component B.
5. A method according to any one of claims 1 to 4 in which component A is a homopolymer of acrylic acid (or salt) or a copolymer of acrylic acid (or salt) with either maleic acid (or salt or anhydride) or itaconic acid (or salt or anhydride).
6. A method according to any one of claims 1 to 5 in which the polymer has a molecular weight in the range 1,500 to 10,000, preferably 2,000 to 5,000.
7. A method according to any one of claims 1 to 6 in which component (B) is a compound according to formula I



wherein M is hydrogen, alkali metal or ammonium and R is selected from the group consisting of -H, -CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub>, -N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub> and -(CH<sub>2</sub>)<sub>6</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub>.

8. A method according to any one of claims 1 to 7 in which component (B) is a compound according to formula II



wherein M is selected from H, alkali metal and ammonium.

9. A method according to any one of claims 1 to 8 in which the antiscalent composition does not contain a mineral acid, selected from hydrochloric acid or sulphuric acid.

10. A method according to any one of claims 1 to 9 in which the antiscalent composition consists essentially of component (A) and component (B).

11. Use of a composition comprising

A) A water soluble polymer of molecular weight below 20,000 and containing anionic groups, and

B) A sequesterant compound containing at least one phosphonate group and salts thereof,

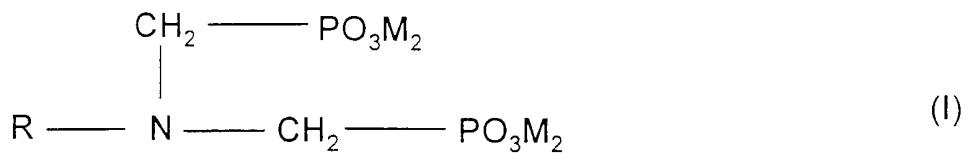
for the treatment of aqueous systems containing struvite, characterised in that component (A) is formed from a monomer or monomer blend consisting of one or more ethylenically unsaturated carboxylic acid monomer(s) and optionally an ethylenically unsaturated water-soluble nonionic monomer.

12. A use according to claim 11 in which the antiscalent composition comprises 25 to 75% by weight of component A and 25 to 75% by weight of component B.

13. A use according to claim 11 or claim 12 in which component A is a homopolymer of acrylic acid (or salt) or a copolymer of acrylic acid (or salt) with either maleic acid (or salt or anhydride) or itaconic acid (or salt or anhydride).

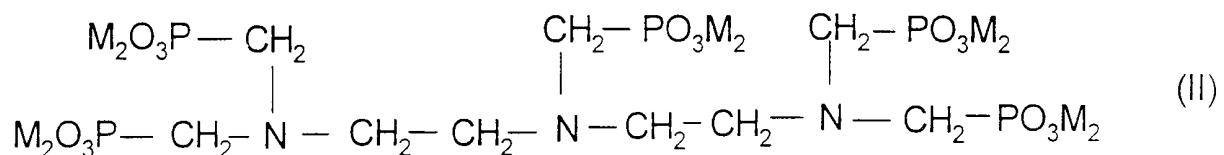
14. A use according to any one of claims 11 to 13 in which the polymer has a molecular weight in the range 1,500 to 10,000, preferably 2,000 to 5,000.

15. A use according to any one of claims 11 to 14 in which component B is a compound according to formula I



wherein M is hydrogen, alkali metal or ammonium and R is selected from the group consisting of -H, -CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub>, -N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub> and -(CH<sub>2</sub>)<sub>6</sub>N(CH<sub>2</sub>PO<sub>3</sub>M<sub>2</sub>)<sub>2</sub>.

15. A use according to any one of claims 11 to 14 in which component B is a compound according to formula II



wherein M is selected from H, alkali metal and ammonium.

16. A use according to any one of claims 11 to 15 in which the antiscalent composition does not contain a mineral acid, selected from hydrochloric acid or sulphuric acid.

17. A use according to any one of claims 11 to 16 in which the antiscalent composition consists essentially of component (A) and component (B).