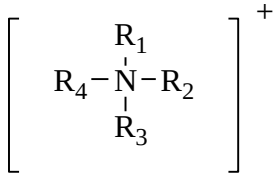
Claims

1. A method for the treatment of wastewater containing at least one organic ammonium ion and optionally impurities such as soluble silica,

which method comprises an electrodialysis of the optionally pretreated wastewater to obtain desalted water having a reduced content of organic ammonium ion and a concentrate containing an organic ammonium ion,

wherein the electrodialysis is carried out in at least one electrodialyser, the membrane stack of the electrodialyser has at least one membrane unit, and the membranes in at least a part of the membrane unit(s) comprise a styrene-type homogeneous cation exchange membrane~~,~~,

wherein the organic ammonium ion is ~~as~~ represented by formula I,



(formula I)

in formula I, R_1, R_2, R_3 and R_4 are independently selected from C_1-C_5 alkyl, and C_6-C_{12} aryl.

2. A method according to Claim 1, ~~wherein~~ one or more of the following features are fulfilled:

the method comprises a pretreatment step, in which the wastewater is subjected to a solid-liquid separation to obtain a solid phase and a liquid phase, and the said liquid phase is delivered to a wastewater treatment step for electrodialysis~~.~~,

~~3. A method according to Claim 2, wherein~~ the wastewater is contacted with at least one precipitant prior to the solid-liquid separation of the wastewater so that the silicon in the wastewater forms a colloid, wherein the precipitant is preferably selected from the group consisting of acid, divalent, trivalent and tetravalent metal salts, more preferably tetravalent metal salts, such as titanium tetrachloride and titanyl sulfate, ~~etc.~~

~~4. A method according to Claim 1, wherein~~ the membrane surface resistance of the styrene-type homogeneous cation exchange membrane is 1-15 Ω·cm2, preferably 3-12 Ω·cm2 and more preferably 4-9Ω·cm2~~.~~,

~~5. A method according to Claim 1, wherein~~ the ion exchange capacity of the styrene-type homogeneous cation exchange membrane is 1-5meq/g dry membrane, preferably 1.5-3meq/g dry membrane and more preferably 1.8-2.6meq/g dry membrane~~.~~,

~~6. A method according to any one of Claim 1 to Claim 5, wherein~~ the electrodialysis is a common electrodialysis performed in the following manner: the membranes in the membrane unit are an anion exchange membrane and a cation exchange membrane; the anion exchange membrane and the cation exchange membrane divide the internal space of the membrane unit into a feed liquid chamber and a concentration chamber; the wastewater enters the feed liquid chamber and water enters the concentration chamber; the said desalted water is obtained from the feed liquid chamber and a concentrate as the alkali liquor is obtained from the said concentration chamber during the electrodialysis~~.~~, or

~~7. A method according to any one of Claim 1 to Claim 5,~~ the electrodialysis is a bipolar membrane electrodialysis which is preferably carried out in one, two or three of the following methods:

Method I: the membrane stack of the bipolar membrane electrodialyser has at least one membrane unit; the membranes in the membrane unit are a bipolar

membrane and a cation exchange membrane; the said bipolar membrane and the cation exchange membrane divide the internal space of the membrane unit into an alkali chamber and a feed liquid chamber; the said wastewater or the said liquid phase enters the feed liquid chamber and water enters the said alkali chamber; an acid liquor is obtained from the feed liquid chamber and an alkali liquor containing an organic ammonium ion is obtained from the alkali chamber during the electrodialysis;

Method II: the membrane stack of the bipolar membrane electrodialyser has at least one membrane unit; the membranes in the membrane unit are a bipolar membrane and an anion exchange membrane; the said bipolar membrane and the anion exchange membrane divide the internal space of the membrane unit into an acid chamber and a feed liquid chamber; the said wastewater or the said liquid phase enters the feed liquid chamber and water enters the said acid chamber; an alkali liquor containing an organic ammonium ion is obtained from the feed liquid chamber and an acid is obtained from the acid chamber during the electrodialysis;

Method III: the membrane stack of the bipolar membrane electrodialyser has at least one membrane unit; the membranes in the membrane unit are a bipolar membrane, an anion exchange membrane and a cation exchange membrane; the said bipolar membrane, the anion exchange membrane and the cation exchange membrane divide the internal space of the membrane unit into an acid chamber, a feed liquid chamber and an alkali chamber; the feed liquid chamber is located between the acid chamber and the alkali chamber; the said wastewater or the said liquid phase enters the feed liquid chamber and water enters the said acid chamber and the alkali chamber respectively; desalted water is obtained from the feed liquid chamber, an acid liquor is obtained from the acid chamber and an alkali liquor containing an organic ammonium ion is obtained from the alkali chamber during the electrodialysis~~.~~,

~~8. A method according to any one of Claim 1 to Claim 7, wherein~~ the concentrate is subjected to a bipolar membrane electrodialysis to produce an

acid liquor, an alkali liquor containing an organic ammonium ion and a second desalted water.

~~9~~3. A method according to ~~any one of~~ Claim 1 ~~to~~or Claim ~~5~~2, wherein one or more of the following features are fulfilled:

the electrodialysis comprises a common electrodialysis and a bipolar membrane electrodialysis; the membranes in the membrane unit of the common electrodialysis are an anion exchange membrane and a cation exchange membrane; the said anion exchange membrane and the cation exchange membrane divide the internal space of the membrane unit into a feed liquid chamber and a concentration chamber;

the membranes in the membrane unit of the bipolar membrane electrodialysis are a bipolar membrane, an anion exchange membrane and a cation exchange membrane; the said bipolar membrane, the said anion exchange membrane and the said cation exchange membrane divide the internal space of the membrane unit into an acid chamber, a feed liquid chamber and an alkali chamber; the feed liquid chamber is located between the acid chamber and the alkali chamber;

the said wastewater is subjected to an electrodialysis in the common electrodialysis to produce a first desalted water and a concentrate having an increased content of organic ammonium ion; the said concentrate is subjected to a bipolar membrane electrodialysis in the bipolar membrane electrodialysis to produce an acid liquor, an alkali liquor and a second desalted water~~.~~,

~~10. A method according to any one of Claim 1 to Claim 9, wherein~~ the voltage applied to each membrane unit of the common electrodialysis during the electrodialysis is 0.1-5V, preferably 0.5-4V and more preferably 1-3V; and/or the voltage applied to each membrane unit of the bipolar membrane electrodialysis is 0.1-8V, preferably 1-6V and more preferably 2-5V~~.~~,

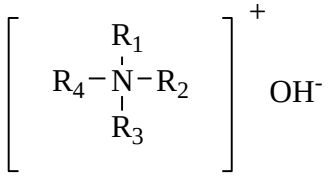
~~11. A method according to any one of Claim 1 to Claim 10, wherein~~ the conditions of the electrodialysis make the content of organic ammonium ion in the desalted water 2000mg/L or less, preferably 1000mg/L or less, and more preferably 500mg/L or less~~.~~.

~~12. A method according to any one of Claim 1 to Claim 11, wherein~~ the concentration of the organic ammonium ion in the wastewater is 1000-35000mg/L, preferably 2000-30000mg/L and more preferably 10000-30000mg/L~~.~~.

~~13. A method according to any one of Claim 1 to Claim 12, wherein~~ the said organic ammonium ion is tetrapropylammonium ion.

~~14~~4. A method according to any one of Claim 1 to Claim ~~13~~3, wherein the wastewater is the wastewater from the preparation of a molecular sieve using organic ammonium hydroxide, preferably a crystallization mother liquor from a crystallization step in the preparation of a molecular sieve using organic ammonium hydroxide, washing wastewater from the washing step in the preparation of a molecular sieve using organic ammonium hydroxide, or a mixture of the said crystallization mother liquor and the said washing wastewater, and the molecular sieve preferably is at least one selected from the group consisting of a titanium silicate molecular sieve, BETA molecular sieve, SSZ-13 molecular sieve and Silicate-1~~.~~.

~~15. A method according to Claim 14, wherein~~preferably the organic ammonium hydroxide is selected from the compound represented by formula II,



(formula II)

in formula II, R_1, R_2, R_3 and R_4 are independently selected from C_1-C_5 alkyl, and C_6-C_{12} aryl;

preferably, the said organic ammonium hydroxide is tetrapropylammonium hydroxide**.**

~~16~~5. A wastewater treatment system~~,~~ (I) or (II),

wherein the ~~said~~system (I) comprises the following features:

the wastewater is the wastewater containing an organic ammonium ion from the preparation of a molecular sieve–, the treatment system comprising a wastewater storage unit, an optional pretreatment unit, a common electrodialysis unit and a bipolar membrane electrodialysis unit as connected in series;

wherein

the wastewater storage unit is used for receiving and storing wastewater;

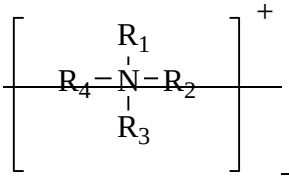
the optional pretreatment unit is used for contacting the wastewater from the wastewater storage unit with at least one precipitant so that after silicon in the wastewater forms a colloid, a solid-liquid separation is carried out to obtain a liquid phase and a solid phase;

the common electrodialysis unit is used for carrying out a common electrodialysis on the wastewater or the said liquid phase to obtain a first desalted water having a reduced content of organic ammonium ion and a concentrate containing an organic ammonium ion;

the bipolar membrane electrodialysis unit is used for carrying out a bipolar

membrane electrodialysis on the concentrate discharged from the common electrodialysis unit to obtain an acid liquor, an alkali liquor containing an organic ammonium ion and an optional second desalted water,

wherein the organic ammonium ion is as ~~represented by formula I,~~defined in claim 1, and the membranes in at least a part of the membrane unit(s) comprise a styrene-type homogeneous cation exchange membrane;



~~(formula I)~~

~~in formula I, R_1, R_2, R_3 and R_4 are independently selected from C_1-C_5 alkyl, and C_6 C_{12} aryl.~~

~~17. The system according to Claim 16, wherein the common electrodialysis unit comprises at least one common electrodialyser wherein the membrane stack of the said common electrodialyser has at least one membrane unit, the membranes in at least a part of the membrane unit are a cation exchange membrane and an anion exchange membrane, and the said cation exchange membrane and the said anion exchange membrane divide the internal space of the membrane unit into a feed liquid chamber and a concentration chamber.~~

~~18. The system according to Claim 16 or Claim 17, wherein the bipolar membrane electrodialysis unit comprises at least one bipolar membrane electrodialyser, the membrane unit of which adopts one, two or three of the following methods:~~

~~Method 1: the membranes in the membrane unit are a bipolar membrane and a cation exchange membrane, and the said bipolar membrane and the said cation exchange membrane divide the internal space of the membrane unit into an alkali chamber and a feed liquid chamber;~~

~~Method 2: the membranes in the membrane unit are a bipolar membrane and an anion exchange membrane, and the said bipolar membrane and the said anion exchange membrane divide the internal space of the membrane unit into an acid chamber and a feed liquid chamber;~~

~~Method 3: the membranes in the membrane unit are a bipolar membrane, an anion exchange membrane and a cation exchange membrane, and the said bipolar membrane, the said anion exchange membrane and the said cation exchange membrane divide the internal space of the membrane unit into an acid chamber, a feed liquid chamber and an alkali chamber, wherein the feed liquid chamber is located between the said acid chamber and the said alkali chamber.~~

~~19. The system according to any one of Claim 16 to Claim 18, wherein the system further comprises a first cycle unit and/or a second cycle unit;~~

~~wherein~~

~~the said first cycle unit is used for delivering an acid liquor discharged from the bipolar membrane electrodialysis unit into the pretreatment unit at least in part as a precipitate;~~

~~the said second cycle unit is used for delivering the first desalted water and/or the second desalted water into the common electrodialysis unit and/or the bipolar membrane electrodialysis unit as water for the common electrodialysis and/or the bipolar membrane electrodialysis.~~

~~20. A wastewater treatment system, wherein~~

wherein the system (II) comprises the following features:

the wastewater is the wastewater containing an organic ammonium ion from the preparation of a molecular sieve, the treatment system comprising a desalination tank, an intermediate salt tank, a common electrodialyser, a

bipolar membrane electrodialyser, an alkali liquor tank, an acid liquor tank and an optional desalted water tank;

wherein

the membranes in the membrane unit of the common electrodialyser are a cation exchange membrane and an anion exchange membrane which divide the internal space of the membrane unit into a feed liquid chamber and a concentration chamber; the membranes in the membrane unit of the bipolar membrane electrodialyser are a bipolar membrane, a cation exchange membrane and an anion exchange membrane which divide the internal space of the membrane unit into a feed liquid chamber, an acid chamber and an alkali chamber, wherein the liquid chamber is located between the said acid chamber and the said alkali chamber;

the desalination tank which is used for receiving wastewater is communicated with the feed liquid chamber of the common electrodialyser in the common electrodialysis unit and provides feed water to the feed liquid chamber and optionally receives an effluent from the feed liquid chamber;

the intermediate salt tank which is communicated with the concentration chamber of the electrodialyser provides feed water to the concentration chamber and receives an effluent from the concentration chamber, and the feed liquid chamber of the bipolar membrane electrodialyser is communicated with the intermediate salt tank to receive a concentrate discharged from the intermediate salt tank as feed water;

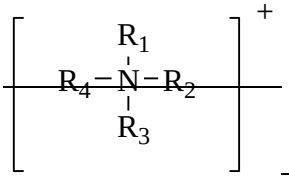
the said alkali liquor tank is communicated with the alkali chamber of the bipolar membrane electrodialyser for receiving an alkali liquor discharged from the alkali chamber of the bipolar membrane electrodialyser and provides feed water to the alkali chamber of the bipolar membrane electrodialyser;

the said acid liquor tank is communicated with the acid chamber of the

bipolar membrane electrodialyser for receiving an acid liquor discharged from the acid chamber of the bipolar membrane electrodialyser, and provides feed water to the acid chamber of the bipolar membrane electrodialyser;

the desalted water tank is communicated with the alkali liquor tank and the acid liquor tank and with the desalination tank or with the feed liquid chamber of the electrodialyser for receiving the first desalted water discharged from the desalination tank or for receiving the first desalted water discharged from the feed liquid chamber of the electrodialyser, while providing feed water to the said alkali liquor tank and the said acid liquor tank,

wherein the organic ammonium ion is as ~~represented by formula I,~~defined in claim 1, and



~~(formula I)~~

~~in formula I, R_1, R_2, R_3 and R_4 are independently selected from C_1-C_5 alkyl, and C_6 C_{12} aryl, and~~

the cation exchange membrane is a styrene-type homogeneous cation exchange membrane.

~~21~~6. The system according to Claim ~~20~~5, wherein one or more of the following features are fulfilled for the system (I):

the common electrodialysis unit comprises at least one common electrodialyser wherein the membrane stack of the said common electrodialyser has at least one membrane unit, the membranes in at least a part of the membrane unit are a cation exchange membrane and an anion

exchange membrane, and the said cation exchange membrane and the said anion exchange membrane divide the internal space of the membrane unit into a feed liquid chamber and a concentration chamber,

the bipolar membrane electrodialysis unit comprises at least one bipolar membrane electrodialyser, the membrane unit of which adopts one, two or three of the following methods：

Method 1: the membranes in the membrane unit are a bipolar membrane and a cation exchange membrane, and the said bipolar membrane and the said cation exchange membrane divide the internal space of the membrane unit into an alkali chamber and a feed liquid chamber;

Method 2: the membranes in the membrane unit are a bipolar membrane and an anion exchange membrane, and the said bipolar membrane and the said anion exchange membrane divide the internal space of the membrane unit into an acid chamber and a feed liquid chamber;

Method 3: the membranes in the membrane unit are a bipolar membrane, an anion exchange membrane and a cation exchange membrane, and the said bipolar membrane, the said anion exchange membrane and the said cation exchange membrane divide the internal space of the membrane unit into an acid chamber, a feed liquid chamber and an alkali chamber, wherein the feed liquid chamber is located between the said acid chamber and the said alkali chamber,

the system further comprises a first cycle unit and/or a second cycle unit;

wherein

the said first cycle unit is used for delivering an acid liquor discharged from the bipolar membrane electrodialysis unit into the pretreatment unit at least in

part as a precipitant;

the said second cycle unit is used for delivering the first desalted water and/or the second desalted water into the common electrodialysis unit and/or the bipolar membrane electrodialysis unit as water for the common electrodialysis and/or the bipolar membrane electrodialysis.

7. The system according to Claim 5, wherein the system (II) further comprises a pretreatment unit which is located upstream of the desalination tank for contacting the wastewater with at least one precipitant so that a solid-liquid separation can be carried out after silicon in the wastewater forms a colloid, and the liquid phase produced from the solid-liquid separation is delivered to the desalination tank.

228. The system according to Claim 205 or Claim 216, wherein the system (II) further comprises an organic ammonium hydroxide recovery tank and an acid recovery tank;

wherein

the said organic ammonium hydroxide recovery tank is used for receiving the alkali liquor discharged from the alkali liquor tank;

the said acid recovery tank is for receiving the acid liquor discharged from the acid liquor tank.;

23. The system according to any one of Claim 20 to Claim 22,preferably wherein the said acid recovery tank is communicated with the pretreatment unit for delivering at least a part of the acid liquor into the pretreatment unit as a precipitant;

the said organic ammonium hydroxide recovery tank is communicated with the synthesis unit for delivering the alkali liquor containing organic

ammonium hydroxide into the synthesis unit;

the said desalted water tank is communicated with one, two or three of the following units: the said synthesis unit for providing water for synthesis to the synthesis unit; the said crystallization unit for providing water for termination of the crystallization to the crystallization unit; the said separation and washing unit for providing washing water to the separation and washing unit, wherein the said synthesis unit, crystallization unit and separation and washing unit refer to the units comprised in the preparation of the molecular sieve.

~~24~~9. The system according to Claim ~~20~~5, wherein the membrane surface resistance of the styrene-type homogeneous cation exchange membrane is 1-15 $\Omega \cdot cm^2$, preferably 3-12 $\Omega \cdot cm^2$ and more preferably 4-9$\Omega \cdot cm^2$; and/or the ion exchange capacity of the styrene-type homogeneous cation exchange membrane is 1-5meq/g dry membrane, preferably 1.5-3meq/g dry membrane, and more preferably 1.8-2.6meq/g dry membrane.

~~25~~10. A method for the preparation of a molecular sieve, comprising a synthetic step, a crystallization step, a separation and washing step and a wastewater treatment step;

wherein

in the synthetic step, a raw material is contacted with water for reaction, wherein the raw material contains a silicon source, an organic ammonium hydroxide and an optional titanium source;

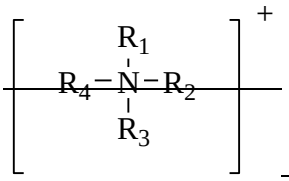
in the crystallization step, the reaction mixture obtained from the synthesis step is crystallized;

in the separation and washing step, the mixture obtained from the crystallization step is brought to a solid-liquid separation to produce a solid

phase and a crystallization mother liquor, and the said solid phase is washed to obtain a molecular sieve and washing wastewater;

in the wastewater treatment process, an alkali liquor containing an organic ammonium ion and desalted water having a reduced content of organic ammonium ion are produced from an electrodialysis of the wastewater, and the said wastewater is the said crystallization mother liquor, the said washing wastewater or a mixture of the crystallization mother liquor and the washing wastewater wherein the wastewater is treated using the method according to any one of Claim 1 to Claim ~~15~~4,

wherein the organic ammonium ion is as ~~represented by formula I,~~



~~(formula I)~~

defined in ~~formula I, R_1, R_2, R_3 and R_4 are independently selected from C_1-C_5 alkyl, and C_6 C_{12} aryl~~claim 1.

~~26~~11. The method according to Claim ~~25~~10, wherein the method further comprises one, two or three of the first cyclic step, the second cyclic step and the third cyclic step;

wherein

in the first cyclic step, the desalted water is recycled in one of the following steps: as water for synthesis in the synthesis step; for termination of the crystallization in the crystallization step; as the washing water in the separation and washing step;

in the second cyclic step, the alkali liquor obtained from electrodialysis is

recycled in the synthesis step;

in the third cyclic step, the acid liquor obtained in the presence of a bipolar membrane electrodialysis is recycled in the pretreatment step at least in part as a precipitant.

~~27~~12. A molecular sieve preparation system which comprises a synthesis unit, a crystallization unit, a separation and washing unit and a wastewater treatment unit;

wherein

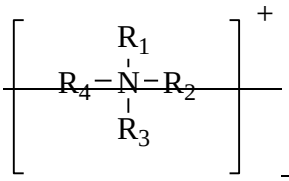
the synthetic unit is used for contacting an raw material with water for reaction, and the said raw material contains a silicon source, an organic ammonium hydroxide and an optional titanium source;

the crystallizing unit is used for crystallizing the reaction mixture obtained from the synthesis step;

the separation and washing unit is used for a solid-liquid separation of the mixture obtained from the crystallization step to produce a solid phase and a crystallization mother liquor, and the solid phase is washed to obtain a molecular sieve and washing wastewater;

the wastewater treatment unit is used for an electrodialysis of the wastewater to produce an alkali liquor containing an organic ammonium ion and desalted water having a reduced content of organic ammonium ion, wherein the said wastewater is the crystallization mother liquor, the washing wastewater or a mixture of the crystallization mother liquor and the washing wastewater, wherein the said electrodialysis is carried out in at least one electrodialyser, the membrane stack of the electrodialyser has at least one membrane unit, and the membranes in at least a part of the membrane unit comprise a styrene-type homogeneous cation exchange membrane,

wherein the organic ammonium ion is as ~~represented by formula I,~~defined in claim 1.



~~(formula I)~~

~~in formula I, R_1, R_2, R_3 and R_4 are independently selected from C_1-C_5 alkyl, and C_6-C_{12} aryl.~~

~~28~~13. The system according to claim ~~27~~12, wherein the electrodialyser is at least one common electrodialyser; the membranes in the membrane unit of the said common electrodialyser are combined in the following manner: the membranes in the membrane unit are an anion exchange membrane and a cation exchange membrane; the anion exchange membrane and the cation exchange membrane divide the internal space of the membrane unit into a feed liquid chamber and a concentration chamber; the feed liquid chamber receives the wastewater~~.~~,

~~29. The system according to claim 27,~~or wherein the electrodialyser is at least one bipolar membrane electrodialyser; the membrane unit of the said bipolar membraneelectrodialyser adopts one, two or three of the following methods:

Method 1: the membranes in the membrane unit are a bipolar membrane and a cation exchange membrane, and the bipolar membrane and the cation exchange membrane divide the internal space of the membrane unit into an alkali chamber and a feed liquid chamber;

Method 2: the membranes in the membrane unit are a bipolar membrane and an anion exchange membrane, and the bipolar membrane and the anion exchange membrane divide the internal space of the membrane unit into an

acid chamber and a feed liquid chamber;

Method 3: the membranes in the membrane unit are a bipolar membrane, an anion exchange membrane and a cation exchange membrane, and the said bipolar membrane, the said anion exchange membrane and the said cation exchange membrane divide the internal space of the membrane unit into an acid chamber, a feed liquid chamber and an alkali chamber, wherein the feed liquid chamber is located between the acid chamber and the alkali chamber~~.~~,

~~30. The system according to Claim 27,~~or wherein the wastewater treatment unit comprises at least one common electrodialyser and at least one bipolar membrane electrodialyser;

the membranes in the membrane unit of said common electrodialyser are an anion exchange membrane and a cation exchange membrane, and the anion exchange membrane and the cation exchange membrane divide the internal space of the membrane unit into a feed liquid chamber and a concentration chamber;

the membranes in the membrane unit of the bipolar membrane electrodialyser are a bipolar membrane, an anion exchange membrane and a cation exchange membrane, and the said bipolar membrane, the said anion exchange membrane and the said cation exchange membrane divide the internal space of the membrane unit into an acid chamber, a feed liquid chamber and an alkali chamber, wherein the feed liquid chamber is located between the acid chamber and the alkali chamber;

the common electrodialyser is used for carrying out an electrodialysis on the wastewater to produce a first desalted water and a concentrate having an increased content of organic ammonium ion, and the said bipolar membrane electrodialyser is used for carrying out a bipolar membrane electrodialysis on the concentrate to produce an acid liquor, an alkali liquor containing an organic ammonium ion and a second desalted water.

~~31~~14. The system according to any one of Claim ~~27 to Claim 30~~12 or 13, wherein the system further comprises a pretreatment unit for contacting the wastewater with at least one precipitant so that at least a part of silicon in the wastewater form a colloid, and a solid-liquid separation is carried out to produce a silicon-containing solid phase and a liquid phase, and the said liquid phase is delivered into the wastewater treatment unit for electrodialysis.

~~32~~15. The system according to any one of Claim ~~27~~12 to Claim ~~31~~14, wherein the wastewater treatment unit further comprises one, two of three selected from a delivery pipeline for desalted water, a delivery pipeline for recovering organic ammonium hydroxide and a delivery pipeline for recovering an acid liquor;

wherein

the said delivery pipeline for desalted water is used for delivering the desalted water recovered by the wastewater treatment unit into one of the following units: the said synthesis unit as water for synthesis; the said crystallization unit as water for termination of the crystallization; the said separation and washing unit as washing water;

the said delivery pipeline used for recovering organic ammonium hydroxide is used for delivering the alkali liquor containing organic ammonium hydroxide obtained from the bipolar membrane electrodialyser in the wastewater treatment unit into the synthesis unit;

the said delivery pipeline for recovering acid is used for delivering the acid liquor obtained from the bipolar membrane electrodialyser in the wastewater treatment unit into the said pretreatment unit at least in part as a ~~precipitate.~~

precipitant.