

**A method for recovering potassium iodide
and boric acid by concentrating iodine waste water
produced by polyvinyl alcohol dyeing**

TECHNICAL FIELD

5 [0001] The present invention relates to processes for the recovery of waste water in the electronics industry and, more particularly, to methods for recovering potassium iodide and boric acid from iodine and boric acid-containing waste waters produced by a related art such as polyvinyl alcohol (PVA) dyeing processes.

BACKGROUND OF INVENTION

10 [0002] The mass production methods of polarizing film mainly can be classified to either extension method or coating method, whereby the extension method is the dominant method in the current market. The mainstream extension methods can be further classified into two sub-categories of dry method and wet method according to the PVA film extension process, or into two sub-categories of iodine staining and
15 dye dyeing according to the PVA film staining process. Iodine staining refers to the process of using iodine and potassium iodide, boric acid as a dichroic medium to produce polarized polarization properties of PVA film in the polarizing film dyeing and stretching process, while dye dyeing method refers to the process comprising the steps of dyeing PVA film as the first step and then followed by stretching, fixing,
20 laminating and drying the PVA film with the aid of an solution environment. Dyeing method has the advantage of that it is easy to obtain a polarization characteristic having a high degree of polarization of 99.9% or more and a high transmittance of 42% or more.

[0003] The general process of dye dyeing is the following. Firstly, to mix the iodine, potassium iodide, boric acid and some other chemicals according to the targeted ratio in the deployment tank, to stir the mixture so that all the chemicals are dissolved completely uniformly and to fine tune the concentration of solutions to meet the predetermined mixture ratio range. Secondly, to use the prepared mixed solution to dye the swelled raw PVA film so that the iodine molecule absorbs the visible light at the specific wavelength and the iodine molecule is assembled in the long chain of PVA to produce the dichroism. Thirdly, to add the boric acid so as to form bonds with PVA and to fix the iodine molecules in the PVA long chains. Finally, to wash away the residual dyeing solution by rinsing the surfaces of PVA films with hot pure water. In the aforementioned processes, the waste water containing iodine and boron during the PVA film dyeing division is thus produced. However, based on to the mainstream wastewater discharge standards adopted in multiple nations including developed and developing countries, the boron content in the discharged waste water should be less than 10 ppm while the iodine content in the discharged waste water should be less than 0 ppm.

[0004] Industrially, recycling treatment approaches of iodine from the iodine-containing solution includes ion exchange method, air blowing method, activated carbon method, precipitation method (eg. silver method and copper method), starch method and organic solvent extraction method. Recovery principles of iodine in these methods are different due to the discrepancy in the source of iodine-containing waste water, the content of iodine in waste water and the form of iodine in the waste water. The recovery methods of iodine are described as the following according to the forms of iodine when separated from the waste water:

[0005] (1) Iodine adsorption method: activated carbon and molecular sieve are widely used as the adsorption medium, although their principles of adsorption are similar: I_2 is absorbed on the surface of the adsorption medium and being enriched

therein; when the enrichment reaches a certain threshold value, I_2 on the adsorption medium is then desorbed into an solution by contacting one or more desorption agents; and the resulted iodine containing solution is then recovered by elution. However, this method is not widely used due to the difficulty in elution of I_2 from the iodine containing solution;

[0006] (2) Iodine extraction method: the commonly used extraction agent of iodine is CCl_4 as iodine can be dissolved in it. The I^- (or IO_3^-) in the iodine solution needs to be oxidized (or reduced) into I_2 before the extraction. The iodine is then distributed physically between the water solution and the CCl_4 in the form of I_2 molecules without chemical reaction. After extraction, the iodine in the extract phase is then recovered by distillation or back extraction process. However, the application of this method is not very extensive as the introduction of CCl_4 is costly and the purify of CCl_4 is also difficult.

[0007] (3) Insoluble iodate precipitation method: it mainly separates iodine from the waste water in the form of insoluble iodate precipitation. The principle is to enrich iodine in the form of I^- by reduction, concentration and other pretreatments, then generated CuI or AgI precipitates by adding copper or silver salts, and finally oxidize the CuI or AgI precipitates with a certain oxidation agents to obtain iodine. However, the drawback of this method is the introduction of copper salt or silver salt which increases the cost.

[0008] (4) Iodine precipitation method: according to the contents of iodine in the waste water, the iodine precipitation method can be divided into two classes, namely, direct precipitation method and reduction precipitation method. For high concentrations of iodine in the iodine-containing waste water, a direct precipitation method normally applies, which is to convert the I^- (or IO_3^-) into I_2 through a certain appropriate treatment process so that I_2 would be crystallized due to the limitation of solubility of iodine in the solution. The reduction precipitation method applies if

iodine concentration in the waste water is low, for instance only a small amount free state form of I_2 is presented. In such a case, an initial enrichment is usually needed. In order to avoid the sublimation loss of I_2 at high temperature, I_2 can be reduced to I^- before concentration. When the concentration is completed, the precipitates of solid iodine from the solution can be obtained by acidification and oxidation. However, this method focuses on the recovery of iodine resources, and generally no boron resources are recycled.

[0009] Industrial treatment of boron-containing wastewater generally includes the following three solutions: (1) for high concentration of boron in the boron-containing waste, typically in the concentration range of hundreds ppm to several thousand ppm, the treatment of adding flocculant (coagulant) is generally used, (2) for low concentration of boron in the boron-containing waste water, typically in the concentration ranges of tens of ppm or less, the ion exchange resin treatment is generally adopted; (3) for medium concentration of boron in the boron-containing waste water, typically dozens of ppm to hundreds of ppm, the treatment usually comprises both the conventional flocculation and the ion exchange resin treatment. However, the recovery efficiency of all resources in the boron-containing waste water is normally not acceptable for the aforementioned methods. For the high boron concentration of boron-containing waste water, an evaporation method also applies, however such a process requires considerable heating energy which increase the operation cost, and moreover the boron residues are present in the evaporation condensate which calls for further processing.

[0010] If the boron and iodine resources can be efficiently recovered from the waste water and then recycled to reuse as raw materials for production, industrial waste can be reduced and the cost of raw materials can also be reduced. In the prior art, JP2001-314864 discloses a method for treating a polarizing plate manufacturing waste water by subjecting the waste water discharged from the polarizing plate

manufacturing process to an electrodialysis process, the waste water is then divided into a desalting solution mainly containing an organic substance component and a desalting solution mainly containing an inorganic component. CN101353804B discloses a method and a system for recycling waste water from a manufacturing process of an iodine-based polarizing film or the like, such method also separates potassium iodide and boric acid as an iodine resource and a boron resource for raw material by processing the solution with an electrodialysis treatment.

[0011] However, the above-described prior art documents have not extensively studied the efficient recycling techniques of iodine and boron in the waste water, not even the detailed conditions for recycling. In order to further reduce both the raw material cost for production and waste treatment cost after production for the PVA dyeing and other related processes, there is a demand for recovering the iodine and boric acid waste water as the society keeps pursuing the construction of environment-friendly manufacturing systems through the reduction of industrial waste. Significantly, the recovery methods for potassium iodide and boric acid are of great practical importance for the development of sustainable green industrial production.

DISCLOSURE OF THE INVENTION

[0012] The present invention provides a method for concentrating and recovering potassium iodide and boric acid from an iodine-containing waste water produced during PVA dyeing to overcome at least the above-mentioned problems existing in the prior art. The method for recycling the iodine and boric acid containing waste water from the electronics industry comprises a series of steps of pH adjustment, reduction, membrane module treatment, evaporation, condensation, crystallization, cooling, recrystallization, resin based adsorption, elution and water reuse.

[0013] Through the desalination, evaporation and condensation, both the

potassium iodide resources and boric acid resources in the waste water can be recovered. The disclosed method is easy to operate and friendly to environment and yet at the same time is a waste resource recovering treatment process with a high degree of resource utilization.

5 [0014] In order to achieve the above-mentioned objects, the technical solution disclosed in the present invention comprises the following aspects. It will be apparent to those skilled in the art that the present invention may be practiced without departing from the scope of the present invention to form numerous deductions or substitutions, which should be considered as falling within the scope
10 of the present invention.

[0015] According to the first aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing, comprising the following steps of:

15 [0016] (1) adjusting pH value of the iodine-containing waste water to be within a range of 3 to 12 with potassium hydroxide to obtain a solution A; In one embodiment of the step described above, the potassium hydroxide is preferably an analytically pure potassium hydroxide solid.

[0017] (2) adding a reducing agent to the solution A obtained in step (1) to reduce I_2 into I^- , stirring the solution A until I_2 is completely reduced to I^- so as to obtain a
20 solution B; In one embodiment of the step described above, the said stirring procedure is conducted for a sufficient duration for complete reduction, preferably 1 to 3 hours.

[0018] (3) separating the solution B obtained in step (2) into a concentrated water C having a concentration of potassium iodide more than 0.1%, preferably 0.1% to
25 10%, and a fresh water D having a concentration of potassium iodide of 0% to 0.01% by a membrane module;

[0019] (4) concentrating the concentrated water C obtained in step (3) by an evaporator to obtain a concentrated solution E having a specific gravity of 1.1 to 1.6 and a condensate water collected from the evaporator is reused, wherein the condensate water is, preferably mixed with raw water, used for production so as to save raw water consumption; In one embodiment, the evaporation is evaporated preferably at a temperature range of 60°C to 100°C.

[0020] (5) analyzing concentration of potassium borate in the concentrated solution E obtained in step (4) and selecting one of the following operating steps according to the obtained concentration of potassium borate:

10 [0021] (A) if the concentration of potassium borate is lower than a threshold concentration, centrifuging the concentrated solution E from step (4) at a temperature of 40°C to 60°C to obtain potassium iodide product and returning residue to mix with the concentrated water C in step (4);

15 [0022] (B) if the concentration of potassium borate is equal to the threshold concentration, centrifuging the concentrate solution E obtained from step (4) at a temperature of 25°C to 35°C to obtain potassium iodide product and a residue solution F, cooling the residue solution F to a temperature of 10°C to 25°C and adding hydrogen iodide acid to adjust the pH value to be within a range of 1 to 4 and centrifuging the residue solution F to obtain boric acid product, and returning
20 residue to mix with the concentrated water C in step (4);

[0023] (C) if the potassium borate content is higher than the threshold concentration, adding water to the concentrate solution E until the concentration of potassium borate equals to the threshold concentration and returning to step (B).

[0024] (6) contacting the fresh water D obtained from step (3) to an ion exchange resin to obtain a resin enriched in potassium iodide and potassium borate, returning
25 the residual directly or mixed with raw water to production so as to save raw water

consumption;

[0025] (7) eluting the enriched resin obtained in step (6) to obtain an eluate G containing both potassium iodide and potassium borate in a concentration range of 1% to 5% and recycling the eluted resin;

5 [0026] (8) returning the eluent G obtained in step (7) to step (4) to be mixed with the concentrated water C for preparation of the concentrated solution E.

[0027] According to the second aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein the said threshold
10 concentration of potassium borate in the concentrated solution E in step (5) is preferably 80 g/L to 160 g/L, more preferably 100 g/L to 140 g/L, and still more preferably 120 g/L.

[0028] According to the third aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water
15 produced by PVA dyeing as described above, wherein in step (1), the final acidity the potassium hydroxide adjusted solution is with a pH value in a range preferably from 6 to 11.

[0029] In one embodiment, when the pH value of the waste solution is adjusted to within the range from 6 to 11 by using the pure potassium hydroxide solid, the
20 consumption of reducing agent in step (2) can be lowered and the reduction efficiency can be significantly improved.

[0030] In practice, the effective utilization rate of the reducing agent can reach to 95% while no additional impurities are introduced to the resolution with the residue of the unconsumed reducing agent.

25 [0031] According to the fourth aspect, the present invention provides a method for

recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein the reducing agent in step (2) is an organic reducing agent or an inorganic reducing agent.

[0032] When an inorganic reducing agent is used, the reducing agent is at least one selected from the groups of formic acid, potassium borohydride, hydrogen gas and potassium sulfite.

[0033] Preferably, when a composite consisting of plural components of formic acid, potassium borohydride, hydrogen gas and potassium sulfite is used as a reducing agent, the effective utilization rate of the reducing agent can reach up to 99% or more, while no additional impurities are introduced to the resolution with the residue of the unconsumed reducing agent.

[0034] According to the fifth aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein the membrane module in step (3) is a permeable membrane module or a membrane separation module suitable for waste water treatment known in the prior art.

[0035] The membrane module, preferably, includes but is not limited to, at least one or more functional units, including such as a coarse filter, a reverse osmosis, a nanofiltration, an ultrafiltration, an ion-exchange membrane and the like.

[0036] According to the sixth aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein the preferred operation conditions of the evaporator in step (4) includes a reduced pressure at a degree of vacuum at a range of 0.01 MPa to 0.09 MPa or at an atmospheric pressure.

[0037] In one embodiment, the evaporator apparatus is selected from, but not

limited to, one or more of mechanical vapor recompression (MVR), single-effect equipment or multiple effect equipment.

[0038] In one embodiment, the material for the equipment apparatus contains at least one or more selected from the groups of enamel, stainless steel and titanium
5 alloyed composite materials.

[0039] According to the seventh aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein the potassium iodide product is obtained from centrifugal separation when concentration of potassium
10 borate in the concentrated solution E of in step (5)(A) is lower than the threshold concentration. A threshold concentration is preferably lower than the saturation concentration. The threshold concentration is 80 g/L to 160 g/L, more preferably 100 g/L to 140 g/L, still more preferably, 120 g/L.

[0040] In one embodiment, potassium borate merely present in the concentrated
15 solution E and the potassium borate crystals are not precipitated during the centrifugal separation of the potassium iodide product, and the potassium iodide product obtained from centrifugal separation is thus without the precipitation of potassium borate crystal, which ensures the purity of the potassium iodide crystals and the purity of potassium iodide crystals can reach to 99% or more.

[0041] According to the eighth aspect, the present invention provides a method for
20 recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein centrifuging the concentrated solution E in step (5)(B) is conducted in a condition that the potassium iodide is crystallized at a characteristic temperature where the solubility of potassium iodide
25 in solution does not change with the temperature as the potassium iodide crystallization is an evaporation crystallization process, while the potassium borate

is crystallized when the potassium borate concentration is lower than the threshold concentration as the potassium borate crystallization is an cooling crystallization process.

[0042] In one embodiment, the characteristic temperature is 20°C to 40°C, more preferably 25 °C to 35 °C, and even more preferably 30°C. In one embodiment, centrifuging the concentrated solution E is conducted at a temperature of 25°C to 35°C to separate the potassium iodide product from the residual solution F.

[0043] In another embodiment, potassium borate is separated from the system as boric acid by controlling the temperature and acidity of the solution with the continuous enrichment of potassium borate.

[0044] In yet another embodiment, the potassium borate content in the solution is equal to the threshold concentration, wherein the threshold concentration is 80 g/L to 160 g/L, preferably, 100 g/L to 140 g / L, and more preferably, 120 g/L.

[0045] In yet another embodiment, the residual solution F is controlled within the characteristic temperature range, preferably 10°C to 25°C, and more preferably, 20 °C. When the solution temperature is lowered from 30 °C to 20 °C, the solubility of potassium iodide in such temperature range is constant so that potassium iodide is not crystallized. When the acidity of the solution is within the characteristic acidity range by adjusting through the addition of hydroiodic acid or other suitable acid sources, whereby the preferred characteristic acidity range is pH value of 1 to 4, more preferably, pH value of 1 to 2, the boric acid is saturated and precipitated to generate a pure boric acid product.

[0046] In yet another embodiment, the boric acid product can be obtained in a purity of 99%, and the residue can be returned to the step (4) to be mixed with the concentrated water C to evaporate and concentrate to prepare the concentrated solution E in the subsequent evaporation step.

[0047] According to the ninth aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein centrifuging the concentrated solution E in step (5)(C) is conducted when potassium borate concentration, which is higher than the threshold concentration, is diluted to the threshold concentration by adding pure water.

[0048] In one embodiment, both the recovery ratio of the iodine resource and the boron resource in the waste water can reach up to 98% or above.

[0049] According to the tenth aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein in step (6), the ion exchange resin comprises at least one of an anion exchange resin and a cation exchange resin.

[0050] In one embodiment, the ion exchange resin comprises at least one anion exchange resin and at least one cation exchange resin. The anions are absorbed by the anion exchange resin while the cations are absorbed by the cation exchange resin.

[0051] In yet another embodiment, both the iodine and boron resources in the waste water can reach a recovery efficiency of 99% or more by setting optimized combinations in quantity and quality of the anion and cation exchange resins in the ion exchange resin.

[0052] According to the eleventh aspect, the present invention provides a method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing as described above, wherein the eluent G in step (7) is obtained from eluting the ion exchange resin comprises eluting the cation exchange resin with an acid such as hydroiodic acid and eluting the anion exchange

resin with a base such as potassium hydroxide to obtain an eluent with a concentration of 1% to 5% potassium iodide and potassium borate.

[0053] In one embodiment, the components of said eluent G are the same as the concentrated water C obtained in the step (3), and can be returned to recover the both products of potassium iodide and boric acid in the subsequent steps.

[0054] In another embodiment, the concentration of hydroiodic acid is 5-50% and the concentration of the potassium hydroxide is 3-60%.

[0055] In yet another embodiment, the recovery efficiency for both the iodine resource and the boron resource in such waste water can reach to 99% by an optimized combination of elution steps.

[0056] The technical advantage of the present disclosed invention includes simple technological processes, zero waste generation, zero waste discharge, full recovery of both potassium iodide and boric acid products and at the same time recovery of the water resource in the waste water, which lead to a significant economic benefit.

BRIEF DESCRIPTION OF THE DRAWINGS

[0057] The invention will now be described in further detail with reference to the accompanying drawing, in which Fig. 1 is a schematic process flow diagram of a method for treating concentrated potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing according to the present invention.

EMBODIMENTS

[0058] For ordinary person skilled in the art, without departing from the inventive concept of the premise, one can also make a number of simple deductions or replacement to carry out the invention which should be considered as belonging to

the scope of the present invention.

Embodiment 1

[0059] A 1000 ml waste water solution that contains both iodine and boron from a
5 PVA production line from an electrolytic plant was selected.

[0060] Added 2g analytically pure solid potassium hydroxide to the solution and
adjust the pH to 10, and obtained the solution A. In the solution A, added potassium
borohydride and stirred for 2 hours until the I_2 content was measured to be zero and
obtained the solution B. Filtered the solution B with two membrane module units
10 comprising a coarse filter and a reverse osmosis to obtain 100 ml concentrated
water C with potassium iodide in a concentration of 3% and 90 ml fresh water D
free of potassium iodide.

[0061] A titanium alloyed multi-effect evaporator was used for evaporation of the
concentrated water C at an evaporation temperature of 60 °C under atmospheric
15 pressure. A 20 ml concentrated solution E with a specific gravity of 1.2 and 80 ml
of condensate water were thus obtained.

[0062] After analysis, the concentration of potassium borate in the concentrated
solution E was 120 g/L. The processing temperature was controlled at 30 °C to
obtain 10g potassium iodide product and 15 ml residue solution F.

20 [0063] Subsequently, the residue solution F was cooled down to 20 °C and
hydroiodic acid was added into the solution to adjust the pH value to 1. After
centrifugation, 0.5 g boric acid product was obtained and 12 ml of residue was
returned to the evaporation process.

[0064] Fresh water D was adsorbed by 2 g anion and cation exchange resin to get
25 2g of resin rich in potassium borate together with 890 ml of recovered water. The

cationic resin and the anion resin were then eluted with 1% hydroiodic acid and 2% potassium hydroxide, respectively, to obtain a 5 ml eluent whose concentration of potassium borate is 2%. As a result of elution, a 2 g of ion exchange resin was also regenerated.

- 5 [0065] The eluent was returned to the evaporation process. Meanwhile, both the fresh water and condensate water were then mixed with raw water and reused in the production line.

Embodiment 2

- 10 [0066] A 2000 ml waste water solution that contains both iodine and boron from a PVA production line from an electrolytic plant was selected.

- [0067] Added 5g analytically pure solid potassium hydroxide to the solution and adjust the pH to 11, and obtained the solution A. In the solution A, added potassium borohydride and stirred for 3 hours until the I₂ content was measured to be zero and
15 obtained the solution B. Filtered the solution B with membrane module units comprising a coarse filtration, ultrafiltration and reverse osmosis to obtain 300 ml concentrated water C with potassium iodide in a concentration of 3% and 1700 ml fresh water D with potassium iodide in a concentration of 0.008%.

- [0068] A MVR evaporator was used for evaporation of the concentrated water C
20 at an evaporation temperature of 100 °C at an atmospheric pressure. A 50 mL concentrated solution E with a specific gravity of 1.4 was and 250 ml of condensate water was thus obtained.

- [0069] After analysis, the concentration of potassium borate in the concentrated solution E was 95 g/L. Centrifuged the concentrated solution E at a temperature of
25 50°C to obtain 28g potassium iodide product and 35 ml residue solution F.

[0070] The residue F is returned to the solution with the concentrated water C and continued to evaporate and concentrate to prepare the concentrated solution E to participate in the subsequent reuse treatment.

- [0071] Fresh water D was adsorbed by 4g anion and cation exchange resin to get 4g of resin rich in potassium iodide and potassium borate together with 1600 ml of recovered water. The cationic resin and the anion resin were then eluted with 2% hydroiodic acid and 3% potassium hydroxide, respectively, to obtain a 12 ml eluent whose concentration of potassium borate is 1% and concentration of potassium iodide is 3%. As a result of elution, a 4g of ion exchange resin was also regenerated.
- [0072] The eluent was returned to the evaporation process. Meanwhile, both the fresh water and condensate water were then reused in the production line directly without mixing with the raw water.

Embodiment 3

- [0073] A 500 ml waste water solution that contains both iodine and boron from a PVA production line from an electrolytic plant was selected.
- [0074] Added 1g analytically pure solid potassium hydroxide to the solution and adjust the pH to 9, and obtained the solution A. In the solution A, added potassium borohydride and stirred for 1 hour until the I_2 content was measured to be zero and obtained the solution B. Filtered the solution B with membrane module units comprising coarse filtration, reverse osmosis, ion exchange membrane and the like to obtain 60 ml concentrated water C with potassium iodide in a concentration of 1.5% and 440 ml fresh water D with potassium iodide in a concentration of 0.007%.
- [0075] A stainless steel single-effect evaporator was used for evaporation of the concentrated water C at an evaporation temperature of 70 °C under a vacuum

degree of 0.09 Mpa. A 10 ml concentrated solution E with a specific gravity of 1.6 and 50 ml of condensate water were thus obtained.

[0076] After analysis, the concentration of potassium borate in the concentrated solution E was 135 g/L. Added a condensate water until the concentration of potassium borate in the concentrate is 115 g/L, and then the concentrate was centrifuged at 35 °C to obtain 5g potassium iodide product and 7 ml residue solution F.

[0077] Subsequently, the residue solution F was cooled down to 20 °C and hydroiodic acid was added into the solution to adjust the pH value to 1.5. After centrifugation, 0.2 g boric acid product was obtained and 5 ml of residue was returned to the evaporation process.

[0078] Fresh water D was adsorbed by 1.5g anion and cation exchange resin to get 1.5g of resin rich in potassium iodide and potassium borate together with 430 ml of recovered water. The cationic resin and the anion resin were then eluted with 2% hydroiodic acid and 4% potassium hydroxide, respectively, to obtain a 4 ml eluent whose concentration of potassium borate is 5% and concentration of potassium iodide is 4%. As a result of elution, a 1.5 g of ion exchange resin was also regenerated.

[0079] The eluent was returned to the evaporation process. Meanwhile, both the fresh water and condensate water were then mixed with raw water and reused in the production line.

CLAIMS

1. A method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing, characterized by comprising the steps of:

5 (1) adjusting a pH value of the iodine-containing waste water to be within a range of 3 to 12 with potassium hydroxide to obtain a solution A;

(2) adding a reducing agent to the solution A obtained in step (1) to reduce I_2 to I^- , stirring the solution A until I_2 is completely reduced to I^- so as to obtain a solution B;

10 (3) separating the solution B obtained in step (2) into a concentrated water C having a concentration of potassium iodide more than 0.1%, preferably 0.1% to 10%, and a fresh water D having a concentration of potassium iodide of 0% to 0.01% by a membrane module;

(4) concentrating the concentrated water C obtained in step (3) by an evaporator to
15 obtain a concentrated solution E having a specific gravity of 1.1 to 1.6 and a condensate water collected from the evaporator is reused, wherein the condensate water is, preferably mixed with raw water, used for production so as to save raw water consumption;

(5) analyzing concentration of potassium borate in the concentrated solution E
20 obtained in step (4) and selecting one of the following operating steps according to the obtained concentration of potassium borate, wherein, the said threshold concentration is 80 g/L to 160 g/L:

(A) if the concentration of potassium borate is lower than a threshold concentration, centrifuging the concentrated solution E from step (4) at a temperature of 40°C to

60°C to obtain potassium iodide product and returning residue to mix with the concentrated water C in step (4);

(B) if the concentration of potassium borate is equal to the threshold concentration, centrifuging the concentrate solution E obtained from step (4) at a temperature of 25°C to 35°C to obtain potassium iodide product and a residue solution F, cooling the residue solution F to a temperature of 10°C to 25°C and adding hydrogen iodide acid to adjust the pH value to be within a range of 1 to 4 and centrifuging the residue solution F to obtain boric acid product, and returning residue to mix with the concentrated water C in step (4);

(C) if the concentration of potassium borate is higher than the threshold concentration, adding water to the concentrate solution E until the concentration of potassium borate equals to the threshold concentration and returning to step (B); (6) contacting the fresh water D obtained from step (3) to an ion exchange resin to obtain a resin enriched in potassium iodide and potassium borate, returning residual directly or mixed with raw water to production so as to save raw water consumption;

(7) eluting the enriched resin obtained in step (6) to obtain an eluate G containing both potassium iodide and potassium borate in a concentration range of 1% to 5% and recycling the eluted resin;

(8) returning the eluent G obtained in step (7) to step (4) to be mixed with the concentrated water C for preparation of the concentrated solution E.

2. A method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing according to claim 1, characterized in that, in the step (1), the final pH value of the iodine-containing waste water adjusted by potassium hydroxide is in a range from 6 to 11.

3. A method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing according to claim 1, characterized in that, in the step (2), said reducing agent comprises an organic reducing agent and an inorganic reducing agent, wherein the said inorganic reducing agent comprises
5 one or more selected from a group consisting of formic acid, potassium borohydride, hydrogen gas and potassium sulfite.

4. A method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing according to claim 1, characterized in that, in the step (3), the said membrane module comprises at least one or more
10 functional unit selected from a group consisting of coarse filtration, reverse osmosis, nanofiltration, ultrafiltration and an ion-exchange membrane.

5. A method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing according to claim 1, characterized in that, in the step (4), the said evaporator is operated under a reduced pressure in a
15 vacuum degree of 0.01 MPa to 0.09 Mpa, or the said evaporator is at least one or more selected from a group consists of mechanical vapor recompression, single-effect equipment and multiple effect equipment, or the material for the said evaporator contains at least one or more selected from the groups of enamel, stainless steel and titanium alloyed composite materials.

20 6. A method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing according to claim 1, characterized in that, in the step (5)(A), the potassium iodide product is obtained from centrifugal separation when concentration of potassium borate in the concentrated solution E is lower than the said threshold concentration, preferably, the said threshold
25 concentration is 120 g/L.

7. A method for recovering potassium iodide and boric acid from an iodine-

containing waste water produced by PVA dyeing according to claim 1, characterized in that, in the step (5)(B), the potassium iodide product is obtained from centrifugal separation when temperature of the concentrated solution E is at a characteristic temperature, preferably, the said characteristic temperature is 30 °C.

5 8. A method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing according to claim 1, characterized in that, in the step (5), the boric acid product is obtained when potassium borate concentration in the concentrated solution E is equal to or higher than the threshold concentration, temperature of the residual solution F is in at a characteristic
10 temperature and acidity of the residual solution F is within a characteristic acidity range, preferably, the said threshold concentration is 120 g/L, preferably, the said characteristic temperature is 20 °C, and preferably, the said characteristic acidity range is pH value of 1 to 2.

9. A method for recovering potassium iodide and boric acid from an iodine-
15 containing waste water produced by PVA dyeing according to claim 1, characterized in that, in the step (6), the ion exchange resin comprises at least one of an anion exchange resin and a cation exchange resin.

10. A method for recovering potassium iodide and boric acid from an iodine-containing waste water produced by PVA dyeing according to claim 9, characterized
20 in that, in the step (7), the eluent G is obtained from eluting the ion exchange resin comprises eluting the cation exchange resin with an acid and eluting the anion exchange resin with a base to obtain, wherein the components of said eluent G are the same as the concentrated water C obtained in the step (3).