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TREATMENT FOR HYDRAZINE-CONTAINING WASTE WATER SOLUTION

N. Yade

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16. Abstract The present invention is concerned with treatment for waste solutions containing hydrazine. The invention attempts oxidation and decomposition of hydrazine in waste water in a simple and effective processing. The method according to this invention pertains to adding activated charcoal to waste solutions containing hydrazine while maintaining a pH value higher than 8, and adding iron salts if necessary. Then, the solution is aerated.			
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54. Treatment for hydrazine containing waste water solution
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 72. Inventor: Dai Yaden, 1-6-9 Miyazaki, Takatsu-ku,
 Kawasaki-shi
 71. Applicant: Narihara Infilco, Inc., 1-1, 1-chome,
 Hitotsubashi, Chiyoda-ku, Tokyo-To
 74. Agent: patent attorney Masahiro Shiozaki

Detailed statement

1. Name of invention:
 Treatment for hydrazine containing waste water solution.
2. Area covered by the present patent application:
 1) Treatment for hydrazine containing waste water which is

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characterized by the following procedure: Active carbon is added to waste solutions containing hydrazine while maintaining the pH value higher than 8 and, if necessary, adding iron salts. Then, aeration is carried out.

2) Treatment for waste solutions containing hydrazine described in item 2 of the present patent application in which the amount of the above-described active carbon is 0.05 ~ 0.5 weight %.

3) Treatment for waste solutions containing hydrazine described in item 1 or item 2 in the area covered by the present patent application in which the above-described iron salts are 100 ~ 1,000 ppm in iron ion concentration.

3. Detailed explanation of the present invention

The present invention is concerned with treatment for waste solutions containing hydrazine.

In testing water pressure and sea water monitoring in electric power plants, water containing hydrazine is used for deoxidation. Since this hydrazine-containing waste water contains the COD components, the components must be decomposed and removed before the waste water is released into rivers.

In the past, treatment of the waste water was oxidation by chlorine gas or sodium hypochlorous acid for decomposition and removal of the components. However, such approaches have difficulties in storage, administration, and handling of the chemicals needed for the processing, and the processing must be done at a very high technical level. Further, when one of the COD components, hydrazine, is oxidized by these chemicals, the latter may remain in the treated waste water. Therefore, another treatment for removal of chlorine and sodium hypochlorous acid, etc., is necessary.

The present invention aims at oxidation and decomposition of hydrazine contained in waste water in a simple and very effective processing and also to greatly simplify the facilities in processing plants.

The present invention is characterized by aeration after adding active carbon in the environment of pH values of more than 8, preferably more than 10, and also, if necessary, adding iron salts to the waste water containing hydrazine.

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Active carbon used for this purpose is powder or granule. The added amount is 0.05 ~ 0.5 wt %. Also, as iron salts, to be added if necessary, are such as iron sulfate I and II, their ammonium salts, and iron chloride I and II. These iron salts are added to reach the ion concentration of 100 ~ 1,000 ppm.

As described above, the present treatment makes it possible to oxidize and remove hydrazine contained in water in a very effective, simple, and economical manner, by aeration, after adding active carbon and if necessary adding iron salts, while keeping the pH value higher than 8. The facilities for this processing are much simpler than those for conventional processings. By adjusting the pH values to a proper value, the pH value of the released waste water without neutralization can match the standard value.

Further, in the present invention, muds created after the above processing and which contain active carbon and iron hydroxide can be used repeatedly. In other words, after separating solids and liquids of the obtained muds, we mix an additional amount of hydrazine-containing liquid and increase the pH value higher than 8 by adding some alkali. Then only aeration is required, and no new addition of processing agents is necessary in repeated uses.

In the following, some examples are shown.

Example 1.

1-1. The method of the present invention.

We used a water solution containing 500 ppm hydrazine for the liquid to be processed. We added iron sulfate I to 5 l of the liquid until the concentration reached 100 ppm. After stirring for 5 minutes, the pH value was adjusted to 10 by adding sodium hydroxide. Then active carbon powder (made by Fuji Pharmaceutical Company (Inc.), Fuji Tansoka B, active carbon 50%) was added up to 0.2 wt % and aeration was done for about 8 hours at the air flow rate of ~ 1.5 l/minute. After keeping the liquid for ~ 2 hours, the supernatant liquid was separated.

1-2. The conventional method.

The pH value of 5 l of the same to-be-processed solution described above was adjusted to 10 by adding sodium hydroxide. Then, we added 93 ml of sodium hydrochlorite (effective chlorine 12%) and stirred for ~ 1 hour. Then the pH value was changed to 8 by hydrochloric acid. The solution was processed by passing through active carbon absorbing layers.

Comparisons of the results by the present and conventional methods are shown in Table 1 and Table 2.

Example 2.

2-1. The present method.

We added iron sulfate I to 5 l of the same to-be-processed liquid as described in Example 1 so that the iron ion concentration became 200 ppm. After stirring for ~ 5 minutes, the pH value was adjusted to 10 by adding sodium hydroxide. Active carbon powder described in Example 1 was added up to 0.2 wt %. Aeration was done for ~ 6 hours at the air flow rate of ~ 1.5 l/minute. After

Table 1. Comparison of processings.

	Present method	Conventional method
Summary of operation	<p>Oxidation</p> <ul style="list-style-type: none"> → Separation of sediments → release into river 	<p>Oxidation</p> <ul style="list-style-type: none"> → pH adjustment → reduction or absorption → release into river
Processing tank	1	3
Difference	<p>Chemicals used for the processing are less and inexpensive.</p> <p>Easy operation and administration</p> <p>Result of the processing is consistent.</p>	<p>Large amounts of expensive chemicals are required.</p> <p>High technologies are required in operation and administration.</p> <p>Result of the processing is less uniform and less consistent.</p>

Table 2. Comparison of the results.

Water quality before processing		Water quality after processing	
		Present invention (1-1)	Conventional method (1-2)
N ₂ H ₄ (ppm)	500	< 1.0	< 1.0
pH	10.1	8.1	8.0
COD (ppm)	230	2.3	5.0

Table 3. Results of the processing.

Water quality before processing		Water quality after processing		
		The present invention (2-1)	Comparison (2-2)	Comparison (2-3)
N ₂ H ₄ (ppm)	500	< 1.0	300	65
pH	10.1	8.1	8.1	8.0
COD (ppm)	230	2.4	150	30

keeping the solution for 2 hours, the supernatant liquid was separated. The results are shown in Table 3.

2-2. Comparison case.

The results of the processing, which was the same as in Example

2-1, except that active carbon powder was not added and the aeration time was changed to ~ 24 hours, are shown in Table 3.

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2-3. Comparison case.

The results of the processing, which was the same as in Example 2-2, except that instead of iron sulfate I iron sulfate II (dissolved in warm water acidified by sulfuric acid) was used, are shown in Table 3.

Example 3.

3-1. The present method.

The pH value of 5 l of the same to-be-processed liquid as in the above examples was adjusted to 10 by sodium hydroxide. The same active carbon powder as described in Example 1-1 was added to 0.3 wt %. Aeration was done for ~ 24 hours at the air flow rate of ~ 1.5 l/minute. After keeping the solution still for ~ 2 hours, the supernatant liquid was separated. The results are shown in Table 4.

3-2. The present method.

The processing was the same as in Example 3-2, except that the pH value was 11 and active carbon powder was added to 0.1 wt %. The results are shown in Table 4.

Example 4.

4-1. The present method.

To 5 l of the same to-be-processed liquid as described in the above examples, iron sulfate II (dissolved in warm water

Table 4. Water quality after processing.

	Present method (3-1)	Present method (3-2)
N ₂ H ₄ (ppm)	< 1.0	< 1.0
pH	8.0	8.1
COD (ppm)	3.0	3.5

Table 5. Water quality after processing.

	Present method (4-1)	Present method (4-2)	Comparison (4-3)
N ₂ H ₄ (ppm)	< 1.0	2.0	150
pH	8.1	6.2	4.5
COD (ppm)	2.2	4.0	70
Aeration time (hr)	6	6	24

acidified by sulfuric acid in advance) was added to 300 ppm. After 5 minutes' stirring, the pH value was changed to 10 by adding sodium hydroxide. Then the same active carbon powder as described in Example 1-1 was added to 0.2 wt %. Aeration was done for ~ 6 hours at the air flow rate of 1.5 l/minute. After keeping the liquid still for ~ 2 hours, the supernatant liquid was separated. The results are shown in Table 5.

4-2. The present method.

Iron sulfate II was added to 200 ppm iron ion concentration, and the pH value was adjusted to 8 by sodium hydroxide. Except for the above two points, the rest of the processing was the same as in Example 4-1. The results are shown in Table 5.

4-3. Comparison case.

Except that the pH value was adjusted to 7 by sodium hydroxide and the aeration time was ~ 24 hours, the processing was the same as in Example 4-2. The results are shown in Table 5. The effectiveness of the processing was significantly reduced at the pH value 7.

Example 5. The present method.

5-1.

To 5 l of the same to-be-processed liquid as in the above examples, iron sulfate I was added to 400 ppm iron ion concentration. After 5 minutes' stirring, the pH value was adjusted to 10 by adding sodium hydroxide. Active carbon powder, the same as described in Example 1-1, was added to 0.2 wt %. Aeration was done for ~ 6 hours at the air flow rate of ~ 1.5 l/minute. After keeping the liquid still for ~ 2 hours, the supernatant liquid was separated. The results are shown in Table 6.

5-2.

In the muds separated in the above example 5-1, 5 l of the /386 fresh, but same to-be-processed, liquid was mixed. The pH value was adjusted to 10 by sodium hydroxide while stirring the mixture.

Aeration was done for ~ 12 hours at the air flow rate of ~ 1.5 l/minute. After keeping the liquid still for ~ 2 hours, the supernatant liquid was separated. The results are shown in Table 6.

5-3.

In the muds separated in Example 5-2, 5 l of the same, fresh, to-be-processed liquid was mixed. The processing was identical to the above. The results are shown in Table 6.

Table 6. Water quality after processing.

	Present method (5-1)	Present method (5-2)	Present method (5-3)
N_2H_4 (ppm)	< 1.0	< 1.0	< 1.0
pH	8.5	7.7	8.1
COD (ppm)	3.0	1.6	2.0
Aeration time (hr)	6	12	12