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Experimental study on removal of mercury in gas field water

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ABSTRACT

The chemical methods which were used to remove the mercury in gas field water were experimentally studied in this paper. The results show that 40% of the total mercury in the gas field water was insoluble or adsorbed in the suspended solids, and they can be removed by filtration. In the basic coagulation and sedimentation, the chemicals types, dosages and pH conditions were determined, and the data indicated that the mercury removal efficiency of basic coagulation and sedimentation was lower than 60%. Furthermore, mercury removal agents (MRA) were added in basic coagulation and sedimentation to form chemical mercury removal I; the data showed that the MRA which contains sulfur group can increase the mercury removal efficiency greatly, and it can attain 89.95%; the suggested addition sequence of MRA was after the coagulants. Lastly, chemical mercury removal II was a combination of oxidant and chemical mercury removal I; the results showed that a part of insoluble mercury can be oxidized to soluble ionic state, and the mercury removal efficiency of chemical mercury removal II was higher than mercury removal I, which reached 98.92%. The results demonstrated that the mercury in gas field water can be removed to satisfy the requirement of discharge standard through chemical method.

Keywords: Gas field water; Mercury; Coagulation; Oxidation; Chemical method

1. Introduction

Mercury is a hazardous element which would cause irreversible harm to humans, and the troubles caused by mercury include the neurological problem, tremors, loss of sensation, vision and hearing impairments, etc. [1–3]. In recent years, mercury is found in the gas field in northwest China, and the mercury content of gas field water can attain 2,000 μg/L through our detection. Because many countries have strict requirements on the content of mercury in wastewater, for instance the integrated wastewater discharge standard of China requires the mercury content to be less than 50 μg/L, so the use and treatment technology about mercury-containing water becomes a difficult problem for these gas fields.

Generally, the mercury-containing gas field water is a mixture of oil, suspended solids, mechanical impurities, mercury and various additives, so the treatment process should combine the traditional water treatment technology with special mercury removal technology (SMRT). Actually, mercury has different existence forms in the water, including elemental mercury, mercury ion, soluble and insoluble mercury compound [4,5]; the removal of mercury has close relations with the properties of its different forms, and both of the traditional water treatment technology and SMRT can remove the mercury to some extent. The traditional water treatment technologies which can be used to remove mercury include separation, coagulation and sedimentation, flotation and filtration. These technologies mainly remove three types of mercury, including elemental mercury and other insoluble mercury by the density differences, or mercury which is adsorbed in the oil and suspended solids by

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filtration, separation and flotation. In these treatment processes, the state of mercury is not changed and it would enter the sludge, and the mercury removal efficiency is mainly determined by the content of different mercury components.

The SMRT for water treatment include adsorption, membrane separation, photo catalysis, ultrasound, etc. [6–9], they can be used to remove mercury in depth. Sharma et al. [10] have reviewed the SMRT from aqueous solution, and they suggested that activated carbon is the most valuable absorbent. Moreover, the adsorbents mainly include activated carbon, clay and nanoparticles; the adsorption capacity of activated carbon can attain 227.3 mg/g [11], it is because the high surface area caused by micropore, and the adsorption capacity of sulfur or silver-impregnated carbon is greater. However, although these SMRT have high mercury removal efficiency, they have some disadvantages also, such as poor stability, high cost, etc., and they are generally used for the advanced treatment of low mercury-containing water [10,12].

To decrease the water treatment cost, the chemical mercury removal method which is based on traditional coagulation sedimentation is studied in this paper. Coagulation sedimentation is a typical water treatment technology, which is mainly used to remove the hydrophobic sol and suspended solids in the water. The sol and suspended solids in the wastewater have certain ability to adsorb the mercury; the removal of sol and suspended solids would lead to the removal of adsorbed mercury. Moreover, the coagulation and sedimentation can be modified by adding oxidant and mercury removal agents (MRA). In this process, the mercury is oxidized to an ionic state at first, and then the ionic mercury reacts with sulfur-containing MRA to form an insoluble compound, which can be removed by coagulation and sedimentation. The chemical mercury removal method for gas field water has series of crucial technical points, including the types of oxidant and MRA, addition sequence of chemicals and the suitable handling conditions. Chen et al. [13] suggested that the mercury removal efficiency can attain 93.66% with the use of mercaptoacetyl polyethyleneimine, but these crucial points are rarely studied, so the experiments about chemical mercury removal method were carried out by us.

2. Experimental

2.1. Water sample and apparatus

The mercury-containing water sample is taken from a gas field in northwest China, and the main water qualities are shown in Table 1. Moreover, the RA-915+ mercury analyzer based on Zeeman effect atomic absorption is used to measure the mercury content of the water; the test procedures include instrument calibration, preheating, moving the supernatant onto the dedicated carrier activated carbon of the mercury analyzer by a pipette, and then input the volume of supernatant as required, the mercury analyzer would analyze and give the total mercury content of the water. Additionally, the filter membranes with a pore size of 0.45 μm were used in the experiment.

Table 1
Main qualities of the mercury-containing water sample

pH	4.78–5.1
Oil (mg/L)	110.5–136.4
Suspended solids (mg/L)	120.15–155.6
Mercury (μg/L)	210.3–355.4

2.2. Removal efficiency

The mercury content, suspended solids content and turbidity of the raw water are used as the initial value, and mercury content, suspended solids content and turbidity of supernatant after treatment are used as the final value. So the mercury removal efficiency, suspended solids removal efficiency and turbidity reduction efficiency can be defined, and they can be calculated using Eqs. (1)–(3):

$$\eta = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

$$\phi = \frac{f_i - f_f}{f_i} \times 100\% \quad (2)$$

$$\zeta = \frac{m_i - m_f}{f_i} \times 100\% \quad (3)$$

where η, ϕ and ζ are the mercury removal efficiency, suspended solids removal efficiency and turbidity reduction efficiency, respectively; C_i, f_i and m_i are the initial value of mercury content, suspended solids content and turbidity; C_f, f_f and m_f are the final value of mercury content, suspended solids content and turbidity.

2.3. Experimental procedures

2.3.1. Determination of the mercury existence form

Testing the mercury content of the gas field water at first, and then the water was filtered by the filter membrane with a pore size of 0.45 μm and testing the mercury content of the filtered water.

2.3.2. Basic coagulation and sedimentation

This experiment was used to screen the types of coagulants and flocculants, and determine the mercury removal efficiency and suitable pH conditions of coagulation and sedimentation. Three types of coagulants were used in the experiment, and they are polymeric aluminum ferric chloride (PAFC), poly aluminum chloride (PAC), and polymerization ferric chloride (PFC). Moreover, the flocculants used in the experiment were polyacrylamides with three different molecular weights.

2.3.3. Chemical mercury removal I

This experiment was a combination of basic coagulation and sedimentation with MRA, and it was used to screen the types of MRA, the addition sequence of chemicals, and determine the mercury removal efficiency of coagulation and sedimentation with MRA. Three types of MRA were used in this experiment, they are SA-630 provided by Nantong Water Treatment Regent Co. (Jiangsu Province, P.R.), SMET-3 provided by SEAJER CHEMICAL Co., and the DTC produced by RUIMEIDI company (Jiangsu Province, P.R.).

2.3.4. Chemical mercury removal II

This experiment was a combination of chemical mercury removal I with oxidant, and it was used to study the effect of oxidant on the mercury, and determine the mercury removal efficiency of chemical mercury removal II. Sodium hypochlorite was used as the oxidant.

3. Results and discussion

3.1. Existence form of mercury

Under the action of membrane filtration, the suspended solids in the water sample were removed, and the mercury which was adsorbed on the suspended solids and other lager size of insoluble mercury were removed at the same time. The use of 0.45 μm membrane is according to the requirement of Chinese standard (GB11901-89) about the measurement of the suspended solids in water.

The existence form of mercury in the gas field water can be determined by the data shown in Table 2. Obviously, the mercury content of the filtered water was lower than the raw water, which indicated that the insoluble mercury and the adsorbed mercury are lower than 40% of the total mercury, and the other 60% of the total mercury can pass through the filter membrane, we thought they were in the soluble ion state. Although the size of the membrane has effect on the determination of the detailed content of mercury with different existence form, we do not consider this factor from the view of engineering point. Moreover, the results also indicated that the single filtering method cannot remove the mercury to satisfy the Chinese discharge standard that requires less than 50 μg/L mercury.

3.2. Results of basic coagulation and sedimentation

3.2.1. Types of coagulants and flocculants

The screening experiments were carried out at room temperature and the pH values were controlled at 7, the procedures include pH regulation at first, and then adding coagulants and flocculants. When screening the types of coagulants, the dosage of all kinds of coagulants was 90 mg/L, and the dosage of flocculants was 4 mg/L, the polyacrylamide with a molecular weight of 18 million was used as the flocculant. Moreover, the suspended solids content, mercury content and turbidity of raw water and the supernatant of treated water were tested, and the experimental data are shown in Table 3. It is obvious that the mercury removal efficiency of PFC is 54.72%, which is higher than PAC and PAFC, and the PFC can remove the suspended solids and reduce the turbidity of water more effectively, so PFC is the most effective among the three coagulants.

When screening the types of flocculants, the coagulants adopt PFC with an experimental dosage of 90 mg/L, and the dosage of different flocculants was 4 mg/L. The experimental data are shown in Table 4. They indicated that the polyacrylamide with a molecular weight of 18 million has a higher ϕ, ζ and η than the other two flocculants, so it is the suitable flocculant for treating the gas field water.

3.2.2. Dosage of coagulants and flocculants

The first two experiments only determined the types of the coagulants and flocculants, and the optimal dosage of the two

Table 3
Screening results of coagulants

Related description	Raw water	Waters treated by different coagulants		
		PAFC	PAC	PFC
Suspended solids, mg/L	136.25	67.62	63.82	44.83
ϕ, %	–	50.37	53.16	67.10
Turbidity, NTU	325	215	180	125
ζ, %	–	33.85	44.62	61.54
Mercury, μg/L	229.5	110.3	107.6	103.9
η, %	–	51.94	53.12	54.72

Table 4
Screening results of flocculants

Related description	Raw water	Waters treated by different flocculants		
		16 million	18 million	20 million
Suspended solids, mg/L	145.36	47.91	43.04	65.78
ϕ, %	–	67.04	70.39	54.75
Turbidity, NTU	340	133	124	196
ζ, %	–	60.75	63.50	42.25
Mercury, μg/L	323.5	146.2	143.5	150.9
η, %	–	54.80	55.65	53.35

Table 2
Mercury content of the raw water and filtered water

Related description	Sample 1	Sample 2	Sample 3	Sample 4
Mercury content of raw water, μg/L	276.3	271.5	320.6	225.2
Mercury content of filtered water, μg/L	187.5	168.6	212.8	149.7
Mercury removal efficiency, %	32.14	37.90	33.62	33.51

chemicals would be determined in this part. For the determination of optimal dosage of coagulants, experiments were conducted with the dosage ranging from 70 to 120 mg/L with an interval of 10 mg/L, and the dosage of flocculants was fixed at 4 mg/L. The three efficiencies mentioned in front were used to determine the optimal dosage of the two chemicals, and they are shown in Fig. 1. Fig. 1(a) shows that the mercury removal efficiency and turbidity reduction efficiency were increased with the PFC dosage at first, and then they decreased, but the trends of them were not obvious. However, the trend of the suspended solids removal efficiency is very obvious, and the optimal dosage of coagulants is 100 mg/L through integrated consideration.

Moreover, when determining the dosage of flocculants, the dosage of coagulants was fixed at 100 mg/L, and the dosage of flocculants was ranging from 1 to 6 mg/L with an interval of 1 mg/L. Then the optimal dosage of flocculants can be determined through Fig. 1(b), and it is 3 mg/L.

3.2.3. Optimal pH conditions

The experimental results in front were used to study the optimal pH value of the coagulation and sedimentation, that is, the dosages of PFC and polyacrylamide were 100 and 3 mg/L, respectively. Moreover, the pH value was adjusted by sodium hydroxide, and it changed from 6 to 9. The data in Table 5 indicated that the optimal pH is 7–7.5. In addition, the experimental results also showed the mercury removal efficiency of single coagulation and sedimentation was lower than 60%. In order to improve the mercury removal efficiency, other chemicals must be used in the coagulation and sedimentation process.

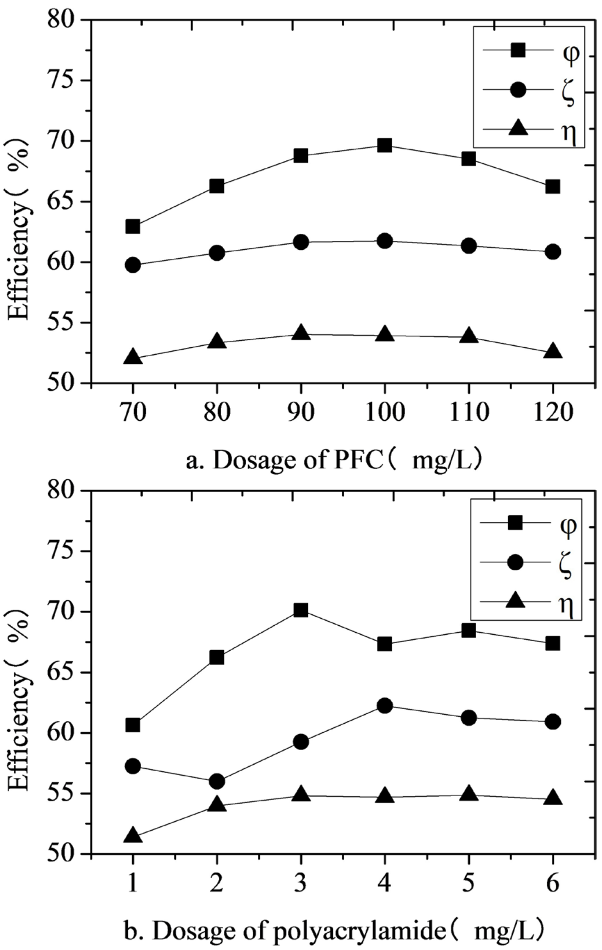

Fig. 1. Effect of the dosages on the efficiency.

3.3. Results of chemical mercury removal I

3.3.1. Types of MRA

This experiment was based on the basic coagulation and sedimentation, except MRA was added to the gas field water at first, and the dosage of MRA was 0.05 mL/L according to the recommended range, the other conditions were same as the optimal conditions of coagulation and sedimentation. Moreover, the mercury removal efficiency was used to evaluate the effect of different MRA.

$$Hg^{2+} + S^{2-} \rightarrow HgS \quad (4)$$

Mercury is a sulfophilic element, so all of the three MRA used in the experiment contain sulfur groups, and the sulfur groups can react with mercury to form mercuric sulfide ($K_{sp} = 4.0 \times 10^{-53}$), which is difficult to dissolve in water, the reaction mechanism is shown in Eq. (4). The data in Table 6 indicated that the mercury removal efficiency was significantly improved after adding MRA, and the treatment effect of SA-630 attained 84.41%, it was the best among the three. However, the excess addition of MRA would produce hydrogen sulfide, and form soluble clathrate to decrease the mercury removal efficiency, so the optimal dosage of MRA should be determined through experiment.

3.3.2. Addition sequence of MRA

Before determining the dosage of MRA, the addition sequence of MRA was studied. Due to the sequence of coagulation and sedimentation is constant, that is, adding coagulants at first and then the flocculants, two addition sequences of MRA were studied in the paper, the first one (I) was adding MRA before coagulants and the other (II) was after it. The dosages of the MRA, coagulants and flocculants were 100, 3 and 0.05 mL/L, respectively. The experimental data are shown in Table 7, they indicate that the addition sequence of MRA has no significant effect on the mercury removal efficiency, and both of them were around 85.2%. However, the coagulants can neutralize the negative electricity of the particles in the water, and causes the particles lose stability, which is beneficial to the reaction of mercury with MRA, so the second addition sequence is recommended.

3.3.3. Optimal dosage of MRA

In this part, the dosages of MRA ranged from 0 to 1 mL/L. As Fig. 2 shows, the mercury removal efficiency rapidly increased when MRA was added, and it attained 85.25% when the dosage was 0.03 mL/L. Moreover, when the dosage was 0.2 mL/L, the best mercury removal efficiency was acquired, and it was 89.95%, the specific data are shown in Table 8. However, when the dosage exceeded 0.2 mL/L,

Table 5
Effect of pH on coagulation and sedimentation

Related description	Raw water	pH					
		6	6.5	7	7.5	8	9
Suspended solids, mg/L	139.85	95.57	76.23	42.25	68.54	82.31	85.63
ϕ, %	–	31.66	45.49	69.79	50.99	41.14	38.77
Turbidity, NTU	330	180	137	128	127	145	152
ζ, %	–	45.45	58.48	61.21	61.52	56.06	53.94
Mercury, μg/L	332.6	159.1	155.8	148.3	148.5	172.2	181.9
η, %	–	52.16	53.15	55.42	55.35	48.23	45.32

Table 6
Effect of different MRA

Related description	Raw water	Mercury removal agents (MRA)		
		SA-630	SMET-3	DTC
Mercury, μg/L	313.1	48.81	61.33	108.05
η, %	–	84.41	80.41	65.49

Table 7
Effect of MRA addition sequence

Related description	Raw water	Addition sequence of MRA	
		I	II
Mercury, μg/L	264.1	39.06	38.66
η, %	–	85.21	85.36

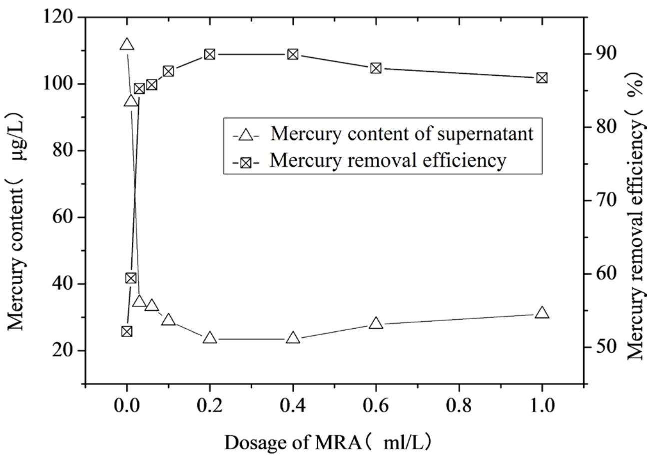

Fig. 2. Effect of the MRA dosages on the efficiency.

the cost of MRA would be very high, and the color of the water changed to yellow, which would deteriorate the water quality. Actually, in the water treatment engineering, the removal of mercury is a combination of chemical method and other SMRT, so the recommended optimal dosages of MRA were between 0.03 and 0.1 mL/L.

Table 8
Mercury content changes with MRA dosage

Dosage of MRA (mL/L)	Mercury content of supernatant (μg/L)	Mercury removal efficiency (%)
0	111.5	52.13
0.01	94.6	59.42
0.03	34.4	85.25
0.06	33.1	85.78
0.1	28.8	87.62
0.2	23.4	89.95
0.4	23.4	89.95
0.6	27.8	88.05
1	30.9	86.72

3.4. Results of chemical mercury removal II

3.4.1. Effect of oxidation

In this part, the effect of oxidation on the state of mercury was studied. The oxidant (10% sodium hypochlorite), coagulants and flocculants were added to the water in sequence, the dosage of coagulants and flocculants was constant, and the dosage of oxidant was changed gradually. Moreover, the oxidation reaction time was 20 min, and it is worth mentioning that MRA were not added in this experiment.

$$Hg + ClO^- + 2H^+ \rightarrow Hg^{2+} + Cl^- + H_2O \quad (5)$$

Fig. 3 shows that the mercury content of the supernatant increased at first, and then it decreased. It indicated that some mercury in the gas field water was oxidized to be soluble ion state according to Eq. (5), and it was the reason for the increase of mercury content in the supernatant. Besides, because the content of alkyl mercury in the raw water was below 2 μg/L through our detection, which was too small to cause the experimental phenomenon mentioned above, the decomposition of organic mercury was not considered. However, the dosage of oxidant was not the more the better, when it exceeded 5 mL/L, the mercury content decreased gradually, because it would deteriorate the effect of coagulation and sedimentation. Moreover, the data also showed that even the optimal dosage of oxidant, 40.79% of the total mercury was insoluble or being adsorbed on the suspended solids, the relative data are shown in Table 9.

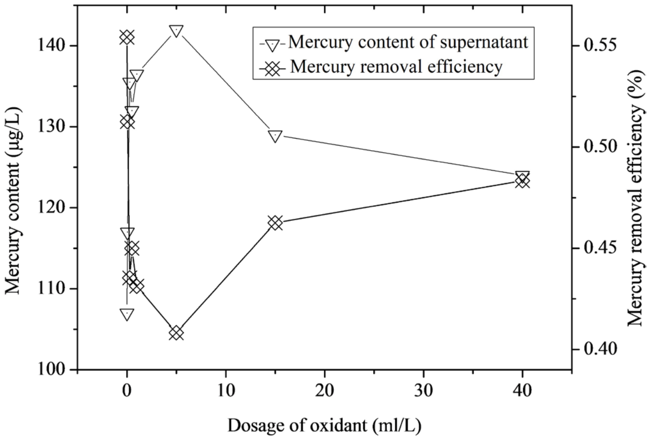

Fig. 3. Effect of oxidant on the efficiency.

Table 9
Mercury content changes with the dosage of oxidant

Dosage of MRA (mL/L)	Mercury content of supernatant (μg/L)	Mercury removal efficiency (%)
0	107.2	55.43
0.05	117.6	51.10
0.3	135.5	43.66
0.5	132.1	45.07
1	136.5	43.24
5	142.4	40.79
15	129.2	46.28
40	124.8	48.11

3.4.2. Effect of chemical mercury removal II

Because the optimal dosage of oxidant had been determined by the above experiment, the effect of chemical mercury removal II can be studied when the MRA are added after the coagulants, that is, the chemicals addition sequence is oxidant, coagulants, MRA and flocculants. Additionally, in order to contrast with chemical mercury removal I, the dosages of oxidant, coagulants, flocculants and MRA were same as section 3.3.3, except the sodium hypochlorite with a dosage of 5 mL/L was added to the water at first.

The mercury removal efficiencies of the two chemical mercury removal processes are shown in Fig. 4. It is obvious that the chemical mercury removal II was more efficient than chemical mercury removal I, and its best mercury removal efficiency can attain 98.92%; it can decrease the mercury of the gas field water from 258.3 to 2.8 μg/L, which satisfies the requirement of the discharge standard in China. Furthermore, alkyl mercury was not detected in the water treated by chemical mercury removal II.

4. Conclusions

This paper experimentally studied the removal of mercury in the gas field water through chemical method, and the main conclusions include: (1) the insoluble mercury and adsorbed mercury in the gas field water were lower than 40% of the total mercury, the other 60% of the total mercury was in soluble ionic state. (2) PFC and polyacrylamide with a molecular weight of 18 million were suitable to treat the mercury-containing gas field water, and the optimal pH condition of coagulation sedimentation was 7–7.5, but the mercury removal efficiency of single coagulation and sedimentation was lower than 60%. (3) MRA were useful to increase the mercury removal efficiency, and the best efficiency of chemical mercury I was 89.95%. (4) Some mercury in the gas field water can be oxidized to be soluble ionic state, and the efficiency of chemical mercury II was higher than chemical mercury I, it can attain 98.92%.

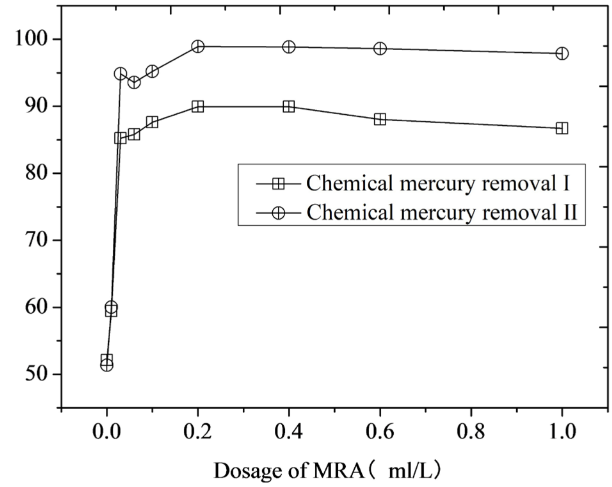

Fig. 4. Comparison of chemical mercury removal methods.

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