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Key methods of drinking water pollution caused by heavy metals

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ABSTRACT

Aiming at the current situation of sudden water pollution in urban water supply system, based on the investigation and study of the main drinking water sources in the northwest China, the potential pollutants along the Yellow River coast were analyzed. First, the sudden heavy metal pollution in the Yellow River was simulated, and its emergency treatment measures were studied. Then, the different concentrations of chromium (VI) pollution in the Yellow River water source were simulated, and the removal method of heavy metals in drinking water sources with sudden heavy metal pollution was studied. Combined with the current water treatment technology commonly used in urban water purification plants in China, a rapid, simple and effective emergency treatment process that can be used directly in water purification plants was studied. The reduction rate of hexavalent chromium can be greatly improved by using ferrous sulfate reduction method. When the concentration of raw water in the hexavalent chromium was 0.25 mg/~2 mg/L, 5 mg/L~16 mg/L ferrous sulfate dosage can make effluent total chromium compliance. For the removal of high standard ratio (1~2 mg/L) of hexavalent chromium, the addition of ferrous sulfate was taken into account. From the economic point of view, 10 mg/L ferrous sulfate was added to a coagulant sedimentation tank. Powder activated carbon (0.035 g~0.35 g) was added to the filter tank to meet the emission standard.

Keywords: Heavy metal pollution; Chemical precipitation; Ferrous sulfate

1. Introduction

Sudden water pollution incident refers to the phenomenon that a liquid or solid containing a high concentration of pollutants suddenly enters a water body, and the water body in a certain water is polluted, thereby reducing or losing functions and being seriously endangered. General pollution is caused by human factors or natural disasters, so that the deterioration of pollutants in the short term seriously affects the water body [1]. The pollution situation is mostly manifested in the uncertainty of occurrence, development and harm, the long-term nature of the impact and the uncertainty of the emergency theme [2]. The number of sudden water pollution incidents in China is increasing. Most of the major sudden water pollution incidents reported in China in the past 20 years have been caused by transportation accidents and enterprise production accidents. Most of the serious pollution of water resources is oil and all kinds of chemicals that are harmful to the people's health. The degree of economic loss caused by pollution incidents is different. Major water pollution events such as Songhua River pollution and Tuojiang River pollution often cause great impact on people's production and life, destroy the ecological environment, and even cause social panic [3]. The increasingly frequent environmental emergencies have become a major obstacle to building a "harmonious society" in China.

In the meantime, heavy metal pollution incidents have occurred in recent years. Timely analysis of the root causes of frequent heavy metal pollution can help to eliminate the hidden dangers of pollution in the bud [4,5]. At present, the heavy metal pollutants removal methods developed and

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applied at home and abroad are mainly chemical, physical and biological methods. It includes membrane separation, activated carbon adsorption, coagulation sedimentation, chemical precipitation and biosorption [6]. The object of this research is to formulate emergency water supply control plan for typical two heavy metal pollution in the Yellow River, and mainly investigate the safety of water supply polluted by heavy metal hexavalent chromium. Therefore, the selection of the treatment plan should be aimed at the characteristics of the Yellow River water itself. The water source of Yellow River has the characteristics of large amount of water, rapid migration and easy pollution. Due to the unpredictable nature of heavy metal pollution, it is only detected after a period of heavy metal pollution accident. In addition, the appropriate treatment method can be used to remove the contaminated object after detection. Therefore, the choice of treatment plan should be considered in a comprehensive way. The treatment plan not only considers the important role of water in ensuring the safety of industry and agriculture and the daily life of the masses, but also has to achieve the effect of removing heavy metals as fast and effectively as possible. In this way, we need to make the best use of the existing processing technology in the water plant in the treatment project, to reduce the construction of the new treatment [7,8]. The powdered activated carbon adsorption method and coagulation – chemical precipitation process method are selected. The two methods are compared and studied through experiments. The adsorption conditions are optimized to achieve the purpose of rapid and effective removal of heavy metal pollution.

2. Materials and methods

2.1. Experimental materials

The main equipment includes the following six parts: 1) 721-spectrophotometer; 2) HY-4 velocity-modulated oscillator; 3) electronic balance, 4) acidity meter; 5) 50 mL comparison tubes; 6) 10 mm cuvette.

The main reagents include the following six parts. The experimental reagent is purchased at the school's reagent laboratory. 1) acetone; 2) sulfuric acid. The sulfuric acid (ρ = 1.84 g/mL) was slowly added to the same volume of water and mixed. 3) phosphoric acid. The phosphoric acid (ρ = 1.69 g/mL) was mixed with an equal volume of water. 4) standard chromium reserve liquid. 0.2829 g potassium dichromate ($K_2Cr_2O_7$, guarantee reagent) that is dried for 2 h at 120°C was weighed After dissolving in the water, potassium dichromate was moved into the 1000 mL capacity bottle. The solution was diluted with water to the marking line and shaken well. Each milliliter of solution contains 0.100 mg hexavalent chromium. 5) chromium standard solution. 5.00 mL chromium standard reserve liquid was absorbed and moved into the 500 mL capacity bottle. The solution was diluted with water to the marking line and shaken well. Each milliliter solution contains 1.00 µg hexavalent chromium. All solutions were prepared on the day. 6) chromogenic agent. 0.2 g diphenylcarbazide ($C_{13}H_{14}N_4O$) was weighed and dissolved in 50 mL acetone. The solution was diluted with water to 100 mL and shaken well. Finally, the solution was stored with brown bottle in the refrigerator. The liquid cannot be used after the color was darkened.

2.2. Experimental methods

Interference and elimination: The iron content is more than 1 mg/L, and the water sample is yellow. The hexavalent molybdenum and mercury also react with the color reagent to produce the colored compound. However, the reaction is insensitive in the chromogenic acidity of this method. Molybdenum and mercury have reached 200 mg/L, which are non-interfering measurements. The mercury is interfering, and its content is higher than 4 mg/L, that is, interference determination. However, when the mercury reacts with the chromogenic agent, it can be dis-colored by itself after 10min. Oxidant and reductive substances, such as ClO^-, Fe^{2+}, SO_3^{2-}, $S_2O_3^{2-}$, and turbid water samples are interfered with the determination and must be pre-treated.

Application scope of the method: This method is suitable for the determination of hexavalent chromium in surface water and industrial waste water. When the sampling volume is 50 mL, the 30 mm cuvette is used. The minimum amount of detection is 0.2 g chromium. The lowest detection concentration is 0.004 mg/L. The 10 mm cuvette is used, and the determination limit is 1 mg/L.

Standard curve: The standard curve part mainly includes coloration and measurement. Coloration: In a set of 50 mL colorimetric tubes, chromium standard solutions with different specifications such as 0, 0.20 mL, 0.50 mL, 1.00 mL, 2.00 mL, 6.00 mL, 8.00 mL and 10.00 mL are added respectively (In the precipitation separation of zinc salt, double standard solution should be added when the standard solution must be pre-added). The solution is diluted with water to the marking line. 0.5 mL (1+1) sulfuric acid solution and 0.5 mL (1+1) phosphoric acid solution are added and shaken well. Then, 2 mL color reagent is added and shaken well. Measurement: After 5~10 min, 10 mm cuvette is used. At 540 nm wavelength, the distilled water is used as the reference ratio. The absorbance is measured, and the blank correction is made. The standard curve of the absorbance to hexavalent chromium is drawn. The standard curve is shown in Fig. 1.

It is calculated that the relationship between the absorbency and the concentration of chromium is y = 0.0119x + 0.0024. in the relation, y is the absorbance after the blank correction, and x is the detection concentration (mg/L) of chromium in the water sample corresponding to y.

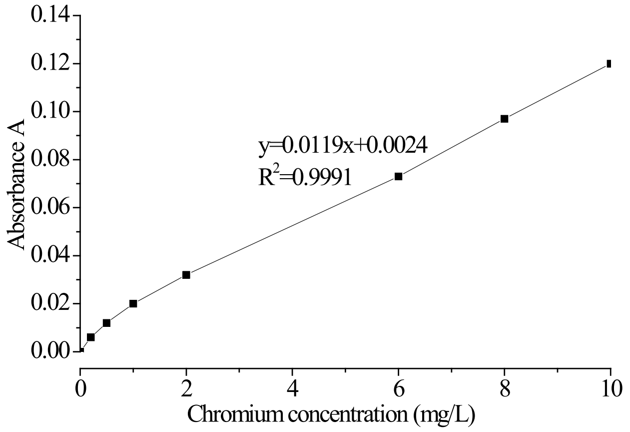

Fig. 1. Standard curve of chromium.

Preparation of excessive water samples: The first step is the water sample. The turbidity of the Yellow River is very large, reaching 1300NTU. Because the natural precipitation time is too long, the suction machine is used to remove the turbidity. Then, the $K_2Cr_2O_7$ is used to prepare the super standard water sample. The molecular weight is 294.18. 707.3 mg, 1415 mg, 2830 mg, 4245 mg and 5660 mg are weighed and dissolved in 1 L water respectively. The 1 m prepared solution was extracted and added into the 1 L volume bottle. Then, the filtered water was added to the scale line and made up of 5 times, that is, hexavalent chromium water with 10, 20, 30 and 40 times. The concentration of hexavalent chromium in water sample is 0.25 mg/L, 0.5 mg/L, 1 mg/L, 1.5 mg/L and 2 mg/L, respectively.

2.3. Removal of chromium from water by ferrous sulfate reduction precipitation method

Because the toxicity of hexavalent chromium is much larger than the trivalent chromium, the hexavalent chromium pollution caused by the sudden incident should be paid enough attention. The effect of using powdered activated carbon to remove hexavalent chromium in water is not good. The dosage of activated carbon is large and the adsorption time is long, which cannot reach the treatment standard. The chemical precipitation method is used to remove the hexavalent chromium in the raw water, and the existing processing technology of the water plant is fully utilized.

In natural water, chromium is mainly adsorbed on suspended matter and colloid substance in water. The proportion of dissolved chromium is very small, and the conventional treatment process can be used to remove it effectively. Chromium is mainly concentrated in the dissolved ion-state such as heavy chromic acid root and chromic acid root in water. However, the treatment process of our existing water plant is poor for the removal of hexavalent chromium. Yan Jiabao and others use the oxidation of hexavalent chromium. By adding ferrous sulfate to water with pH value of 2.0~3.0, the hexavalent chromium is reduced to trivalent chromium. Then, the pH value is adjusted to alkaline to produce chromium precipitation to achieve the removal effect. There is a problem here. It is unrealistic to adjust the pH to below 3 for the water plant. The use of drugs is large and uneconomical. The strong acidity will corrode the equipment and structures of the water plant. Secondly, after converting hexavalent chromium into trivalent chromium, the pH will also be adjusted to alkaline. Therefore, a large amount of alkali is consumed and the pH value of the effluent is high.

The method of removing hexavalent chromium in this experiment: The activated carbon adsorption method and ferrous sulfate reduction method are used. The activated carbon itself has a certain adsorption. It can adsorb hexavalent chromium and trivalent chromium. The hexavalent chromium in the water is reduced to trivalent chromium by ferrous sulfate. Trivalent chromium is easily formed in the chromium hydroxide precipitation, and it can be removed in the process of coagulation precipitation. However, in ferrous sulfate, Fe^{2-} is oxidized to Fe^{3-} and become coagulant. Thus, the removal efficiency is improved. The hexavalent chromium in the water is reduced to trivalent chromium by ferrous sulfate. The pH value is adjusted and the trivalent chromium forms precipitation.

2.4. Removal of chromium in water by powdered activated carbon adsorption

The measurement step is divided into three steps: First, a 100 mL cylinder was used to measure 100 mL hexavalent chromium solution with different times. The excessive hexavalent chromium water samples were placed in seven 250 mL conical flasks. The powdered activated carbon with different weights was weighed by the electronic balance. It was added to the conical bottle containing the water sample and numbered. Then, the solution bottle was sealed and the solution was placed on the oscillator for 30 min. The solution was filtered sequentially and the filtrate was taken after the oscillation. 10 mL solution was removed with 50 mL plugged colorimetric tube and diluted with distilled water to the marking line. Then, 0.5 mL (1+1) sulfuric acid solution and 0.5 mL (1+1) phosphoric acid solution were added and shaken well. 2 mL color reagent was added and shaken well. Finally, the solution was placed for 5~10 min. 10 mm cuvette was used. At 540 nm wavelength, the distilled water is taken as a reference. The absorbance was measured and a blank correction is made.

3. Result and discussion

3.1. Effect of pH value of raw water on removal of chromium

As shown in Fig. 2, the content of hexavalent chromium in the raw water is 0.5 mg/L, and the amount of ferrous sulfate is 6 mg/L. When the pH value of raw water is less than 6.5, the total concentration of chromium in the effluent is very high. When pH is between 6.5~8.0, the total concentration of chromium in the effluent is not very different. It meets the *Drinking Water Health Standards* (GB5749-2006). The limit of hexavalent chromium is 0.05 mg/L.

The experiment found that the lower the pH value of raw water is, the faster the water sample changed from colorless to light yellow after adding ferrous sulfate is. In other words, the faster the ferrous iron is oxidized, and the faster the hexavalent chromium is reduced. Therefore, the raw

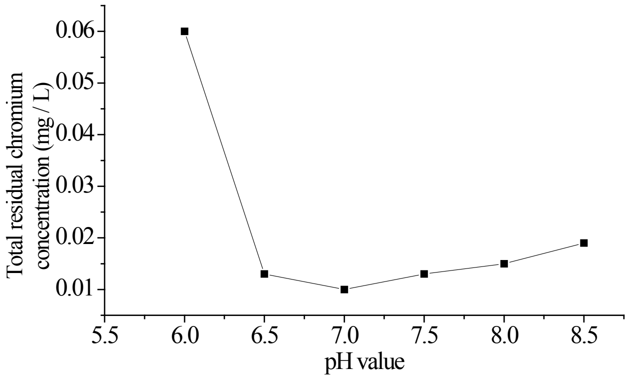

Fig. 2. Comparison of chromium removal effect under different pH values.

water pH value between 6.5 to 8.0 is the best. The Yellow River water in the experiment is neutral. It is suitable for adding ferrous sulfate directly to remove hexavalent chromium. As shown in Table 1, the dosage of ferrous sulfate is determined by experimental result. After repeated experiments, it is concluded that the addition of ferrous sulfate is: $FeSO_4{\cdot}7H_2O{:}Cr^{6+}$ (mass ratio) ≥16.

The hexavalent chromium is removed by the method of adding ferrous sulfate. The effluent meets the limit of hexavalent chromium stipulated in the *Drinking Water Health Standards* (GB5749-2006) as 0.05 mg/L. The highest chromium concentration that can be removed is the excessive chromium with 40 times.

3.2. Adsorption of hexavalent chromium by activated carbon

The results show that the adsorption effect of activated carbon on hexavalent chromium is not good. The group formed by hexavalent chromium is a negative ion, and activated carbon is positively charged due to its surface functional groups, such as acidic functional groups (carboxyl, phenolic hydroxyl) and basic functional groups. Therefore, the adsorption of positive ions is determined. Therefore, it is not good to use activated carbon to adsorb hexavalent chromium ions in water. As shown in Fig. 3, the initial hexavalent chromium concentration in the raw water is 0.25 mg/L. With the increase of the dosage of activated carbon, the concentration of hexavalent chromium is reduced. When the dosage reaches 0.07 g, the concentration of hexavalent chromium is no longer reduced. This shows that the adsorption of activated carbon has reached saturation state and is no longer adsorbed. At this time, the effluent concentration is still a little high and cannot reach the effluent discharge standard.

Table 1
Initial hexavalent chromium concentration and ferrous sulfate dosage

Initial hexavalent chromium conc. (mg/L)	Ferrous sulfate dosage (mg/L)	Effluent conc. (mg/L)
0.25	5	0.019
0.5	7	0.019
1	11	0.019
1.5	14	0.019
2	6	0.019

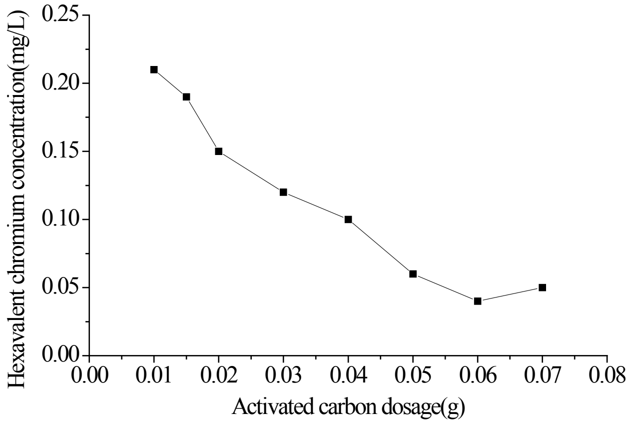

Fig. 3. The dosage of activated carbon and the concentration of hexavalent chromium.

3.3. Combination of powdered activated carbon adsorption and ferrous sulfate reduction

When the exceeding standard concentration of hexavalent chromium with high concentration (1~2 mg/L) is treated, only ferrous sulfate can be used to get the water to reach the standard. But considering that the dosage of ferrous sulfate is not large enough, the chroma of the effluent is not satisfied. Therefore, the powdered activated carbon adsorption and ferrous sulfate reduction are combined. This method is a little more complicated than only adding ferrous sulfate to meet the discharge standard. But it can be used. The dosage of ferrous sulfate is 10 mg/L, and the different powder activated carbons are added to the exceeding standard hexavalent chromium raw water with 20, 30 and 40 times. The specific relation is shown in Figs. 4 and 5:

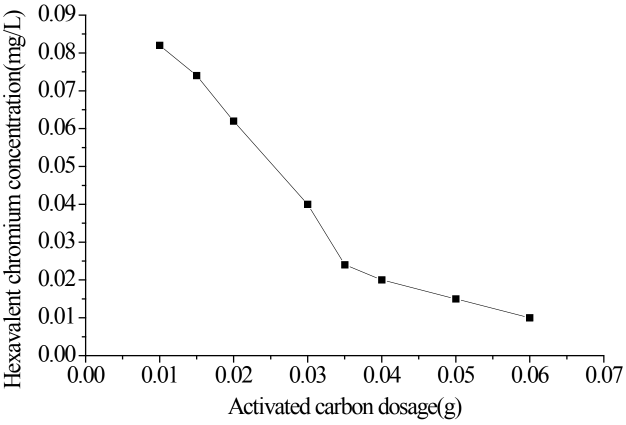

Fig. 4. Comparison of removal effect of different activated carbons when hexavalent chromium exceeded 20 times.

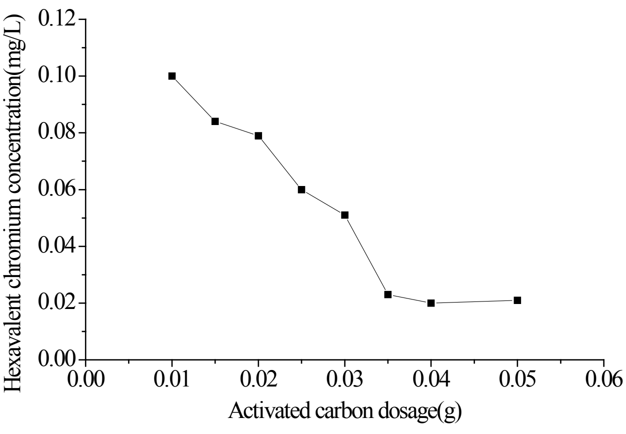

Fig. 5. Comparison of removal effect of different activated carbons when hexavalent chromium exceeded 60 times.

As shown in Figs. 4 and 5, the combination of powdered activated carbon adsorption and ferrous sulfate reduction can also reach the treatment standard. For the treatment of hexavalent chromium raw water with high exceeding standard, the ferrous sulfate reduction method, powdered activated carbon adsorption and ferrous sulfate reduction can be combined. When the concentration of hexavalent chromium is 20~40 times (1~2 mg/L), the dosage of ferrous sulfate is 10 mg/L and the dosage of powdered activated carbon is 0.035 g~0.35 g. Currently, the treatment water reaches the standard.

4. Conclusion

To remove heavy metals in drinking water, aiming at the events of drinking water treatment and sudden heavy metal pollution occurring in heavy metal contaminated area, based on the current water treatment technology widely used in waterworks, a practical and quick start-up method that can be accepted by water plants is studied. In the experiment, Cr (VI) is selected as the target for the heavy metal which is easy to appear in the Yellow River basin of northwest China. The powder activated carbon adsorption method and precipitation method are used. The dosage of activated carbon and the pH value of water sample are adjusted. Meanwhile, different amounts of ferric chloride and ferrous sulfate coagulant are added and the better result is finally achieved. After treatment, the effluent reaches the standard.

The study finds the following points: First, under the condition that pH is weak alkaline, the removal effect of powdered activated carbon on hexavalent chromium is not ideal. The removal of six valent chromium should be carried out under suitable pH condition. Therefore, adding activated carbon is necessary. Secondly, the experiment made full use of the existing processing technology in the water plant. However, when hexavalent chromium is removed by ferrous sulfate reduction method, the original pre-oxidation process of water plant should be suspended. Again, the hexavalent chromium in water is reduced to trivalent chromium that is easy to form precipitation by ferrous sulfate. At the same time, the floc can adsorb chromium hydroxide and improve the removal efficiency. When the concentration of hexavalent chromium in the raw water is 0.25~2 mg/L, the amount of the corresponding ferrous sulfate is 5~16 mg/L, and the total chromium in the effluent can reach the standard. The addition point is selected in front of the coagulant pool. At the same time, for the removal of chromium in the polluted water (1~2 mg/L) with exceeding standard hexavalent chromium, the pH value should be greatly adjusted after the reduction of ferrous sulfate. Considering the guarantee of treatment effect, a small amount of ferrous sulfate can be added to the coagulating sedimentation tank, and a proper amount of powdered activated carbon is added before in front of the filter tank to achieve the discharge standard. In addition, when the pH value of the original water is 3~4, the hexavalent chromium is reduced to trivalent chromium. However, this is not conducive to the formation of chromium hydroxide, and the removal effect is not good. The pH value of the appropriate raw water is between 6.5~8.0. Finally, the ferrous sulfate precipitation method and the powder activated carbon method are used. This method has the advantages of convenient economy, small dosage and good removal effect. Moreover, this combined method is suitable as an emergency treatment for the treatment of hexavalent chromium pollution in drinking water source.

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