ABSTRACT

The Yellow River which flows through several provinces is an important water source in North China. With the rapid development of cities along the Yellow River, arsenic pollutants which were discharged from chemical, textile, glass, leather industries polluted the water and destroyed the ecological environment. The adsorption of sediment on arsenic pollutants depends on many factors, such as sediment composition, sediment concentration, sediment grain size, temperature, pH value, adsorption time, etc. In order to research of the sediment environment, preservation the water quality and protection of ecological environment, study on various factors of arsenic adsorption by sediment in the Yellow River is very necessary. The adsorption characteristics of sediment on arsenic were obtained in the hydrostatic and dynamic adsorption experiments. The main results are as follows. ①The adsorption can reach equilibrium in 5 minutes when the sediment concentration is below 200 kg/m³. ②During the same concentration conditions, the rule of adsorption amount is fine sand > medium sand > coarse Sand. ③A logarithmic growth trend of adsorption amount is obtained with the increasing of sediment concentration in the hydrostatic and hydrodynamic conditions. ④15~20 kg/m³ is a very important cut-off point in the adsorption by coarse sediment. ⑤The adsorption rate is higher in hydrodynamic condition than in hydrostatic condition.

Keywords: prototype sand; arsenic; hydrostatic adsorption experiment; dynamic adsorption experiment

INTRODUCTION

The Yellow River which flows through several provinces is an important water source in North China. It supplies the 15% cultivated land and 12% people of China. As a drinking water source of cities along the Yellow River, its water quality security is important. But with the rapid development of the Yellow River coastal economic, chemical, textile, glass, leather, industrial wastewater and agricultural non-point source sewage discharged into the Yellow River. These heavy metals, especially arsenic pollutants are in the water and sediments, causing water quality deterioration[1-6]. The sources of arsenic in the Yellow River are background arsenic and outside arsenic. Background arsenic stems from runoff which contains arsenic from soil erosion. Outside arsenic stems from human activities (arsenic industrial wastewater discharge, arsenical pesticide use, farmland irrigation water). Investigation shows that the average concentration of arsenic was 10.38 ppm in the sediment of the loess plateau. According to the 16 tons sediment discharge per annual, the total arsenic is up to 16000 tons from the loess plateau to the Yellow River per annual. With the arsenic pollution increasing, the ecological environment and the drinking water source are threatened. The average arsenic concentration of the surface sediments is 1.93~15.11 mg/kg in downstream of the Yellow River.

In order to research of the sediment environment, preservation the water quality of high sediment laden rivers and protection of ecological environment, the study on the sediment adsorption of arsenic come to be practical significance. In this paper, some key factors on the sediment adsorption of arsenic pollution are studied.
systematically, such as contact time, sediment concentration, sediment grain size, flow state and etc.

EXPERIMENT SECTION

Methods

An important research is solid phase adsorption in environmental science, soil chemistry and geochemistry. The past research mainly concentrated in the adsorption of heavy metals by suspended matter\(^7\), sediment, soil and so on\(^8-13\). Now, the research has begun to expand the forms of heavy metals, the change in charge distribution, and other disciplines such as chemical plant nutrition\(^14-17\). Research shows that, the adsorption of sediment on heavy metal depends not only on the sediment itself, but also restricted by many factors in water environment. The main influencing factors are the sediment composition, sediment concentration, sediment grain size, temperature, pH value and adsorption time. In order to research the sediment adsorption law on arsenic in the natural water, experiments are conducted. The adsorbing material is the Yellow River prototype sand. Influences of sediment concentration, sediment grading, contact time and flow state in the sediment adsorption of arsenic are researched in a focused way.

Experimental sediment

The Yellow River prototype sand is selected as adsorbent in this experiment. Sediment samples are from the Huayuankou section of the Yellow River. The sediment characteristics are associated with the flooding and sedimentation, and the bedding deposition is showed because of the grain size of sediment. So, sediment of different grain size is collected by layered gathering. The Yellow River sediment mainly comes from the Quaternary sediments of the Loess Plateau, and the main minerals are illite, quartz, chlorite, calcite, feldspar, etc. Different mineral content decides different sediment grading. Research shows that the sediment of the Yellow River has high CaCO\(_3\) (about 10%), low organic matter (<1%), and the pH value was slightly alkaline (7.9~8.3).

According to the size of sediment, prototype sand is divided into coarse, medium and fine sand, and the medium sand is 1:1 mixture material by coarse sand and fine sand. The sediment grading of coarse, medium and fine sand is acquired by the photoelectric particle detector. The nonuniform coefficients \(K_f (K_f = \sqrt{\frac{d_{75}}{d_{25}}})\) of coarse, medium and fine sand are 1.26, 1.53 and 2.95, and medium diameter are 10.02 \(\mu\)m, 17.32 \(\mu\)m, 35.84 \(\mu\)m respectively.

In order to find out the background arsenic of sand sample itself, leaching tests were performed. Coarse, medium and fine sand which had been weighed (3 grams) were put into Erlenmeyer flask, then added 300ml distilled water and shock 2h in the constant temperature oscillator (25 °C). After shocking, let stand for 24 hours, then supernatant is measured. The results showed that the leaching of arsenic from sediments is extremely small. The leaching amount from coarse sand is not detection, and the leaching amount from medium and fine sand is 0.26 \(\mu\)g/L and 1.81 \(\mu\)g/L respectively.

Experimental device

The test devices comprise static adsorption test devices and dynamic adsorption test devices.

(1) static adsorption test device

The static adsorption test device is a transparent cylindrical organic glass cylinder. In this experiment, water surface of organic glass cylinder should be maintained in a constant level. Based on the above consideration, the effective volume of test device is 14L, the total height is 102cm, effective height is 93cm, internal diameter 13.9cm, external diameter 14.8cm. Sedimentation cylinders are vertically placed with 9 sampling nozzles. The sampling outlets are arranged on the side wall of the glass cylinder. The fourth sampling nozzle is selected in this experiment which is 60cm height from the bottom.

The sampling outlets made of organic glass are perpendicular to the wall. Suspensoid is mixed with a agitator which has full of holes before experiment. The difference of upper and lower concentration should be not more than 1%, in order to ensure the initial sediment concentration is same in the vessel.

(2) Dynamic adsorption test device

The dynamic adsorption test device is a six combined agitator. A single agitator has 1L effective volume, 17.8cm high, 11cm external diameter, 10cm internal diameter, and the sampling outlet is 10.7cm high from the bottom.
Testing method and instrument
The arsenic of sediment could not leach easily in the slightly alkaline condition of the Yellow River. Selecting clarified water or centrifugal water as detection water sample is reasonable, which can meet the drinking, irrigation, fisheries, industrial water demand. Therefore clarified water is selected as detection water sample in this experiment, without acid and high temperature digestion.

Arsenic content in the experiment clarified water was determined by atomic fluorescence spectrometer (model: AFS-8220). The $R^2$ value of standard curve reaches 0.999.

DISCUSSION

Adsorption time
According to figure 1~3, when the concentration of sediment is $15 \text{kg/m}^3$~$25 \text{kg/m}^3$, adsorption and desorption of arsenic is active, the adsorption rate fluctuated slightly. With other sediment concentration, the sediment adsorption rate is relatively stable. It shows that the adsorption process of sediment on arsenic is very fast. And the adsorption can reached saturation within 5 minutes.

The sediment of the Yellow River stems from the Loess Plateau. It has higher Fe, Al, Cu and other metal compounds which are good adsorbents of arsenic. When adding arsenic standard solution into vessels, the physical and chemical interactions among the arsenic anion and metal cations are completed quickly. Arsenic pollutants which are adsorbed by sediments are not easy to be leached again. Therefore arsenic adsorption rate almost does not change with time after 5 minutes.
Sediment grading and concentration
When the sediment concentration is 1 kg/m$^3$, the adsorption rate is low. The adsorption rates of coarse, medium and fine sand were 19%, 11% and 5% respectively. With the increase of sediment concentration, adsorption rate rises steadily. When the sediment concentration is 200 kg/m$^3$, the adsorption rates of coarse, medium and fine sand were up to 97%, 97% and 87% respectively, exceeding 85%. Adsorption of arsenic by coarse sediment has two phases, as shown in figure 3. When the sand content is $\leq$15 kg/m$^3$, the adsorption rate is relatively low, below 40%. When the sediment concentration $\geq$20 kg/m$^3$, the adsorption rates are improved obviously, more than 70%. It shows that 15–20 kg/m$^3$ is a very important cut-off point. A tiny change of sediment concentration will cause a great change of adsorption rate during this area.

According to figure 4, sediment grading and sediment concentration could influence the arsenic amount of adsorption strongly. If sediment concentration is same, with the sand size is smaller the adsorption quantity is well increase. The rule of adsorption amount is fine sand > medium sand > coarse Sand. When the sediment concentration is same, the smaller particle has larger surface area, then it has more adsorption point and is apt to adsorption. If sediment gradation is same, with the sediment concentration increased the adsorption amount was increased. When the sediment concentration is 1-25 kg/m$^3$, the adsorption amount increases rapidly. But when the concentration is higher than 25 kg/m$^3$, concentration increased slowly with the increasing of adsorption of sediment. With the increase of sediment concentration, the adsorption amount of different sand showed a logarithmic growth equation, shown in Figure 4. The regression judgment coefficient $R^2$ was 0.9218, 0.9306 and 0.8434 respectively.

Flow state
The experiment shows that the adsorption rate is higher in hydrodynamic condition than in hydrostatic condition. The adsorption rate increased from 8.58% to 82.76% during the hydrostatic test condition, and adsorption rate increased from 15.54% to 96.07% during the hydrodynamic test condition, as shown in Fig.5. When the flow is...
turbulent state, arsenic pollutants and sediment can fully contact and adsorb more pollutants. By fitting the experimental data, a logarithmic growth trend of arsenic amount by sediment adsorption is obtained along with the increase of sediment concentration in the hydrostatic and hydrodynamic conditions. The coefficients $R^2$ of regression equations are 0.9633 and 0.9308 respectively. This conclusion do not match the statement, "sediment concentration and arsenic show linear positive correlation" which is presented by Wang Zhimin. The mainly cause is that Wang Zhimin experimented within low sediment concentration (below 70kg/m$^3$) and did not discount the high sediment concentration (e.g. 200 kg/m$^3$).

**CONCLUSION**

In this paper, adsorption properties of the Yellow River prototype sand on arsenic are studied in the hydrostatic and dynamic conditions. Some key factors on the sediment adsorption of arsenic pollution are studied systematically, such as contact time, sediment concentration, sediment grain size, flow state and etc.

The main results are as follows.

a. The adsorption of sediment on arsenic is quickly. It can reach the adsorption equilibrium in 5 minutes when the sediment concentration is below 200kg/m$^3$.

b. During the same concentration conditions, the rule of adsorption amount is fine sand > medium sand > coarse Sand.

c. A logarithmic growth trend of arsenic amount by sediment adsorption is obtained along with the increase of sediment concentration in the hydrostatic and hydrodynamic conditions.

d. 15~20kg/m$^3$ is a very important cut-off point in the adsorption by coarse sediment. A tiny change of sediment concentration will cause a great change of adsorption rate during this area.

e. The adsorption rate is higher in hydrodynamic condition than in hydrostatic condition.

**Fund project:** sediment laboratory of the ministry of water resources (2010002)

**REFERENCES**