



## Study on Arsenic (III) Sorption Behaviour by River Sediment

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Nat. Env. & Poll. Tech.  
Website: [www.neptjournal.com](http://www.neptjournal.com)

Received: 17-10-2013

Accepted: 25-11-2013

### Key Words:

Arsenic (III)  
River sediment  
Sorption  
pH  
Temperature

### ABSTRACT

The present study deals with sediment sorption of arsenic onto sediments from the middle Yellow River and major affecting factors (such as temperate, pH, particle size and sediment dose have been studied by isothermal sorption and single factor experiments. The results showed that sorption equilibrium time of each dose and particle size sediment was 5-10 min. expect  $1\text{kg/m}^3$ . When the sediment dose was  $1\text{kg/m}^3$ , the sorption equilibrium time was about 180min. The retention rate of As(III) increased with respect to sediment dose while the retention quality of per sediment decreased. As the sediment concentrations are the same, the smaller the particle size, the more the retention quality. The order for sorption As(III) was fine sediment>medium sediment>coarse sediment. When  $\text{pH}<7$ , the percentage of As (III) removal was higher compared to pH 7. A general increase was there in sorption with respect to pH above 7.0 for both the fractions of the sediment. It is evident that the pH for minimum uptake of As (III) is 7.0, and for maximum uptake is 9.0. At the same time, temperate as the main factor for sorption was also studied. The temperate experiments showed that the temperature is of significance to sorption. When temperatures between  $10\text{-}15^\circ\text{C}$ , the higher the temperature, the lower the removal rate. When temperatures between  $15\text{-}20^\circ\text{C}$ , the higher the temperature, the bigger the removal rate. After temperature greater than  $20^\circ\text{C}$ , temperature change effects on arsenic sorption rates do not remain obvious.

### INTRODUCTION

For many years, the annual average natural runoff of the Yellow River has been 58 billion  $\text{m}^3$ , carrying 1.6 billion tons of sediment. At Huayuankou Station, the sediment concentration in water is no more than  $2\text{ kg}\cdot\text{m}^{-3}$ , the whole 80% in a year after the operation of Xiaolangdi reservoir (Zeng Yong et al. 2006). Under water-sediment regulation, the sediment in the Xiaolangdi reservoir can be discharged with average sediment concentration at  $13.3\text{-}31.1\text{ kg/m}^3$  (Li & Sheng 2011).

Arsenic (As) is a well known water contaminant that causes toxicological and carcinogenic effects (Shipley et al. 2010). Recently, with the development of industry, arsenic contamination of groundwater has been reported in more than ten provinces and municipalities of China. (Ma & Tu 2011, Wang & Lin 2012). Mean values of As concentration in the Yellow River delta has been increased from  $13.07\text{mg/kg}$  in 1996 to  $40.75\text{ mg/kg}$  in 2007 (Bai & Xiao 2012). Arsenic as the first class carcinogen, in January 2006, the U.S.EPA lowered the maximum contaminant level (MCL) from 50 to  $10\text{ }\mu\text{g/L}$ . Many countries, including the USA, now face the dilemma of treating their drinking water

to achieve regulatory standards. Arsenic removal methods are needed because millions of people in Southeast Asia and 13 million people in the USA are exposed to arsenic concentration greater than  $10\text{ }\mu\text{g/L}$  in their drinking water (World Health Organization 2001). The Yellow River is the main drinking water source of Zhengzhou. The search for safe and effective ways to remove As from drinking water requires an ongoing international effort.

It is well known that sediment is a good adsorbent of drinking-water treatment residual, with large specific surface area. Sediment surface exists in a variety of activity substances, which have a strong surface conjugation with heavy metals (Xiong & Yang 2003, Yuan Hao et al. 2008, Wang Zhaoyin et al. 2007, Zhao Rong et al. 2003). Sorption phenomenon plays a major role in hazardous material reduction for water resources management and planning (Sun Jianhui et al. 2010). Many years of research by the Yellow River Conservancy Commission (YRCC) reveals that the water and sediment regulation of Xiaolangdi reservoir has played an important role on water quality of the lower reaches of the Yellow River (Yang Ziliang et al. 2010). Heavy metals could enter the sediment surface through different biogeochemical processes such as

deposition and precipitation onto the water-sediment interface (Li Xue et al. 2011). Therefore, the study of sediments and their sorptive properties can provide valuable information relating to the tolerance of the system to the added heavy metal load and may determine the fate and transport of pollutants in the aquatic environment. However, little information is available about sediment sorption on arsenic. We hypothesized that differences would also exist in the efficacy of sediment concentration and sediment grading to adsorb As from water. Also, the factors such as pH and temperature would influence As removal. Thus, the objectives of this study were (1) to compare the As removal efficacy and As sorption capacity by sediment concentration and sediment grading; (2) to understand the effect of pH and temperature on the As removal.

## MATERIALS AND METHODS

**Sorption experiments:** Freshly deposited sediments from shallow water near the bank of Yellow River at Huayuankou were collected in polyethylene bags and brought to the laboratory. Samples were taken from the upper 5 cm of the sediments. Different particle size fractions of the sediment were distributed for: the coarse, medium and fine sands. The coarse, medium and fine sediment size were respectively 35.84 $\mu\text{m}$ , 17.32 $\mu\text{m}$ , 10.02 $\mu\text{m}$ . The sediment was composed of 10%  $\text{CaCO}_3$  and 1% organic matter with pH of 7.9–8.30.

**Single factor effect experiments:** The dried fine sands were crushed by the pulverizer for 2–3 minutes and got through 500mesh, 325mesh, 200mesh and 125 mesh purpose points sample screen to obtain < 0.0375 mm, 0.0375–0.088 mm, 0.088–0.15 mm, 0.15–0.3 mm, 0.3–0.45 mm and 0.45–2 mm size sediment. The sands were baked for 6h at 105°C and cooled to the room temperature in dryer. This material was kept for the pH and temperature experiment.

The reaction vessel used in this study was a transparent container system. It is a 14 litre glass container with 108cm height. Atomic fluorescence spectrophotometer was used for determination of concentration of arsenic (III). Quantification of arsenic (III) was based upon calibration curves of standard solutions of arsenic (III) ion. The detection limit for arsenic (III) was 0.01 mg/L. The correlation coefficients were generally 0.9998. The Relative Standard Deviation of three replicate analyses was always below 1%. At the same time, four water samples were selected, which were set as four parallel samples respectively, to run the addition and recovery experiment. The results indicated that the recovery rate was in the range of 97.489%–105.303%, the accuracy of the method was good and met the accuracy requirement of the analysis method. An Orion-Ross combination glass electrode was used to measure the pH of the

solution. The glass electrode was calibrated at 25°C using 4, 7, and 10 pH buffers.

The As(III) removal from the water was calculated as % As(III) removal = 100%  $(C_0 - C_t)/C_0$  and the adsorptive uptake of As(III) by sediment (g/L) (mg/g), was calculated as

$$qt = (C_0 - C_t)V/W$$

Where,  $C_0$  is the initial As(III) concentration (mg/L),  $C_t$  is the As(III) concentration (mg/L) at any time, V is the volume of the solution (L) and W is the mass of the adsorbent (g).

## RESULTS AND DISCUSSION

**Sorption equilibrium time:** Sorption experiments were conducted on arsenic contaminated the Yellow River water at pH 7.70. The experiments were conducted at 25°C and at a pH of 8.00 $\pm$ 0.04 buffered with 0.01 M tris (hydroxymethyl) aminomethane (THAM) buffer. The pH adjustment of the solution was accomplished with either 1N NaOH or 6N  $\text{HNO}_3$ . Respectively, sorbent dose of 1 kg/m<sup>3</sup>, 5 kg/m<sup>3</sup>, 10 kg/m<sup>3</sup>, 15 kg/m<sup>3</sup>, 20 kg/m<sup>3</sup>, 25 kg/m<sup>3</sup>, 100 kg/m<sup>3</sup> and 200 kg/m<sup>3</sup> of coarse, medium and fine sediment concentration was prepared and activated with water for 24 hours. The solution was then added to the vessel for a fixed initial concentration of As(III) (0.2 mg/L). Typically, samples were collected at 5, 10, 15, 20, 25, 30, 60, 120, 180, 240, 300 and 360 minutes. Samples (10 mL) were taken from the vessel and filtered through a 0.45- $\mu\text{m}$  Nalgene SCFA filter. The water samples were taken in the fourth outlet in the distance 60 cm to the bottom. After filtration, the supernatant fluid was measured to test the water phase As concentration and calculated the sorption of arsenic of per unit weight of the sediment. The pH was checked at the end of each experiment to confirm that negligible pH change had occurred, less than about  $\pm$  0.05. The solution pH was generally 8.00 $\pm$ 0.04 measured at the end of the 1-h experiment.

The variation of arsenic adsorptive capacity of unit mass of coarse (Fig. 1) medium (Fig. 2) fine sediment (Fig. 3) with time showed that when the concentration value of sediments is 1kg/m<sup>3</sup>, the arsenic sorption quantity to per unit of mass of the coarse, medium and fine sediment, all presented a clear tendency of waving increase, but all of them could achieve a dynamic sorption equilibrium after 180min, and the sorption quantity is stable, being in a range from 35 to 45mg/kg. When the concentration value of sediments is 5, 10, 15, 20 and 25mg/kg, the arsenic sorption quantity to per unit of mass of the coarse, medium and fine sediment, all reached an equilibrium after 5 minutes, and the sorption quantity is approximately stable, being in a range from 5 to 12mg/kg. The asymptotic nature of the plot indicates that there is no appreciable change in the remaining concentration after 5 minutes. After that, with the increasing

of time, the sorption quantity is approximately stable, the sorption is in a dynamic equilibrium; the arsenic sorption quantity to per unit of mass of the coarse, medium and fine sediment decreased with the increase of sediment concentration.

**Holding rules of As (III) sorption by different sediment concentrations:** The experiments were conducted at 25°C and at a pH of 8.00±0.04. The pH adjustment of the solution was accomplished with either 1N NaOH or 6N HNO<sub>3</sub>. Respectively, sorbent dose of 1, 5, 10, 15, 20, 25, 100 and 200 kg/m<sup>3</sup> of coarse sediment, medium and fine sediment concentration value was prepared and activated with water for 24 hours. The solution was then added to the vessel for a fixed initial concentration of As (III) (0.2mg/L). Typically, samples were collected at the equilibrium time.

The effect of percentage sorption and per unit weight of sorbent Fig. 4(a,b) showed that the sorption of As(III) per unit weight of sorbent decreases with increasing the concentration of sediments. On the other hand, percent sorption increases from 93.5 to 97.5% for the fine sediment with increasing the concentration of sediments from 0.5 to 2.5 g/L. Accordingly, percent sorption increases from 93.5% to 97.5% for the coarse sediment with increasing the concentration of sediments from 0.5 to 2.5 g/L.

In view of the concentrations of the different elements measured in the sediment, it is clear that the arsenic physical (fine sand > medium sand > coarse sand) sorption to sediments is related to specific surface area. The finer the particles are, the larger their specific surface areas are, the more sorption sites they have, and the larger the sorption quantity is. But the chemical sorption is related to the active ingredients contained by the sediment particles, generally, finer particles contain more active ingredients, and sorption capacity is stronger; coarser particles contain more original minerals, and sorption capacity is weaker. The sorption quantity decreases with the increase of concentration value of sediments. The increase of sand quantity may induce the decrease of specific surface areas of sorbents, and the sorption quantity decreases with specific surface areas do.

**Effect of pH on As (III) sorption by sediment:** Sorption experiments were conducted in a series of Erlenmeyer flasks of 500mL capacity covered with a teflon sheet to prevent contamination for a fixed initial concentration of As (III) (0.1 mg/L) and sorbent dose of 5, 10, 15, 20, 25 kg/m<sup>3</sup> at a particle size of <0.025mm. Experimental pH were designed at 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0 and 9.5. At the same time, experiments were conducted with the absence of arsenic standard solution as a contrast. At the temperature of 30°C, the solution was shaken for 15 min at 200 RPM. Then, the samples were taken from the vessel and filtered through the

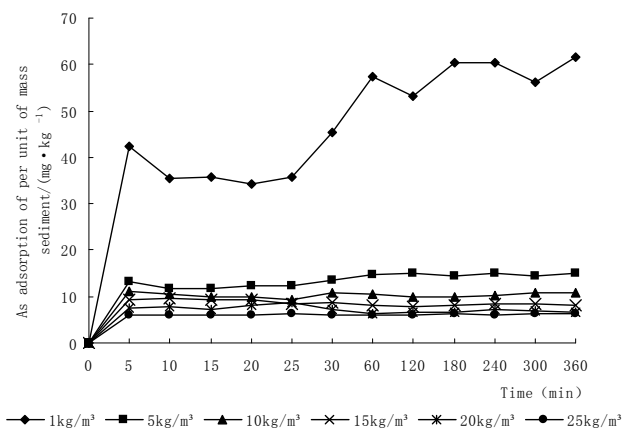


Fig. 1: Variation of arsenic adsorptive capacity of unit mass of coarse sediment with time.

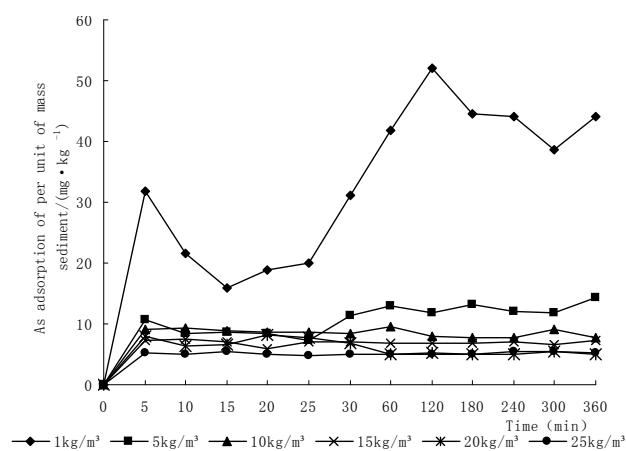


Fig. 2: Variation of arsenic adsorptive capacity of unit mass of medium sediment with time.

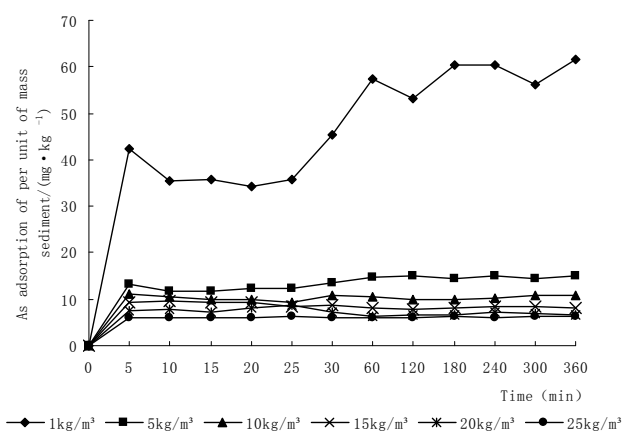


Fig. 3: Variation of arsenic adsorptive capacity of unit mass of fine sediment with time.

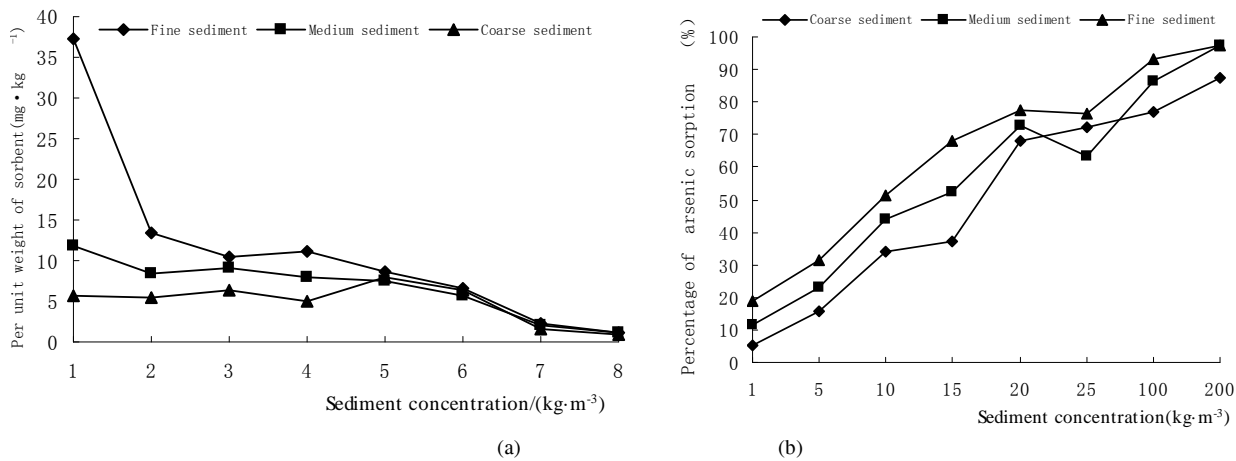


Fig. 4 Variation of arsenic sorption rate with sediment concentration

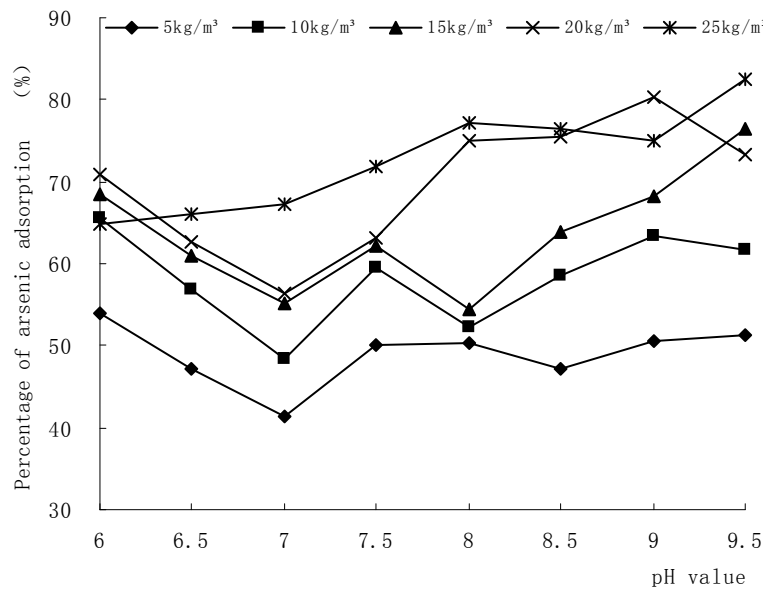


Fig. 5: The influence on the sorption of arsenic under different pH in 15min.

0.45- $\mu$ m filter. Acid was added to the solution for reserve. Arsenic concentrations were measured by ASF.

From the effects of pH on the sorption of As(III) (Fig. 5), it is evident that the pH for maximum uptake of As(III) is 9.0 and the minimum uptake is 7.0. Further, it is apparent that the sorption of As(III) rises from 46.66% at pH 7.0 to 87.22% at pH 9.0 in the case of sorbent dose of 20 kg/m<sup>3</sup>. The pH values in the range of 6~7 were disadvantage to the sorption of the sediment arsenic (III) pollutants, the removal rate was low. Minimum 46.66% of arsenic was removed at pH 7. The growth of pH between 7 and 7.5 was favourable for the sorption of the arsenic, when the pH of the samples were be-

tween 7.5 and 8, sorption showed no appreciable change, the removal rate was more than 60%, when the pH>8, the sorption effect of the arsenic (III) pollutant was good, the highest can be 87.22%. This high As(V) sorption potential could be related to the fact that, at alkaline pH, the predominant As(V) species is HAsO<sub>4</sub><sup>2-</sup>, which could bind to the surface of sediment by means of inner sphere complexes with the octahedral As.

**Effect of temperate on As(III) sorption by sediment:** Sorption experiments were conducted in a series of Erlenmeyer flasks of 500 mL capacity covered with a teflon sheet to prevent contamination for a fixed initial concentration of

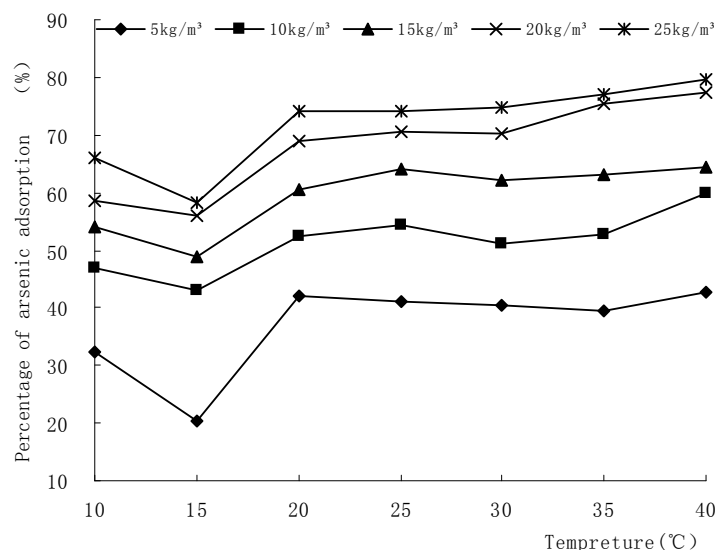


Fig. 6: The influence on the sorption of arsenic under different temperature in 15min.

As(III) (0.1 mg/L) and sorbent dose of 5, 10, 15, 20 and 25 kg/m<sup>3</sup> at a particle size of <0.025mm. Experimental temperatures were designed at 10, 15, 20, 25, 30, 35 and 40°C. At the same time, experiments were conducted with the absence of arsenic standard solution as a contrast. The solution was shaken for 15 min at 250 RPM. Then, the samples were taken from the vessel and filtered through the 0.45- $\mu$ m filter. Acid was added to the solution for reserve. Arsenic concentrations were measured by ASF.

The effect of temperature on the sorption of sediment (Fig. 6) systematically demonstrated the effect that in the temperature at 10°C different concentrations of sediment removing rate was between 32.38% and 65.98%, which was relatively low; when temperature rises from 10 to 15°C, the removing rate decreased with it and reached the lowest point at 15°C, in this condition, just 20.38%~58.25% could be adsorbed on; whereas temperature is between 15~20°C, the removing rate increased faster with the rise of temperature and could reach 42.01~74.19%, when temperature is higher than 20°C, the removing rate is approximately stable at the level of 20°C. This shows that the influence of temperature on arsenic sorption to sediments followed a same law: when being in a range from 10~15°C, the rise of temperature goes against the arsenic sorption, when being in a range from 15~20°C, the rise of temperature contributes to the arsenic sorption, when temperature is higher than 20°C, the change of temperature has no obvious influence on the removing rate of arsenic.

## CONCLUSION

These results demonstrate the ability of the sediment to

remove As (III) from potable water. For coarse sand, medium sand and fine sand whose concentration values are 1kg/m<sup>3</sup>, the arsenic sorption quantity to per unit of mass of medium sand presented a clear tendency of waving increase and could reach a dynamic equilibrium in 180 minutes; for coarse sand, medium sand and fine sand who have different concentration values, 5-10minutes would be taken to achieve a dynamic sorption equilibrium.

1. Accompanied by the rise of sediments concentration value, the rate of arsenic adsorbed to coarse sand, medium sand and fine sand increased, but the quantity of arsenic adsorbed to per unit of mass sediments decreased. When the sediments concentration values are same, the absorption rate increased with the decrease of sediments gradation, the smaller the gradation is, the higher the rate of arsenic absorption to equivalent sediments is, the larger the sorption quantity is. It was presented as a law that micro sand > medium sand > coarse sand.
2. A pH value between 6 and 7 is against the pollutant arsenic (III) sorption to sediments and has a low removing rate, the lowest removing rate is when the pH value is 7, then after that, the sorption rate increased with pH value. When pH value is higher than 8, the effect of arsenic (III) sorption to sediments is satisfactory.
3. In different sampling time, the influence of temperature on arsenic sorption to sediments has a same law, presented as: when temperature ranging from 10 to 15°C, the increment is against the sorption, when temperature range from 15 to 20°C, the increment promote the sorption, and when temperature is higher than 20°C, change

of temperature has no obvious influence on the removing rate of arsenic.

It may be concluded from the study that though As(III) has more affinity for the fine fraction of the sediment, the sorption data suggests that the pH of the solution is the most important parameter in the control of metal pollution. The percentage sorption increases with increasing sorbent doses.

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