Original Research Paper

Influence of Coexistent Ions Fe³⁺ and Mn²⁺ on Arsenic (III) Adsorption Behaviour onto River Sediment

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ABSTRACT

To understand the influencing factors of the sediment adsorption of As^{3+}, prototype sand of the Yellow River was taken as the material. The effects of sediment adsorption saturation time and adsorption regularities were investigated when coexisting ions Fe^{3+} and Mn^{2+} existed. The results show that: (1) when there was only As^{3+} existing alone, the saturation time was 60 min; when Fe^{3+} and Mn^{2+} were added, the saturation time was 90 min; (2) when Fe^{3+} existed, the sediment adsorption laws of As^{3+} were as follows: during the initial period, with the increasing concentration of Fe^{3+}, the adsorption decreased; when the concentration of Fe^{3+} was more than 0.4mg/L, the adsorption capacity increased with the increasing concentration of Fe^{3+}; when there was Mn^{2+} existing, the regulation also showed that it initially decreased slightly and then increased, i.e., when Mn^{2+} was less than 1.0mg/L, the adsorption capacity decreased with the increasing concentration of Mn^{2+}; when Mn^{2+} was higher than 1.0mg/L, the adsorption capacity increased with the increasing concentration of Mn^{2+}; when Fe^{3+} and Mn^{2+} coexisted, the sediment adsorption of As^{3+} increased with the increasing concentration of the coexisting ions; (3) when the coexisting ion concentration was 0.2-0.4mg/L, the removal rate of Fe^{3+} was less than that of Mn^{2+}, and also less than that of the coexistence of Fe^{3+} and Mn^{2+}. When the concentration of coexistent ions is less than 0.2 or more than 0.4 mg/L, the removal rate of Mn^{2+} was less than Fe^{3+}, and also less than that of the coexistence of Fe^{3+} and Mn^{2+}.

INTRODUCTION

The Yellow River is an important drinking water source for the north and northwest China, and it is also the rare sediment-laden river in the world. Since the Xiaolangdi reservoir was operated, the average sediment concentration of the Yellow River is 13.3~31.1kg/m³ in the non-regulation period (Li & Sheng 2011, Li 2014). The sediment particles, whose surface exists in a variety of activity substances, have a large specific surface area, and a strong surface conjugation with heavy metals (Yuan et al. 2008, Wang et al. 2007, Huang et al. 1994, Zhao et al. 2003). Studies have shown that heavy metal pollution of the Yellow River, especially arsenic pollution, is more prominent (Bai & Xiao 2012, Yang et al. 2010, Sun et al. 2010). Heavy metal pollution in water and sediment environment has been concerned with a lot of academics all the time (Liu et al. 2007, Ma 2011). The scholars at home and abroad, mainly deal with sediment sorption concerning heavy metals from water, focusing Cu, Cd, Pb and Cr etc. (Xia et al. 2011, Xu et al. 2009, Zhang et al. 2011, Natalia et al. 2012, Shipley et al. 2010, Achour et al. 2011, Jin et al. 2009), however, for the absorption of As contaminant in river sediment, little attention has been paid (He & Li 2004, Huang & Wan 1995). China, America and EU have a drinking water standard that requires arsenic concentration from 0.01 up to 0.05mg/L (GB5749-2006). The new drinking water standards further strengthen the urgency of arsenic wastewater treatment.

In summary, this paper investigates the sediment adsorption capacity of As and influencing factors of Huayuankou section of the Yellow River and conducts a study on the regularities that coexisting ions Fe^{3+} and Mn^{2+} have an effect on As sorption by different concentration sediment, which provides the scientific basis for the transportation of As contaminant in heavily slit-carrying river and harnessing water sources.

MATERIALS AND METHODS

Experimental Materials

The experimental materials are sediments taken from shallow water near the bank of the Yellow River at Huayuankou during the process of natural air drying. The dried sands were crushed by the pulverizer in 2~3 minutes and got through 325 mesh sample sieve to obtain 0.0375~0.088mm size sediment. The sands were baked for 6 hours in 105°C and cooled to the room temperature in a dryer. This material was reserved for the pH and temperature experiment. In order to prevent the test interference arising from the arsenic pollutants, which is original in sediment, the sediment which is processed and soaked was used to conduct the blank parallel determination in order to take out the blank and remove the interference.

Determination Method

Atomic fluorescence spectrophotometer (model 8220) was used to determine the concentration of arsenic (III). Quantification of arsenic (III) was based upon the calibration curves of standard solutions of arsenic (III) ion. The equation of calibration curve was $y = 44.268x\text{-}33.533$, and the detection limit of arsenic (III) was 0.01mg/L. The correlation coefficients were approximately 0.9998. The relative standard deviation of the three replicates was always below 1%. At the same time, four water samples were selected, which were set for four parallel samples respectively in order to run the addition and recovery experiment. The results indicated that the recovery rate was in the range of 97.489% to 105.303%. The accuracy of the method was good and satisfied the accuracy requirement of the analysis method.

Experiment Scheme

Experiment scheme of the effect of adsorption equilibrium time of coexistent ions: To make sure the arsenic solution's adsorption equilibrium time of arsenic, arsenic+Fe^{3+} and arsenic+Fe^{3+}+Mn^{2+}, the experiments were conducted under the condition of 25°C, pH of 8.00±0.04, vibration velocity of 150r/min and size of sediment 0.0375~0.088mm. A sorbent dose of 5kg/m³, 10kg/m³, 15kg/m³, 20kg/m³ and 25kg/m³ of sediment concentration was prepared, respectively. Typically, samples were collected at 5, 10, 15, 30, 45, 60, 90, 120 minutes. Experiment scheme is given in Table 1.

Experiment scheme of the effect of arsenic adsorption from sediment on coexistent ions: Arsenic's adsorption equilibrium time was 90 minutes, which can be obtained under the above experimental conditions. The study on the effect of arsenic adsorption was conducted at the equilibrium time of 90 minutes, under four conditions of arsenic, arsenic+Fe^{3+}, arsenic+Mn^{2+} and arsenic+Fe^{3+}+Mn^{2+} and at sediment concentration of 5kg/m³, 10kg/m³, 15kg/m³, 20kg/m³ and 25kg/m³, respectively. Experiment scheme is given in Table 2.

RESULTS AND DISCUSSION

The Influence of Adsorption Equilibrium Time on Coexistent Ions

The arsenic removal rate which is corresponding to five sediment concentrations for different sampling times of arsenic, arsenic and Fe^{3+}, arsenic and Mn^{2+}, arsenic+Fe^{3+}+ Mn^{2+} solution as per above mentioned experimental scheme was plotted and different ion concentrations of five sediment concentrations of arsenic removal rate curve were obtained and shown in Figs. 1, 2, 3, 4, respectively.

The plot in Fig. 1 indicated that the percentage of arsenic adsorption did not appreciably change with the change in time about 5 minutes to 10 minutes. This instable As sorption potential could be related to the fact that the reaction which was in an adaptation period was just beginning. When the time rose from 10 to 60 minutes, the percentage of arsenic adsorption increased with it at different sediment concentrations. Whereas during 60 to 120 minutes, the arsenic adsorption rate was approximately stable. This result showed that arsenic adsorption equilibrium time from sediment was 60 minutes.

From the effects of coexistent ions on the sorption of As(III) (Figs. 2, 3, 4), it was evident that the percentage of arsenic adsorption did not appreciably change in 5 to 15 minutes. But it presented a clear tendency towards increasing during 15 to 90 minutes at different sediment concentrations. After that, when the time was about 90 to 120 minutes, the arsenic sorption quantity was approximately stable; all of them could achieve sorption equilibrium at different sediment concentrations respectively. These results demonstrated that arsenic adsorption equilibrium time of each dose from sediment was all 90 minutes under the conditions of arsenic+Fe^{3+}, arsenic+Mn^{2+} and arsenic+Fe^{3+}+Mn^{2+}.

The Influence of Arsenic Sorption by Sediment on Coexistent Ions

The influence of arsenic sorption by sediment in the presence of Fe^{3+}: Fe^{3+} was added to water samples in the known

Table 1: Experiment scheme of determination of adsorption equilibrium time

Arsenic concentration (mg/L)	0.1	0.1	0.1	0.1
Coexistent ions concentration (mg/L)		$Fe^{3+} = 0.5$	$Mn^{2+} = 0.5$	$Fe^{3+} = 0.5 Mn^{2+} = 0.5$

Table 2: Experiment scheme of the influence on the sediment adsorption of arsenic when Fe^{3+} and Mn^{2+} exist.

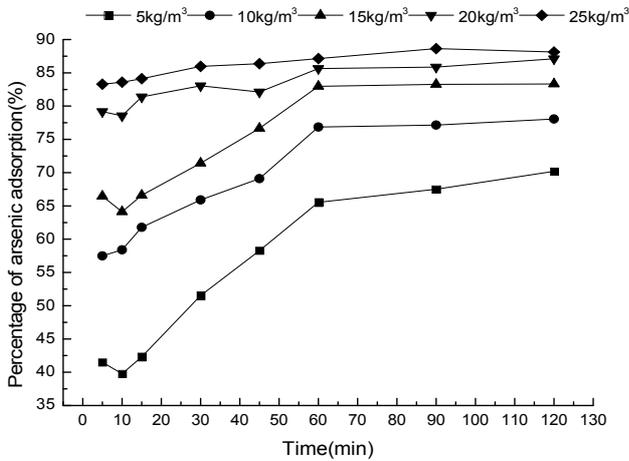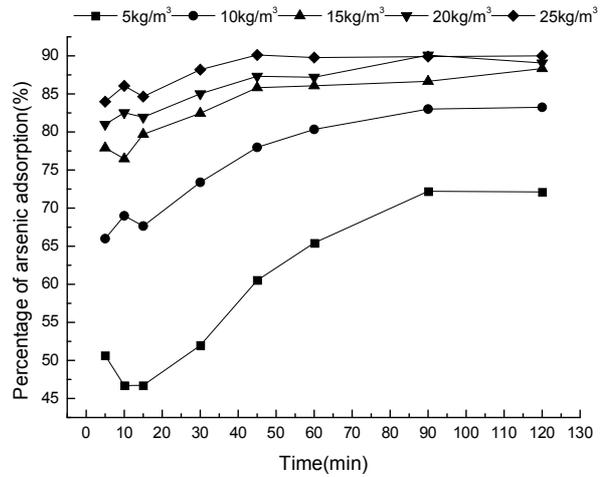| Experiment conditions	As, Fe^{3+}	As, Mn^{2+}	As, Fe^{3+}, Mn^{2+}
Fe^{3+} concentration (mg/L)	0.1, 0.2, 0.3, 0.4, 1.0, 1.5, 2.0	0	0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5
Mn^{2+} concentration (mg/L)	0	0.1, 0.2, 0.3, 0.4, 1.0, 1.5, 2.0	0.1, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5

Fig. 1: Arsenic is 0.1mg/L.

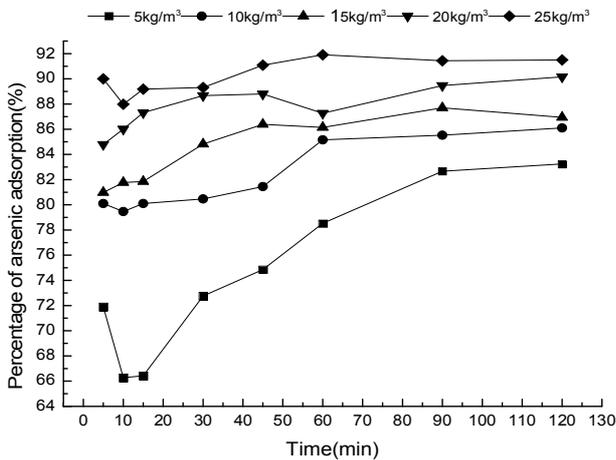Fig. 3: Arsenic is 0.1mg/L and Mn²⁺ is 0.5mg/L.

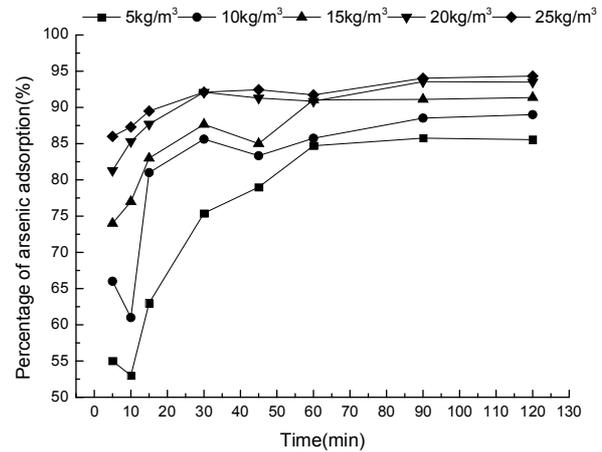Fig. 2: Arsenic is 0.1mg/L and the Fe³⁺ is 0.5mg/L.

Fig. 4: Arsenic is 0.1mg/L, Fe³⁺ and Mn²⁺ are 0.5mg/L.

experimental conditions. Fe^{3+} concentration of 0.1, 0.2, 0.3, 0.4, 1.0 and 2.0mg/L, respectively. The contents of arsenic before and after adsorbing were detected, and the percentage of As adsorption was calculated. Percentage of As adsorption change curve of different sediment concentrations with the change in Fe^{3+} concentration is exhibited in Fig. 5.

Fig. 5 showed that the sorption of As(III) removing rate decreased initially and then increased with the increasing concentration value of Fe^{3+} under the same sediment concentration. The sorption of As(III) reduced from 65.88% to 63.36% and then rose to 85.72% in the case of sorbent dose of 5kg/m³. When the concentration value of sediments of 10, 15, 20, 25kg/m³ followed the same law, further at the concentration value of sediments of 5, 20, 25kg/m³, the removing rate reached the lowest point at 0.4mg/L, whereas the lowest point at 0.3mg/L in the case of sorbent dose of 10

and 15kg/m³. This was due to the low concentration of Fe^{3+}, the condition where water pH value was equal to 8 is weakly alkaline, a small amount of ferric hydroxide precipitation formed and was allowed to settle, being coupled with the competitive adsorption of Fe^{3+} ions caused by a low concentration of Fe^{3+}. As the Fe^{3+} concentration increases, the removal rate of As falls; then sudden increase in the Fe^{3+} concentration to more than double of the original value, Fe^{3+} hydrolysis generated a large amount of iron hydroxide adsorbing the heavy metal As, which results in increased rate of arsenic removal.

The influence of arsenic sorption by sediment on the presence of Mn²⁺: Following the procedures in the above section, the Fe^{3+} standard solution as the standard Mn^{2+} solution with the other conditions unchanged was replaced, and the experiment was finished. When the sampling time is 90
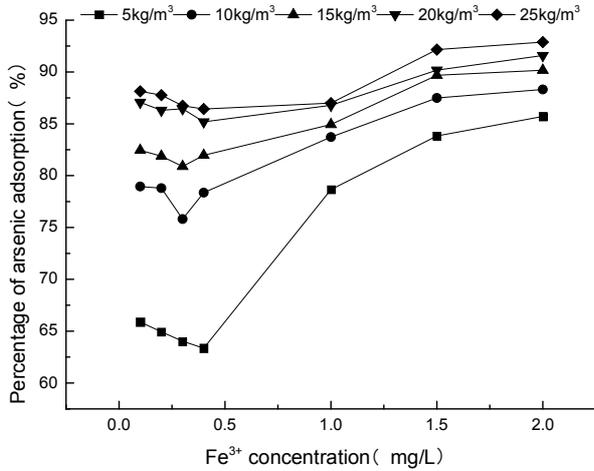
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Fig. 5: The arsenic removal rate changes with Fe³⁺concentration under different sediment concentrations.

Fig. 7: The arsenic removal rate changes with Fe^{3+} and Mn^{2+} concentration under different sediment concentrations when the sampling time is 90mins.

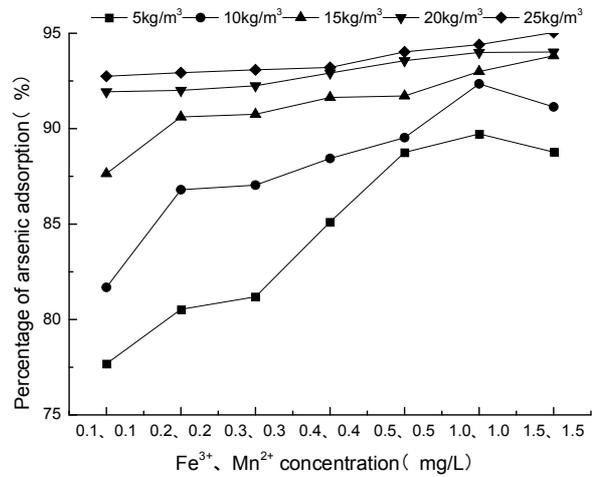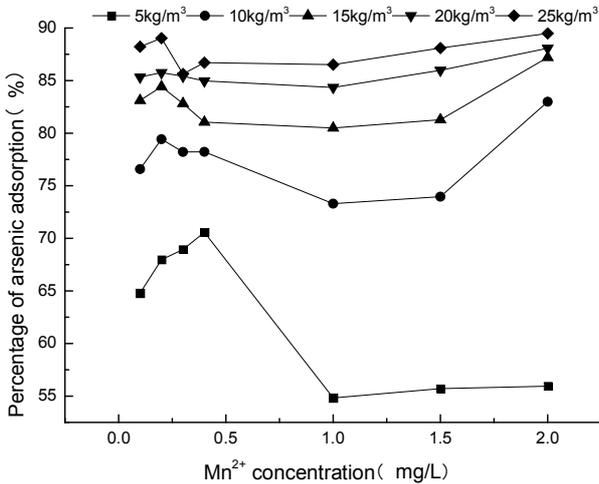Fig. 6: The arsenic removal rate changes with Mn^{2+} concentration under different sediment concentrations when the sampling time is 90min.
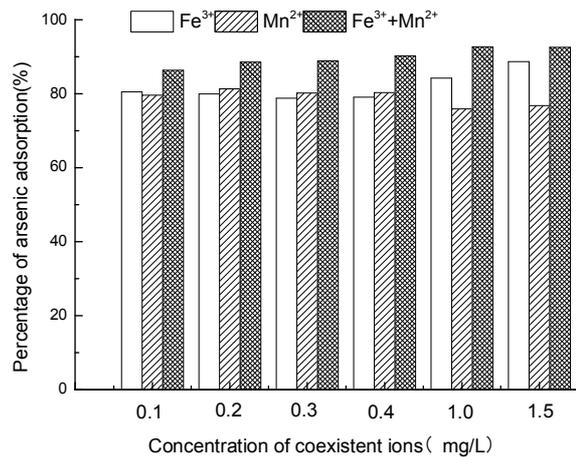

Fig. 8: When sediment concentration is 15kg/m³, the variation of arsenic removal rate along with the concentration of coexistent ions.

minutes, the arsenic removal rates in different sediment concentrations changed with Fe^{3+} concentration curve, as shown in Fig. 6.

Fig. 6 systematically demonstrates that the As(III) removing rate increased initially, then decreased and finally increased again with the increasing concentration of Mn^{2+}. Furthermore, it was apparent that the sorption of As(III) rose from 64.8% when Mn^{2+} was 0.1mg/L to 70.6% when Mn^{2+} was 0.4mg/L, then decreased to 54.8% when Mn^{2+} was 1.0mg/L, increased to 55.9% when Mn^{2+} was 2.0mg/L in the case of sorbent dose of 5kg/m³ in the end. The influence of Mn^{2+} on the arsenic sorption at the concentration value of sediments of 10, 15, 20 and 25 kg/m³ followed the same law: when Mn^{2+} ranged from 0.1 to 0.2mg/L, arsenic sorption

increased; when Mn^{2+} ranged from 0.2 to 1.0mg/L, arsenic sorption decreased; when Mn^{2+} ranged from 1.0 to 2.0mg/L, arsenic sorption increased. After Mn^{2+} was added in the experiment water samples, the concentration of Mn^{2+} increased in water samples, and there was a stage where it firstly decreased and then increased, and the turning point appeared when the concentration of Mn^{2+} was 1.0mg/L. The reason was that its hydrolysis is of smaller intensity; when the concentration of Mn^{2+} was low, its hydrolytic strength was weaker; when the concentration of Mn^{2+} was less than 1.0 mg/L, Mn^{2+} generated less manganese hydroxide, and the hydrogen ions produced by hydrolysis reduced the pH value of water. It is assumed that the water sample is neutral, the conclusion is based on the effect of pH on sediment adsorp-

tion of As that when the concentration of Mn^{2+} increases, the acidity is strengthened and the removal rate of As decreases; when the concentration of Mn^{2+} was higher than 1.0mg/L, the hydrolysis was full, and massive production of the hydroxide of manganese adsorbed the arsenic as one kind of new absorbent, with the increase in Mn^{2+} concentration. If the amount of adsorbent increases, then the removal of arsenic will increase.

The influence of arsenic sorption by sediment on the presence of Fe^{3+} and Mn^{2+}: The experiment was conducted according to the experimental protocol, so as to obtain the change curves of arsenic removal rates in different sediment concentrations with Fe^{3+} and Mn^{2+} concentration and is shown in Fig. 7.

From the effects of Fe^{3+} and Mn^{2+} on the sorption of As(III), it was evident that the percentage of arsenic adsorption increased with the increase in the concentration value of Fe^{3+} and Mn^{2+}, only at the concentration value of sediments of 5, 10kg/m^3 of Fe^{3+} and Mn^{2+} 1.5mg/L, the removing rate of As(III) declines slightly. This is due to the fact that when Fe^{3+} and Mn^{2+} are hydrolysed into hydroxides as the new adsorbent, except sediment, and it can absorb large amount of arsenic. When the concentration of Fe^{3+} and Mn^{2+} increases, the production of adsorbent increases, then the water removal rate of arsenic also increases.

The Variation of Arsenic Removal Rate Along With the Concentration of Coexistent Ions

To further explore the effect of Fe^{3+} and Mn^{2+} on sediment adsorption of arsenic, the sediment concentration of 15kg/m^3 was selected, the sampling time was 90 minutes, the Fe^{3+} standard solution, the Mn^{2+} standard solution and the Fe^{3+} + Mn^{2+} standard solution were added in the same concentration water sample and compared with the removal rate. The variation of arsenic removal rate along with the coexistent ion concentration was obtained and is shown in Fig. 8.

It can be seen from Fig. 8, when the concentration of coexistent ion is constant, by adding Fe^{3+}, Mn^{2+} and adding Fe^{3+} and Mn^{2+} at the same time, the effects of arsenic on the removal rate are not the same. When the coexistent ion concentration is 0.2 to 0.4mg/L, the removal rate of Fe^{3+} is less than Mn^{2+}, and less than that of the coexistence of Fe^{3+} and Mn^{2+}. When the concentration of coexistent ions is less than 0.2 or greater than 0.4 mg/L, the removal rate of Mn^{2+} is less than Fe^{3+}, and less than that of the coexistence of Fe^{3+} and Mn^{2+}. This is because under the condition of adding these two ions, the amount of formed absorbent is higher than that of adding one kind of ion alone. The amount of adsorbent is higher, and the removal rate of arsenic is higher. When the concentration of coexistent ion is larger or smaller, the

removal rate of arsenic with adding Fe^{3+} is higher than Mn^{2+}. The reason is that the Fe^{3+} hydrolysis intensity is higher than Mn^{2+}. The production of iron hydroxide is greater than the manganese, large concentrations of arsenic adsorption, and higher removal efficiency; when the coexistent ion concentration is 0.2 to 0.4mg/L, the removal rate of arsenic Mn^{2+} is higher than Fe^{3+} in the water sample. It may be due to the manganese hydroxide adsorption arsenic whose ability is better than the iron hydroxide.

CONCLUSION

To explore the regularities that coexistence of ions Fe^{3+} and Mn^{2+} have an effect on As sorption by different concentration sediment, firstly, arsenic solution adsorption equilibrium time was confirmed through experiments on the conditions of arsenic, arsenic+Mn^{2+}, arsenic+Fe^{3+} and arsenic+Fe^{3+}+ Mn^{2+}. The results demonstrate that:

- The adsorption equilibrium time of arsenic was 60 minutes, when only arsenic was in the solution. At the same time, arsenic adsorption equilibrium time from sediment was all 90 minutes on the conditions of arsenic+Fe^{3+}, arsenic+Mn^{2+} and arsenic+Fe^{3+}+Mn^{2+}.

- As (III) removal rate increased initially, then decreased and finally increased again with the increase of the concentration value of Mn^{2+} at the sample time of 90 minutes.

- The sorption of As (III) removing rate decreased initially and then increased with the increase of the concentration of Fe^{3+} under the same sediment concentration.

- Accompanied by the rise of concentration of Fe^{3+} and Mn^{2+}, the rate of arsenic adsorption increased. But at the concentration value of sediments of 5, 10kg/m^3 of Fe^{3+} and Mn^{2+} 1.5mg/L, As(III) removing rate slightly decreased.

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REFERENCES

Achour, Terbouche, Ramdane-Terbouche, C. A., Hauchard, D. and Djebbar, S. 2011. Evaluation of adsorption capacities of humic acids extracted from Algerian soil on polyaniline for application to remove pollutants such as Cd (II), Zn (II) and Ni (II) and characterization with cavity microelectrode. Journal of Environmental Sciences, 23(7): 1095-1103.

Bai, J. H. and Xiao, R. 2012. Arsenic and heavy metal pollution in wetland soils from tidal freshwater and salt marshes before and after the flow-sediment regulation regime in the Yellow River delta. China Journal of Hydrology, 450: 244-253.

GB5749-2006, Drinking Water Sanitary Standard.

Huang, Sui-liang, Wan, Zhao-hui and Wang and Lan-xiang 1994. Studies on heavy metal pollutant adsorption by sediment in the laboratorial static experiments. Advances in Water Science, 5(4): 271-279.

Huang, Sui-liang and Wan, Zhao-hui 1995. Study on the effects of concentrations of heavy metals in sediment and initially in water phase on their absorption. Advances in Water Science, 15(1): 66-76.

He, Yong and Li, Yi-tian. 2004. Study of the model of heavy metal pollutants transport. Advances in Water Science, 15(5): 576-583.

Heather, J., Shipley, Sujin, Yean, Amy, T. Kan and Tomson, M. B. 2010. A sorption kinetics model for arsenic adsorption to magnetite nanoparticles. Environ. Sci. Pollut. Res., 17: 1053-1062.

Jin, Sheng-sheng, He, Ji-zheng, Zheng, Yuan-ming and Zhang, L. M. 2009. Adsorption of heavy metals by biogenic manganese oxides. Acta Scientiae Circumstantiae, 29(1): 132-139.

Liu, Cheng, Wang, Zhao-yin, Huang and Wen-dian et al. 2007. Water and sediment pollution at river mouths of Haihe River basin. Journal of Hydraulic Engineering, 38(8): 920-925.

Ma, L. and Tu, S.X. 2011. Removal of arsenic from aqueous solution by two types of nano TiO_2 crystals. Environmental Chemistry Letters, 9: 465-472.

Li, G. Y. and Sheng, L X. 2011. Model of water-sediment regulation in Yellow River and its effect. Science China Technological Sciences, 54(4): 924-930.

Li, Hai-hua, Meng, Rui-jing, Huang Qiang and Qiu Lin. 2014. Study on arsenic (b™) sorption behavior by river sediment. Nature Environment and Pollution Technology, 13(2): 1-6.

Natalia, Seco-Reigosa, Susana, Peña-Rodríguez, Juan, Carlos Nóvoa-Muñoz, Arias-Estévez, M., Fernández-Sanjurjo, M. J., Álvarez-Rodríguez, E., & Núñez-Delgado, A. 2012. Arsenic, chromium and mercury removal using mussel shell ash or a sludge/ashes waste mixture. Environ. Sci. Pollut. Res., 20(4): 2670-2678.

Sun, Jian-hui, Chai, Yan and Wang, Guo-liang 2010. Review on effects of sediment on the water quality of the Yellow River. Journal of Sediment Research, 1(1): 72-77.

Wang, Zao-yin, Wang, Wen-long and Tian and Shi-min 2007. Mineral composition and distribution of the sediment in the Yellow River basin. Journal of Sediment Research, 10(5): 1-8.

Xu, R. K., Wang, Y. and Tiwari, D. and Houyan, Wang 2009. Effect of ionic strength on adsorption of As(III) and As(V) on variable charge soils. Journal of Environmental Sciences, (21): 927-932.

Xia, Jian-xin, Yu, Liang and Ren, Hua-tang 2011. Analysis of the effect factor when using nature sand to remove heavy mental from water body. Journal of Basic Science and Engineering, S1: 1-4.

Yuan, H., Wang, Y. C., Gu, S. Y., Lu, J., Zhou, H. D. and Wan, X. H. 2008. Chemical forms and pollution characteristics of heavy metals in Yellow River sediments. Chinese Journal of Ecology, 27(11): 1966-1971.

Yang, Zi-liang, Yue, Bo and Yan, Da-hai 2010. Leaching characteristic and environmental risk analysis of arsenic in resource recovery products using arsenic-containing waste. Research of Environmental Sciences, 23(3): 293-297.

Zhao, Rong, Ni, Jin-ren, Sun, Wei-ling and Zhang, L. 2003. Copper sorption by sediments from the middle Yellow River. Acta Scientiae Circumstantiae, 23(4): 441-446.

Zhang, H., Luo, Y., Song, J., Zhang, H., Xia, J. and Zhao, Q. 2011. Predicting As, Cd and Pb uptake by rice and vegetables using field data from China. Journal of Environmental Sciences, 23(1): 70-78.