



Adsorption Performance of Polyvinyl Alcohol onto Sediments of Yellow River

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ABSTRACT

In this study, adsorption performance of polyvinyl alcohol (PVA) onto sediments of Yellow River was systematically investigated. Results showed that the sediments could effectively adsorb PVA so as to decrease its dissolved amount in the natural water. Kinetic experiments indicated that a rather rapid uptake of PVA occurred and the removal percentage could reach 60.2% by 24 h. Non-linear fitting method succeeded in discerning that both Toth and Koble-Corrigan models best fitted the experimental data, indicating the possible mono layer and physical adsorption of PVA on the sediments. Langmuir isotherm model also simulated the adsorption isotherm data better, and at 288 K, the maximum adsorption capacity of 356.56 mg/g for PVA uptake was obtained by Langmuir isotherm model. Both, the increase of temperature and solution pH values, would reduce the uptake of PVA. At the same time, the co-existing anions could inhibit the uptake of PVA to some extent. This research would be useful in the risk assessment and subsequent treatment and utilization of the Yellow River. It could also be a reference for other pollution adsorption performances onto the sediments in different rivers.

INTRODUCTION

The Yellow River is the second largest river in China. It flows through nine provinces and autonomous regions of China, bringing together many small rivers and eventually flowing into the Bohai Sea. It is an important irrigating river in China. The Yellow River has a mean annual natural runoff of 58 billion m³ and a mean annual suspended sediment load of 1.6 billion tonnes, which makes it ranking the first of all the world's rivers in terms of sediment load (Wang et al. 2009, Xu et al. 2007). The sediment of the Yellow River contains complex components, including clay minerals, organic matters and active oxide metals, etc., and it can result in a series of complicated reactions such as physical, chemical and biochemical reactions under the water, which is very important for the distribution, migration and transformation of various types of pollution in water (Xia et al. 2010, Sun et al. 2016). It is found that the adsorption action of the various pollutions on the sediments directly affect their mobility, volatilization, biodegradation and biological toxicity in the environment. When the environmental factors change, the adsorptive pollution by the sediments may happen to be desorption, which will not only contaminate the water again, but also generate negative effects on benthos (Ren et al. 2010). So the investigation of the adsorption performance of pollution on the sediments is vital to the risk assessment and subsequent treatment of the water.

Polyvinyl alcohol (PVA) was chosen as the adsorbate here because it is widely used in many branches of an

industry. It has extensive use in the production of adhesives, coatings, medicines, paints, paper, oils, fibres and hydrogels (Hsu et al. 2011, Wisniewska et al. 2016, Chou et al. 2010). PVA is also used in food industry as an agent to retain satisfactory taste, texture and quality of the food (Gupta et al. 2011). PVA has good flexibility, high tensile strength, chemical stability, water-solubility and good film-forming capability (Yan et al. 2007). However, PVA is a refractory organic and difficult to be biodegraded. A lot of discharged PVA is harmful to the environment and could accumulate in the human body via the food chain (Meng et al. 2016, DeMerlis et al. 2003).

In this paper, the adsorption performance of PVA onto sediments of Yellow River was studied. The resulting sediments were characterized by SEM, XRD and FTIR analysis to assure the structure and property of the sediments. Efficient adsorption removal of PVA from aqueous solution was observed. To better understand the adsorption behaviour and mechanism of PVA on the sediments, the adsorption kinetics and adsorption isotherms were investigated. The effects of Zeta potential, solution pH and ionic strength were explored as well. This study was supposed to provide reference for the adsorption performance of pollution on the river sediments.

MATERIALS AND METHODS

Materials: Polyvinyl alcohol (PVA, 95.5%) was purchased from Tianjin Kemio Chemical Reagents Co., Ltd. (Tianjin,

China). Sediment of Yellow river was collected from the part of Huayuankou in Zhengzhou. Before it was used, the sediment had experienced cleaning and drying. All the chemicals used were of analytical grade. Deionized (DI) water was used to prepare all solutions.

Adsorption experiments: A stock PVA solution with a concentration of 500 mg/L was prepared by dissolving PVA in DI water. It was stored in a refrigerator and used up within three days. Adsorptive removal of PVA was determined by batch experiments in conical flasks at 25°C. For the tests of adsorption isotherms for ionic strength effect, pH effect and coexisting ion effect, 100 mg of PVA was added into 50 mL of PVA solution with a concentration of 20 mg/L. For the kinetics study, 2000 mg of sediment was added into 1000 mL of PVA solution with a concentration of 20 mg/L. These mixtures were shaken at 145 rpm. The temperature was controlled at a constant temperature of 298 K. The solution pH adjustment was conducted by adding HNO₃ or NaOH solution. All the solution pH values were maintained at neutral pH except for the pH effect study.

Analyses: Samples were collected and filtered through a 0.45 µm membrane before analysing. According to the procedures described by Finley (Finley et al. 1961), boric acid and iodine solutions were added into the pretreated samples, and then the PVA concentration was determined by measuring the absorbance at a fixed wavelength (690 nm) using an UVmini-1240 spectrophotometer (Shimadzu).

RESULTS AND DISCUSSION

Characterization of Yellow River sediment: Fig. 1 showed the SEM morphologies of Yellow River sediment before and after PVA adsorption. These raw sediment particles were irregular and most of them were within the range of 50 µm. After PVA adsorption, there was lack of fine particles and these particles became bigger, which might be attributed to the binding force of PVA. Furthermore, the EDX spectra of Yellow River sediment were measured and presented in Fig. 2. In the raw sediment, as shown in Fig. 2a, the atomic ratios of C, O and Si achieved 23.5%, 47.8% and 14.9%, respectively. After PVA adsorption, as shown in Fig. 2b, these atomic ratios of C, O and Si were 8.7%, 54.3% and 35.2%, respectively. The spectra of Ca, Fe and Mg had almost disappeared. This indicated that the adsorption of PVA onto Yellow River sediment had altered the component of the sediment surface due to the PVA covering onto the sediment.

The X-ray diffraction patterns of the raw Yellow River sediment are illustrated in Fig. 3. As stated above, the main component of Yellow River sediment was SiO₂. The peaks at 2θ = 20.9°, 26.6°, 50.1° and 59.9° were attributed to that of quartz (JCPDS NO. 46-1045), in which the peak at 2θ =

26.6° was the strongest peak. Other components such as illite, plagioclase and dolomite are also illustrated in Fig. 3. The above indicated that the main component of the sediment was quartz.

Adsorption kinetics: The effect of reaction time on PVA adsorption on Yellow River sediment was investigated at pH = 4.0, 7.0 and 10.0. The adsorption kinetics at pH = 7.0 is shown in Fig. 4. Adsorption kinetics was used to evaluate the performance of an adsorbent.

The nonlinear pseudo-first-order model can be expressed as below:

$$q_t = q_e (1 - e^{-k_1 t}) \quad \dots(1)$$

The nonlinear pseudo-second-order model can be expressed as below:

$$q_t = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)} \quad \dots(2)$$

The mathematical representations of the linear models of pseudo-first-order and pseudo-second-order kinetics are given in the following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(4)$$

Where, q_e and q_t are the adsorption capacities (mg/g) of the adsorbent at equilibrium and at time t (min), respectively; and k_1 (min⁻¹) and k_2 [g/(mg.min)] are the related adsorption rate constants for the pseudo-first-order and pseudo-second-order model, respectively (Sun et al. 2015a, Qian et al. 2015).

It could be seen from Fig. 4, that the adsorption process typically consists of an initial, rather rapid uptake and a subsequent smooth increase to equilibrium within 24 h, while 39.4% of the PVA molecules were adsorbed in the initial 120 min, and 60.2% of the PVA molecules were adsorbed in 1440 min. Using the nonlinear regressive method, the experimental kinetic data for PVA adsorption at pH 7.0 were simulated by pseudo-first-order and pseudo-second-order. The parameters for the two models at pH 4.0, 7.0 and 10.0 are summarized in Table 1 for comparison. From Fig. 4, it was evident that the kinetic curve simulated by the pseudo-second-order was the best to describe the experimental points as the experimental data were closer to the fitted pseudo-second-order curve. Further, judging from the values of regression coefficient (R^2), it could be observed that the pseudo-second-order model fitted the experimental data better than the pseudo-first-order model at all the pH conditions using both nonlinear and linear regressive meth-

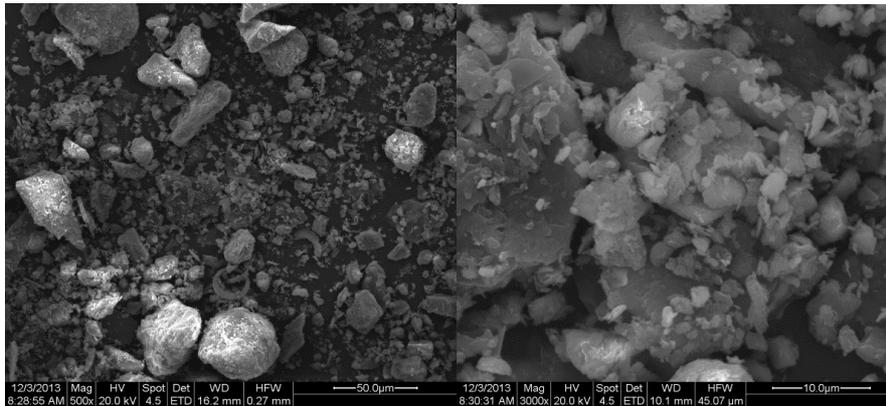


Fig.1(a)

Fig.1(b)

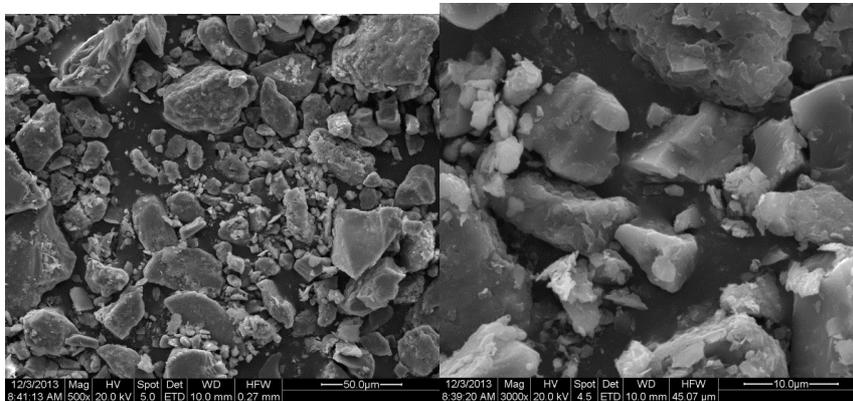


Fig.1(c)

Fig.1(d)

Fig. 1: SEM images of (a, b) raw Yellow River sediment and (c, d) exhausted Yellow River sediment after PVA adsorption. (a) and (c) were magnified 500 times while (b) and (d) were magnified 3000 times.

ods. Usually, the pseudo-second-order kinetics model was used to describe chemisorption of pollutants from aqueous solution onto sorbent. So the adsorption process of PVA onto the sediment of Yellow River might be a significant chemisorption process (Mi et al. 2016).

Adsorption isotherms: In order to find the optimal design of the adsorption system for the removal of PVA, it was necessary to establish the most appropriate correlation for the equilibrium data. The adsorption isotherm was investigated at 15°C, 25°C and 35°C, respectively. For simplicity, only the adsorption isotherm at 25°C was illustrated and simulated in Fig. 5. Six isotherm models were used to fit the experimental data, and the parameters for all of models are listed in Table 2. The non-linear forms of all models are listed below (Sun et al. 2015b, Cao et al. 2015):

$$\text{Langmuir isotherm } q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad \dots(5)$$

$$\text{Freundlich isotherm } q_e = k_F C_e^{\frac{1}{n}} \quad \dots(6)$$

$$\text{Koble-Corrigan } q_e = \frac{AC_e^n}{1 + BC_e^n} \quad \dots(7)$$

$$\text{Toth isotherm } q_e = \frac{q_m C_e}{(k_{Th} + C_e^t)^{\frac{1}{t}}} \quad \dots(8)$$

$$\text{Redlich-Peterson isotherm } q_e = \frac{AC_e}{1 + BC_e^g} \quad \dots(9)$$

$$\text{D-R isotherm } q_e = q_m e^{(-k \ln^2(1+1/c_e))} \quad \dots(10)$$

Where, q_e is the amount of the adsorbed adsorbate (mg/g) at equilibrium, q_m is the monolayer adsorption capacity of the adsorbent (mg/g), C_e is the concentration of adsorbate in the solution at equilibrium (mg/L), K_L is the Langmuir isotherm constant (L/mg) that is related to the

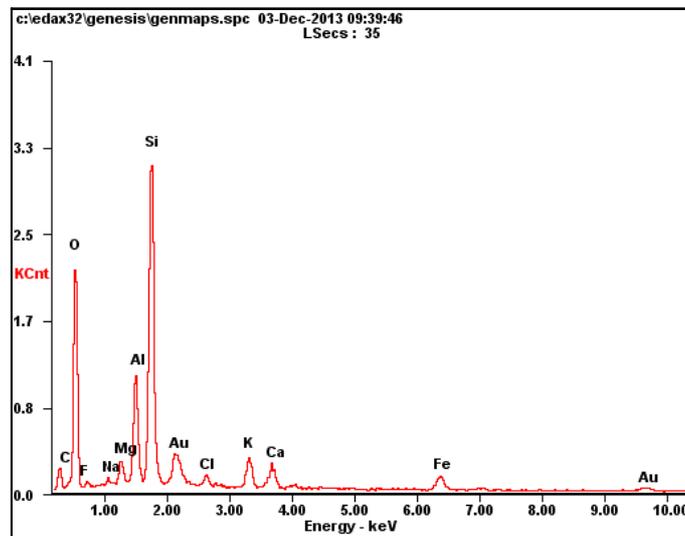


Fig. 2(a)

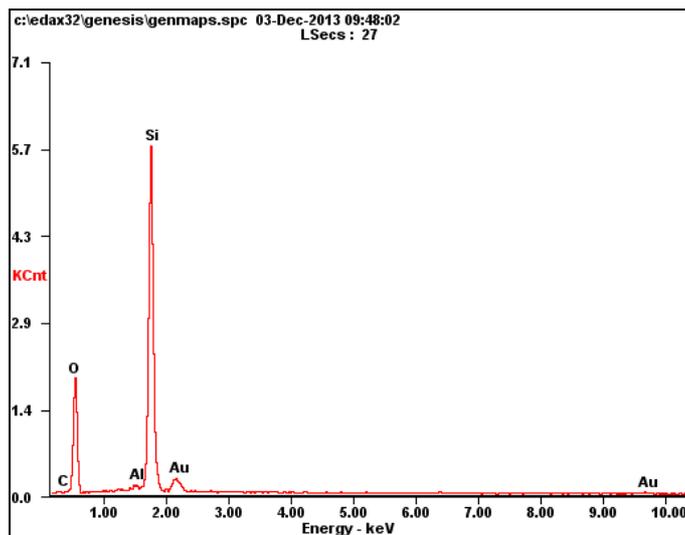


Fig. 2(b)

Fig. 2: EDX graphs of (a) raw Yellow River sediment and (b) exhausted Yellow River sediment after PVA adsorption.

adsorption energy, K_F is the Freundlich constant that is related to the adsorption capacity, $1/n$ is the adsorption intensity, kTh is the Toth constant, while A and B are the isotherm constants.

The adsorption isotherms can provide information about the surface properties and adsorption behaviour of adsorbent. Judging from the experimental data and fitted isotherm curves in Fig. 5, all of the isotherm models fitted the experimental data rather well, except the Freundlich isotherm model, and the correlation order of the models according to the R^2 values in Table 2 was Toth (0.987) and Koble-Corri-

gan (0.987) models, Redlich-Peterson (0.984) model, Langmuir (0.973) model, D-R (0.959) model and Freundlich (0.907) model at 25°C, and the results implied that the adsorption process of PVA onto sediments was monolayer and physical adsorption. At the same time, as presented in Table 2, no matter by Langmuir, Toth or D-R models, the calculated maximal adsorption capacities of Yellow River sediments decreased along with the increase of the temperatures, which indicated that the adsorption process was exothermic (Guo et al. 2016).

Zeta potential and FTIR measurements of the sediments:

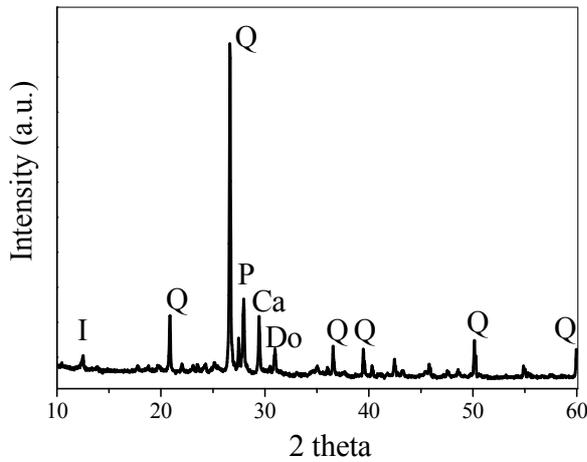


Fig. 3: XRD patterns of raw Yellow River sediment. Q (quartz), I (illite), P (plagioclase), Do (dolomite).

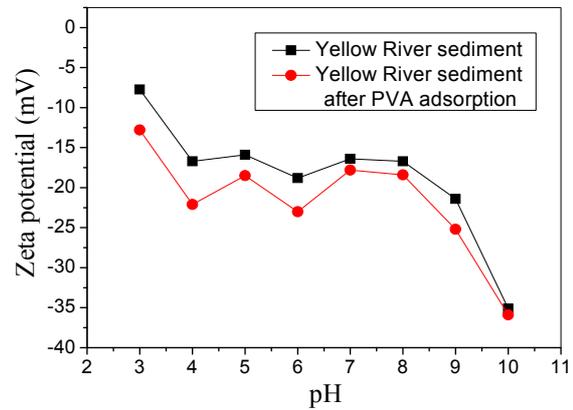


Fig. 6: Zeta potential of Yellow River sediment before and after PVA adsorption (conditions: adsorbent dosage 200 mg/L, ionic strength 0.01 mol/L, equilibrium time 48 h).

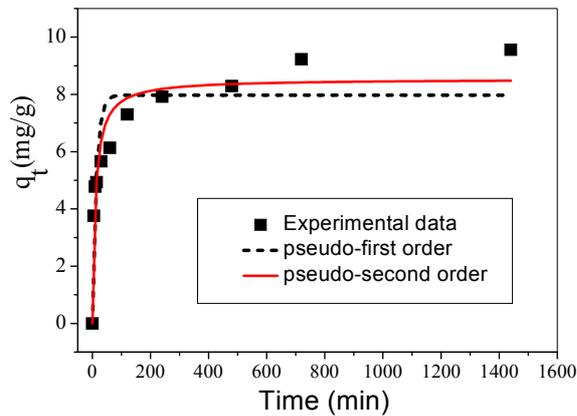


Fig. 4: PVA adsorption kinetics onto Yellow River sediment (conditions: initial PVA concentration 20 mg/L, pH = 7.0, at 25°C).

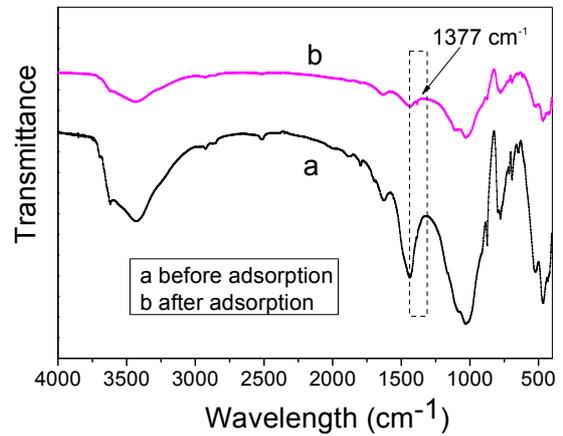


Fig. 7: FTIR spectra of Yellow River sediment before and after PVA adsorption.

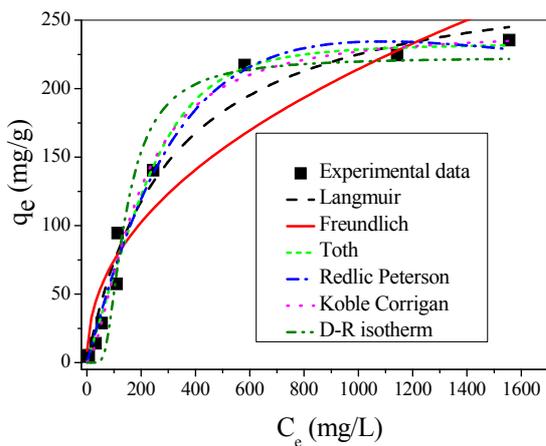


Fig. 5: The non-linear fitted curve with different models for PVA adsorption onto Yellow River sediment (conditions: pH = 7.0, 298 K).

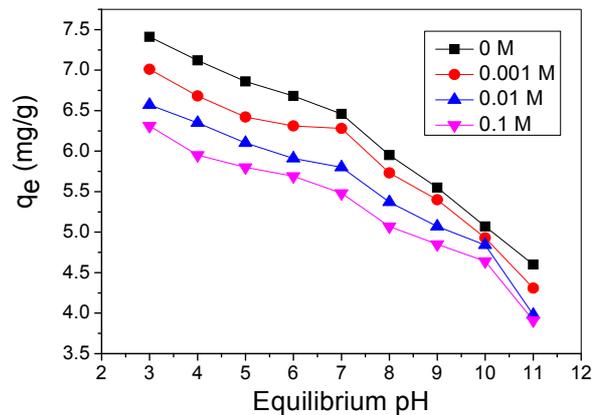


Fig. 8: Adsorption of PVA on the sediments of Yellow River at different ionic strength and equilibrium pH (conditions: initial PVA concentration 20 mg/L, at 25°C)

Table 1: Parameters for the nonlinear and linear kinetic models including pseudo-first-order and pseudo-second-order with initial PVA concentration of 20 mg/L.

	Non linear			Linear		
	pH=4	pH=7	pH=10	pH=4	pH=7	pH=10
Pseudo-first-order						
k1 (min ⁻¹)	0.068	0.072	21.859	0.00236	0.00371	0.00509
qe (mg/g)	5.446	7.797	20.706	3.975	5.129	13.130
R ²	0.706	0.827	0.976	0.830	0.887	0.912
Pseudo-second-order						
k2 (g·mg/min)	0.015	0.011	0.075	0.00388	0.00354	0.01127
qe (mg/g)	5.868	8.537	21.240	6.963	9.621	22.036
R ²	0.995	0.923	0.990	0.992	0.997	0.999

Table 2: Parameters of the six isotherm models for the adsorption of PVA on the sediments.

	288 K	298 K	308 K
Langmuir			
q _{max} (mg·g ⁻¹)	356.56	291.63	145.17
k _L (L·mg ⁻¹)	0.0039	0.0033	0.0039
R ²	0.980	0.973	0.985
Freundlich			
k _F (mg·g ⁻¹)	12.01	9.02	6.19
n	0.454	0.458	0.414
R ²	0.914	0.907	0.972
Toth			
K _{th}	1.52×10 ⁶	1.71×10 ⁷	0.63×10 ⁵
q _{max} (mg·g ⁻¹)	289.57	232.84	125.14
t	2.501	2.832	1.908
R ²	0.992	0.987	0.989
Redlich-Pererson			
A	1.098	0.723	0.443
B	3.11×10 ⁻⁴	1.12×10 ⁻⁴	6.61×10 ⁻⁴
g	1.317	1.422	1.205
R ²	0.969	0.984	0.988
Koble-Corrigan			
A	0.103	0.056	0.187
B	3.43×10 ⁻⁴	2.31×10 ⁻⁴	1.4×10 ⁻³
n	1.571	1.599	1.228
R ²	0.994	0.987	0.987
D-R isotherm			
k	11751	14901	21663
q _{max} (mg·g ⁻¹)	277.96	223.03	118.69
R ²	0.959	0.959	0.931

Zeta potential is a function of surface coverage by charged species at a specified pH, and it is theoretically determined by the adsorption of chemical reagents or polymers at the surface either non-uniformly or uniformly (Moayedid et al. 2011, Das et al. 2013). It had been reported that the effect of pH on the zeta potential was more important than electrolyte concentration in the adsorption process (Markiewicz et al. 2013), so the changes of zeta potential along with the varied pH under the fixed concentrations of sediments and PVA were investigated, and the results are shown in Fig. 6. It could be seen from Fig. 6 that the Yellow River sediment

after PVA adsorption had more negative charge than the one before PVA adsorption when the pH values changed from 3.0 to 6.0, after pH 6.0, the differences were lessened. And when the pH increased continually to 10.0, the zeta potential values of sediment before and after PVA adsorption overlapped, which implies that the pH played a very important role in the adsorption performance of PVA onto the sediments of Yellow River.

The adsorption of PVA was also investigated by detecting the FTIR spectra of Yellow River sediment before and after PVA adsorption, as illustrated in Fig. 7. Typically, af-

ter PVA adsorption, these FTIR absorption bands of the exhausted Yellow River sediment became weaker compared with those of raw Yellow River sediment. Both, the raw sediment and the used sediment for PVA adsorption shared most of the absorption bands. The absorption band at 1142 cm^{-1} was considered by some researchers as an indication of PVA structures due to the semi-crystalline nature of the synthetic polymer (Mansur et al. 2004). However, there was no other related absorption band generated after PVA adsorption. Additionally, only one new band appeared at 1377 cm^{-1} , which was attributed to CH_2 wagging of PVA (Hema et al. 2009). Anyhow, the above indicated the existence of PVA adsorbed onto the Yellow River sediment.

Effect of ionic strength on adsorption effects: As ions are commonly existent in the polluted water, and its strength could affect the adsorption performance obviously, so the effect of different ionic strengths under diverse equilibrium pH was investigated and the results are illustrated in Fig. 8. It could be seen from Fig. 8 that the ionic strength (NaNO_3) was changed from 0.001 to 0.1 M while the equilibrium pH was from 3.0 to 11.0, and the adsorption capacity of PVA on the sediments of Yellow River decreased significantly. This result indicated that the adsorption capacity was very sensitive to the ionic strength. As to the inner layer adsorption, higher ionic strength could obviously promote the adsorption ability or have little impact while outer-sphere association suppresses the adsorption when increasing the ionic strength (Al-qodah et al. 2000). It could get the conclusion that the adsorption of PVA on the sediment was outer layer adsorption by forming outer-sphere complex.

CONCLUSION

PVA is widely used in many branches of industry. However, it is difficult to biodegrade. Yellow River as the second largest river in China, its sediments were abundant and full of active oxide metals which could be an excellent adsorbent. Results showed that the sediments of Yellow River indeed had remarkable adsorption effects on the PVA. The Toth and Koble-Corrigan kinetics models better fitted the experimental data, which indicated that the adsorption of PVA on the sediments was possibly monolayer and physical. Langmuir isotherm model also simulated the adsorption isotherm data better and the maximum adsorption capacity of 356.56 mg/g for PVA uptake was obtained by Langmuir isotherm model at 288 K. Both, the increase of temperature and pH values would decline the adsorption ability. Meanwhile, the co-existing anions could inhibit the uptake of PVA to some extent. This research would enlighten some measures for the treatment of the pollution with the river sediments.

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