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Original Research Paper

# Study on the Absorption Mechanism of the Sediment to Phosphorus in Yangtze River Yibin Section

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## ABSTRACT

Through laboratory study, the isothermal absorption characteristics and dynamics characteristics of sediment to phosphate in Yangtze River Yibin Section were analysed. The study shows that the absorption curve of sediment is in good compliance with Langmuir and Freundlich isothermal absorption curves, which means that the sediment can absorb the phosphate spontaneously, and the absorption is done by polymolecular layer, for which the maximum theoretical absorption amount is 13.969mg/g, and the empirical constant n>1, which shows the sediment in Yangtze River Yibin Section has great absorption activity. Through analysis of primary and secondary dynamics model, it shows that the absorption of phosphorus is divided into fast absorption and slow absorption period, and the secondary dynamics equation can simulate the process more accurately. Under different sediment and water ratio, the relative error of theoretical equilibrium concentration and experimental equilibrium concentration calculated from the equation is less than 5%.

## INTRODUCTION

The occurrence and development of eutrophication is affinitive with the development of nutrient salt; some studies show that when there is no exterior sources input, the nutrient salt in the sediment might be the main factor for causing eutrophication, especially at the interface of water and sediment. The recycle of nutrients plays a very important role in the process of eutrophication (Sondergaard 1996). As the total phosphorus in the water of Yangtze River Yibin Section has been over the standard in recent years, in order to examine the contribution of sediment to eutrophication in Yangtze River Yibin Section, a simulation indoor experiment was carried out; in the early days of the study, the sediment from Yangtze River Yibin Section does not release nitrogen, phosphorus or heavy metals, etc, and the sediment has good absorption activity to phosphate. Also in the study, the impact on the absorption of sediment to phosphate by pH, temperature, DO, turbulence, etc. was analysed. This paper aims at studying furthermore the absorption mechanism of sediment to phosphate in Yangtze River Yibin Section through isothermal absorption characteristics and dynamics.

## MATERIALS AND METHODS

**Collection and treatment of sediment:** Sediment was collected from the river bed 500m from the downstream of Yibin Yangtze River bridge. It is also in the downstream of the city, and no pollution discharges nearby. Column type sediment sampler was used to collect 20-25cm thickness sample from the surface of the river bed. Totally 15 samples were collected. Treating of the sediment refer to Inspection Specification of Lake Eutrophication.

**Analysis of the physico-chemical properties of sediment:** Colour of sediment is light green gray, in clay condition with light fishy smell. Using weight method to measure the water ratio, and the wet density was calculated through water ratio conversion. pH was measured using pHs-3c acidometer. Ignition loss was checked at 550°C in muffle furnace, and measurement of heavy metal was done by flame atomic absorption method after the sediment was digested.

From the Table 1, it can be seen that the water ratio and ignition loss is very low, which shows that the organics and heavy metal density is very low, and the sediment is in alkali property. The heavy metal is normally contained in the particles, and settled in the sediment, and comparatively stable, with very small variation. According to the quality classification standard of Yangtze River stream area (Jiang 2012) and the sand quality specification of National Oceanic and Atmospheric Administration (NOAA) (Gao 2001, Chen 2001), it shows that the pollution of the sediment and water in this section is not so serious, and there is no heavy metal pollution. Based on the sediment integral evaluation method (Liu 2005), the quality condition of the sediment in Yibin Section was evaluated, which shows that the quality of the sediment is in First class, and has a very small possibility of hazardous impact.

Table 1: Physico-chemical property of sediment in Yangtze River Yibin Section.

| Property | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|---|---|---|---|---|
| Water ratio | 1.97% | 1.12% | 0.42% | 0.85% |
| Ignition loss | 5.85% | 5.96% | 4.49% | 4.08% |
| pH | 8.26 | 8.27 | 8.26 | 8.26 |
| Cu, mg/g | 0.98 | 0.92 | 0.83 | 0.66 |
| Cd, mg/g | 0 | 0 | 0 | 0 |
| Pb, mg/g | 0.25 | 0.2 | 0.18 | 0.15 |
| Zn, mg/g | 0.53 | 0.51 | 0.42 | 0.59 |
| Fe, mg/g | 15.58 | 15.43 | 11.35 | 9.043 |
| Mn, mg/g | 28.25 | 24.74 | 27.5 | 16.73 |
| Cr, mg/g | 0.06 | 0.06 | 0.02 | 0.03 |
| Ni, mg/g | 0.02 | 0.02 | 0.01 | 0.01 |

**Isothermal absorption experiment:** Twelve standard $PO_4$-P liquid were made by 110°C dried $KH_2PO_4$, i.e., 0.00mg/L, 0.05mg/L, 0.10mg/L, 0.20mg/L, 0.50mg/L, l.00mg/L, 1.50mg/L, 2.00mg/L, 4.00mg/L, 6.00mg/L, 8.00mg/L and 10.00 mg/L. From naturally dried sediment sample after grinding and screened by 100 eye screen, take 0.5g sediment samples and put them into 12 pieces 50mL centrifugal tube with scale and add 25mL above mentioned $PO_4$-P liquids respectively. Put the centrifugal tubes on a water based homothermal oscillator, and vibrate continuously for 24h at frequency of 145 per minute and temperature 20°C. Centrifuge for 30min with 4000r/min and take the upper clean liquid. Filtrate the upper clean liquid with 0.45μm filter and take 5mL, then examine the concentration of $PO_4$-P and the balance mass concentration is obtained. Ammonium molybdate spectrophotometric method was used to examine the phosphate concentration.

**Absorption dynamics experiment:** Prepare 1.50mg/L $PO_4$-P liquid with 110°C dried $KH_2PO_4$ for use. Weigh the sediment samples of 0.00g, 0.50g, 1.00g, 1.50g and 2.00g after screening through 100 eye screen, and put them into 250mL conical flask with plug, make the sediment flat, and put in above prepared 150mL $PO_4$-P liquid. Put the plugged conical flask on a water based homothermal oscillator for vibrating at frequency of 145 per minute and temperature 20°C. Centrifuge for 30min with 4000r/min and take the upper clean liquid. Filtrate the upper clean liquid with 0.45μm filter and take 5mL immediately. Put it into refrigerator, then examine the density of $PO_4$-P. The time for taking the sample is: 0h, 2h, 4h, 6h, 8h, 10h, 22h, 34h, 46h, 58h, 82h, 106h and 154h. Ammonium molybdate spectrophotometric method was used to determine the phosphate concentration.

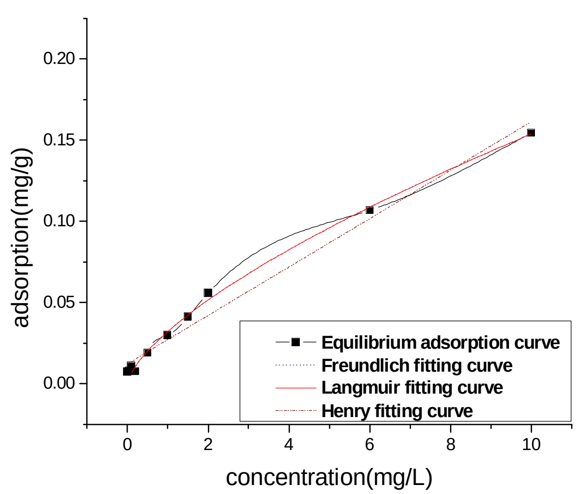


Fig. 1: Isothermal absorption curve of phosphorus by sediment.

## ISOTHERMAL ABSORPTION OF PHOSPHORUS TO SEDIMENT AND ANALYSIS

According to the experiment design, the absorption amount of phosphate by sediment with time is shown in Fig. 1.

Isothermal equation of absorption of phosphate by sediment is given in Table 2. From Fig. 1 of balance absorption curve, it can be seen that for water samples with different phosphate concentrations, the sediment has shown absorption property to phosphate; with the increase of the concentration of overlying water, the unit absorption amount is going up. When the concentration is lower than 2mg/L, the unit absorption amount is going up in linear with the increase of the concentrations; and for this part, it shows more of the characteristics of Henry type curve. However, when the concentration is higher than 2mg/L, the increasing rate of absorption amount is decreasing gradually, and it shows the characteristics of Freundlich curve. The reason probably is that at the beginning stage, because the surface absorption activity of the sediment is not saturated and the molecules show linear absorption increase at this stage, but with the increase of the concentrations of overlying water, the surface absorption is gradually saturated, and there is some resolution of phosphonium ion, which makes the unit absorption rate to decrease.

From Fig. 1 and Table 2, it can be seen that the standard deviation or relevancy $R^2$ of the isothermal absorption equation are all higher than 0.95, and can well describe the isothermal property of absorption of phosphate. And in the three curves, Freundlich isothermal absorption curve is optimal followed by Langmuir curve and Henry curve. The relevancy between the absorption curve of sediment and Freundlich curve and Langmuir curve are all higher than 0.995, which shows that using these two curves can describe the absorption property of sediment more suitably. According to Langmuir absorption theory, the absorption intensity factor $k_2$ = 0.00231, which is positive showing that under

Table 2: Fitting parameters of isothermal absorption of phosphate by sediment.

| Type | Henry fitting curve | Freundlich fitting curve | Langmuir fitting curve |
|---|---|---|---|
| K | 0.015 | - | - |
| $k_1$ | - | 0.0322 | - |
| N | - | 1.473 | - |
| $k_2$ | - | - | 0.00231 |
| $Q_m$ | - | - | 13.969 |
| Equation | y = 0.0124 + 0.15x | $y = 0.0322x^{0.679}$ | $y = 118.240x^{0.68}/(3672.18 + x^{0.68})$ |
| Relevancy ($R^2$) | 97.85 | 99.58 | 99.52 |

the experimental condition, the absorption can proceed spontaneously. However, the value of $k_2$ is comparatively small, which means the binding ability of sediment and phosphate is small, and easy for resolving. Using Langmuir isothermal absorption equation, the maximum theoretical absorption amount of phosphate by sediment can be calculated as 13.969mg/g. The absorption curve conform to Freundlich curve, which means the absorption of phosphate by sediment is polymolecular layer absorption, and the empirical constant n>1, which means that the sediment in Yangtze River Yibin Section has great absorption activity, and can be used as good sorbent.

## ABSORPTION DYNAMICS OF ABSORPTION OF PHOSPHATE BY SEDIMENT

**Absorption dynamics model:** The dynamics process of absorption of pollutant by sediment can be described by first-order kinetic equation and quasi second kinetic equation.

1. Differential form of first-order kinetic equation is:

$$\frac{dq_t}{dt} = k(q_e - q_t)$$

Integral form is:

$$q_t = w(1 - e^{-kt})$$

2. Differential form of quasi second kinetic equation is:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

Integral form is:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}$$

In the above two integral forms:

$q_t$- absorption amount of solvent by sorbent, mg/g
$q_e$- balance absorption amount of solvent by sorbent, mg/g
k- speed constant
w- constant related to the initial density of solvent, mg
t- time of absorption process, min

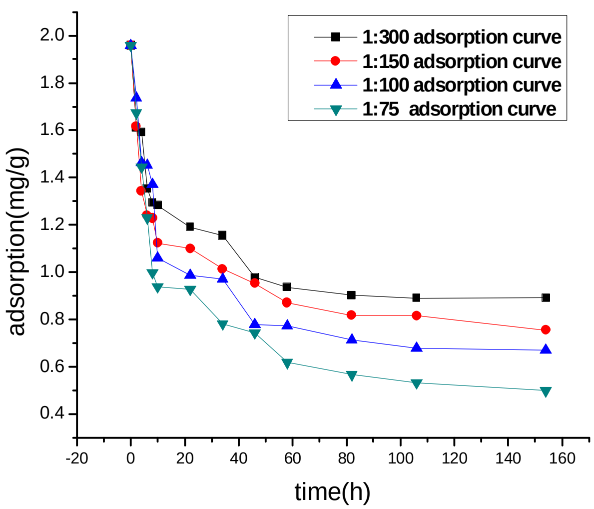


Fig. 2: Absorption curve of phosphorus by sediment under different sediment and water ratio.

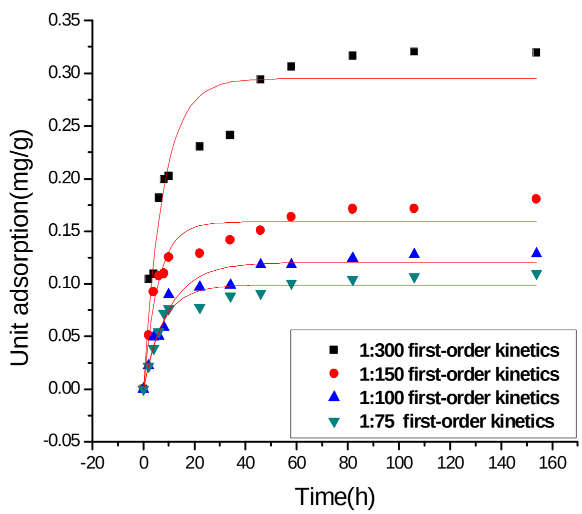


Fig. 3: First-order kinetics fitting curve of absorption experiment under different sediment and water ratio.

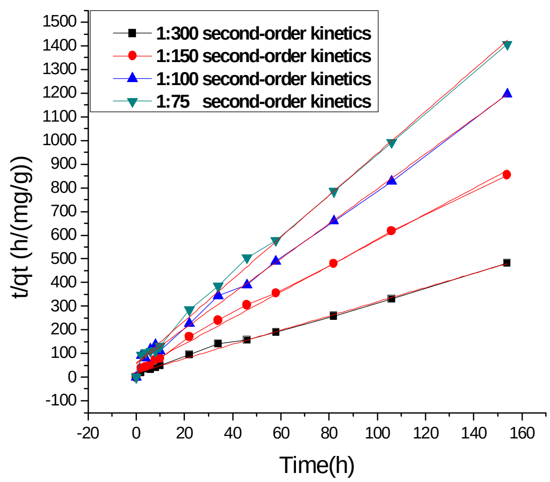


Fig. 4: Second kinetics fitting curves of different sediment and water ratio.

Table 3: Absorption of phosphate by sediment under different sediment and water ratio (mg/L).

| Time of sample (h) | Vacant | Sediment and water ratio 1:300 | Sediment and water ratio 1:150 | Sediment and water ratio 1:100 | Sediment and water ratio 1:75 |
|---|---|---|---|---|---|
| 0 | 1.9582 | 1.9582 | 1.9582 | 1.9582 | 1.9582 |
| 2 | 1.5971 | 1.6098 | 1.6162 | 1.7373 | 1.6735 |
| 4 | 1.4824 | 1.5928 | 1.3422 | 1.4633 | 1.4441 |
| 6 | 1.4505 | 1.3528 | 1.2402 | 1.4526 | 1.2296 |
| 8 | 1.4038 | 1.2933 | 1.2275 | 1.3698 | 0.9981 |
| 10 | 1.3655 | 1.2827 | 1.1234 | 1.0597 | 0.9386 |
| 22 | 1.2976 | 1.1914 | 1.1000 | 0.9874 | 0.9280 |
| 34 | 1.2912 | 1.1552 | 1.0129 | 0.9704 | 0.7814 |
| 46 | 1.2721 | 0.9789 | 0.9534 | 0.7793 | 0.7431 |
| 58 | 1.2466 | 0.9365 | 0.8706 | 0.7729 | 0.6178 |
| 82 | 1.2678 | 0.9025 | 0.8175 | 0.7134 | 0.5668 |
| 106 | 1.2891 | 0.8897 | 0.8154 | 0.6773 | 0.5329 |
| 154 | 1.2678 | 0.8918 | 0.7559 | 0.6709 | 0.4989 |

Table 4: Absorption kinetics fitting equation and relevancy.

| Sediment and water ratio | First-order kinetic equation | $R^2$ | Quasi second kinetic equation | $R^2$ | $q_e$, mg/g |
|---|---|---|---|---|---|
| 1:300 | $y = 0.295 \times (1-e^{-0.131x})$ | 91.8% | y = 18.127 + 3.000x | 99.5% | 0.333 |
| 1:150 | $y = 0.159 \times (1-e^{-0.173x})$ | 92.7% | y = 30.685 + 5.479x | 99.6% | 0.183 |
| 1:100 | $y = 0.0.120 \times (1-e^{-0.099x})$ | 95.5% | y = 56.910 + 7.388x | 99.5% | 0.135 |
| 1:75 | $y = 0.099 \times (1-e^{-0.133x})$ | 94.7% | y = 59.558 + 8.855x | 99.6% | 0.113 |

The set of coordinate of first-order kinetic equation is y-x: qt-t, the set of coordinate of second kinetic equation is y-x: t/qt-t.

**Analysis of the Absorption Dynamics Experiment of Sediment to Phosphorus:** Under 20°C and different sediment and water ratio conditions, the absorption amount of phosphate by sediment is as follows:

According to data from experiment, with the help of Origin software, the absorption curve has been drawn for different sediment and water ratios (Fig. 2), and kinetics fitting was conducted and shown in Figs. 3 and 4.

Table 3 and Fig. 2 show the absorption of phosphate under different sediment and water ratios with time. It can be seen that under different sediment and water ratios, with the increase of sediment density, the time that reaches the balance absorption density is postponed, and the final balance absorption density is quite different from each other, and the sediment density is inversely proportional to balance phosphorus concentration in overlying water. Under different sediment and water ratios, the absorption of phosphorus all show fast absorption and slow absorption stage.

In the kinetics fitting curves (Figs. 3 and 4), it reflects that at the beginning stage, the absorption speed is the highest in the whole absorption process. As the absorption amount increases, the speed goes down, and with the increase of sediment density, the absorption amount of unit sediment is also going down. According to fitting curve, the equations of absorption kinetics mode of phosphate absorption by different sediment densities are given in Table 4.

According to the related coefficient of kinetics, although the related coefficients of both first-order kinetic model and second kinetic model are higher than 91%, but comparatively, quasi second kinetic model can describe the absorption of phosphorus by sediment more accurately. The related coefficient is higher than 99.5%, and from this it can be seen that no matter how much the sediment density is, they all fit quasi second kinetic equation. The balance absorption amount $q_e$ under different sediment and water ratios is calculated with quasi second kinetic equation, and is shown in Table 4. The deviations of experimental balance density and theoretical density are 3.9%, 1.6%, 4.4%, 2.7% respectively. Therefore, the quasi second kinetic equation can be used to describe the absorption characteristics of phosphorus by sediment.

## CONCLUSION

Microorganism absorb phosphorus in water to compound its nutrient, the main used part is resolvable phosphate, and therefore, the change of resolvable phosphate can reflect eutrophication level more accurately. The study shows that the sediment water ratio, organics, and heavy metals in the sediment of Yangtze River Yibin Section are all very low, and in alkali condition. The sediment has good absorption activity, and the absorption characteristics match Freundlich absorption; the absorption can happen spontaneously, and belongs to polymolecular layer absorption. The maximum theoretical absorption is 13.969mg/g.

Under different sediment and water ratios, with the increase of sediment, the time that reaches balance absorption density is postponed, and the final balance density is quite different from each other. From the fitting of different sediment and water ratios experiment, according to first-order kinetics and quasi second kinetics, it shows that the speed of beginning stage of absorption is the maximum phase, and with the increase of absorbing amount, the speed goes down, and with the increase of sediment, the absorbing amount of unit sediment shows a going down trend. The absorption at different sediment and water ratios, all fit quasi second kinetic equation, the deviation of theoretical balance density calculated by this equation and the experimental density is less than 5%, which means that the sediment in this section has a function of restraining eutrophication.

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## REFERENCES

Chen, J.S., Wang, L.X. and Hong, S. 2001. The difference of aquatic sediment quality criteria and the reason analysis. Environment Chemistry, 5: 417-424.

Gao, H., Bao, W. Y., Zhang, S.G., Li, Y.T., Peng, B. and Zhou, H.D. 2001. Sandy River Pollution Chemical and Eco-toxicological Research. Yellow River Water Conservancy Publishers, Zhengzhou.

Jiang, Y. X., Liu, Y. and Deng, C. 2012. Effect of environmental factors on segment phosphorus adsorbed sediment in Yibin section of the Yangtze River. Sichuan Environment, 2: 45-49.

Liu, C., Wang Z.Y. and He, Y. 2005. The research of water sediment quality criteria for sediment. Sediment Research, 2: 54-60.

Sondergaard, M. and Windolf, J.J.E. 1996. Phosphorus fractions and profiles in the sediment of shallow Danish lakes as related to phosphorus load, sediment composition and lake chemistry. Water Research, 4: 992-1002.