Effects of sediment particle morphology on adsorption of phosphorus elements

Hong-wei FANG\textsuperscript{1}, Ming-hong CHEN\textsuperscript{2}, Zhi-he CHEN\textsuperscript{3}, Hui-ming ZHAO\textsuperscript{4}, and Guo-jian HE\textsuperscript{5}

Abstract
Sediment particle surface morphology affects phosphorus adsorption. This paper studied the phosphorus adsorption on sediment particle by using a Scanning Electron Microscope (SEM) and an Energy Dispersive X-ray Spectroscopy (EDS). Sediment samples from the Yangtze, Yellow and Yongding rivers in China were chosen to measure the particle surface morphology, surface gray scale and element distribution maps. These samples were firstly cleaned and put into phosphate solution for adsorption. Both the Langmuir equation and Freundlich equation were used for descriptions of adsorption-desorption isotherms for sediments. Particles were then dried and scanned. The results show that the adsorption of phosphorus depends on the surface morphology of particles. Phosphorus exists mostly in the ridges and channels, while a few exist in the slopes, and casually in the peaks, passes and pits.

Key Words: Surface morphology, Scanning electron microscope, Adsorption, Element distribution

1 Introduction
Sediment particle surface morphology plays an important role on sediment transport research (Graf, 1971; Yalin, 1977; Chien and Wan, 1999). Despite the numerous experimental results concerning physico-chemical processes on the surfaces of fine sediment particles and nano-particles, especially for adsorption (Gupta et al., 2001; Liu et al., 2008), our understanding of the surface physico-chemical processes still relies on the traditional double electric layer and adsorbed water film analysis. In the previous study, the sediment particles were analyzed as a ball and the particle surface morphology was largely unknown (Reiner and Radke, 1993; Mohan and Singh, 2002).

As pointed out by Krinsley and Doornkamp (1973) and Vilks and Wang (1981), almost all the sediment particles studied have a rather irregular outline and show primary glacial features. These features include not only relict conchoidal fractures and dish-shaped concavities but also less frequently parallel steps or striae. Because of long distance transport, many exposed particle surfaces have current markings, particularly mechanical V-marks, superimposed on the glacial features. Furthermore, angular edges have been rounded due to mechanical abrasion. In addition, surface solution and silica coating occur during surface physico-chemical processes, thus producing pits, pores and deposits. All these features have a strong impact on the interface actions on sediment surfaces, including physical action, chemical action and biofilm growing on the surface. This paper focused on the adsorption and desorption action and element distribution on the sediment surface influenced by sediment surface morphology. The development of observation devices made it possible to figure out the mechanical process of adsorption and desorption directly. The mathematic statistics method was then applied to analyze the static results of adsorption and attempt to determine rules for these complex physico-chemical processes.

2 Research methods
A super high resolution Field Emission Gun Scanning Electron Microscope (S5500) was used for investigating particle surface texture. This system scans an electron beam across the sediment particle line by line, collecting the electrons emitted from the particle (Buzio et al., 2003; Athene, 2003; Gillies and Prestidge, 2004). The highest resolution of this

\begin{thebibliography}{99}
\bibitem{1} Prof., Department of Hydraulic Engineering, the State Key Laboratory of Hydro Science and Engineering, Tsinghua University, Beijing 100084, China
\bibitem{2} Assoc., Prof., College of Water Resources and Civil Engineering, China Agricultural University, Beijing 100083, China; Corresponding author, E-mail: chemminghong@cau.edu.cn; Tel: +86 10 62738486
\bibitem{3} Instructor, Department of Water Resources and Environment, Sun Yat-sen University, Guangzhou 510275, China
\bibitem{4} Ph.D., Department of Hydraulic Engineering, the State Key Laboratory of Hydro Science and Engineering, Tsinghua University, Beijing 100084, China
\bibitem{5} Assoc. Prof., Department of Hydraulic Engineering, the State Key Laboratory of Hydro Science and Engineering, Tsinghua University, Beijing 100084, China
\end{thebibliography}
microscope can reach to 0.4nm (30kV). SEM sample preparation should be made to sediment samples before observation. Because sediment particles are not conductive in the vacuum chamber, the microscope cannot capture a clear image. It is better to coat the surface of the sample with gold film when only the morphology measurement is required. The image of the particle surface is clear but does not affect the surface morphology because of the strong conductive performance of gold film. If element distribution detecting is required, the sample should be coated with carbon film.

Figure 1 shows some typical SEM images of sediment particles from (a) the Yangze River, (b) the Yellow River and (c) the Yongding River in China. These figures show various particle forms with very complex surface morphologies. Most features, such as primary glacial features, mechanical V-marks and silica coating, can be clearly seen from images. The compositions of features, however, are different from each other.

![Fig. 1 SEM pictures of fine sediment particles](image)

(a) the Yangze River  (b) the Yellow River  (c) the Yongding River

Close-up SEM images of the sediment particle surface are shown in Fig. 2. These two images show that the particle surface consists of many small holes approximately several nanometers in size. A very complex interface is formed because of these holes or pores. These pores can be open to different directions, closed or connected (Fang et al., 2009). However, it is not easy to investigate these pores visually.

![Fig. 2 Magnified SEM pictures of particle surface](image)

The sediment samples from the Yongding River are often coated with organic compounds, as well as adsorbing nitrogenous and phosphorus compounds and heavy metal ions. Natural sediment samples need to be “washed” as described by Wang et al. (1982) to reduce the effect of these contaminants on experimental results. These particles were boiled in high concentration of hydrochloric acid for 10 min, washed with distilled water, boiled in stannous chloride for 20 min, then reworshed with distilled water, boiled in 30% hydrogen peroxide for 10 min, and finally washed with distilled water again and thoroughly dried. Organic and inorganic compounds and heavy metal ions were washed out after this sequence, making sediment particles return to a clean state. Their major components and main structure are not destroyed.

The washed and dried sediment samples were used in a series of adsorption-desorption isotherm experiments. Weighted sediment particles were dissolved in water in a container originating from the same site as the sediment samples. A certain amount of phosphorus solution with a certain concentration was added to this suspension liquid.
container was then put in a homothermal machine at 20°C for 24 hours shaking. The total phosphorus concentration of filtrate was measured after being filtrated by a 0.45μm micro-pore filter. The adsorption amount could thus be calculated according to the mass conservation principle.

Experiments were divided into four groups under conditions summarized in Table 1. The mean grain size of samples was 0.014mm and maximum grain size was 0.02mm. Higher concentrations of phosphorus than found in natural river systems were designed in order to ensure enough mass for element scanning on particle surfaces.

<table>
<thead>
<tr>
<th>Group No.</th>
<th>Sediment concentration (g L⁻¹)</th>
<th>Initial concentration of phosphate (mg L⁻¹)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.0</td>
<td>0.0, 0.5, 1.0, 1.5, 2.0, 2.5</td>
<td>6~7</td>
</tr>
<tr>
<td>2</td>
<td>10.0</td>
<td>1.0, 2.0, 3.0, 4.0, 5.0, 8.0, 10.0</td>
<td>6~7</td>
</tr>
<tr>
<td>3</td>
<td>15.0</td>
<td>1.0, 2.0, 3.0, 4.0, 5.0, 8.0, 10.0</td>
<td>6~7</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>1.0, 2.0, 3.0, 4.0, 5.0, 8.0, 10.0</td>
<td>6~7</td>
</tr>
</tbody>
</table>

We used an EDS system to produce element maps. The Scanning Electron Microscope mentioned above was equipped with this EDS system. An element map is an image showing the spatial distribution of elements in a sample and is extremely useful for displaying element distributions in textural context, particularly for showing compositional zonation. The image is produced by progressively rasterizing the electron beam point by point over an area of interest. Think of an element map as a pixel by pixel image based on chemical elements. Resolution is determined by beam size, and relative response of each element is determined by how long the beam dwells on each point and of course the actual concentration. Greater distinction can be made by longer analysis, but at the cost of time. Elements in low concentration may not give a response. After more than ten minutes scanning over the particle surface, a series of maps for specific elements can be obtained. Maps of different elements over the same area can help to determine what phases are present.

3 Results and analysis

3.1 Adsorption isothermal curve

Langmuir equation and Freundlich equation were used to describe the adsorption isotherm data herein.

In the Langmuir equation,

\[
C_s = \frac{S_m K_f C_e}{1 + K_f C_e} \quad (1)
\]

\(C_s\) (mg g⁻¹) is the equilibrium solution phase concentration; \(C_e\) (mg g⁻¹) is the equilibrium absorbed concentration; \(S_m\) (mg g⁻¹) is the maximum adsorption capacity for sediment; and \(K_f\) is a coefficient.

In the Freundlich equation,

\[
C_s = K_f C_e^n \quad (2)
\]

\(K_f\) and \(n\) are constants.

Each of these equations has two constant parameters to be fitted, \(S_m\) and \(K_f\), \(n\), respectively. Adsorption isotherms for samples from four groups are plotted in Fig. 3. The constants of the equations are given in Table 2. It is noteworthy that these samples have background values of phosphorus concentration measured as 0.08 mg g⁻¹.

<table>
<thead>
<tr>
<th>Sediment concentration (kg m⁻³)</th>
<th>Parameters for Langmuir equation</th>
<th>Parameters for Freundlich equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(S_m)</td>
<td>(K_f)</td>
</tr>
<tr>
<td>5.0</td>
<td>0.474</td>
<td>0.548</td>
</tr>
<tr>
<td>10.0</td>
<td>0.415</td>
<td>1.060</td>
</tr>
<tr>
<td>15.0</td>
<td>0.377</td>
<td>1.335</td>
</tr>
<tr>
<td>20.0</td>
<td>0.269</td>
<td>21.477</td>
</tr>
</tbody>
</table>

It can be seen from the table that high values of the correlation coefficient show a good agreement with adsorption data and isotherm equations. Both the Langmuir equation and Freundlich equation can be used for descriptions of adsorption-desorption isotherms for sediments from the Yongding River. The Langmuir equation provides an even better fit.
3.2 Element distributions on particle surface

Element maps for specific elements can be determined once the surfaces of particles are scanned. Herein, we are concerned with the mapping of phosphorus because much phosphate has been adsorbed on the particle surface in previous adsorption experiments. The polluted sediment from Group 1 in Table 1 was selected and made into samples for element scanning. Figures 4 (a) and (b) show an SEM image of an original sediment particle and a map of phosphorus distribution on its surface. To observably display the distribution of phosphorus on the surface, irrelevant background information around the particle was removed. A Sobel operator in digital image processing was used to sketch out the edge of the particle projection. The area outside of the particle edge but inside the SEM picture was set to white. In Figs. 4 (a) and (b), the size of the image in its entirety is 512 pixels by 384 pixels and the scale is 10 \( \mu \text{m} \).

Laplace transformation was applied to enhance the image signal of the element map to avoid random noise. All interferential points having low brightness were directly removed. The black points in Fig. 4 (b) indicate that phosphorus atoms were detected.

In order to clearly observe the distribution of phosphorus on the surface and find the correlation between phosphorus distribution and particle surface morphology, two images were digitalized and processed (Chen et al., 2009). Figure 4 (c) and (d) show a spatial surface built from a partial area of the SEM image in gray scale and the addition of an element map to the surface. Fluctuations and sunken places can be found on the surface in Fig. 4 (c). Black circles in Fig. 4 (d)
are phosphorus atoms interspersed among these fluctuations and sunken places. It is found that these atoms concentrate in the middle concave area while a great amount of atoms also exist on convex places. Phosphorus atoms seldom appear in relative flat areas. The role of distribution in quantity will be described in a following section.

4 Discussions

4.1 Description of sediment surface morphology

The SEM images of particles captured by a scanning electronic microscope are gray pictures and consist of several grid shaped pixels. The difference between gray values indicates relative height difference on particle surface to some extent. SEM images of particles have more pixels if the scanning electronic microscope has a higher resolution. Therefore, the images are clearer for information processing.

The surface of particles is so concave-convex and fluctuant from SEM images that a simple mathematical surface in the three-dimensional Euclid space could not express the features of the surface. However, supposing the surfaces of particles is local, smooth and continuous, it can even be mathematically described by some equation. Theoretically, a surface in the Euclid space can be approached with any precision by a high order polynomial no matter how complex it is. However, high order polynomials have more coefficients which are physically ambiguous. Therefore, the quadratic surfaces with their deformation are practically used to express surface features. In the gray charts, any point from surfaces and its neighboring eight points form a continuous surface which is able to describe the local geometrical feature of that point. According to the idea of differential geometry, the equation of the quadratic surface is assumed as $z = z(x, y)$, where $x, y$ are the coordinates of the points in the image matrix (Wood, 1996).

For a surface modeled by the quadratic,

$$Z(x, y) = ax^2 + by^2 + cxy + dx + ey + f$$

coefficients $a, b, c, d, e, f$ are determined with neighboring points.

Some characteristic parameters describing morphology of the sediment particle surface, such as slope in degree $\beta$, cross sectional curvature $C_s$, minimum and maximum profile convexity $C_{\min}$ and $C_{\max}$, can be defined by the coefficients in Eq. (3).

Slope in degree:

$$\beta = \tan^{-1} \sqrt{\frac{\Delta^2 + e^2}{\Delta^2 + e^2}}$$

Cross sectional curvature:

$$C_s = GS \times \frac{bd^2 + ae^2 - cde}{d^2 + e^2}$$

Maximum profile convexity:

$$C_{\max} = GS \times \left(-a - b + \sqrt{(a-b)^2 + c^2}\right)$$

Minimum profile convexity:

$$C_{\min} = GS \times \left(-a - b - \sqrt{(a-b)^2 + c^2}\right)$$

where, $GS$ is the grid size of image pixel.

One of the most widely used set of morphometric characteristics is the subdivision of all points on a surface into one of peaks, ridges, channels, passes, pits and slope (Zhou and Liu, 2006); see Table 3. These morphometric features are described by slope, cross sectional curvature, and minimum and maximum profile convexity.

<table>
<thead>
<tr>
<th>Feature name</th>
<th>Slope in degree $\beta$</th>
<th>Cross sectional curvature $C_s$</th>
<th>Maximum profile convexity $C_{\max}$</th>
<th>Minimum profile convexity $C_{\min}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak</td>
<td>0</td>
<td>--</td>
<td>&gt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Ridge</td>
<td>&gt;0</td>
<td>--</td>
<td>&gt;0</td>
<td>0</td>
</tr>
<tr>
<td>Channel</td>
<td>0</td>
<td>&gt;0</td>
<td>&gt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Pass</td>
<td>0</td>
<td>&lt;0</td>
<td>&gt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Pit</td>
<td>0</td>
<td>&gt;0</td>
<td>&lt;0</td>
<td>&lt;0</td>
</tr>
<tr>
<td>Slope</td>
<td>&gt;0</td>
<td>0</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

4.2 Phosphorus distribution statistics

Based on the SEM images and morphometric method, four polluted samples from Group 1 in Table 1 (0.5, 1.0, 1.5,
2.0 mg L\(^{-1}\)) were selected. For each sample, ten images were captured and statistics were compiled. All images including original sediment particle images and element mapping images were digitalized and analyzed. The points on the surface where phosphorus atoms were located were classified by local morphometric features of the surface which centered at these points. The statistical results are listed in Table 4. This table shows the number and the percentage of phosphorus atoms located at each morphometric feature.

<table>
<thead>
<tr>
<th>Feature name</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atom number</td>
<td>%</td>
<td>Atom number</td>
<td>%</td>
</tr>
<tr>
<td>Peak</td>
<td>49</td>
<td>0.50</td>
<td>14</td>
<td>0.06</td>
</tr>
<tr>
<td>Ridge</td>
<td>4,722</td>
<td>48.11</td>
<td>11,270</td>
<td>47.66</td>
</tr>
<tr>
<td>Channel</td>
<td>4,577</td>
<td>46.63</td>
<td>10,939</td>
<td>46.26</td>
</tr>
<tr>
<td>Pass</td>
<td>37</td>
<td>0.38</td>
<td>12</td>
<td>0.05</td>
</tr>
<tr>
<td>Pit</td>
<td>21</td>
<td>0.21</td>
<td>9</td>
<td>0.04</td>
</tr>
<tr>
<td>Slope</td>
<td>409</td>
<td>4.17</td>
<td>1,402</td>
<td>5.93</td>
</tr>
<tr>
<td>total</td>
<td>9,815</td>
<td>100</td>
<td>23,646</td>
<td>100</td>
</tr>
</tbody>
</table>

It can be seen from Table 4 that phosphorus exists mostly in the ridges and channels, with a few in the slopes, and casually in the peaks, passes and pits. So it can be concluded that the ridges and channels have more active adsorption sites and are suitable for adsorption of phosphorus. The structure of clay minerals and their complex changes in water lead to greater distribution of local permanent charges and other functional groups in these two kinds of positions, which will influence the adsorption properties of clay particles.

Looking back at Table 3, both the ridges and channels have one main profile convexity valued 0 with another main profile convexity positive or negative. In differential geometry, the geometric meaning of the absolute Gaussian curvature value \((C_{\text{max}} \times C_{\text{min}})\) of a point on a surface is the bending degree of the surface at that point. Therefore, the change rate of curvature goes against the adsorption of contaminants. The peaks, passes and pits have a great curvature change rate and adsorb less amounts of phosphate.

Furthermore, comparing the percentage of phosphorus atoms at each morphometric feature in four samples, it can be found that the slopes adsorb more phosphate ions with the increase of initial phosphate concentration. We can infer that the ridges and channels have a great competitive advantage. In the adsorption process, the ridges and channels capture the phosphate ions first. When they are gradually saturated, the slopes begin to adsorb more ions.

### 4.3 Relationship between phosphorus distribution and surface morphology

Experimental results show that the adsorption of phosphate on sediment particle surfaces depends on the surface morphology. A quantitative relationship should be established with the variables to represent the main characteristics of these two objects. Firstly, non-spherical curvature is introduced for describing how close the local surface structure approaches a spherical surface. The non-spherical curvature \(C_{u}\) is defined as,

\[
C_u = \frac{1}{2}(C_{\text{max}} - C_{\text{min}})
\]

On the spherical surface, the maximum profile convexity equals the minimum profile convexity, i.e. \(C_u = 0\). A greater value of \(C_u\) indicates greater roughness on the surface. Figure 5 plots the relationship between \(C_u\) and the amount of adsorption, where \(N_i\) is the amount of phosphate adsorbed on each small surface with the non-spherical curvature \(C_u\); \(N\) is the total amount of phosphate adsorbed on this particle. A distribution function is selected to fit the statistical data with an acceptable correlation coefficient. This exponential function is,

\[
\frac{N_i}{N} = 0.77e^{-0.68C_u} - 0.82e^{-1.27C_u}
\]

It can be seen from Fig. 5 that the amount of phosphate ions adsorbed grows with the increase of curvature value ranging from 0 to 1.1 and decreases when the curvature value is greater than 1.1. Especially when \(C_u > 6.5\), the amount of ions is very low. The complexity of surface morphology plays an important role in ions adsorption. For a certain range of \(C_u\), the phosphate ions are easily adsorbed on surfaces with ridges and channels. However, excessively great values of \(C_u\) go against the adsorption.

In the classic double layer theory, solid particles are supposed to be spheres with electric charge distributed uniformly on the surface. Actually, the sediment particle surface is non-uniform as can be observed using the SEM system. The charges, consequently, distribute non-uniformly on the surface which result in difference of adsorption potential on each local site. Double layer theory may not be suitable for describing the adsorption process of phosphate while complex theory is (Stumm, 1987, 1990; Ditoro, 2001). However, the importance of surface morphology in complex theory is the...
same as in double layer theory. Seen from the experiment results and analysis, the ridges and the channels on the surface have great adsorption potential but do not desorb ions as easily as the peaks and the pits. When active adsorption sites on the ridges and channels are saturated, more ions turn to the slopes which have slightly smaller adsorption potential.

Fig. 5  Statistics and distribution fitting of non-spherical curvature

Most of the sediment particles which we are concerned about and study are clay particles. The structure of clay minerals and the lattice substitution in the weathering process lead to more distribution of local permanent charges and other functional groups in some positions, which will influence the adsorption properties remarkably.

For the resolution of SEM measurement, the conclusion is correct in the statistical sense. The selective adsorption of phosphorus depends on the microtopography distribution on the surface.

Statistics and analysis should be conducted on more sediment samples in the future to strengthen our conclusion on distribution law. The law, however, should be extended to mathematical sands in flow-sediment-contaminant models, because only mathematical sands can represent different types of natural particles with complex surface superior to traditional particles. Once a mathematical sand particle is obtained, the value of non-spherical curvature at each point of the surface can be calculated and the phosphorus can be redistributed on its surface by obeying the law. The subsequent work will be to obtain mathematical sands which are reconstructed by capturing thousands of SEM images and modeling them with both image processing and Fourier series methods. This portion of the work will be conducted in the near future.

5 Conclusions

The intention of these experiments was to observe and measure the surface morphology and determine the relationship between particle surface morphology and phosphorus distribution. A scanning electron microscope was used to capture some gray images of sediment particles with different resolutions. Most features, such as primary glacial features, mechanical V-marks and silica coating, can be clearly seen from images.

Adsorption experiments were conducted on sediment samples from some Chinese rivers. The results show that both the Langmuir equation and Freundlich equation can be used for descriptions of adsorption-desorption isotherms for samples in phosphate solutions.

The phosphorus distributions on particle surfaces were measured using an EDS system after phosphorus adsorption on sediment particles. The results indicate that phosphorus exists mostly in the ridges and channels, while a few exist in the slopes, and casually in the peaks, passes and pits. For a certain range of non-spherical curvature, the phosphate ions are easily adsorbed on the surface by the ridges and channels. However, excessively great values of non-spherical curvature go against the adsorption.

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References


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Wrong affiliation:
1 PhD candidate, School of Environmental and Rural Science, University of New England, E-mail: ahaddad3@une.edu.au
3 Assis., Prof., Dept. of Irrigation Engineering, University of Gorgan, E-mail: amirahmad.dehghani@gmail.com

Correct affiliation:
1 PhD Candidate, Australian Rivers Institute, Griffith University, Nathan, QLD 4111, Australia. Corresponding author, E-mail: arman.haddadchi@griffithuni.edu.au
3 Assis., Prof., Department of Water Engineering, Gorgan University of Agricultural Sciences and Natural Resources, Golestan, Iran, E-mail: a.dehghani@gau.ac.ir