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Zeolite (Na) modified by nano-Fe particles adsorbing phosphate in rainwater runoff

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Abstract
Zeolite (Na) modified by self-synthesized nano-Fe particles was used as infiltration media to adsorb phosphate in rainwater runoff. The adsorption capacities increased up to 75 times that of natural zeolite at a saturated equilibrium phosphate concentration of 0.42 mg/L. The correlation of capacity and material-specific surface area indicated that specific surface area was not the key factor contributing to the capacity improvement. SEM and XRD analysis showed that chemical reaction between Fe and P to form new products like cacoexinite is the main reason for the increased capacity, and that the method of adding metal ions or particles to improve the adsorption capacity for phosphate is feasible.

Key words: rainwater runoff; phosphate adsorption; nano-iron modification

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Introduction
There are two main types of sources of phosphorus water pollution: point sources and non-point sources. With the accelerating process of urbanization, urban water-impervious area has increased rapidly, which reduces rainfall infiltration and increases surface runoff. With the increase in rainwater runoff, the phosphorus pollution loading into water bodies is rising dramatically. Research (Dong et al., 2008) showed that in Beijing in 2006, the average total phosphorus concentration in roof rainfall runoff was 0.71 mg/L, while the average total phosphorus concentration in road rainfall runoff was 0.49 mg/L. Compared to a currently accepted total phosphate concentration threshold for eutrophication of 0.02 mg/L (US EPA, 1999; Schauser et al., 2006), if such untreated stormwater runoff is directly discharged into a water body, severe eutrophication problems will be caused. Thus, there is an urgent need to find an effective but affordable treatment process to remove phosphorus from stormwater runoff. In a previous study by our group, the phosphorus adsorption characteristics of 12 common materials were studied, such as activated carbon, brick, anthracite, and quartz sand, and some were chosen as filtration media for rainwater infiltration ponds to remove phosphorus in the runoff. However, the adsorption capacities of these materials were highly limited. For example, assuming an annual rainfall of 1154 mm with soluble P concentration of 0.42 mg/L, these materials in a 100 m² infiltration pond with a catchment area of 10,000 m² will be saturated in just 5–10 months (Bai, 2010). Therefore, the phosphorus adsorption material used in such an infiltration process should be modified to achieve a much higher adsorption capacity to meet the engineering demand.

The average phosphorus concentration in rainwater runoff is normally lower than the concentration in industrial, municipal or rural wastewater. Many studies have been carried out focused on increasing the adsorption capacity for removal of P from municipal and rural wastewater, but the effluent P concentration cannot reach levels lower than 0.02 mg/L since the discharge standards for municipal and rural wastewater are not as strict as the eutrophication threshold. According to the basic principle of adsorption, the absorption capacity is correlated with the equilibrium concentration, which is the effluent concentration or discharge concentration (Tchobanoglous et al., 1991), and a low equilibrium concentration indicates a low adsorption capacity of a given adsorbent at this concentration. So the challenge for adsorbent modification for the treatment of rainwater runoff is how to increase the adsorption capacity at a relatively low equilibrium concentration level.

This goal can be approached empirically from two directions. One is to increase the specific surface area of the absorbers. The larger the surface area is, the more active sites can react with the target compounds. The smaller the particle size that can be obtained, the larger specific...
surface area the particle has. Nano-materials would have a huge specific surface area due to their very small size scale. The other approach is to add certain compounds which have high reactivity with the target compounds; metal ions such as Fe$^{3+}$, Al$^{3+}$, Ca$^{2+}$, Mg$^{2+}$, are usually chosen to modify the adsorbers removing phosphate since metallic phosphate salts can be easily precipitated, which changes the adsorption process into an absorption process. A better solution is to combine the two approaches to find a reactive metallic nano-material to get both a huge specific surface area and a high reactivity with phosphate in order to achieve a large adsorption capacity at a low equilibrium concentration.

Lab-synthesized nano-Fe particles (usually coated with Pd, Pt, etc. to form bimetallic particles) are often used as photo-degradation catalysts for dehalogenation (of compounds such as polychlorinated biphenyls, PCBs) (Liu et al., 2009; Li et al., 2008, Wang et al., 1997), but it is seldom reported that nano-Fe is directly used as an adsorption medium to treat phosphate. Because of the size of the nano particles, if they are directly added to the infiltration tanks, they are easily washed away. Therefore the nano particles should be fixed on a natural carrier medium, and zeolite, shale ceramisite and quartz sand are commonly used as infiltration media.

In this article, self-synthesized nano-Fe particles were used as the additive agents to modify natural zeolite (Na) infiltration media. The adsorption capacities of modified adsorbents were calculated and compared with ferric chloride-modified products and other natural materials. The mechanisms of how nano-Fe increased the capacity were discussed.

1 Materials and methods

1.1 Nano-Fe synthesis

The nano-Fe particles were prepared through the ferric solution reduction process by NaBH$_4$ (Lien and Zhang, 2001). The reaction equation is shown below:

$$4\text{Fe}^{3+} + 3\text{BH}_4^- + 9\text{H}_2\text{O} \rightarrow 4\text{Fe} \downarrow + 3\text{H}_2\text{BO}_3^- + 12\text{H}^+ + 6\text{H}_2 \uparrow$$

(1)

The reaction was conducted in a water-in-oil microemulsion environment, which consisted of 60 wt.% isooctane as the oil phase, 5 wt.% n-butanol as cosurfactant, and Span 80 with Tween 80 as surfactants to achieve a final Hydrophile-Lipophile Balance (HLB) value around 9 (Zarur and Ying, 2000). The microemulsion was ultrasonically emulsified before use.

The NaBH$_4$ microemulsion was titrated into the ferric microemulsion, and the precipitates were separated by magnet, rinsed with de-oxidized deionized water three times and then absolute ethanol three times. The products were stored in ethanol and dried in a vacuum centrifugal concentrator (5301, Eppendorf, Germany) before use.

The oxidized nano-Fe particles were prepared from the newly-made nano-Fe particles after a 24-hour-exposure-in-air step.

The crystallite size of the nano-Fe particles used in this article was 13±0.6 nm, calculated using the Scherrer Equation (Scherrer, 1918).

1.2 Carrier modification

Sodium zeolite (hereafter zeolite) was used as the carrier of the modification products, and was ground and screened to a size of 1.4–3.0 mm. Two different modified products were prepared through the following methods:

Method 1: The carrier was mixed with nano-Fe particles in water with a mass ratio of 6:1, and after 2-hr stirring, the product was dried at 105°C for 2 hr; the product was named nano/zeolite #1.

Method 2: 20 g carrier material was soaked in 500 mL FeSO$_4$ solution with a concentration of 2 mol/L, and after stirring for 2 hr, the raw product was dried at 105°C for 2 hr. The dried raw product was soaked in NaBH$_4$ solution and stirred for 24 hr, and the product was dried in the vacuum drying oven to constant weight; the product was named nano/zeolite #2.

1.3 Ferric chloride modification

Twenty gram of carrier material was soaked in 500 mL FeCl$_3$ solution with a concentration of 2 mol/L, and after stirring for 2 hr, the raw products were dried at 105°C for 2 hr, and then rinsed with deionized water; the product was named FeCl$_3$/zeolite.

1.4 Phosphate adsorption experiment

One gram samples of all the products were put in rainwater runoff with a final PO$_4^{3-}$ (as in KH$_2$PO$_4$) concentration of 0.16, 0.40, 0.60, 0.80, 1.20 and 1.60 mg/L in a 150 r/min shaker at 25°C for 24 hr, and the phosphate concentrations in the filtrates after a 0.45-μm filtration were measured using the malachite green-molybdophosphate method (Ministry of Environmental Protection, 2002) as the adsorption equilibrium concentration. The adsorption isotherms were plotted to calculate the adsorption capacity according to the Langmuir or Freundich models (Tchobanoglous et al., 1991). Besides the nano-Fe- and FeCl$_3$-modified zeolites, the capacities of several other materials, such as granular activated carbon (GAC), FeCl$_3$/GAC, shale ceramisite, and FeCl$_3$/shale ceramisite, were also measured for comparison.

1.5 Phase property analysis

For specific surface area analysis the tests were carried out on a N$_2$ adsorption surface area and pore size analyzer (QuadraSorb SI, Quantachrome, USA), according to the standard ISO 9277:2010 (ISO, 2010). For scanning electron microscopy (SEM) analysis, the tests were carried out on a scanning electron microscope (S4500, Hitachi, Japan) under a normal inorganic material analysis procedure. For X-ray diffraction (XRD) analysis, the tests were carried out on an X-ray diffractometer (MAXima, X XRD-7000, Shimadzu, Japan) under a normal inorganic crystal analysis procedure (Cu $K\alpha$ radiation with 20 from 10° to 90°). The XRD pattern identification analysis was carried out by the
2 Results and discussion

According to previous studies (Bai, 2010) of rainwater runoff monitoring in a southern Chinese city, the phosphate concentrations ranged from 0.17–0.66 mg/L in 2009, and the annual flow rate weighted average concentration was 0.42 mg/L. According to fixed-bed adsorption theory, the adsorption packing media in a filtration or infiltration tank will reach its maximum adsorption capacity at breakthrough where the adsorption equilibrium concentration equals the influent concentration (Tchobanoglous et al., 1991). Therefore, the concentration of 0.42 mg/L was chosen as the equilibrium concentration to calculate the capacity in the case of the Chinese city. The adsorption capacities and specific surface areas of modified materials are shown in Table 1.

From Table 1, we can see that the capacities of the nano-Fe-modified and FeCl₃-modified zeolites increased compared to natural zeolite. Among them, the nano/zeolite #1 reached a 75-fold capacity, five times higher than nano/zeolite #2, which indicates that the procedure of simply mixing the nano-Fe particles may be superior to reducing the Fe³⁺ in situ on the carrier surface. A possible reason is that the severe reduction reaction of Fe³⁺ when contacted with NaBH₄ can form a dense Fe layer clogging the micro pores in the natural carrier, preventing further reduction of Fe³⁺ beneath the carrier surface. For nano-Fe itself, the apparent capacity values of nano-Fe and oxidized nano-Fe particles show that the unoxidized nano-Fe capacity was 1.25 times that of the oxidized particles per unit mass of the materials. However, the mass of the element Fe only contributes 0.7 of the Fe₂O₃ mass, so based on the unit mass of Fe, the capacity of the oxidized particles exceeded the unoxidized one up to 5.997 mg/g Fe, indicating the oxidized Fe³⁺ has a higher capacity than the unoxidized Fe⁰. This result can satisfy the purpose of the adsorbent usage, because when the adsorbent is used as the packing media in a filtration or infiltration tank to treat rainwater runoffs, the nano-particles will undergo the natural oxidation process, and eventually become oxidized particles. The result shows there will be no significant decrease of capacity during the oxidation process based on Fe mass, so it is feasible to put the particle in practical application. Unfortunately, the tiny nano-Fe particle by itself cannot stay very long in an infiltration tank through the filtration process, thus a carrier is still necessary. It is not possible to calculate the binding efficiency of the nano particles and the carrier, so it is difficult to compare the capacity per unit mass Fe in the nano-particles and in the bound product. But if we assume the capacity of Fe per unit mass does not change during the fixation process, the binding efficiency can be derived from the apparent capacity values. In practice, a higher ratio of nano-particle to carrier and a longer fixation time can help nano-particles dominate in the capacity contribution.

There will be a linear relationship or positive correlation between the adsorption capacity and the specific surface area, if the adsorption process is a simple physical adsorption. Therefore, the capacities were plotted versus specific surface areas to determine whether the process is a physical adsorption process for phosphate. From Fig. 1, it can be concluded that there is no positive correlation between the capacity and specific surface area (with a correlation coefficient of −0.14), which shows that the process is not a simple physical adsorption process, and that a chemical process may contribute to the results. Especially for nanoparticles, compared to GAC, the specific surface area is an order of magnitude less, but the capacity is nearly ten times greater.

Figure 2a, b shows SEM images of oxidized nano-Fe particles before and after adsorption. After the adsorption, a new product was formed on the surface to form a dense structure. The analysis of XRD graph of Fig. 2c, d shows that the new product is a kind of cacoxenite without Al, with a stoichiometric formula of Fe₄+3(PO₄)₃(OH)₁₂H₂O. This confirms that a chemical reaction was definitely carried out during the adsorption process, or we can say that besides the physical adsorption, there was also chemical absorption in this process, which validates the approach of adding ions like Fe to increase the capacity of the absorber. The very low solubility of cacoxenite implies that the desorption process for phosphate can

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Capacity (mg/g)</th>
<th>Capacity ratio to zeolite</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td>0.008</td>
<td>1.00</td>
<td>28.29</td>
</tr>
<tr>
<td>Nano-Fe</td>
<td>5.244</td>
<td>655.50</td>
<td>32.38</td>
</tr>
<tr>
<td>Oxidized nano-Fe</td>
<td>4.198</td>
<td>524.75</td>
<td>104.88</td>
</tr>
<tr>
<td>Nano/zeolite #1</td>
<td>0.604</td>
<td>75.50</td>
<td>54.33</td>
</tr>
<tr>
<td>Nano/zeolite #2</td>
<td>0.100</td>
<td>12.50</td>
<td>29.01</td>
</tr>
<tr>
<td>FeCl₃/zeolite</td>
<td>0.041</td>
<td>5.13</td>
<td>87.67</td>
</tr>
<tr>
<td>Granular activated</td>
<td>0.898</td>
<td>112.25</td>
<td>757.61</td>
</tr>
<tr>
<td>carbon (GAC)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeCl₃/GAC</td>
<td>0.071</td>
<td>8.88</td>
<td>812.58</td>
</tr>
<tr>
<td>Shale ceramisite</td>
<td>0.088</td>
<td>11.00</td>
<td>3.99</td>
</tr>
<tr>
<td>FeCl₃/shale ceramisite</td>
<td>0.001</td>
<td>0.13</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Fig. 1 Correlation of specific surface area and adsorption capacity.
**Fig. 2** SEM pictures and XRD pattern of oxidized nano-Fe before (a, c) and after (b, d) KH$_2$PO$_4$ adsorption.

**Fig. 3** SEM pictures and XRD pattern of FeCl$_3$/zeolite before (a, c) and after (b, d) KH$_2$PO$_4$ adsorption.
be ignored. The whole process can be expressed as follows:

\[
\text{Fe} + \text{PO}_4^{3-} \quad \xrightarrow{\text{adsorption}} \quad \text{complex} \quad \xrightarrow{\text{desorption}} \quad \text{Cacoxenite} \quad \quad (2)
\]

Similarly, from the SEM images (Fig. 3) of FeCl₃/zeolite, new crystals were formed after adsorption, and XRD (Fig. 3d) is consistent with the stoichiometric formula of KFeH₁₄(PO₄)₈·4H₂O, where the potassium came from the zeolite. The reason why the two adsorption products are different may be the different forms of Fe on the two modified products.

Since there is a strong bond between Fe and P, the adsorption products are not easily desorbed, which will bring out the questions of whether and how the modified adsorbent should be renewed. In our related research, the desorption processes of the adsorption products are still under study in normal rainfall and acid rain scenarios.

3 Conclusions

After modification with ferric chloride and self-made nano-Fe particles, the adsorption capacities of zeolite were greatly improved from 0.008 to 0.041 and 0.604 mg/g, respectively. The chemical absorption process between Fe and phosphate played a decisive role and dominated the contribution to increased capacity over the effect of the specific surface areas, and the capacity of oxidized particles exceeded that of unoxidized ones up to 5.997 mg/g Fe. Cacoxenite is the product of nano-Fe adsorption while complex KFeH₁₄(PO₄)₈·4H₂O is the result of FeCl₃ adsorption.

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References


Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues. The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

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