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Title	Phosphate removal from water using zirconium-based mesoporous materials [an abstract of dissertation and a summary of dissertation review]
Author(s)	Pitakteeratham, Niti
Citation	. ( ) 11577
Issue Date	2014-09-25
Doc URL	http://hdl.handle.net/2115/57229
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Type	theses (doctoral - abstract and summary of review)
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Niti Pitakteeratham

Phosphate removal from water using zirconium-based mesoporous materials
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The element phosphorus (P) is essential to all life (e.g. plants, animals and bacteria) and is a key ingredient in fertilizers to sustain high crop yields. However, the lifetime of exploitable reserves of natural ore deposits containing P is estimated to range from the next few decades to several hundreds of years, since P is intensively used in agriculture and other industries. The use of P yields large amounts of P-containing wastewater. P discharged form municipal and industrial wastewater treatment plants as sludge and water is approximately estimated to be 40,000 tons P par year in Japan. Hence, the wastewater can be considered an alternative source of P to phosphate rock. Since the release of P-containing wastewater into water bodies leads to deterioration in water quality, such as eutrophication, P in the wastewater also has to be removed from an environmental point of view. Therefore, substantial attention has been paid to the efficient removal and recovery of P from wastewater and then recycling of P. P can be removed from both raw wastewater and P rich side-streams in wastewater treatment plants by chemical precipitation with addition of Fe, Al(III) or Ca salt, biological processes, adsorbents and ion exchangers. Considering the reuse of the P recovered from the wastewater, concentrations of impurities, such as heavy metals, toxic organic materials and pathogens, should be very low. Hence, the solution used for the phosphate recovery should be clear. In addition, high phosphate concentration is beneficial for effective phosphate removal. Therefore, we applied zirconium sulfate-surfactant micelle mesostructure (ZS) as an ion exchanger to recover orthophosphate from P rich water. Although the use of ion exchangers for P recovery is relatively expensive, they have advantages of easy operation, high selectivity, high efficiency and no sludge production over other processes to obtain concentrated phosphate solution in high purity. Since a typical influent concentration of total P in sewage wastewater ranges from 5 mg-P/L to 10 mg-P/L, ZS was applied to the wastewater at higher phosphate concentration, such as reject water from an anaerobic digestion process. This thesis started with characterization (ion exchange capacity, sorption isotherm, effects of pH and interfering ions, desorption capacity) of ZS. Then ZS powders were immobilized on polymer matrix to avoid decomposition of ZS structure in regeneration process. P-ZS was used for recovery of phosphate in artificial solution and ground water containing phosphate of about 10 mg-P/L. Furthermore, we tried to obtain phosphate rich solution without suspended solid from excess sludge generated in a membrane bioreactor (MBR) by anaerobic digestion with an anaerobic MBR (AnMBR).

We investigated characterization of ZS. Ion exchange process reached to equilibrium within 60 min. The sorption isotherms could be described by the Langmuir model. The kinetic parameters were evaluated according to the pseudo-second order equations. The ZS was an effective ion exchanger for phosphate with a very high sorption capacity (114 mg P/g ZS). The sorbed phosphate was desorbed effectively (85%) using NaOH solution at pH of higher than 13.3. In the regeneration process, the breakage of ZS particles occurred and the size of ZS powders regenerated with NaOH was below 0.5 μm. We can conclud that ZS is a highly effective ion exchanger for phosphate and enables the removal of phosphate from water. However, decomposition of ZS structure made difficult to recover the regenerated ZS, for example by filtration or sedimentation.

To realize the reuse of ZS, ZS was immobilized on a polymer matrix (Aramid-Polymer). Scanning electron microscopy images of the cross-section of polymer-coated ZS (P-ZS) showed the ZS particles had angular outline and sharp edges, and the dimensions of ZS were in the range of 20 to 100 mm. Some smaller ZS particles still existed. ZS was densely packed with the polymer. P-ZS

had considerable numbers of pores and skin surface, which could facilitate transfer of phosphate and prevent leakage of ZS particles that were broken down during the desorption process. As expected, the sorption kinetics of P-ZS for phosphate were slow and it took 120 min for P-ZS to achieve equilibrium. This is probably explained by mass transfer resistance within the polymer structure. However, the contact time of 120 min is likely sufficient for P-ZS to achieve sorption equilibrium, because the amount of phosphate per unit mass of ZS for P-ZS in equilibrium was comparable to the ZS at 120 min. The phosphate sorption capacity increased with decrease in pH and the phosphate sorption capacity was highest at pH 3.0. Considering the acid dissociation constant values of phosphoric acid, the fraction of each phosphate species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}) of the total orthophosphate, which was defined as the sum of these four chemical species, was calculated. A decrease in pH from 7.2 inevitably resulted in the formation of more $H_2PO_4^-$ than HPO_4^{2-}, indicating preferable sorption of $H_2PO_4^-$ to ZS. This result indicates that phosphate removal by ZS requires pH adjustment to optimize phosphate removal efficiency. Since anions (e.g., bicarbonate, nitrate, chloride and acetate) other than phosphate were present in environmental waters, the interfering effect of the anions was investigated. The uptake and distribution coefficients (K_d) of these anions were evaluated. The selectivity order based on the K_d values was phosphate ($K_d = 3390$) $\approx$ bicarbonate ($K_d = 3340$) $\gg$ nitrate ($K_d = 109$) $\approx$ acetate ($K_d = 84$) > chloride ($K_d = 1.7$). At equilibrium, P-ZS sorbed 65.5 mg P/g-ZS while 16.5 mg P/g-ZS of phosphate was sorbed in presence of carbonate. P-ZS was subjected to a 50-cycle sorption-desorption test to investigate P-ZS reusability. The overall amount of phosphate adsorbed and desorbed in 50 cycles was 1300 and 1141 mg P/g P-ZS, respectively. The P-ZS retained its functionality and sorption and desorption capacities over 50 cycles. An artificial phosphate solution and groundwater, both of which contained phosphate of about 10 mg P/L, was treated in columns packed with P-ZS. The phosphate could be removed completely onto P-ZS up to 1020 (an artificial solution) and 241 (groundwater) bed volumes, respectively. The reason for the lower removal efficiency was the presence of bicarbonate. These results indicated that P-ZS was a highly effective ion exchanger for phosphate and enabled the removal of phosphate from water.

AnMBR (20L) was operated for 165 days. Excess MBR sludge, which contained P at a relatively high concentration, was fed to the AnMBR at a sludge-loading rate of 3.8 g SS/reactor/day. COD removal efficiencies were > 88%. The average biogas production rate was 432 mL/reactor/day. Sludge has not been withdrawn except samples (500 mL) for analysis. P was released from the MBR sludge and collected as permeate of membrane. Concentration of phosphate in the permeate was 74 ± 19 mg P/L. However, by anaerobic digestion, 37% of P present in the MBR sludge was not transformed to soluble phosphate that could be filtered. The permeate was fed to the P-ZS column with a flow rate of 5 mL4/hr (2 h of hydraulic retention time). Breakthrough occurred at 196 BV, during which 71 mg P of phosphate per g ZS in P-ZS was sorbed.

In summary, ZS could recover phosphate in pure water, transparent ground water and even filtered rejected water by an ion-exchange process with high sorption capacity. Bicarbonate was the sole interfering anion among the anions tested. Phosphate sorbed could be desorbed from the ZS using NaOH solution. The P-ZS could be reused at least 50 times without loss of original functionality. A column packed with P-ZS could remove phosphate completely in groundwater (about 10 mg P/L of phosphate) and filtered reject water (88 mg P/L of phosphate) up to 241 and 196 bed volumes, respectively. Therefore, we concluded that ZS is a highly effective ion exchanger for phosphate and enabled the removal of phosphate from water. From an economic point of view, modification was required, such as simplification of the system and further increase in the number of reuse of P-ZS.