Recovery of Inorganic Phosphorus Using Copper-Substituted ZSM-5

Michael J. Manto,[†] *Pengfei Xie,*[†] *Mitchell A. Keller, Wilhelm E. Liano, Tiancheng Pu, Chao Wang*[*]

Department of Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland 21218, United States

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Abstract. Efficient and cost-effective separation of phosphorus (P) from aqueous solutions possesses great value in addressing the challenges in sustainability. Not only does it mitigate the pollution caused by phosphate in agricultural runoffs, but it also provides a renewable source for production of phosphorus-based chemicals and fertilizes. Here we report on the use of copper-substituted zeolites, Cu-ZSM-5, as sorbents for recovery of P. Fast capture and release of phosphate anions are demonstrated with >90% efficiency of recovery using synthetic solutions of Na_2HPO_4 and NaCl, respectively. The zeolite sorbents are also found to be recyclable and sustain high recovery efficiencies after multiple capture-release cycles. Cu(II) species in the zeolites are identified to be the active sites for anion adsorption, and based on this finding a ligand exchange mechanism is proposed for ion exchange involved in the capture and release of phosphorus.

INTRODUCTION

Interest is growing in the development of separation processes for the efficient removal and regeneration of P from wastewaters.[1-2] Dissolved P, including phosphate (PO_4^{3-}), hydrogen phosphate (HPO_4^{2-}) and dihydrogen phosphate ($H_2PO_4^-$), is a primary source of water contamination originating from industrial wastewater and agricultural runoffs.[3-5] The presence of high levels of P in ponds, rivers and lakes can lead to eutrophication, threatening the existence of fish and other aquatic life.[6-8] On the other side, P is broadly used as fertilizers in agriculture to promote the growth of crops and the demand continues to escalate as the population grows. The world's supply of P today, however, relies on depleting feedstocks such as phosphate rocks.[9-11] It thus becomes imperative, not only for pollution mitigation, but also for the sustainable production of fertilizers, to develop efficient and cost-effective methods for separation of P from aqueous solutions.

The most common method of phosphorus separation is chemical precipitation, typically in the form of struvite.[12-13] Although feasible for implementation, this method consumes valuable feedstocks such as ammonia and/or magnesium salts.[14-16] Meanwhile, struvite precipitation requires operation under high-pH conditions and precise control over the molar ratio of ammonium (NH_4^+), magnesium (Mg^{2+}), and phosphates, which add challenges to the process design and incur additional costs for scale-up applications.[17-20] The use of other cations, such as Al^{3+} and Fe^{3+} that are capable of precipitating phosphate under more robust conditions, however, generates products undesired for agricultural purposes.[21-22] In light of the challenges present in chemical precipitation, efforts have been devoted to the development of new separation processes, such as using sorbents for capture of phosphate anions.[23]

Zeolites have attained great attention as ion-exchange materials due to their chemical and structural stability, tunable and selective adsorption properties, employment of naturally abundant elements, and environmental compatibility.[24-25] Natural zeolites such as clinoptilolite and gibbsite have previously been reported for capture and release of phosphates.[24,26-29] Their limited capacity and specificity, however, have inspired the exploration of more robust sorbents. Synthetic zeolites[30-35] have been demonstrated to have high capacity for P capture, yet with poor efficiency (<10%) of release. Recently, synthetic zeolites modified with high-valence metal cations such as La^{3+} have been reported to possess high capacity of phosphate adsorption and release efficiencies as high as 100%.[36-40] Despite the demonstrated potential for P separation, these sorbents still involve rare-earth elements and fundamental questions about the mechanisms of capacity enhancement persist.

Here we report on the study of copper-substituted Zeolite Socony Mobil-5 (Cu-ZSM-5) as sorbents for the recovery of inorganic P from aqueous solutions. ZSM-5 represents an industrially important type of aluminosilicate with the general chemical formula of $Na_nAl_nSi_{96-n}O_{192}\cdot16H_2O$. Isomorphous substitution of Si^{4+} by Al^{3+} produces a negative charge on the framework, which is usually compensated by adsorbed cations (H^+, NH_4^+ or Na^+). Substitution of these cations with Cu^{2+} produces Cu-ZSM-5, with the introduced Cu sites believed to be active for anion exchange. Capture and release of phosphates are systematically studied using synthetic solutions to evaluate the dependences of adsorption capacity and release efficiency on the loading of sorbent and the extent of Cu substitution. The nature of the active sites is depicted by tuning the conditions of pretreatment and examining the effect of Cu oxidation state on P capture, leading into discussion of the mechanism for anion exchange. Finally, using the Cu-ZSM-5 sorbents to recover P from complex media is demonstrated with synthetic solutions containing competing anions or real wastewater.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cu-ZSM-5. Commercial NH_4-ZSM-5 (Si/Al molar ratio of 11.5) was purchased and converted into Cu-ZSM-5 through a series of treatments. The as-received NH_4-ZSM-5 was first calcined to obtain H-ZSM-5 and then exchanged in a solution of sodium nitrate to produce Na-ZSM-5.[41-42] Na-ZSM-5 was further subjected to cation exchange in solutions of copper(II) acetate to form Cu-ZSM-5 (Scheme 1, see the Methods for more details of the synthesis). Na-ZSM-5 was employed for Cu substitution because the cation exchange in this case is more facile than that for H-ZSM-5.[43]

Three types of zeolites with different contents of Cu were obtained by tuning the conditions of synthesis, with the weight percentages of Cu determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis to be 3.43%, 3.53% and 3.98%. From the results of elemental analysis, the Cu/Al ratios are determined to be 0.43, 0.45 and 0.51, corresponding to Cu site densities of 539, 556 and 626 μmol$_{Cu}$/g$_{zeolite}$ for the three types of zeolites, which are denoted as Cu-ZSM-5(1), Cu-ZSM-5(2) and Cu-ZSM-5(3), respectively, in the following discussion (Table 1). The obtained Cu-ZSM-5 preserved the particle size (~1 μm) and the morphology of the commercial NH_4-ZSM-5 (Figures 1a-c). XRD patterns show neither significant change to the crystal structure of ZSM-5 nor the formation of copper oxides after the Cu substitution, and the major peaks can be assigned to the MFI type of zeolite framework (JCDPS No. 37-0359) (Figure 1d). The specific surface areas estimated by the Brunauer–Emmett–Teller (BET) analysis are nearly consistent in the range of 365 – 373 m^2/g for the three types of zeolites, as compared to 376 m^2/g for Na-ZSM-5, which are also in line with the previously reported results on Cu-ZSM-5[42,44] (Table 1). Similar situations are also observed for the microporous volumes calculated by the t-plot method.[45]

These characterizations suggest that the ZSM-5 has been successfully modified with atomic Cu species, with the microporous structure of the zeolites remaining intact. In the MFI framework of ZSM-5, the 10-membered rings form three-dimensional micropores of 5.4 to 5.6 Å in diameter, which are sufficiently large to allow for diffusion of phosphate anions in and out of the zeolites.[27,46] In addition to the characterizations discussed above, the oxidation state of Cu in the obtained Cu-ZSM-5 has also been characterized by using X-ray photoemission spectroscopy (XPS), which will be detailed in the discussion below on the active sites for phosphate adsorption.

P Capture in Synthetic Solutions. Capture of P was carried out with the Cu-ZSM-5 sorbents in synthetic solutions of Na_2HPO_4. In a typical process, 300 mg of zeolite is used for 10 ml of Na_2HPO_4 solution (1 g-P/L, pH = 8.6). During the adsorption process, aliquots of solution were collected at various time intervals and after separation of the sorbent, the concentrations of dissolved P remaining in the solution were measured by using a molybdenum blue assay.[47-48] The amounts of P captured by the zeolites were then determined as the difference between the initial and remaining concentrations of P in the solution (see the Methods and Figure S1).

Figure 2a shows the kinetic results for the three types of zeolite. A two-stage behavior is consistently observed: the amount of captured P has a rapid increase in the first ~15 min, and then the rate of sorption dramatically slows down. These two kinetic regimes can be ascribed to film and pore diffusion, which is confirmed by fitting the time-dependent adsorption curves with the intra-particle model[30,36] (Figure S3). For all the sorbents, the calculated coefficients for pore diffusion ($k_{d.p}$) are generally 2 – 3 times smaller than those for film diffusion ($k_{d.f}$), indicating that the diffusion through the micropores within the zeolites is the rate-limiting step (Table S1). Furthermore, it is shown that $k_{d,p}$ increases as the Cu content in the zeolite increases, suggesting that a hopping-type of mechanism, i.e., migration of adsorbate between adjacent Cu sites, may facilitate the diffusion of phosphates through the micropores.[49-51] Within the studied period (1.5 h), uptake capacities of ca. 27, 30 and 33 mg-P/$g_{zeolite}$ were achieved by using 300 mg of Cu-ZSM-5(1), Cu-ZSM-5(2) and Cu-ZSM-5(3), corresponding to capture of ca. 84.5, 91.2 and 98.9% of the dissolved inorganic P in the solutions, respectively. The trends of uptake capacity and capture efficiency are in line with the order of Cu site density in the zeolites (Table 1).

With the given amount of dissolved P (10 mg), the efficiency of P capture is highly dependent on the sorbent mass, with more P captured as the mass of applied zeolite increases (Figure 2b). In the case of Cu-ZSM-5(1), the efficiency of P capture varies from ~9% to ~99% as the applied amount of sorbent increases from 10 to 500 mg. While compared at the other loadings, the trend of capture efficiency is consistent with that observed when 300 mg of zeolite is used, namely Cu-ZSM-5(3) > Cu-ZSM-5(2) > Cu-ZSM-5(1). For the former two types of zeolite, the maximum efficiency, ~99% of the dissolved P (nearly complete sorption), is reached at sorbent loadings ≥200 mg, whereas it requires >400 mg of loading for Cu-ZSM-5(1) to reach the same efficiency.

Release of P. Release of the captured P is crucial for the recovery of nutrients and for the development of cost-effective, reusable sorbent materials. To desorb the phosphate anions, the Cu-ZSM-5 sorbents are isolated from the capture solution and re-dispersed in a brine solution. The chloride anions exchange with the adsorbed phosphate, and the P released into the brine solution is again analyzed by using a molybdenum blue assay. Typically, 10 ml of NaCl solution (10 g/L) is used for 300 mg of sorbent. Figure 3 presents the percentages of P released during the desorption process. For all the three types of zeolite sorbent, the release follows a two-stage behavior similar to that for capture, with a rapid release of nearly 80% of the captured P within the initial ~15 min. The consistent fast kinetics of P release may be a result of the rather high concentration of NaCl in the brine solutions, which provides high chemical potentials to drive the ion diffusion and exchange in the zeolites. The release of P is found to be independent of the Cu content in the zeolite and the loading of sorbent (10 – 500 mg), and the three types of zeolites have a consistent efficiency of release at ~87%. The time-dependent desorption behavior can also be fitted by the film and pore diffusion model, with the trends of diffusion coefficients found to be consistent with those derived from adsorption (Figure S3 and Table S1). It should be pointed out that the captured P may also be released in acidic or basic electrolytes, e.g., using HCl to generate phosphoric acid and applying ammonia to make $(NH_4)H_2PO_4$ or $(NH_4)_2HPO_4$, which is advantageous for production of pure phosphorus chemicals.

Recyclability of Cu-ZSM-5. After demonstrating the capture and release of P, recyclability of the sorbents is further studied by applying the Cu-ZSM-5 zeolites to successive capture and release cycles. Each cycle is carried out under the standard conditions, i.e., 300 mg of sorbent, 10 ml of Na_2HPO_4 solution (1 g/L) for capture and 10 ml of NaCl solution (10 g/L) for release.

Figure 4 summarizes the results of recyclability studies for the three types of Cu-ZSM-5 sorbent and compares the amounts of captured and released P within 20 capture-release cycles. All the three types of zeolite exhibit great recyclability. The drop of uptake capacity is only marginal in the first 10 cycles, although it becomes more substantial in subsequent cycles (Figure 4a). For example, Cu-ZSM-5(3) has an uptake of 32.6 mg-P/$g_{zeolite}$ in the first cycle, and sustained ~95% and ~78% of this capacity by the 10th and 20th cycle, respectively. In comparison, Cu-ZSM-5(1) and Cu-ZSM-5(2) have initial uptake capacities of ~28 and ~30 mg-P/$g_{zeolite}$, with ~61% and ~64% retention of the initial capacity in the 20th cycle, respectively. The release of P is found to follow a similar trend as that for capture, with 13.1, 13.5 and 22.4 mg of P recovered from each gram of Cu-ZSM-5(1), Cu-ZSM-5(2) and Cu-ZSM-5(3) sorbent in the 20th cycle, respectively (Figure 4b). These values correspond to ~53%, ~55% and ~31% retention of the amounts of P recovered in the first cycle.

The recyclability performances are further illustrated by the plots of release and recovery efficiencies over the course of the 20 capture-release cycles (Figure 4c). Here, the efficiency of release represents the ratio between the released and captured amount of P in each cycle, whereas the recovery efficiency indicates the percentage of net recovered P compared to the initial amount of dissolved P in the starting solution (10 ml of Na_2HPO_4 solution at 1 g-P/L, using 300 mg of sorbent). For all three types of zeolite, the release efficiency is consistently at 80 – 90% throughout the recyclability studies. In contrast, the efficiency of recovery drops from ~73% to ~39% for Cu-ZSM-5(1), from ~79% to ~41% for Cu-ZSM-5(2), and from ~88% to ~67% for Cu-ZSM-5(3) in

20 cycles. From XRD analysis after the recyclability studies, the Cu-ZSM-5 sorbents retained their crystal structures throughout the capture-release cycles (Figure S4). These observations suggest that the recyclability may not be limited by the desorption of phosphate, but rather by the capacity of capture. The latter can be correlated to the loss of Cu content throughout the capture-release cycles, as characterized by ICP-MS analysis for the cycled sorbents (Figure 4d). The Cu site densities preserved after 20 cycles are found to be 524, 551 and 564 $\mu mol_{Cu}/g_{zeolite}$ for the three types of zeolites, with the order still being consistent with that for the recovery efficiency at the end of the recyclability studies, namely Cu-ZSM-5(3) > Cu-ZSM-5(2) > Cu-ZSM-5(1).

It is noticed that the Cu leached out of the sorbent may cause secondary contamination to the water during P recovery. Part of the leached Cu may come from non-specifically (or loosely) bound Cu species on the surface or trapped in the zeolites, which could be mitigated by applying pretreatments such as immersion in and wash with NaCl solutions. Nevertheless, the amount of Cu leached out during each cycle is quite small. The loss of Cu is up to 10% for Cu-ZSM-5(3) after 20 cycles, which is corresponding to <2% in each single capture-release cycle. This sorbent has the highest content of Cu and probably also the most non-specifically bound Cu. In contrast, Cu-ZSM-5(2) has merely <1% loss for the Cu content within 20 cycles, and the concentration of leached Cu in the capture and release solutions is estimated to be in the ppm level.

Phosphate Adsorption. The above discussions have revealed a strong correlation of the capacity of P capture to the density of Cu sites for the Cu-ZSM-5 sorbents, suggesting that Cu functions as the active sites for phosphate adsorption. Although this may be explicit considering the atomic structures of Cu-ZSM-5, it is noted that pristine zeolites (without metal substitution) have also been reported to be capable of capturing P.[28,52-57] Our control experiments on using H-ZSM-5 or Na-ZSM-5 show very limited capacity of P capture (<10%, Figure S5), indicating that the monovalent cations (H^+ and Na^+) are not beneficial for anion adsorption and the small capacity may be ascribed to hydrogen bond interactions between the phosphate anions and the framework oxygen.[27] In Cu-ZSM-5, the substituted Cu(II) is known to be chelated on the –O–Al–O– site in the 10-membered ring and create positive charge centers.[58-61] It is thus speculated that these positively-charged sites accommodate anion adsorption and facilitate ion exchange. To validate this scheme, comparative studies are further performed on Cu-ZSM-5 subjected to different pretreatment conditions.

Cu-ZSM-5 with the Cu/Al ratio of 0.51 is used as the example here. The Cu-ZSM-5(3) sorbent mentioned in the above discussion was prepared by calcination at 100°C in air for overnight. Pretreatment at 500°C in static air or in He was also applied to the zeolite with the same Cu/Al ratio, with the obtained products denoted as Cu-ZSM-5(3A) or Cu-ZSM-5(3B), respectively (Table 2). The oxidation state of Cu in these zeolites was characterized by using XPS (Figure 5a). Based on the previous studies, the Cu $2p_{3/2}$ peak is deconvoluted on the basis of Cu(I) at the binding energy of 933.3 eV and Cu(II) at 935.4 eV, with the deconvoluted peak areas used to determine the molar fractions of Cu(I) and Cu(II) in the zeolites (Table 2).[62-65] It is revealed that >90% of the Cu species in Cu-ZSM-5(3) and Cu-ZSM-5(3A) is in the +2 state, whereas a significant portion (~80%) of Cu is converted into +1 state in Cu-ZSM-5(3B). These observations are in line with the previous studies reported on Cu-ZSM-5.[66-68]

Figure 5b shows the comparison of P capture by using the three types of Cu-ZSM-5 with the same Cu/Al ratio (0.51). It is found that Cu-ZSM-5(3) and Cu-ZSM-5(3A) have similar kinetic behaviors and capacities for P capture, reaching an uptake of ~31 mg-P/$g_{zeolite}$, whereas Cu-ZSM-5(3B) has only a low uptake of ~5 mg-P/$g_{zeolite}$. By plotting the uptake of P and the ratio of Cu(II) (in the total amount of Cu species) together, a strong correlation is clearly seen between these two values (Figure 5c). This finding, together with the observation that the Cu species is also predominantly Cu(II) in Cu-ZSM-5(1) and Cu-ZSM-5(2) (Figure 5a), thus validates that the phosphate adsorption sites are associated with Cu(II) in the Cu-ZSM-5 sorbents.

Mechanism for Ion Exchange. With Cu(II) determined to be the active site for phosphate adsorption, a ligand exchange mechanism is proposed for anion exchange on Cu-ZSM-5. As shown in Scheme 2, the first step of P capture (at pH = 8.6 ± 0.1) is believed to involve the reaction

$$=\mathrm{Cu{-}OH} + \mathrm{Na}^+ + \mathrm{HPO_4}^{2-} \rightarrow =\mathrm{Cu{-}HPO_4}\cdots\mathrm{Na} + \mathrm{OH}^- \qquad (1)$$

where =Cu represents the positively charged Cu(II) site on the ZSM-5 framework, with the hydroxyl group introduced for charge balance. This hydroxyl group could undergo ligand exchange with hydrogen phosphate ($\mathrm{HPO_4}^{2-}$) anions in the solution phase, assisted by solvated Na^+ cations for charge balance.[27,30,39] The release of OH^- from this step is confirmed by the rise of pH to 9.5 ± 0.1 after capture (Table 3). After the initial capture, the release of P in NaCl solution could be written as

$$=\mathrm{Cu{-}HPO_4}\cdots\mathrm{Na} + \mathrm{Cl}^- \rightarrow =\mathrm{Cu{-}Cl} + \mathrm{Na}^+ + \mathrm{HPO_4}^{2-} \qquad (2)$$

and the following P capture then takes place by the reversed process

$$=\mathrm{Cu{-}Cl} + \mathrm{Na}^+ + \mathrm{HPO_4}^{2-} \rightarrow =\mathrm{Cu{-}HPO_4}\cdots\mathrm{Na} + \mathrm{Cl}^- \qquad (3)$$

where Na^+ is also introduced for charge balance. These ion exchange reactions are also confirmed by the changes of solution pH measured during the capture-release cycles. After release of the hydrogen phosphate, the pH of the brine solution is raised by about one unit, whereas the pH of the $\mathrm{Na_2HPO_4}$ solution drops from ~8.6 to ~7.1 after the P capture. These pH changes are consistent with the expectations considering the alterations of phosphate concentrations in the cyclic process.

It should be noted that the stoichiometries of these reactions may differ from eq. (1-3) and the number of phosphate (and chloride) anions adsorbed per Cu(II) site could be >1. For example, the molar ratio between P and Cu (P/Cu) calculated based on the measured uptake (Figure 2a) is about ~1 at the mass loading of 100 mg for all the three types of zeolites, which suggests monolayer coverage being dominant in this situation. When the loading of sorbent is reduced, the P/Cu ratio becomes larger, reaching as high as ~2.5 for Cu-ZSM-5(1) at the loading of 10 mg. The adsorption of multiple phosphate anions on one Cu(II) site could be stabilized by the formation of hydrogen bonds between phosphates, as well as between phosphate and the framework, polymerization between phosphates, and/or involvement of multiple Na^+ cations in the inner sphere.[27,69-71]

P Capture in Complex Media. After studying the capture and release of P in synthetic solutions, we further apply the Cu-ZSM-5 sorbents to complex media, including synthetic solutions of phosphate in the presence of competing anions and real wastewater containing various inorganic and organic impurities, which is believed to be important for practical applications.

The effects of coexisting ions have been extensively studied for ion exchange using zeolites.[30,35-36,38] For anion (phosphates) adsorption, the concern of competing ions is primarily on the presence of other anions such as SO_4^{2-}, $C1^-$, NO_3^- and HCO_3^-, which may compete with phosphates for adsorption on the cationic Cu sites in the zeolitic sorbents. To examine the effects of competing adsorption on P capture, synthetic solutions containing 1000 mg-P/L (equivalent to 32.3 mmol-P/L) and 5 – 50 mmol/L of Cl^-, NO_3^-, HCO_3^- or SO_4^{2-} are treated with 500 mg of Cu-ZSM-5(1). The introduction of these anions led to drop in the efficiency of P capture, with the loss in capture capacity increasing at higher concentrations of competing anions (Figure 6a). The drop of capture efficiency is rather marginal when the concentrations of competing anions are below that for phosphate, i.e., <25% in general, but becomes substantial if the competing anions are more abundant than phosphate, up to 40% drop when 50% mmol/L of SO_4^{2-} is present. From Figure 6a, it can also be seen that the affinity of anions on Cu-ZSM-5 follows the order PO_4^{3-} >> SO_4^{2-} > HCO_3^- > NO_3^- > Cl^-, with SO_4^{2-} having the largest and Cl^- having the least effect on the P capture.

Wastewater is a complex media containing various organic and biomolecular impurities besides competing anions.[37-38] To demonstrate the potential for practical applications, we have applied the Cu-ZSM-5 sorbents to recover P from real wastewater (derived from the Back River Wastewater Treatment Plant in Baltimore, MD). This plant employs anaerobic digestion to break down sewage wastes and the effluents contain low concentrations of phosphate (8.1 mg-P/L) and various organic impurities. The Cu-ZSM-5 sorbent is capable of recovering up to ca. 40% of P from the anaerobic digestion effluents (Figure 6b). This efficiency is considered to be significant since the P content in the wastewater may be present in the organic form, which may be inaccessible for ion exchange. The sorbents are also found to be recyclable, with less than ~5% drop in recovery efficiency within 5 cycles of capture and release, indicating that Cu-ZSM-5 is resistant to fouling for recovering P from wastewater (Figure 6b).

CONCLUSION

We have performed systematic studies of Cu-ZSM-5 as sorbents for phosphorus recovery. Fast capture of phosphorus from synthetic solutions of Na_2HPO_4 and release of the captured phosphorus in brine solutions have been demonstrated with a net efficiency of recovery >90%. The zeolite sorbents have also been shown to be recyclable and sustain high recovery efficiency after multiple capture-release cycles. Comparative studies of phosphorus capture using the zeolites subjected to different pretreatments, in combination with XPS analysis for the oxidation state of Cu in the sorbents, reveal that Cu(II) species are the active sites for anion adsorption, which serve as a basis for a proposed ligand exchange mechanism for the capture and release of phosphorus. The Cu-

ZSM-5 sorbents have also been demonstrated for P capture in the presence of competing anions and recovery of P from real wastewater. Our work highlights the tremendous potential of metal-substituted zeolites as sorbents for anion exchange and the recovery of nutrients from wastewater streams.

METHODS

Materials and Chemicals. The following materials were purchased and used as-received without further purification: L-ascorbic acid ($C_6H_8O_6$, reagent grade, Sigma), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}$-$4H_2O$, ACS reagent, 81.0-83.0% MoO_3 basis, Sigma-Aldrich), copper(II) acetate monohydrate ($Cu(CO_2CH_3)_2$-H_2O, $\geq$ 99.0%, Sigma-Aldrich), nitric acid (HNO_3, ACS grade, Fisher), sodium bicarbonate ($NaHCO_3$, ACS grade, VWR), sodium chloride (NaCl, $\geq$ 99.0%, Fisher), sodium nitrate ($NaNO_3$, $\geq$ 99.0%, Sigma-Aldrich), sodium phosphate dibasic (Na_2HPO_4, $\geq$ 98.5%, Sigma), sodium sulfate (Na_2SO_4, anhydrous, ACS grade, VWR), sulfuric acid (H_2SO_4, ACS grade, BDH), Zeolite Socony Mobil-5 (ZSM-5, ammonium, Si/Al = 11.5, Alfa Aesar), and anhydrous ethanol (C_2H_5OH, 200 proof, ACS/USP grade, Pharmco-Aaper). Deionized water was collected from an ELGA PURELAB flex apparatus.

Synthesis of Cu-ZSM-5. Commercial NH_4-ZSM-5 (Alfa Aesar, Si/Al = 11.5) was calcined at 450°C for 4 h in static air, which is converted into H-ZSM-5. Na-ZSM-5 was prepared by dispersing H-ZSM-5 in 1 M $NaNO_3$ solution (about 10 ml solution was used per gram of zeolite), which was held at 80°C under stirring for 4 h. The Na-ZSM-5 was further exchanged with Cu^{2+} cations by using three different protocols. Cu-ZSM-5(1) and Cu-ZSM-5(2) were prepared by exchanging two or three times, respectively, in a 0.01 mol/L copper(II) acetate solution at 25°C for 24 h. Cu-ZSM-5(3) was prepared by exchanging three times in a 0.1 M copper(II) acetate solution at 25°C for 24 h. After each step of exchange, the sorbents were rinsed with deionized water three times. The obtained Cu-ZSM-5 sorbents were dried at 100°C overnight in static air.

Characterization. Scanning electron microscopy (SEM) images were taken on a JEOL 6700F field emission electron scanning microscope operating at 10.0 kV. Transmission electron microscopy (TEM) images were taken on an FEI Tecnai 12 operating at 100 kV. X-ray diffraction (XRD) patterns were obtained from a PANalytical X'Pert^3 X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5406 Å). Nitrogen adsorption measurements were measured on a Micromeritics ASAP 2010 instrument with the samples degassed under vacuum at 300°C for 4 h. Specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller (BET) theory. The Cu and Al contents were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a PerkinElmer Elan DRC II Quadrupole ICP-MS after dissolution of the zeolites in HF. X-ray photoelectron spectroscopy (XPS) spectra were collected on a PHI 5400 X-ray photoelectron spectrometer equipped with an Al K_α X-ray source.

Inorganic P Capture and Release. Synthetic solutions of 1000 mg-P/L (calculated on the basis of elemental P) were prepared by dissolving Na_2HPO_4 in deionized water. In a typical capture process, 300 mg of Cu-ZSM-5 sorbent was added to 10 mL of the Na_2HPO_4 solution. The formed mixture was stirred (700 rpm) at room temperature for up to 1.5 h for P capture. After separation of the sorbent by centrifugation, P release was performed by mixing the sorbent with 10 mL of NaCl solution (10 g/L). At designated time intervals during the capture and release, aliquots of the solutions were extracted from the mixture and centrifuged to remove the sorbent. The obtained supernatants were treated with a molybdenum blue assay, and ultraviolet-visible (UV-Vis) absorption spectra were collected on these treated supernatants using a Promega GloMax Multi

Detection System to determine the concentration of inorganic P.[47-48] Experiments and/or measurements were repeated for a total of three runs each to determine standard errors.

Inorganic P Capture and Release in Complex Media. For examining the effect of competing anions, synthetic solutions containing 1000 mg-P/L (32.3 mmol-P/L) and 5 – 50 mmol/L of Cl^-, NO_3^-, HCO_3^- or SO_4^{2-} were treated with 500 mg of Cu-ZSM-5(1). For recovery of P from wastewater, samples derived from the Back River Wastewater Treatment Plant (Baltimore, MD) was centrifuged to remove the bulk biosolids and then employed for P capture using 500 mg of Cu-ZSM-5(1).

ASSOCIATED CONTENT

Supporting Information. More details about the experimental methods and additional results of material characterization. This material is available free of charge via the Internet at http://pubs.acs.org

AUTHOR INFORMATION

Corresponding Author

*Email: chaowang@jhu.edu

Author Contributions

The manuscript was written with contributions from all the authors. All the authors have given approval to the final version for submission.

†These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

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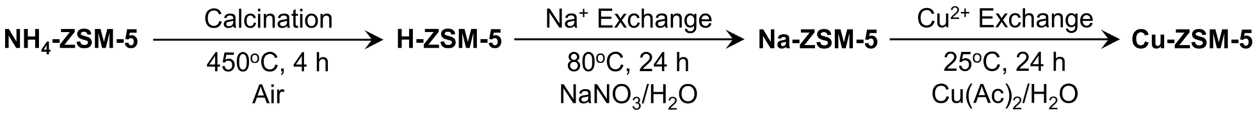
Scheme 1. Synthesis protocol for the preparation of Cu-ZSM-5.



Scheme 2. Proposed mechanism of P capture and release using Cu-ZSM-5.

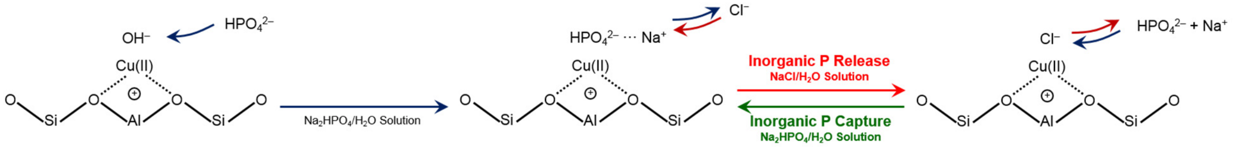


Table 1. Summary of Si/Al and Cu/Al molar ratios, Cu site density and BET surface areas for the Cu-ZSM-5 sorbents.

Sample	Si/Al Molar Ratio	Cu/Al Molar Ratio	Cu Site Density ($\mu mol_{Cu}/g_{zeolite}$)	BET Surface Area (m^2/g)	V_{micro}[a] (cm^3/g)
Na-ZSM-5	11.5	–	–	376	0.163
Cu-ZSM-5(1)	11.5	0.43	539	373	0.163
Cu-ZSM-5(2)	11.5	0.45	556	369	0.161
Cu-ZSM-5(3)	11.5	0.51	626	365	0.160

[a] Calculated by the t-plot method.

Table 2. Preparation method, Cu site density, and ratios of Cu(I) and Cu(II) in Cu-ZSM-5(3), Cu-ZSM-5(3A) and Cu-ZSM-5(3B).

Sample	Preparation After Cu^{2+} Exchange	Cu Site Density ($\mu mol_{Cu}/g_{zeolite}$)	Cu(I) Ratio (%)	Cu(II) Ratio (%)
Cu-ZSM-5(3)	100°C Overnight, Static Air	626	5.8	94.2
Cu-ZSM-5(3A)	500°C 2 h, Static Air	626	6.2	93.2
Cu-ZSM-5(3B)	500°C 2 h, He	626	79.2	20.8

Table 3. Measured solution pH during initial and subsequent capture/release cycles.

Cycle	Solution	Stage	pH
First Capture-Release Cycle	Na_2HPO_4/H_2O	Before Capture	8.6 ± 0.1
		After Capture	9.5 ± 0.1
	$NaCl/H_2O$	Before Release	6.9 ± 0.1
		After Release	8.3 ± 0.1
Subsequent Capture-Release Cycles	Na_2HPO_4/H_2O	Before Capture	8.6 ± 0.1
		After Capture	7.1 ± 0.1
	$NaCl/H_2O$	Before Release	6.9 ± 0.1
		After Release	8.0 ± 0.1

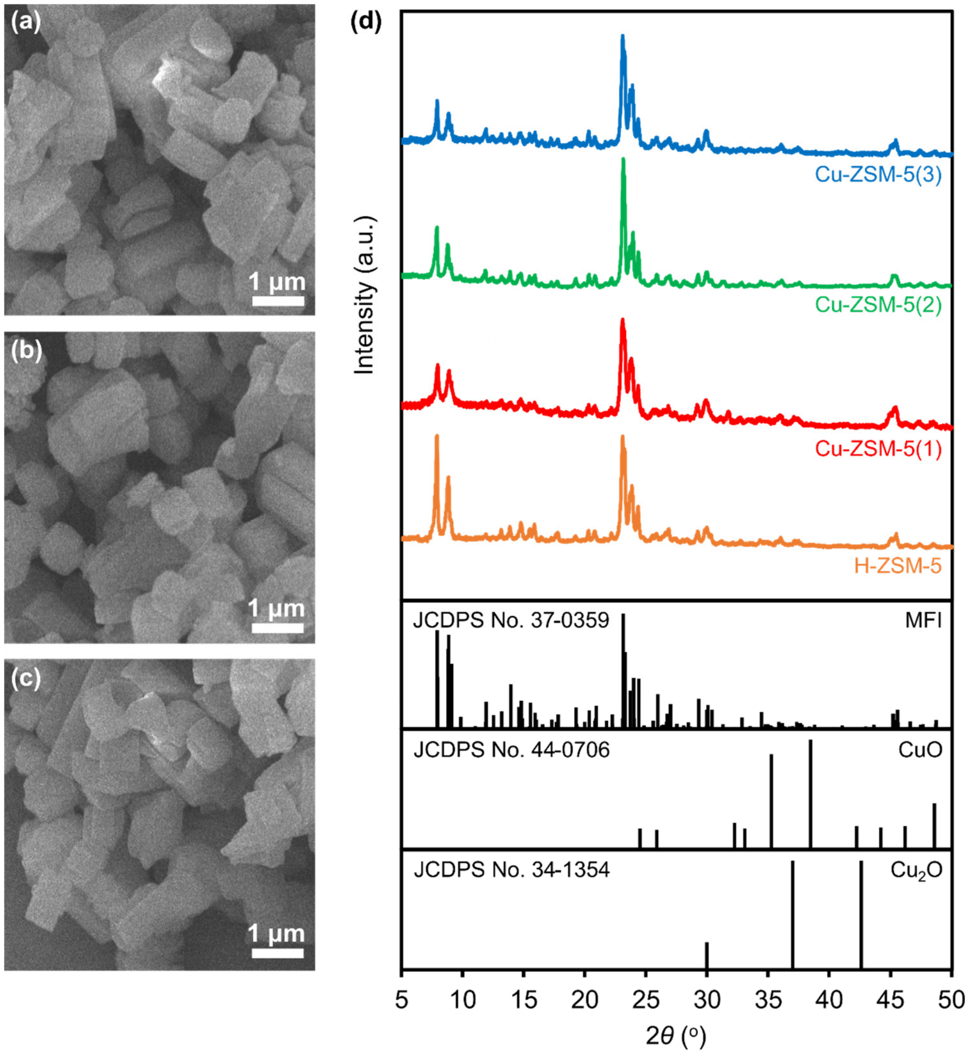


Figure 1. SEM images of (a) NH_4-ZSM-5, (b) H-ZSM-5 and (c) Cu-ZSM-5(3). (d) XRD patterns of the intermediate H-ZSM-5 and Cu-ZSM-5 sorbents compared to JCDPS PDF patterns for MFI, CuO and Cu_2O.

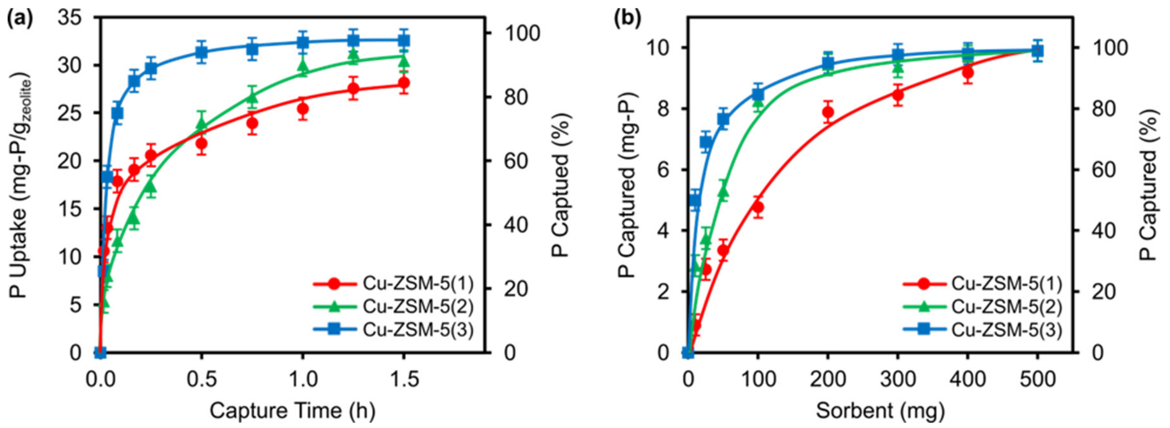


Figure 2. (a) Uptake and captured percentage of the P from 10 mL of Na_2HPO_4 solutions (1 g-P/L) by using 300 mg of each Cu-ZSM-5 sorbent. (b) The dependence of P capture using various loadings of Cu-ZSM-5 sorbents.

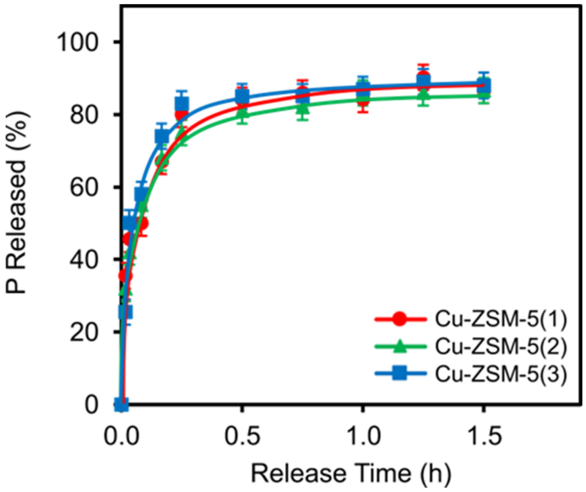


Figure 3. Percentages of released P (versus the captured P) from 300 mg of each Cu-ZSM-5 sorbent in 10 mL of NaCl solution (1 g/L) after the capture shown in Figure 2a.

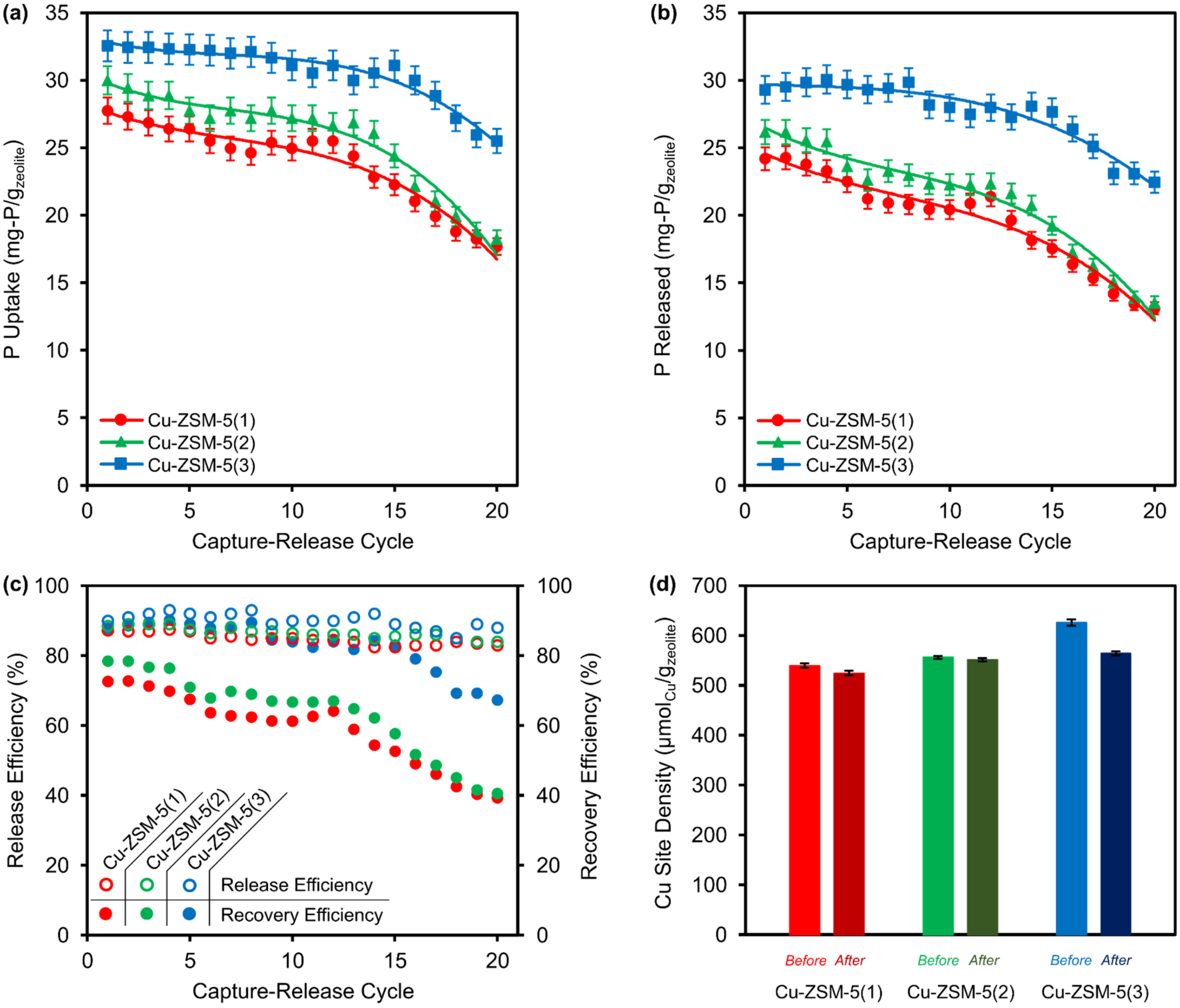


Figure 4. Recyclability analysis of each Cu-ZSM-5 sorbent showing the capacities of (a) P uptake and (b) P release over a total of 20 capture-release cycles. (c) Release efficiency and recovery efficiency of each Cu-ZSM-5 sorbent recorded over the capture-release cycles. (d) Changes in Cu site density determined by ICP-MS for each Cu-ZSM-5 sorbent before and after the recyclability studies.

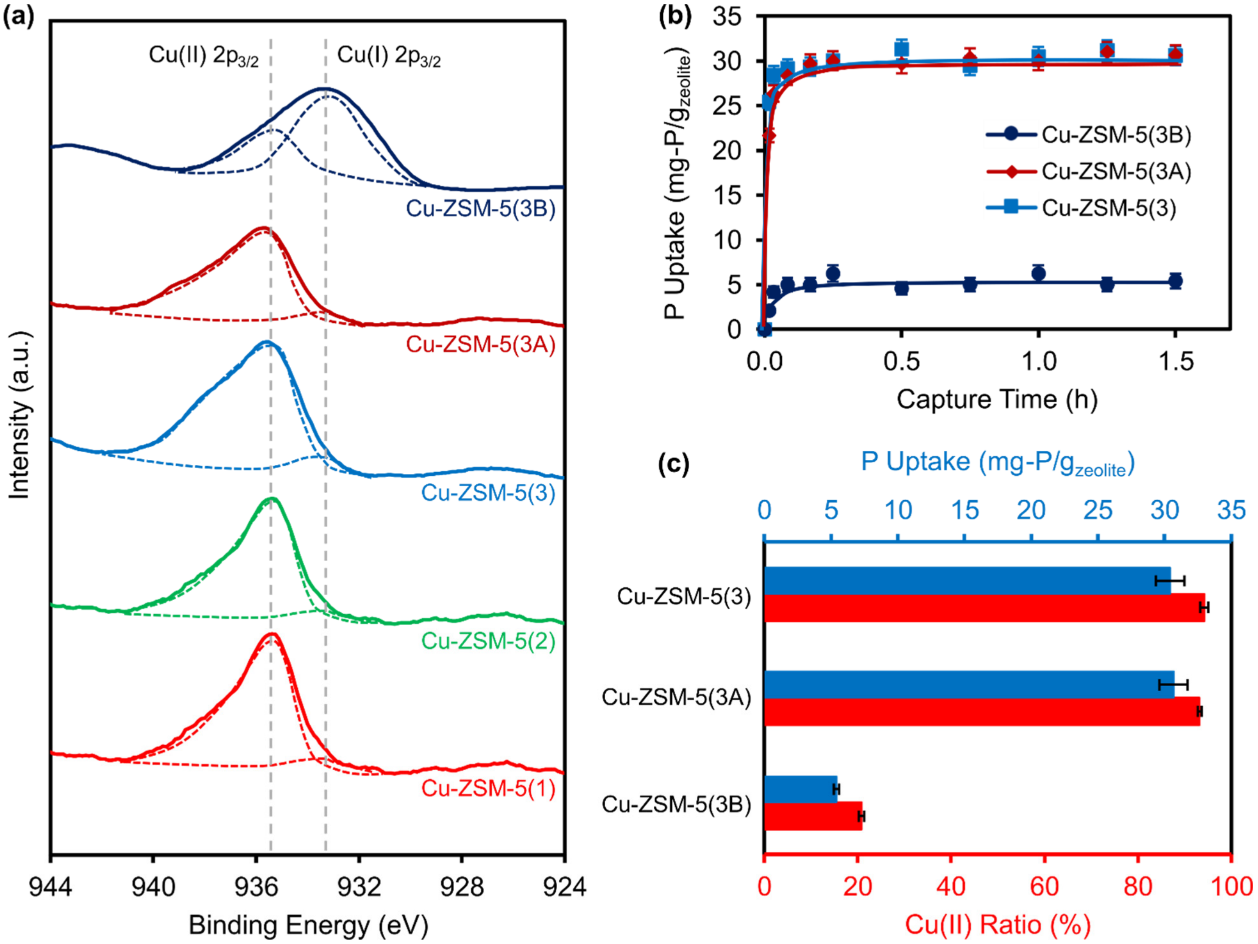


Figure 5. (a) XPS spectra showing the Cu $2p_{3/2}$ peaks for Cu-ZSM-5 sorbents. (b) P uptake using 300 mg of Cu-ZSM-5(3), Cu-ZSM-5(3A) or Cu-ZSM-5(3B). (c) Correlations between the capacity of P uptake and the ratio of Cu(II) in the Cu species plotted for the three types of zeolites with Cu/Al ratio equal to 0.51.

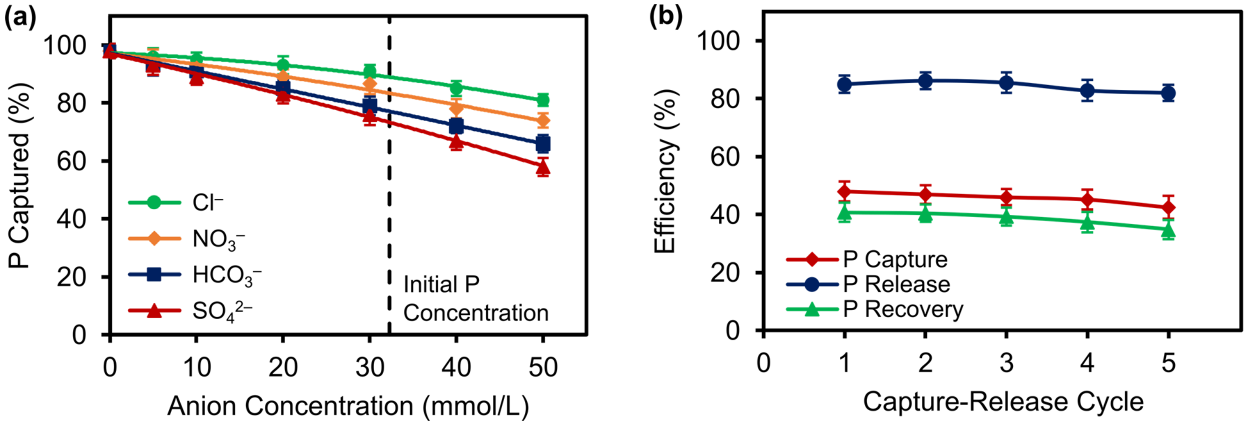


Figure 6. (a) P capture using 500 mg of Cu-ZSM-5(1) in the presence of various concentrations of competing anions. (b) Capture, release, and recovery efficiencies using 500 mg of Cu-ZSM-5(1) from wastewater (8.1 mg-P/L, see the Methods).

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