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# Surfactant-Modified Zeolite as a Slow Release Fertilizer for Phosphorus

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The feasibility of using surfactant-modified zeolite (SMZ) as a carrier for fertilizer and for slow release of phosphorus (P) was investigated. Zeolite-A was modified by using hexadecyltrimethylammonium bromide, a cationic surfactant, to modify its surface to increase its capacity to retain anion, namely, phosphate ( $PO_4^{3-}$ ). SMZ was thoroughly characterized using X-ray diffraction, Fourier transform infrared, and scanning electron microscopy to study the effect of surfactant modification. Zeolite-A and SMZ were then subjected to P loading by treating them with fertilizer (KH<sub>2</sub>PO<sub>4</sub>). It was observed that the P loading on SMZ increased by a factor of 4.9 as compared to the unmodified zeolite-A. A comparative study of the release of P from fertilizer-loaded unmodified zeolite-A and SMZ and from solid KH<sub>2</sub>PO<sub>4</sub> was performed using the constant flow percolation reactor. The results show that the P supply from fertilizer-loaded SMZ was available even after 1080 h of continuous percolation, whereas P from KH<sub>2</sub>PO<sub>4</sub> was exhausted within 264 h. The results indicate that SMZ is a good sorbent for PO<sub>4</sub><sup>3-</sup>, and a slow release of P was achievable. These properties suggest that SMZ has a great potential as the fertilizer carrier for slow release of P.

KEYWORDS: Surfactant-modified zeolites; slow release fertilizers; phosphate

# INTRODUCTION

Excessive use of chemical fertilizers causes serious environmental hazards as only a fraction is really absorbed by the soil. The excess fertilizer is washed off and leads to high concentrations of elements such as nitrogen, phosphorus, and potassium in surface water bodies, leading to eutrophication. The nutrients may also reach groundwater, leading to excessive dissolved solids such as nitrates in groundwater (1). Soil salinization by the excess fertilizer and damage to seedlings in arid zones by poor water quality also pose severe threats to mankind (2). The aforementioned problems can be resolved using slow release fertilizers (SRFs) (3-6). Recently, several types of SRFs have been developed and tested, including SRFs using various zeolites (7-15). However, SRFs are often expensive and the release of nutrients is slow at the time of high nutrient need (16).

Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, with a three-dimensional lattice, furrowed by an inner network of pores and channels. Zeolites have a high cation exchange capacity and have often been used as inexpensive cation exchangers for various applications (17). The studies on SRFs based on zeolites are limited to nutrients, which can be loaded in cationic forms such as  $NH_4^+$  and  $K^+$ . However, if the nutrients are in anionic forms such as  $NO_3^-$  or  $PO_4^{3-}$ , the loading is negligible on unmodified zeolites. Therefore, it is imperative that the material should have adequate affinity for anions so that the anionic nutrients can be efficiently loaded for its use as SRFs. Anionic properties can easily be imparted on the zeolitic surface using the concept of surface modification using surfactant. In 1994, Haggerty et al. reported surfactant-modified zeolite (SMZ), a type of inexpensive anion exchanger, to remove anionic contaminants from water (18). Since then, SMZs have been studied extensively for sequestration of various anions (19-26). The surfactant molecules form bilayers on zeolite external surfaces with the lower layer held by electrostatic interaction between the negatively charged zeolite surface and the positively charged surfactant headgroups while the upper layer is bound to the lower layer by hydrophobic forces between the surfactant tail groups in both layers (22). Under the surfactant bilayer configuration, the zeolite reverses its surface charge, resulting in a higher affinity for negatively charged anions, and the sorption and retention of anions are attributed to surface anion exchange. Because the surfactants are attached only on the external surface of the zeolite, the cation exchange sites situated inside the pores are still available for cation exchange. Therefore, loading of cationic nutrients such as K in the pores can be achieved simultaneously with the anionic nutrients such as NO3<sup>-</sup> or PO4<sup>3-</sup> on their surface. It has also been reported that the use of SMZ as anion exchanger is economically more feasible as compared to synthetic anion exchange resins (24). It may also be emphasized that zeolites are commonly used as soil conditioners and therefore are very suitable for this application. Thus, SMZs offer a great promise as anion carriers for slow release of nutrients.

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Figure 1. Experimental setup of the percolation reactor for nutrient uptake.

The present study deals with the synthesis and characterization of SMZ. Nutrient uptake capacities of unmodified zeolite and SMZ modified with different surfactant loading were also studied. To study the slow release of nutrients, we used the percolation reactor at a constant flow of solution, so that the actual field conditions can be simulated to evaluate the nutrient supply capacity of SRFs. A comparative study of nutrient leaching from nutrient-loaded unmodified zeolite, SMZ, and pure fertilizer was also undertaken.

### MATERIALS AND METHODS

Synthesis of SMZ. The commercial zeolite-A used was procured from Degussa (Germany). Surfactant modification of the zeolite was carried out using the surfactant, hexadecyltrimethylammonium bromide (HDTMABr) (E. Merck, Germany). A preweighed quantity of washed zeolite sample was mixed with HDTMABr solution in a 1:100 (solid: liquid) ratio. The concentrations of HDTMABr solutions used for preparation of SMZ-1, SMZ-2, and SMZ-3 were 50, 100, and 200 mg/ L, respectively. The solution was agitated for 7-8 h at 150 rpm on an orbital shaker. The solution was then filtered, and the solid residue was washed with double-distilled water and air-dried for 4-6 h. The synthesized SMZ was then mechanically ground with a mortar and pestle to a fine particle size. As the surfactant is the only source of carbon in the system, the surfactant loading was monitored by total organic carbon (TOC) analysis of the initial and final solutions obtained during the synthesis of SMZ. The TOC analysis was carried out using a Shimadzu TOC analyzer (model: TOC-V<sub>CPH</sub>). SMZs with surfactant loadings of 1.7, 3.8, and 4.6 mg g<sup>-1</sup> of zeolite were designated as SMZ-1, SMZ-2, and SMZ-3, respectively. The unmodified zeolite-A and SMZ-3 were characterized using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared analysis (FTIR), and Brunauer-Emmett-Teller (BET) surface area estimation. Various physicochemical properties of the unmodified zeolite and SMZ-3 are given in Table 1.

**Synthesis of SRFs.** The SMZs with different loadings of HDTMABr were subjected to treatment with KH<sub>2</sub>PO<sub>4</sub> to prepare the nutrient-loaded SRFs. To study the sorption behavior of phosphate on various zeolites, different quantities of zeolite were added to centrifuge tubes containing



Figure 2. XRD patterns of unmodified zeolite-A and SMZ-3.

Table 1. Physicochemical Properties of Unmodified Zeolite and SMZ-3

property	unmodified zeolite-A (Degussa)	SMZ-3
appearance average particle size (µm)	white 2–3	white 4–6 276
(mequiv/100 g dry sample) density (g/cm <sup>3</sup> ) pH of 1% slurry	2.03 9.5	2.8 11.2
crystalline form crystallinity (percent) SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> molar ratio	A type zeolite 96–99 1.93	A type zeolite 85 1.93
surface area (m <sup>2</sup> /g) TCLP test <sup>a</sup>	590 -Ve	521 -Ve

<sup>a</sup> TCLP-ve; no toxic elements were leached.

Table 2. Physicochemical Properties of Soil

parameter	measurement values
water holding capacity (%)	61.30
pH (1: 1 soil: water)	8.6
electrical conductivity (dS/m)	0.63
organic carbon (%)	0.91
porosity (%)	56.01
specific gravity (g/cm <sup>3</sup> )	1.80
particle density (g/cm <sup>3</sup> )	2.29
bulk density (g/cm <sup>3</sup> )	1.01
Ca (mg/kg)	20490
Fe (mg/kg)	397
Al (mg/kg)	59080

50 mL of KH<sub>2</sub>PO<sub>4</sub> solution and the mixture was stirred for 12 h at 150 rpm. The mixtures were then centrifuged, and the phosphate solution concentration was analyzed by addition of using ammonium molybdate and stannous chloride solution, which results in development of a blue colored complex. The absorbance of the solutions was measured at 690 nm using UV–visible spectrophotometer (Chemito, model UV 2100) (*30*). The amount of phosphate sorbed was calculated from the difference between the initial and the equilibrium solution concentrations.

To prepare SRFs, required quantities of SMZ were stirred with 1.0 M solution of KH<sub>2</sub>PO<sub>4</sub> for 8 h and filtered, washed three times with deionized water, and air-dried. The solid:liquid ratio used was 1:10 for the synthesis of phosphate-loaded zeolites. Similarly, nutrient loading was also carried out on unmodified zeolite to study the effect of surface modification on nutrient uptake capacity and slow release of nutrients as compared to SMZ. The amount of  $PO_4^{3-}$  sorbed was calculated from the difference between the initial and the equilibrium solution concentrations.

**Soil.** The soil was collected locally from a nearby garden. The soil was thoroughly characterized for various parameters using standard procedures (*31*). Bulk density, specific gravity, pore space percent, and water holding capacity were determined using a Keen–Raczkowski box experiment. pH and electrical conductivity were determined from water extracts of the soil prepared from a 1:2.5 soil:water suspension. The pH and electrical conductivity meter (WTW), respectively. The percent organic carbon was determined by dichromate oxidation. The Ca, Fe, and Al were determined by inductuvely coupled plasma optical emission spectroscopy (Perkin-Elmer, model Optima 4100). Various soil properties are shown in **Table 2**. Soil was added to simulate the actual field conditions to study the release of P from various fertilizers.

**Experimental Setup of Percolation Reactor for Nutrient Uptake.** The experimental setup was basically the same as reported by Pino et al., except that the Teflon reactor was replaced by a glass column reactor and the pumped flow was replaced by flow under gravity with precise flow controllers (3). The chemical reactor (Figure 1) consisted of a glass column (internal diameter = 1.5 cm; height = 25 cm) through



Figure 3. SEM of unmodified zeolite-A and SMZ-3.

the top of which deionized water was continuously supplied at a flow rate of  $72 \pm 1$  mL day<sup>-1</sup>. Inside the reactor, 10 g of soil overlaid with 1.0 g of fertilizer was placed. The leachates were collected to determine PO<sub>4</sub><sup>3-</sup> (as P) using the UV-visible spectrophotometric method. Three tests were performed as follows: two SRFs prepared from unmodified zeolite and SMZ and another with pure KH<sub>2</sub>PO<sub>4</sub>. A test was also performed using pure soil with no fertilizer added, to determine the contribution of P from soil. Parallel reactors were set up to perform the tests in duplicate, and average values are reported. The mean temperature during the experiment was  $30 \pm 0.2$  °C.

# **RESULTS AND DISCUSSION**

Zeolite Characterization. To monitor the effect of surfactant modification on structure stability, the powder XRD analysis (using Cu K $\alpha$  as the source for X-rays) of unmodified zeolite-A and SMZ-3 was performed. The XRD patterns of unmodified zeolite-A and SMZ-3 are presented in Figure 2. The d spacing values used for reference are as follows:  $12.20 \pm 0.20$ ,  $8.60 \pm$  $0.20, 7.05 \pm 0.15, 4.07 \pm 0.08, 3.68 \pm 0.07, 3.38 \pm 0.06, 3.26$  $\pm$  0.05, 2.96  $\pm$  0.05, 2.73  $\pm$  0.05, and 2.60  $\pm$  0.05 Å. The closely matching d spacing values of all of these zeolites prove that structure has been retained. The surface morphology of SMZ-3 was examined by SEM and is presented in Figure 3. The cubical geometry of zeolites has not changed much; probably, there are changes in sharp edges and corners. FTIR spectra obtained using KBr pellets of unmodified zeolite-A and SMZ-3 are presented in Figure 4. The IR pattern of SMZ-3 shows the characteristic peaks at wavenumbers 3402, 1651, 1004, 559, and 464  $cm^{-1}$  reported for zeolite-A (27). Besides, the peaks at 2923 and 2856  $cm^{-1}$  in SMZ-3 can be assigned to HDTMABr sorbed on the zeolite surface as the corresponding peaks are also observed in the IR pattern of HDTMABr only



Figure 4. FTIR spectra of SMZ-3 and HDTMABr.

(peaks at 2918 and 2848 cm<sup>-1</sup> in **Figure 4a**). The presence of characteristic peaks of zeolite-A confirms the structural stability of zeolite after surfactant modification. Also, the presence of HDTMABr peaks in the IR spectra of SMZ indicates the sorbed HDTMABr on the zeolite surface.

The surfactant loading was confirmed by using TOC analysis, as mentioned earlier. A substantial decrease in surface area was observed for SMZ-A as compared to unmodified zeolite-A, which is due to coverage of HDTMABr molecules (head size of about 6 Å) on the external surface (**Table 1**).

**Phosphate Loading on SMZ.** The sorption of  $PO_4^{3-}$  on unmodified zeolite and SMZs with different loadings of HDTMABr is shown in **Figure 5**. As evident from the figure, the surfactant modification greatly enhances anion sorption on zeolite. Furthermore, it is observed that the amount of phosphate sorbed increases with the increase in surfactant loading on zeolite, and a maximum sorption of 454.5 mmol g<sup>-1</sup> is observed for SMZ-3. The percent loading of P on SMZ-3 has increased by a factor of 4.9 as compared to unmodified zeolite. Similar results have been reported for other oxyanions such as chromate (19).

The sorption of anionic species on zeolitic surfaces can be well-described by the Langmuir sorption isotherm:

$$S = \frac{K_{\rm L} S_{\rm m} C}{1 + K_{\rm I} C} \tag{1}$$



Figure 5. Sorption of P on unmodified zeolite and SMZs with different surfactant loading.

where *S* is the amount of anions sorbed on solid surfaces at equilibrium (mmol  $g^{-1}$ ), *C* is the equilibrium anion concentration (mmol  $L^{-1}$ ), *S*<sub>m</sub> is the maximum sorption capacity (mmol  $g^{-1}$ ), and *K*<sub>L</sub> is the Langmuir sorption coefficient (mmol<sup>-1</sup>).

Langmuir coefficients, maximum sorption capacity, and the coefficient of regression are listed in **Table 3**. Because the

**Table 3.** Sorption Maxima ( $S_m$ ), Langmuir Sorption Coefficients ( $K_L$ ), and Coefficients of Regression for P Sorption on SMZ ( $r^2$ )

fertilizer	$S_{\rm m}$ (mmol g <sup>-1</sup> )	$K_{\rm L} ({\rm mmol}^{-1}  imes 10^{-3})$	r <sup>2</sup>
unmodified zeolite	92.6	0.23	0.97
SMZ-1	131.6	0.35	0.99
SMZ-2	147.1	0.29	0.99
SMZ-3	454.5	0.38	0.99



Figure 6. P release from pure fertilizer, unmodified zeolite-A, and SMZ-3.

SMZ-3 shows the highest phosphate sorption, it was selected for further study.

Slow Release of Phosphorus. The pure fertilizer (KH<sub>2</sub>PO<sub>4</sub>), P-loaded unmodified zeolite-A and SMZ-3 were subjected to desorption using the chemical reactors. The reactor with soil and without fertilizer did not provide any detectable amount of P. Therefore, all of the P measured from the leachates obtained from reactors having soil plus fertilizer can be attributed to the fertilizer source exclusively. The variation of P concentration with time for the three fertilizers is presented in Figure 6. It can be observed from the data that at the start of the experiment, a maximum concentration of 44.5 mmol  $L^{-1}$  P is observed in the leachate from pure KH<sub>2</sub>PO<sub>4</sub> followed by 31.7 and 20.1 mmol  $L^{-1}$  from unmodified zeolite and SMZ-3, respectively. Furthermore, it can be seen that in the initial stage, P dissolution, from all three fertilizers, occurs rapidly and attains a concentration between 4.6 and 3.5 mmol L<sup>-1</sup> at about 120 h, after which slow release is observed. The data also reveal that all of the available P in pure KH<sub>2</sub>PO<sub>4</sub> is exhausted after 264 h while the release of P from unmodified zeolite continues till 624 h, beyond which the concentration of P reached below detectable limits. However, the release of P from SMZ-3 is continued even after 1080 h, with concentrations ranging from 1.8 to 1.4 mmol  $L^{-1}$ . The results clearly demonstrate the slow release of P from SMZ-3. Also, the level of P released is sufficient for soil microbial activity and plant growth (2).

In general, the desorption is somehow instantaneous, making it very difficult to fit the observed data to any desorption models. However, it has been reported that the slow release of fertilizers normally follows a first-order kinetics (3). Figures 7-9 show the kinetics of P release from KH<sub>2</sub>PO<sub>4</sub>, P-loaded unmodified zeolite, and SMZ-3, respectively. The results show that the release takes place in different stages according to the solubility of the different fractions, so that the readily soluble P is leached



Figure 7. Kinetics of P release from pure KH<sub>2</sub>PO<sub>4</sub>.



Figure 8. Kinetics of P release from unmodified zeolite.



Figure 9. Kinetics of P release from SMZ.

first. However, only one stage is observed for pure  $KH_2PO_4$ , characterized by a steep slope with a decay time of 264 h. The corresponding rate constant is also higher for the pure  $KH_2PO_4$  than for any of the zeolite-based fertilizers (**Figures 7–9**),

indicating the instantaneous desorption of P. Two stages are observed for unmodified zeolite with a decay time of 624 h after which the P concentration reaches below detectable limits. It can be assumed that the available P has been completely released. SMZ-3 also shows leaching of P in two stages (Figure 9). Stage one corresponds to fast release of P similar to unmodified zeolite. However, from 120 h onward, the P release curve for SMZ-3 stabilizes progressively and a P concentration of about  $1.8-1.4 \text{ mmol } L^{-1}$  is continued even after 1080 h. The SMZ-3 presents a leaching pattern, which is in accordance with that of an SRF, characterized by two stages in which a first-order kinetic law describes the release process. The fast release of P in the first stages, in both cases, may be attributed to the readily soluble form of the salt that covers the zeolite particles and that has not been completely removed by the previous washing. Furthermore, the values of rate constants for initial stages for unmodified zeolite and SMZ-3 are comparable to the rate constant values obtained for pure fertilizer, which confirms that the initial stage corresponds to unadsorbed, unwashed P present on the zeolite surface.

No attempt has been made in the present paper to explain the nature or desorption mechanism of P since it is welldocumented and reported elsewhere (28, 29). However, it is worth pointing out that SMZ-3 fertilizer provides a nutrient supply, high enough to sustain a suitable plant development, even at the simulated field conditions such as those used in this work. The study has proved the efficacy of SMZ-3 for slow release of nutrients like P. Moreover, the most favorable characteristic of zeolite, for its application as SRF, is the fact that it also functions as a soil conditioner. Besides, the composition of zeolites does not differ significantly from that of soil. It is, therefore, not expected to alter its characteristics, thus ensuring physicochemical stability and consequently higher plant growth.

#### **ABBREVIATIONS USED**

SMZ, surfactant-modified zeolite; SRF, slow release fertilizer; HDTMABr, hexadecyltrimethylammonium bromide; XRD, powder X-ray diffraction; FTIR, Fourier transform infrared analysis; SEM, scanning electron microscopy; BET surface area, Brunauer–Emmett–Teller surface area; TOC, total organic carbon.

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