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Use of surfactant-modified zeolite to carry and slowly release sulfate

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ABSTRACT

Use of water soluble fertilizers could result in increased loss of plant nutrient during irrigation and cause non-point source groundwater contamination. In this study the feasibility of using surfactant-modified zeolite (SMZ) as fertilizer additives to control sulfate release was tested in batch and column leaching experiments. The zeolite was able to carry as much as 5, 15, and 25 mmol/kg of sulfate when modified to 100%, 150% and 200% of its external cation exchange capacity (ECEC). Batch tests showed an almost instantaneous and partially reversible sulfate release. Leached with 50 pore volumes (PVs) of water, 70% and 85% of the loaded sulfate was still remained on SMZ modified to 150% and 200% ECEC, respectively. The initial sulfate concentration in leachate was reduced by a factor of three when sulfate loaded SMZ was used compared to mixtures of soluble sulfate and zeolite of the same loading in column leaching experiments. Mass balance showed a 31% recovery after the columns were flushed with 60 PVs of water, similar to the observation in batch tests. The results indicated that SMZ could be a good carrier for sulfate. Thus, leaching of sulfate can be greatly reduced and slow release of sulfate can be achieved if SMZ is used as fertilizer additives.

Keywords: Slow release fertilizer; Sulfate; Surfactant; Zeolite

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1. Introduction

Many of the plant nutrients are in anionic forms such as nitrate, sulfate, and phosphate. Furthermore, many plants assimilate nitrogen in nitrate form and sulfur in sulfate form [1]. As they are mobile, it would be of great interest to find some inexpensive materials to serve as carriers to control the leaching of these compounds and to slowly release them to meet the nutrition needs for plants growth.

Because of its high cation-exchange capacity, clinoptilolite, a natural occurring zeolite, has often been used as an inexpensive slow release fertilizer (SRF) carrier to carry and slowly release NH_4^+ [2–4]. In addition, mixing NH_4-saturated clinoptilolite with phosphate rock could provide slow release of both P and N [5,6]. Zeolite could also serve as a carrier for occlusion of ammonium nitrate to achieve slow release of both ammonium and nitrate [7,8].

Surfactant-modified zeolite (SMZ) has been studied extensively in the last 15 years due to its high capacity of sorption and retention of oxyanions [9,10]. Positive results have been reported on retention of chromate [11–13], nitrate and sulfate [10], and phosphate [14]. In addition, surfactant micellar enhanced ultrafiltration could also remove phosphate [15] and color dyes [16] from treated domestic wastewaters. However, most of these researches were focused on using SMZ

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to remove contaminants from water. Tests on using SMZ as fertilizer carriers for SRF were only limited on release of nitrate [17] and phosphate [14]. A 20 fold reduction in nitrate concentration in the effluent was achieved and a stable supply of 0.3 mmol/L of nitrate up to 50 pore volumes (PVs) could be maintained when nitrate-loaded SMZ was used in comparison to that when water soluble nitrate of the same loading was used [17]. Phosphorus supply from phosphate-loaded SMZ was available even after 1080 h of continuous percolation, whereas P from KH_2PO_4 was exhausted within 264 h [14].

Sulfur is an essential element for growth and physiological functioning of plants. But its content varied greatly between plant species and ranged from 0.1% to 6% of the plants' dry weight [18]. Sulfate taken up by the roots was the major sulfur source for growth, though it had to be reduced to sulfide before being metabolized [19]. Although animal manure contained sulfur, only 5% of total sulfur in manure slurry was plant available [20]. The primary source of sulfur in nitrogen fertilizer was ammonium sulfate, ammonium bisulfite, and thiosulfate while other sulfur fertilizers including potassium sulfate, magnesium sulfate, and potassium magnesium sulfate were also good sulfur providers [21]. The sulfur in sulfate fertilizers had the advantage of being immediately available to plants following their dissolution, while the disadvantage was a relatively large dose of sulfate released to the soil over a short period of time which was likely lost beyond the root zone of plants by leaching [1]. Thus, an inexpensive fertilizer carrier that can curtain the sulfate release rate would be of great value. This research aims at evaluating retention of sulfate on and leaching of sulfate from SMZ under batch and column conditions so that the transport behavior of sulfate in SMZ could be determined and the slow release effect of sulfate from SMZ assessed.

2. Materials and methods

2.1. Zeolite

The zeolite aggregates (from the St. Cloud mine in Winston, New Mexico) were 0.42–0.83 mm in size, contained 74% clinoptilolite, 12% feldspar, 12% quartz and cristobalite, and trace amounts of clay minerals [22]. The external cation exchange capacity (ECEC) was 100 meq/kg with major exchangeable cations being K^+ and Ca^{2+} [11].

2.2. Preparation of SMZ

Hexadecyltrimethylammonium (HDTMA) bromide (from Aldrich, Milwaukee, WI), a cationic surfactant, was used for surface modification of zeolite. Previously results showed that at HDTMA loading maximum of 200 mmol/kg, corresponding to 200% of the zeolite's ECEC, a surfactant bilayer would form and the surface was reversed to positive [11]. However, in this study, the zeolite was modified by HDTMA to 100%, 150%, and 200% of its ECEC to determine the optimal HDTMA loading for sulfate upload and release. To each 250 mL centrifuge bottle, 60 g of raw zeolite and 180 mL of HDTMA solution with concentrations of 33, 50, 67 mmol/L were mixed on a reciprocal shaker for 24 h at 150 rpm. The mixture was then centrifuged at 5000 rpm for 20 min and the HDTMA solution concentration analyzed by an HPLC method [11]. The equilibrium HDTMA concentration was nondetectable for the low treatment levels and less than 0.3 mmol/L for the higher treatment level, indicating that targeted HDTMA loading levels were achieved.

2.3. Determination of sulfate carrying capacity on SMZ

To each 40-mL centrifuge tube, 2.0 g of SMZ and 20 mL of 1, 2, 3, 4, 6, 8, or 10 mmol/L K_2SO_4 solution were mixed for 24 h at 150 rpm. The mixtures were then centrifuged and the sulfate analyzed by an HPLC method [11]. The amount of sulfate loaded was calculated from the difference between the initial and equilibrium solution concentrations.

2.4. Preparation of sulfate loaded SMZ

To each 250-mL centrifuge bottle, 40 g of SMZ modified to 100%, 150%, or 200% ECEC was mixed with 200 mL of 10 mmol/L K_2SO_4 solution for 24 h at 150 rpm. The mixture was then centrifuged, the sulfate concentration analyzed and the solid air-dried. The final sulfate loadings were 16 and 21 mmol/kg on SMZ at surfactant loadings of 150% and 200% ECEC.

2.5. Batch sulfate release

Batch sulfate release experiments were conducted as functions of time, pH, ionic strength, and numbers of release cycles. To each 40-mL centrifuge tube, 2.5 g of sulfate-loaded SMZ and 25 mL of deionized water or solutions with pH 4 (30 mmol/L acetic acid/3 mmol/L sodium acetate), 7 (33 mmol/L NaCl), or 10 (16.5 mmol/L Na_2CO_3/16.5 mmol/L $NaHCO_3$); or solutions with ionic strengths of 3.3, 10, or 33 mmol/L of NaCl as the background electrolyte were mixed for 1/4, 1/2, 1, 2, 4, 8, 16, and 32 h at 150 rpm. The mixture was then centrifuged at 5000 rpm for 20 min and 20 mL of supernatant was removed. The sulfate concentrations were analyzed by an HPLC method [9,11]. Then 20 mL of fresh solution was added followed by shaking

Table 1
Flow conditions for column sulfate leaching tests

Settings	Unmodified Zeolite	Modified Zeolite
Solid weight (g)	61	74
Pore volume (mL)	31	29
Porosity	0.51	0.38
Flow rate (mL/min)	0.44	0.44
Sulfate input (mmol)	1.1	1.3
Sulfate output (mmol)	0.75	0.4
Recovery (%)	71	31

the mixtures for the same amount of time. The above procedure was repeated for two more cycles for each treatment condition and each shaking time.

2.6. Column sulfate leaching test

The columns used were 60-mL plastic syringe sleeves, each packed with 60 mL of zeolite or SMZ. For the unmodified zeolite columns, about 60 g of raw zeolite blended with 18 mmol/kg of K_2SO_4 was used. For SMZ columns, each was filled with 76 ± 1 g of SMZ of the same sulfate loading. The columns were flushed with distilled water using a four-head peristaltic pump. The sulfate concentrations in leachate were analyzed by an HPLC method [11] at every 1/4 PV for the mixture and sulfate loaded SMZ at the early stage. Detailed flow and transport conditions are listed in Table 1.

3. Results and discussion

3.1. Loading of sulfate on SMZ

Loading of sulfate on SMZ modified to >100 % ECEC was well characterized by the Langmuir sorption isotherm (Fig. 1). The sulfate loading capacity (S_m) (Fig. 1) was lower than that of nitrate on SMZ [17], comparable to that of phosphate on two out of three SMZ [14], and higher than chromate sorption [9,11]. Under normal lyotropic series, divalent anions should have a higher selection coefficient over monovalent anions. The loading capacity of sulfate compared to nitrate on SMZ may be attributed to the charge effect of the anions. Each HDTMA molecule contributes one positive charge, which needs only one negative charge to balance. Sulfate is divalent and thus, needs two HDTMA molecules to neutralize. Meanwhile, the HDTMA surface configuration is not rigid because of the surfactant tail-tail interaction. Thus, bridging two HDTMA molecules with one sulfate may be less favored compared to 1:1 neutralization of HDTMA by nitrate.

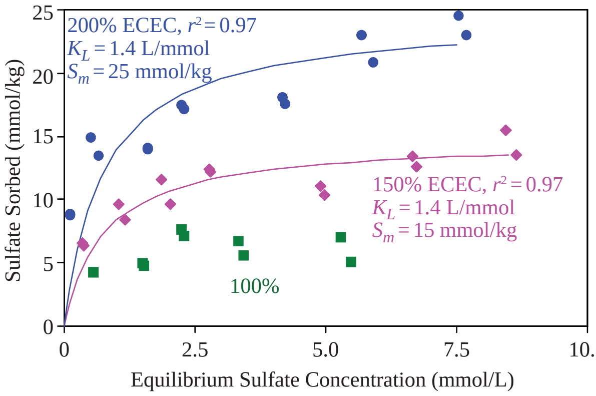

Fig. 1. Loading of sulfate on SMZ modified to 100% (■), 150% (◆), and 200% (●) ECEC. Solid lines are the Langmuir fit to the observed data. K_L is the Langmuir sorption coefficient.

3.2. Release of sulfate from sulfate-loaded SMZ

The liquid used in each desorption cycle corresponded to 17 PVs of SMZ. The kinetics of sulfate release by deionized water was more or less instantaneous (Fig. 2). The mean percentages of sulfate release were 31 ± 5% and 15 ± 3% from SMZ modified to 150% and 200% ECEC, respectively. More sulfate was released when surfactant loading was at 150% ECEC, at which, the surfactant bilayer formation was incomplete. A surface adjustment of the sorbed surfactant molecules from patchy bilayer to a monolayer could release the counterion (sulfate in this case) associated with the patchy bilayer [23]. At 200% ECEC, the surfactant bilayer formation is complete. The surface

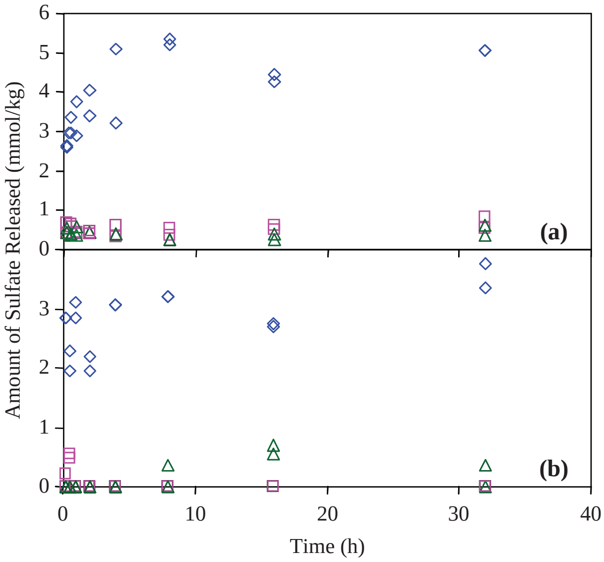

Fig. 2. Sulfate release by deionized water from SMZ modified to 150% (a), and 200% ECEC (b) under first (◇), second (□), third (△) release cycles.

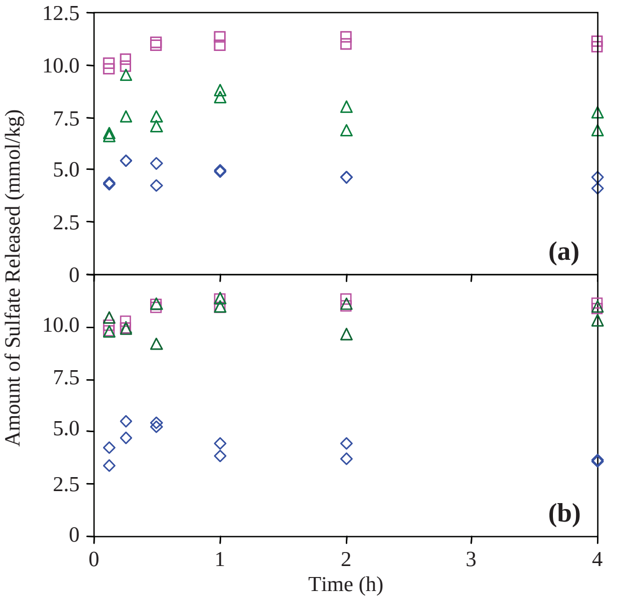

Fig. 3. Kinetics of sulfate release from zeolite modified to 200% ECEC with initial sulfate loading of 21 mmol/kg at (a) ionic strengths of solutions of 33 mmol/L (□), 10 mmol/L (△), and 3.3 mmol/L (◇) of NaCl and (b) pH of solutions at 4 (◇), 7 (□), and 10 (△).

becomes more positively charged, resulting in more sulfate retention and less release from sulfate-loaded SMZ.

3.3. Influence of solution pH and ionic strength on sulfate release

Release of sulfate from SMZ modified to 200% ECEC was further tested under different initial pH and ionic strength conditions. As the ionic strength of the solution increased, sulfate release increased (Fig. 3a). Since the sorption and desorption of anionic species on SMZ surfaces were attributed to surface anion exchange [9], an increase in ionic strength of the solution will result in competition between background electrolyte chloride against sulfate for sorption sites, thus resulting in more sulfate release. At approximately the same background electrolyte concentrations (about 33 mmol/L), more sulfate was released at pH 7 and 10 compared to pH 4 (Fig. 3b). This difference may be attributed to the type of background electrolytes present in the solution under different pH conditions. Similar results were observed for nitrate release from SMZ surfaces [17].

3.4. Column leaching tests

Column leaching tests showed that at the same initial sulfate loading of 18 mmol/kg, the initial sulfate concentration in leachate was about 40 mmol/L when mixtures of zeolite and soluble sulfate were used. In contrast, the initial sulfate concentration in leachate was only 18 mmol/L when sulfate-loaded SMZ was used (Fig. 4). It took about 2 PVs to reduce the effluent sulfate concentration to 0.05 mmol/L when soluble sulfate blended with zeolite was leached. On the other hand, 20 PVs were needed to reach the same effluent sulfate concentration from sulfate-loaded SMZ.

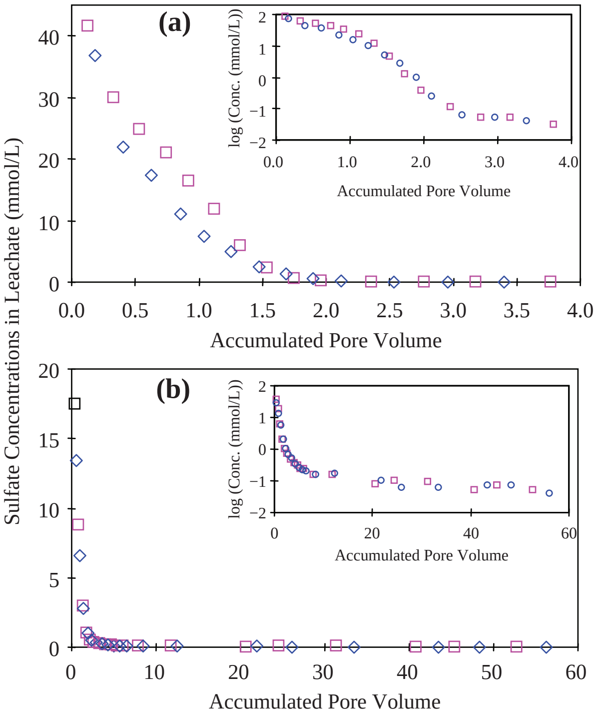

Fig. 4. Sulfate release from columns packed with raw zeolite blended with K_2SO_4 (a) and with sulfate-loaded SMZ (b). Data are duplicates with each type of symbol representing a single column. Inserts are plots on log (concentrations).

Mass balance analyses indicated that 70% of the input sulfate leached out from unmodified columns. Visual inspection of the leachate solution showed white precipitation at about 1.5 PVs. It is not surprised to see the precipitation as the major exchangeable cation in the zeolite is Ca and K. With relative high concentration of sulfate in the leachate, the ion activity product of sulfate and calcium may reach or exceed 2.13×10^{-5} to 2.79×10^{-5}, the solubility product of gypsum [24]. As the leachate was filtered before HPLC analyses, the precipitates retained on the filter were not determined and not accounted in mass balance calculation. This may account for the difference between the input and output sulfate mass. For modified columns, 67% of input sulfate still remained on the SMZ after being flushed with 60 PVs of water (Table 1). White precipitation was not seen in the leachate. Previous results showed that nitrate was significantly retarded by SMZ and nitrate-loaded SMZ could be used as SRF to provide prolonged nutrition of nitrogen in nitrate form [17]. The leaching test data from this study again indicate that sulfate release could be significantly reduced when SMZ was used. Slow release of sulfate could also be achieved as sulfate is the sulfur form ready for plant absorption [19].

3.5. Fitting of column release data to kinetic models

Different kinetic models were used to describe sorption and desorption of ions from soils and soil minerals [25–27]. Although the goodness of fitting to models was expressed by the coefficient of determination (r^2), a high r^2 value for a particular model did not necessarily mean that this model was the best [26]. A relative higher r^2 value only indicated that the model successfully described the kinetics of sorption and desorption [27].

First-order kinetic models have been applied extensively to cation and anion sorption in soils. The first-order rate model for desorption is [27]

$$\ln\left(\frac{S_t}{S_0}\right) = -k_d t, \tag{1}$$

where S_0 and S_t are the initial sulfate loading and sulfate loading at time t, while k_d is the apparent release rate constant. If the sulfate release rate from sulfate-loaded SMZ followed first-order kinetics, a plot of ln (S_t/S_0) against t should yield a linear relationship. The fitting of the experimental data to the first-order kinetic model revealed two segments (Fig. 5), agreeing well with a two segment plot to characterize the phosphate release from SMZ [14]. The data for nitrate release from nitrate-loaded SMZ [17], though not fitted in the original article, could also be fitted to two segments. A four to five fold reduction in k_d was found for sulfate release from SMZ at the early stage of leaching experiment, reflecting a significant reduction in sulfate release.

Elovich model was used to study the phosphate sorption on soil [25] and the sorption of NH_4^+ on zeolite [27]. The Elovich model for desorption is [26,27]

$$S_0 - S_t = a \ln(t) + b. \tag{2}$$

In Eq. (2), a and b are constants. Although their chemical significance was not clearly resolved [26]), the a value may be related to the apparent rate constant for release.

Fitting of the experimental data to Elovich model also resulted in two segments (Fig. 6). A two segment fitting was used to characterize the release of nitrate from nitrate-loaded SMZ [17] and from occluded zeolite [8], too. A four to seven fold reduction in a value was seen for sulfate release from sulfate-loaded SMZ, reflecting a significant reduction in sulfate release rate.

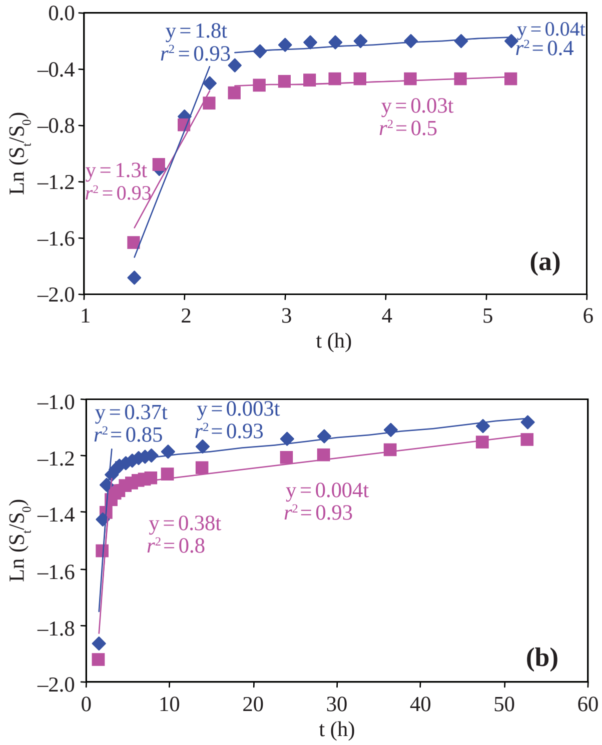

Fig. 5. First-order kinetics fits to the column test results for raw zeolite blended with K_2SO_4 (a) and sulfate-loaded SMZ (b). Data are duplicates with each type of symbol representing a single column.

Fitting of sulfate leaching data to different kinetic models showed about the same results, i.e., a reduction of sulfate release constant by a factor of four to seven in the early stage of the leaching, which may correspond to the irrigation after first application of sulfate fertilizers. This reduction in rate constant could curtain sulfate percolation, thus reducing potential groundwater contamination by a non-point source on one hand, and minimize fertilizer use, thus saving the cost on yield. Greenhouse tests on reduction of nitrate leaching using SMZ showed similar plant heights and dry mass [17]. Results from this study indicate SMZ is also an effective carrier as SRF to control sulfate release.

4. Conclusion

Studies of retention and release of sulfate from SMZ showed that SMZ was a good carrier for sulfate with a loading capacity of 15 and 25 mmol/kg on SMZ modified to 150% and 200% ECEC. The sulfate uptake was well characterized by the Langmuir sorption isotherm at >100% ECEC. Release of sulfate form SMZ surface

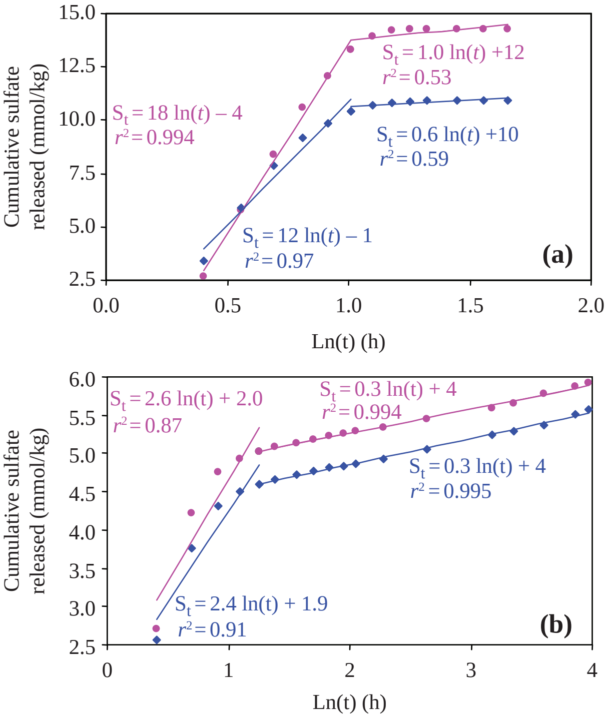

Fig. 6. Elovich fits to the column test results for raw zeolite blended with K_2SO_4 (a) and sulfate-loaded SMZ (b). Data are duplicates with each type of symbol representing a single column.

was almost instantaneous. Higher ionic strength and higher pH enhanced sulfate desorption. Compared to water soluble sulfate, the sulfate sorbed on SMZ could be slowly released. After equilibrated with 50 PVs of water in batch tests, 70% and 85% of the loaded sulfate still remained on SMZ modified to 150% and 200% ECEC, respectively. Column leaching tests confirmed that the sulfate release rate could be reduced by five to seven folds when SMZ was used. The results suggest that SMZ could be used as carriers for SRF to control nitrate, sulfate, and phosphate release.

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