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Enhanced Reduction of Chromate and PCE by Pelletized Surfactant-Modified Zeolite/ Zerovalent Iron

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The current research focuses on enhanced removal of chromate and perchloroethylene from contaminated water by a combination of a reduction material (represented by zerovalent iron, ZVI) and a sorption material (represented by surfactant-modified zeolite, SMZ). Natural zeolite and ZVI were homogenized and pelletized to maintain favorable hydraulic properties while minimizing material segregation due to bulk density differences. The zeolite/ZVI pellets were modified with the cationic surfactant hexadecyltrimethylammonium bromide to increase contaminant sorption and, thus, the contaminant concentration on the solid surface. Results of chromate sorption/reduction indicate that the chromate sorption capacity of pelletized SMZ/ZVI is at least 1 order of magnitude higher than that of zeolite/ZVI pellets. Compared to SMZ pellets, the chromate removal capacity of SMZ/ZVI pellets in a 24-h period is about 80% higher, due to the combined effects of sorption by SMZ and reduction by ZVI. The chromate and PCE degradation rates with and without surfactant modification were determined separately. The pseudo-first-order reduction constant increased by a factor of 3 for PCE and by a factor of 9 for chromate following surfactant modification. The enhanced contaminant reduction capacity of SMZ/ZVI pellets may lead to a decrease in the amount of material required to achieve a given level of contaminant removal.

Introduction

Permeable barrier technologies for groundwater remediation have recently drawn great attention owing to their potential for effective contaminant containment/destruction and low maintenance costs. Barrier materials can be classified into two general categories based on the interactions between the barrier materials and the contaminants. The removal of contaminants from groundwater by the first type of barrier material is mainly due to the sorption of contaminants. Sorption capacity determines the potential use of the sorbent.

Thus, high sorption capacity and low material cost are the keys for sorbent selection. Surfactant-modified zeolite (SMZ) has been shown to be an effective sorbent for multiple types of contaminants (*1–6*). The removal of contaminants from groundwater by the second type of barrier material is due to destruction of the contaminants, and the final product is environmentally innocuous. The reaction kinetics requires a minimum residence time of a contaminant within the barrier to complete the reaction. Often the rate of reaction may be very slow, and thick barriers may have to be used to provide the required the residence time, which results in an increase in barrier cost. Zerovalent iron (ZVI), which has been shown effective for degradation of chlorinated compounds in groundwater, has been studied extensively (*7–9*). Although degradation of highly chlorinated methanes is fast, the degradation of chlorinated ethenes is relatively slow (*10*). Thus, efforts have been made to increase the reaction rate of chlorinated solvents with ZVI by combining ZVI with other metals such as Ni or Pd (*11, 12*). In studying of the reactions of chlorinated solvents with ZVI, it was found that ZVI had a limited sorption capacity for perchloroethylene (PCE) and trichloroethylene (TCE), perhaps due to the presence of impurities, yielding apparent reaction orders different from one (*13*). The sorption of halocarbons was attributed to nonreactive sites (*13*). The observed degradation constants of chlorinated solvents by ZVI varied considerably in the literature. However, once the observed rate constants were normalized to the surface area and the mass concentration of the ZVI, the variation was limited to 1 order of magnitude (*10*). Synergistic and inhibitive effects on reduction of chlorinated solvents in the presence of other species such as dissolved and sorbed surfactants were also studied. It was found that in the presence of hydroxypropyl-β-cyclodextrin, the PCE degradation rate decreased due to partitioning of PCE molecules into the hydrophobic interiors of the cyclodextrin molecules (*14*). Investigation into the influence of corrosion inhibitors on the degradation of carbon tetrachloride by ZVI showed that strong complexation of both redox-active and nonredox-active ligands at the oxide-electrolyte interface blocked the interaction sites and thus decreased the degradation rate constant. In contrast, a concomitant addition of chloride enhanced the degradation reaction (*15*). An increase of three in PCE reduction rate constant was noted when surfactant-modified ZVI rather than raw ZVI was used for PCE reduction. The reduction rate of TCE was not increased by the addition of surfactant to the ZVI, resulting in TCE accumulation due to degradation of PCE (*16*).

Chromium exists as two major species, Cr(VI) and Cr(III), in natural waters and soils. Chromate is highly water soluble and mobile. Efforts have been made to remove chromate from groundwater either by sorption or by reduction. Due to the positive charge of the outermost surface, SMZ has been proved an effective sorbent for chromate and other oxyanions (*3, 4*). In the presence of zerovalent iron, chromate can be reduced to Cr(III), which will combine with Fe(III) to form $(Cr, Fe)(OH)_3$ precipitates (*17*).

The current research focused on combining SMZ as a sorbent and ZVI a reductant for contaminant removal from water. The two materials were mechanically mixed and pelletized to maintain favorable hydraulic properties while minimizing material segregation due to bulk density differences. Chromate and PCE, representing two different types of contaminants, were used in the experiments to investigate the overall efficiency of SMZ/ZVI pellets for contaminant sorption and destruction.

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Experimental Section

Pellet Preparation. A natural clinoptilolite-rich zeolitic tuff ("zeolite") with a particle size of less than 0.4 mm was obtained from the St. Cloud Mine, Winston, NM. The zeolite consists of about 74% clinoptilolite, 5% smectite, 10% quartz and cristobalite, 10% feldspar, and 1% illite, based on internal standard X-ray diffraction analysis (18), and has a BET surface area of 15.7 m²/g (19). The ZVI was obtained from USMetal (New Britain, PA). Ninety-five percent of the iron particles passed a 100-mesh (0.13-mm diameter) sieve. The mean surface area of the ZVI is 2.8 m²/g, based on single point BET measurement.

The process to make the pellets involved in addition of a hydrogel to bind ZVI and zeolite together homogeneously while maintaining a high surface area. The hydrogel was formed by controlled blending of soluble sodium silicate and sodium aluminate. Under some circumstances, a foaming agent (Al metal) was added to promote larger pellet surface area. When mixed in the proper proportions the mixture gels in a controlled, reproducible amount of time, binding the ingredients added prior to mixing (20). The combined mixture of hydrogel and zeolite/ZVI was homogenized and pelletized in a rotating disk pelletizer to yield aggregates of 2- to 5-mm diameter. The pellets were baked at 170 °C under nitrogen and then leached with deionized water to remove excess sodium hydroxide, leaving the pellets in the sodium form. Alternatively, the pellets were leached with CaCl₂ or NH₄Cl solutions to convert them to the calcium or ammonium form. The final composition of the pellets (by weight) was approximately 5% sodium aluminosilicate, 25% zeolite, and 70% ZVI (about 50% ZVI by volume). For comparative purposes, zeolite pellets without ZVI were also prepared using the procedures described above.

Surfactant Modification. The surfactant used was hexadecyltrimethylammonium (HDTMA) bromide, a cationic surfactant from Aldrich (Milwaukee, WI). The HDTMA sorption isotherm for the zeolite/ZVI pellets is determined using initial HDTMA concentrations in the range 0–20 mmol/L. Duplicates were prepared for each initial concentration. For each sample, 5.00 g of zeolite/ZVI pellets and 20.0 mL of HDTMA solution were placed in a 50-mL screw-top, polyallomer centrifuge tube and shaken in an orbital shaker at a speed of 75 rpm and a temperature of 30 °C for 24 h, a period shown sufficient to obtain sorption equilibrium. After shaking, the samples were filtered, and the filtrate was analyzed by an HPLC method (3) for the equilibrium HDTMA concentration in solution. The amount of HDTMA sorbed was determined by the difference between the initial and equilibrium HDTMA concentrations.

Surfactant modification of the pellets was performed by equilibrating the pellets with a 20 mmol/L aqueous HDTMA solution at a solid-to-liquid ratio of 1:4. The mixture was shaken for 24 h at 30 °C and 75 rpm, followed by centrifuging and washing with two portions of type I water from a Milli-Q system. The modified samples were air-dried before use. The final HDTMA loadings were 60 mmol/kg for zeolite pellets and 30 mmol/kg for zeolite/ZVI pellets.

Chromate Sorption/Reduction. Chromate solution was prepared by dissolving K₂CrO₄ (Fisher Scientific) into type I water. For the chromate sorption/reduction study, 2.50 g of SMZ/ZVI pellets and 10.0 mL of aqueous chromate solution with initial concentrations in the range of 0–480 mg/L were placed in polyallomer centrifuge tubes. The samples were shaken at 75 rpm and 25 °C for 24 h and then filtered, and the filtrates were analyzed for chromate concentration. For the chromate reduction rate determinations, 2.50 g of solid and 10.0 mL of 100 mg/L chromate solution were shaken at 75 rpm and 25 °C for 0–16 h, filtered, and analyzed for chromate concentration. Duplicates were prepared for each
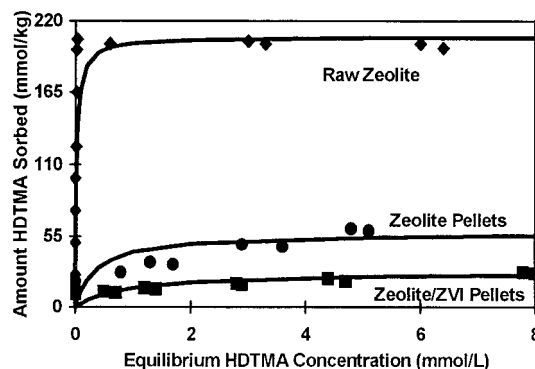

FIGURE 1. HDTMA sorption on raw zeolite, zeolite pellets, and zeolite/ZVI pellets. Solid lines are Langmuir fits to the observed data.

initial concentration and each sampling time. Each sample was sacrificed for analysis.

PCE Sorption/Reduction. PCE solutions were also made using type I water. For the PCE sorption/reduction study, 2.00 g of SMZ/ZVI and 10.0 mL of aqueous PCE solution with an initial concentration of 20 mg/L were put into 12-mL glass headspace vials and sealed with PTFE-lined septa. The samples were shaken at 75 rpm and 25 °C for 0–78 h and then centrifuged at 3600g for 20 min. The PCE concentrations in the supernatants were analyzed by GC. Triplicates were prepared for each initial concentration and sampling time. Each sample was sacrificed for analysis.

Methods of Analysis. Chromate was analyzed by HPLC using a Waters Nova-Pak C18 narrow bore column (15-cm × 2 mm id). The mobile phase was 5 mM tetrabutylammonium hydrogen sulfate in water with 10% acetonitrile (v/v). At the detection wavelength of 365 nm and flow rate of 0.5 mL/min, the chromate retention time was 2.5 min, and the linear response was 0.5–240 mg/L based on peak area (3, 4). The PCE and TCE concentrations were analyzed by a Hewlett-Packard 5890 GC with a 0.53-mm × 15-m HP-5 capillary column and an FID detector. The oven, injector, and detector temperatures were 40, 240, and 300 °C. The head pressures for air, hydrogen, and helium were 250, 125, and 150 kPa, respectively. The retention times for PCE and TCE were 3.9 and 1.9 min. The linear response range is 0–200 ppm for PCE and 0–110 ppm for TCE.

Calibration curves for each analate were prepared using four to six standards. Straight lines were fitted with coefficients of determination of (r^2) no less than 0.999 for chromate and 0.99 for PCE and TCE.

Results and Discussion

HDTMA Sorption on Zeolite/ZVI Pellets. It has been found that HDTMA has strong affinity to zeolite, and the sorption of HDTMA by zeolite follows a Langmuir sorption isotherm (1–4)

$$C_S = \frac{S_m K_L C_L}{1 + K_L C_L} \tag{1}$$

where C_S is the amount of solute sorbed and C_L is the equilibrium solute concentration. K_L is the sorption intensity reflecting the affinity of the solute for the solid surface, and S_m is the sorption capacity, the sorption plateau on the sorption isotherm. Sorption of HDTMA on raw zeolite, zeolite pellets, and zeolite/ZVI pellets can be seen in Figure 1. The sorption capacities, calculated by fitting eq 1 to the observed data, are 200, 60, and 25 mmol/kg, respectively. Compared to raw zeolite, the HDTMA sorption maximum on zeolite pellets was much lower. Thus, pelletization resulted in blocking some of the HDTMA sorption sites on the zeolite

description of pellets	pellet size	150 rpm	100 rpm	75 rpm
foamed/calcium form	−3 + 8 mesh	U	U	NT
foamed/calcium form	−12 + 20 mesh	U	U	NT
nonfoamed, porous NH_4^+ form	−3 + 8 mesh	U	U	NT
nonfoamed, porous NH_4^+ form	−12 + 20 mesh	U	U	NT
foamed/sodium form	−3 + 8 mesh	U	U	S
foamed/sodium form	−8 + 12 mesh	U	U	S
nonfoamed/sodium form	−12 + 20 mesh	U	U	S
nonfoamed/sodium form	−3 + 8 mesh	U	U	S
nonfoamed/calcium form	−12 + 20 mesh	S	S	S
nonfoamed/calcium form	−3 + 8 mesh	S	S	S

[a] U = unstable (>5% generation of fines after 1 h), S = stable (<5% generation of fines after 1 h), and NT = not tested at this shaking rate.

surface. When iron was added to the mixture at a zeolite-to-iron ratio of 1:3 by weight, the HDTMA sorption maximum decreased to 25 mmol/kg. Since the HDTMA sorption capacity of USMetal ZVI is about 4 mmol/kg (*16*), retention of HDTMA by the zeolite/ZVI pellets was due to sorption on both the zeolite and the ZVI. Some HDTMA sorption capacity in both the zeolite and zeolite/ZVI pellets was likely added by the aluminosilicate binder.

Stability of SMZ/ZVI Pellets. To evaluate the suitability of the pellets for permeable barriers or other packed bed applications, it was necessary to determine their mechanical stability under saturated conditions. Several variables contributed to zeolite/ZVI pellet stability, including the zeolite to ZVI ratio, types of exchangeable cations, ZVI source, use of a foaming agent, pellet size, and shaking rate. Pellets made under different conditions were tested at different shaking speeds at an initial HDTMA concentration of 100 mmol/L. Mechanical breakdown was evidenced by a decrease in mean pellet size accompanied by the generation of fines. The qualitative results are summarized in Table 1. Nonfoamed sodium-saturated pellets were mechanically stable (estimate <5% of the pellets reduced to fines after 1 h) up to a shaking speed of 75 rpm. However, significant breakdown of the sodium and ammonium pellets began after 1 h shaking at a rate of 100 rpm. In contrast, nonfoamed calcium-saturated pellets remained intact (estimated <2% loss by mass) at all shaking speeds. Most foamed pellets were unstable regardless of saturating cation or shaking rate, making them unsuitable for further testing.

Chromate Sorption/Reduction. Due to the presence of ZVI in the pellets, chromate removal from water represents the combined effects of sorption and chemical reduction. The sorption/reduction of chromate by zeolite/ZVI pellets after 24 h can be seen in Figure 2. The 24-h sorption/reduction capacities are the plateaus in Figure 2. For zeolite/ZVI pellets the sorption/reduction capacity was 0.5 mmol/kg. The zeolite pellets modified with surfactant had a capacity of 10 mmol/kg, while the SMZ/ZVI pellets had a capacity of 15 mmol/kg. The greater capacity of SMZ/ZVI pellets compared SMZ pellets was due to an enhanced chromate reduction in addition to chromate sorption by the SMZ/ZVI pellets.

The pseudo-first-order rate model for sorption and reduction can be expressed as (*21*)

$$\frac{\mathrm{d}[C]}{\mathrm{d}t} = -k[C] \qquad (2)$$

where $[C]$ is the solute concentration at time t, and k is the apparent reaction rate constant. Integration of eq 2 yields

$$\ln[C] - \ln[C]_0 = -kt \qquad (3)$$

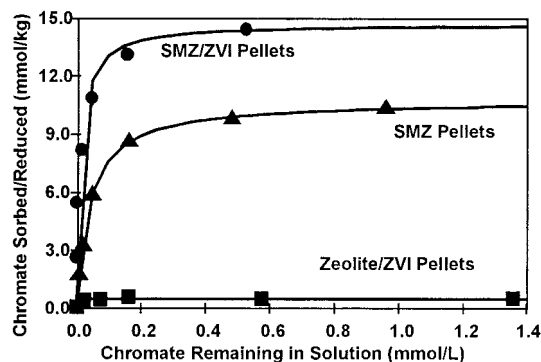where $[C]_0$ is the initial concentration at $t = 0$. Thus, if the

FIGURE 2. Chromate sorption/reduction by zeolite/ZVI pellets, SMZ pellets, and SMZ/ZVI pellets in a 24-h period. Each symbol is an average of duplicates. Solid lines are Langmuir fits to the observed data.
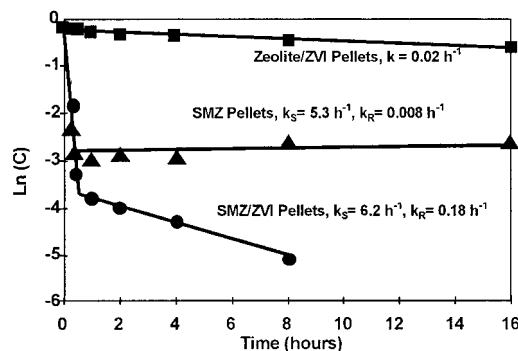

FIGURE 3. Chromate solution concentration vs time for chromate sorption and reduction by zeolite/ZVI pellets, SMZ pellets, and SMZ/ZVI pellets. Each symbol is an average of duplicates. The k_S and k_R values are rate constants for sorption and reduction.

concentration is plotted on a log scale and the time on a linear scale, a straight-line regression of observed data indicates a pseudo-first-order reaction.

Figure 3 shows the data for chromate removal from solution as a function of time for zeolite/ZVI, SMZ, and SMZ/ZVI pellets. For zeolite/ZVI pellets, the concentration versus time data followed a single straight-line relationship, with a first-order rate constant of 0.02 h^{-1}. This behavior represented the chemical reduction of chromate by the ZVI, with essentially no sorption of chromate. For SMZ and SMZ/ZVI pellets, the observed data could be divided into two segments, each of which followed a straight-line relationship with an associated rate constant (Figure 3). In each case the rate constant was much larger for the early-time segment. For the SMZ pellets, chromate removal from solution was rapid for the first 0.5 h (rate constant 5.3 h^{-1}), after which the chromate concentration in solution remained essentially unchanged (rate constant less than 0.01 h^{-1}). The pattern reflected first-order sorption by the SMZ pellets with equilibrium attained in 0.5 h and no chemical reduction of chromate. This rapid sorption of chromate by the SMZ pellets was similar to that observed for chromate sorption by unpelletized SMZ (*1*). The SMZ/ZVI pellets also showed an initial rapid decrease in chromate concentration, with a rate constant (6.2 h^{-1}) that was similar to that for the SMZ pellets (Figure 3). After the initial rapid concentration decrease, presumably due to sorption, removal of chromate continued with a rate constant of 0.18 h^{-1}. This second phase of chromate removal from solution by the SMZ/ZVI pellets was due to chemical reduction. The rate constant of chromate reduction was about nine times greater for the SMZ/ZVI pellets than for the zeolite/ZVI pellets, suggesting an enhancement in chromate reduction when chromate is
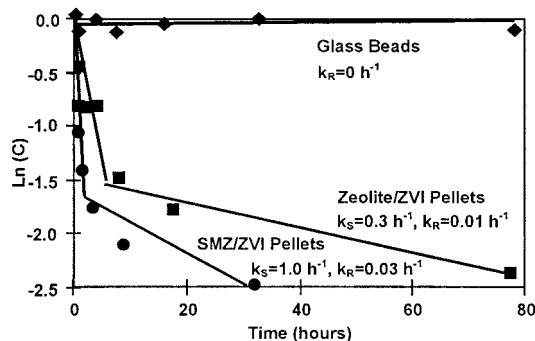
FIGURE 4. PCE solution concentration vs time for PCE sorption and reduction by zeolite/ZVI pellets, SMZ/ZVI pellets, and a glass bead control. Each symbol is an average of triplicates.

FIGURE 5. Production of TCE vs time due to PCE reduction. Each symbol is an average of triplicates. C_0 is the initial PCE concentration.

sorbed. The enhancement may have been due to an increased local concentration of chromate in solution that promoted electron transfer for chromate reduction and iron oxidation or to direct reduction of sorbed chromate.

PCE Sorption/Reduction. The PCE removal vs time can be seen in Figure 4. The glass beads served as controls. Similar to chromate reduction, data for both zeolite/ZVI pellets and SMZ/ZVI pellets can be divided into two sections, and both show initial rapid decreases in PCE solution concentration. As noted by Burris et al. (*13*), ZVI has the ability to sorb PCE, presumably due to presence of carbon in the iron metal. Thus, the initial steep decrease in PCE solution concentration with zeolite/ZVI pellets may be attributed to PCE sorption by iron. Following the decrease in solution PCE concentration by sorption, additional PCE removal continued via chemical reduction at a rate of 0.01 h^{-1} for zeolite/ZVI. The SMZ/ZVI pellets showed a sorption rate constant more than three times greater and a reduction rate constant (0.03 h^{-1}) about three times greater than the zeolite/ZVI pellets. Previous results indicated that the PCE reduction rate constant for unmodified ZVI and surfactant-modified ZVI was 0.012 and 0.033 h^{-1}, respectively (*16*). The similarity between these two results suggests that surfactant-modified iron enhance PCE reduction, in contrast to the situation when PCE is sorbed to nonreactive sites of ZVI (*13*). In this case the SMZ in the pellets merely caused initial PCE removal from solution via rapid sorption. As pointed by Bizzigotti et al. (*14*), PCE is sorbed to the iron surface first, followed by the reaction of the sorbed PCE to form products, initially TCE and chloride. In a similar study involving reduction of nitroaromatic compounds by ZVI, it was postulated that the electron transfer occurred on the sorbed phase (*22*). In another study, it was speculated CCl$_4$ was sorbed to the surface via hydrophobic interactions prior to reduction by ZVI (*15*). Bound HDTMA molecules would enhance the hydrophobic sorption of PCE on iron surface. The enhanced sorption of PCE due to the presence of HDTMA, therefore, appears to be responsible for the enhanced PCE degradation.

The increase in the PCE reduction rate constant also may be explained as an increased local PCE concentration in the vicinity of iron surface, promoting the electron transfer for PCE reduction. The sorbed HDTMA molecules form admicelles on zeolite and ZVI surfaces (*1–6, 16*). Admicelle solubilization (adsolubilization) of hydrophobic compounds by sorbed surfactant micelles can dramatically increase the surface concentration of hydrophobic compounds (*23*). Such admicelles have also been used as two-dimensional templates for reactions. Admicelle catalysis using sodium dodecyl sulfate sorbed on high surface area alumina was studied for the hydrolysis of trimethyl orthobenzoate to methyl benzoate by Yu and Lobban (*24*). The enhanced PCE removal by SMZ/ZVI may also be attributed to admicelle-catalyzed reduction by ZVI.
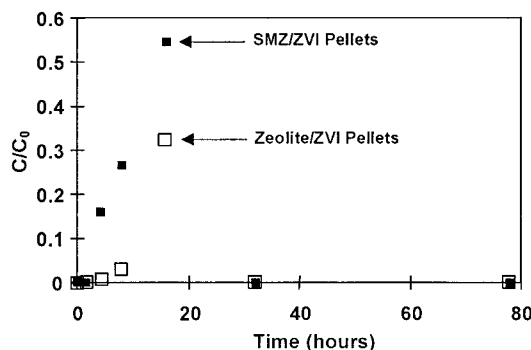
The TCE production due to reduction of PCE was monitored. The results are shown in Figure 5. As the aqueous PCE concentration decreased, the TCE concentration started to increase. The net TCE production rate was greatest at early times, when the PCE concentration was high. At later times the apparent TCE production rate slowed as the PCE concentration decreased and as TCE was reduced to less chlorinated products, which were not monitored in this study.

In summary, results of chromate and PCE interactions with SMZ/ZVI pellets indicate that SMZ/ZVI may be an effective sorbent/reductant for water decontamination. Surfactant modification not only increased the sorption rate and capacity compared to raw ZVI or zeolite/ZVI pellets but also increased the reduction rate constant by factors of 3–9 for PCE and chromate, respectively. Therefore, SMZ/ZVI pellets have the potential to lower the amount of reactive material required to achieve a target level of contaminant reduction along a flow path.

Acknowledgments

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