Removal of cationic surfactants from water using clinoptilolite zeolite

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ABSTRACT

Batch and column experiments were conducted to evaluate the efficiency of a clinoptilolite zeolite as an inexpensive sorbent material to remove cationic surfactant from water. With an initial surfactant concentration greater than its critical micelle concentration, the removal of surfactant is achieved by admicellar sorption onto the zeolite surface. Although the sorption capacity of hexadecyltrimethylammonium by zeolite of different aggregate size is about the same (200 mmol/kg), the finer particles had a much higher capacity at breakthrough point and almost twice the column efficiency compared to the coarse aggregates.

1. INTRODUCTION

Natural zeolite as an inexpensive sorbent has been studied in great detail for its potential use to remove a broad spectrum of environmental contaminants including heavy metal from waste water [1], ammonium from sewage [2] and azo dyes from aqueous solution [3]. The main process to remove these contaminants was through cation exchange and specific sorption due to higher cation exchange capacity and larger surface area of the zeolite.

Studies on quaternary ammonium sorption on zeolite were focused on the potential use of quaternary ammonium modified zeolite as sorbent to remove organic contaminants and inorganic anions [4-5]. The sorption of hexadecyltrimethylammonium (HDTMA), a cationic surfactant, is strongly affected by the type of counterions with a higher HDTMA sorption being achieved when bromide is the counterion [4]. The sorption of HDTMA is fast when the initial input of HDTMA is much less than the external cation exchange capacity (ECEC) of the zeolite and longer time is needed to reach equilibrium as the total surfactant increased progressively [6]. As the surfactant chain length increased, the amount of surfactant increased [7-8].

The use of surfactant is a major cause for lake eutrophication [9]. Activated clays have been proposed for potential use to remove surfactants from tannery waste water [10]. However, the use of zeolite for direct removal of surfactant from water has not been studied in great detail, particularly in column tests.

In this study, a natural clinoptilolite zeolite was tested in batch studies to remove cationic surfactants under different initial surfactant concentrations, total surfactant inputs, and surfactant chain lengths, and in column transport studies with different particle size of the zeolite aggregates, so that the mechanism of surfactant removal by zeolite can be elucidated.

2. MATERIALS AND METHODS

2.1. Materials

The zeolite (from St. Cloud Mine in Winston, NM) aggregates having particle sizes of 0.4 – 1.4 and 1.4 – 2.4 mm were used without pre-treatment. The material contains 74% of clinoptilolite, 10% of feldspar, 10% of quartz, and 5% smectite and has an ECEC of 90-110 mmol/kg [5]. K^+ and Ca^{2+} are the major exchangeable cations. The surfactants used include HDTMA bromide and chloride, dodecyltrimethylammonium (DDTMA) bromide, and octyltrimethylammonium (OTMA) bromide.

2.2. Batch surfactant sorption

Two grams of zeolite and 20 mL of surfactant solution were mixed in 50 mL centrifuge tubes with initial concentrations of 4, 8, 12, 16, 20, 24, and 28 mM for HDTMA and DDTMA, and 1, 3, 6, 9, 12, 15, 18, and 21 mM for OTMA. The mixtures were shaken at 150 rpm for 24 h, centrifuged at 4000 rpm for 30 min, and the supernatant analyzed after being filtered through a 0.45 μm syringe filter.

2.3. HDTMA sorption kinetics

To each 50 mL centrifuge tube, 10 mL of 20 mM HDTMA solution and varying amounts of zeolite were combined to achieve initial inputs of 25, 75, and 200 mmol/kg. These loading levels would result in a monolayer to a bilayer surfactant surface coverage. The mixtures were shaken at 150 rpm for varying amounts of time, centrifuged, and then filtered before the supernatant was analyzed. When the mixing time was less than 15 minutes, the samples were filtered and then analyzed.

2.4. Column HDTMA transport

Surfactant transport experiments were performed using plastic columns of 2.54 cm in diameter and 14.2 cm in length. Duplicate columns were packed with 0.4 – 1.4 and 1.4 – 2.4 mm zeolite. A 4-head peristaltic pump was used for surfactant solution (5 mM) delivery at 20 mL/h in upward direction. Detailed column and flow parameters are listed in Table 1. Both HDTMA and counterion bromide concentrations were analyzed for the effluent.

Table 1
Transport parameters of HDTMA through zeolite columns

Columns	Density	Porosity	K_L (L/kg)	S_m (mmol/kg)	Dispersivity, α_L	r^2
1	1.04	0.66	0.59 (±0.06)	250 (±40)	13 (±3)	0.992
2	1.02	0.61	0.51 (±0.19)	180 (±45)	12 (±5)	0.994
3	1.00	0.67	0.65 (±0.33)	206 (±80)	3.2 (±0.7)	0.997
4	1.01	0.67	0.47 (±0.19)	206 (±60)	3.2 (±0.6)	0.99

2.5. Chemical analysis

The HDTMA solution concentration was analyzed using an HPLC method with a Nucleosil CN column from Sigma-Aldrich (St. Louis, MO), a Shimadzu 9-A autoinjector, a Linear 100 UV-Vis detector at detection wavelength of 254 nm. The mobile phase was 5 mM p-toluenesulfonate in 45% water and 55% methanol. At a flow rate of 1 mL/min, the retention time was 2.2, 2.6, and 3.2 min for OTMA, DDTMA, and HDTMA, respectively. A dilution at 1/10 ratio was made for concentrations greater than 2 mM. Bromide and chloride analysis was

performed in another HPLC system using a Shimadzu 9-A autoinjector, a Hamilton PRP-X100 anion chromatographic column, and an Alltech electric conductivity detector. The mobile phase was 2 mM potassium phthalate with pH 6 adjusted by NaOH. At a flow rate of 2 mL/min, the retention time was 2.1 and 3.1 min for chloride and bromide, respectively.

All experiments were performed in duplicate and standard curves were fitted based on 4-6 standards with the linear coefficient of determination (r^2) not less than 0.999. The amount of surfactant and counterion sorbed was calculated from the difference between the initial and final solution concentrations.

2.6. Simulation of HDTMA transport

HYDRUS-1D version 2.01 [11], which uses the following partial differential equation to describe the transport of a solute undergoing equilibrium sorption, was used to simulate the HDTMA breakthrough data:

$$\frac{\partial C}{\partial t} + \frac{\rho_b}{\theta}\frac{\partial S}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \tag{1}$$

where C and S are the solute concentrations in aqueous and solid phases, t the travel time, ρ_b the media bulk density, θ the porosity, D the hydrodynamic dispersion coefficient, v the mean pore velocity, and x the travel distance. The sorption of HDTMA on zeolite is governed by the Langmuir sorption isotherm by which HDTMA sorption on zeolite follows [4]:

$$S = \frac{K_L S_m C}{1 + K_L C} \tag{2}$$

where S_m is the solute sorption capacity or sorption maximum and K_L the Langmuir coefficient. The retardation factor of a solute, whose sorption on solid is governed by the Langmuir sorption isotherm, is a function of effluent solution concentration:

$$R = \frac{\rho_b}{\theta}\frac{S_m K_L}{(1 + K_L C)^2} \tag{3}$$

3. RESULTS AND DISCUSSION

The length of surfactants' hydrophobic chain had a significant effect on their removal from water by zeolite (Figure 1). The sorption capacities on zeolite are 200, 160, and 70 mmol/kg for HDTMA, DDTMA, and OTMA, respectively. The HDTMA and DDTMA sorption capacities exceede the ECEC while that of OTMA is less than the ECEC of the zeolite. Accompanying surfactant removal, simultaneous sorption of counterion bromide is also achieved (Figure 1). The counterion sorption capacities are 140, 70, and 0 for HDTMA, DDTMA, and OTMA, respectively. The ratio of HDTMA sorbed/Br sorbed on zeolite was 4/3, indicating an admicelle formation. The ratio of DDTMA sorbed/Br sorbed was 1/1 at higher concentration, revealing a less dense bilayer formation. However, OTMA mainly forms monolayer as Br sorption is minimal due to monomer sorption and surface cation exchange.
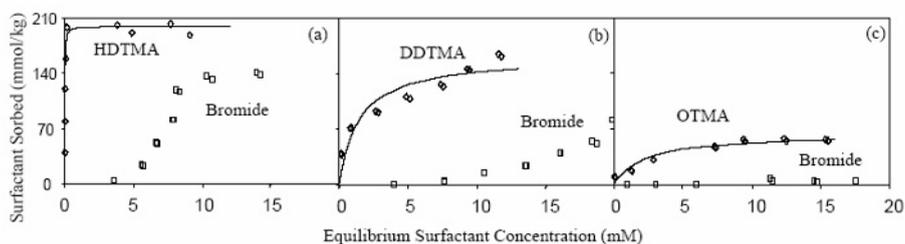
Fig. 1. Sorption isotherm of HDTMA (a), DDTMA (b), OTMA (c) and counterion bromide on zeolite. The lines are Langmuir fit to the observed data.

The admicellar sorption was further revealed in kinetics study as concurrent removal of both surfactant and counterion was achieved (Figure 2). Surfactant removal was fast when the initial surfactant input was low. A later arrangement of surfactant molecules on zeolite surfaces resulted in a slight desorption of counterions from the admicelle when the input surfactant was 75 and 133 mmol/kg, less than 200% of the ECEC of the zeolite (Figure 2b). For example, at an HDTMA input of 75 mmol/kg, the highest counterion sorption occurred at 1 hour, beyond which the counterion sorption dropped from 24 mmol/kg to 8 mmol/kg. When the HDTMA input was 133 mmol/kg, the highest counterion sorption occurred at 8 hour, after which the counterion sorption dropped from 49 mmol/kg to 38 mmol/kg. (Figure 2b).
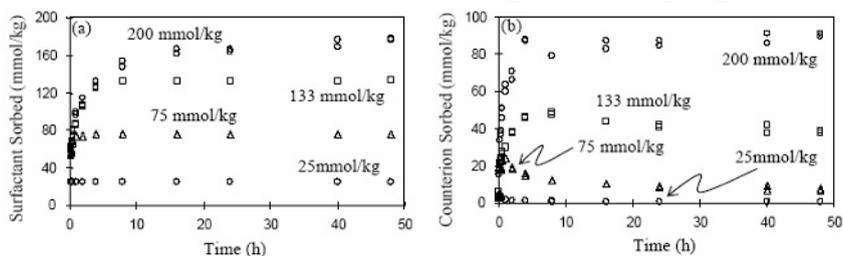

Fig. 2. Sorption of HDTMA (a) and counterion chloride (b) as a function of time at different initial inputs. The values are initial surfactant input.

The transport of HDTMA followed a typical solute breakthrough curve (Figure 3). The capacity of the adsorbent in the breakthrough point C_B is defined as the amount of solute sorbed when the effluent concentration reaches 5% of the input concentration, while the capacity in the exhaustion point C_E corresponds to the amount of solute sorbed when the effluent HDTMA concentration reaches 95% of the input concentration. The C_B value is 82-83 mmol/kg and the C_E is about 185-187 mmol/kg for the 1.4 – 2.4 mm zeolite. In contrast, the 0.4 – 1.4 mm zeolite has the C_B value of 140 – 160 mmol/kg and C_E value of 195 – 210 mmol/kg. The degree of saturation or column efficiency ε can be calculated as: $\varepsilon = C_B / C_E$. The ε values are 0.44 – 0.45 for 1.4 – 2.4 mm zeolite and 0.72 – 0.76 for 0.4 – 1.4 mm zeolite.
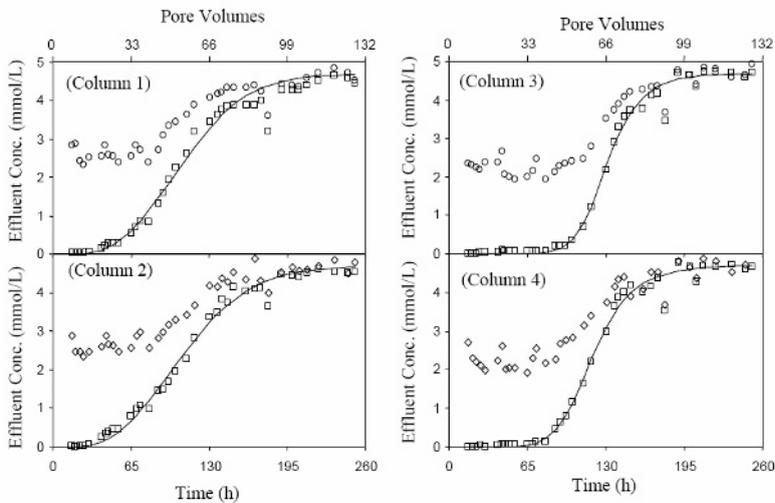
Fig. 3. Transport of HDTMA (□) and counterion bromide (◇) through duplicate zeolite columns of 1.4 – 1.4 mm (Column 1 and 2) and 0.4 – 1.4 mm (Column3 and 4).

The breakthrough curve for counterion bromide is completely different from that of HDTMA (Figure 3). While the effluent HDTMA concentration was minimal in the early stage of the column experiment, an immediate breakthrough of bromide at 50% of the input concentration could be seen. The results also support admicellar sorption of HDTMA on zeolite, by which 50% of the counterion could be initially sorbed.

The HDTMA retardation factor R can be estimated by the number of pore volumes it takes for the effluent concentration to reach half of the input concentration. Using this method, the R value is about 50 for the 1.4 – 2.4 mm zeolite and 60 for the 0.4 – 1.4 mm zeolite.

The following parameters were estimated using HYDRUS-1D [11]: longitudinal dispersivity, α_L, $K_L S_m$, and K_L by inverse modelling of the observed breakthrough data. Both particle sizes had similar K_L and S_m values but different dispersivity value (Table 1). More dispersion is seen for the zeolite aggregates with larger particle sizes. The calculated S_m value is about 210 mmol/kg, very close to the value determined from batch tests.

The accumulative sorption of HDTMA and counterion bromide on zeolite from the columns tests is plotted in Figure 4. The total HDTMA loading at the end of experiment is 190 and 220 mmol/kg for the 1.4 – 2.4 and 0.4 – 1.4 mm zeolite, respectively. These values are close to the HDTMA sorption capacity of 200 mmol/kg, determined from batch tests (Figure 1) and to the values simulated by HYDRUS-1D (Table 1). Accompanying HDTMA sorption, concurrent counterion bromide sorption also occurs. At any given time the ratio of HDTMA sorbed to that of counterion bromide sorbed is about 2 to 1, again verifying surfactant admicelle sorption when the initial surfactant concentration is greater than the CMC of the surfactant. At the surfactant sorption maximum, bromide sorbed is 105 and 125 mmol/kg for 1.4 – 2.4 and 0.4 – 1.4 mm zeolite, further indicating sorbed surfactant bilayer formation on zeolite (Figure 4).
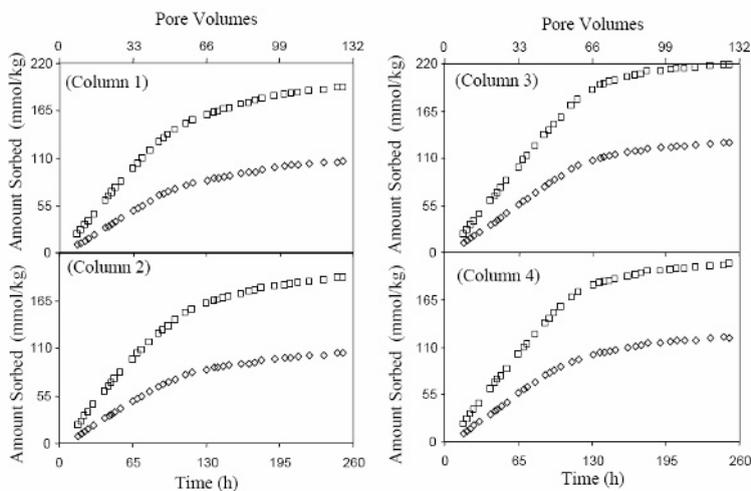
Fig. 4. Accumulative HDTMA (□) and counterion bromide (◇) sorption on 1.4 – 1.4 mm (Column 1 and 2) and 0.4 – 1.4 mm zeolite (Column 3 and 4).

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