

Desorption Of (HDTMA) Hexadecyltrimethylammonium from Charged Mineral Surfaces and Desorption Of Loaded Modified Zeolite Minerals

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ABSTRACT:

The use of surfactant-modified zeolites as sorbents to remove multiple types of contaminants from water has attracted great attention recently. Sorption of cationic surfactants onto negatively charged zeolite and clay mineral surfaces is controlled by cation exchange and hydrophobic interactions. When surfactant loading is less than the cation exchange capacity (CEC) of the substrate, the retention of surfactant is via cation exchange. Once the surfactant loading exceeds the CEC of the substrate, further retention of surfactant is governed by hydrophobic interactions among surfactant tail groups, and the sorbed surfactant molecules form a bilayer on mineral surfaces, which is responsible for retention of anionic contaminants. To evaluate the feasibility of using surfactant modified clays and zeolites for environmental remediation, the desorption of sorbed surfactant from these mineral surfaces needs further study, particularly from column flow-through desorption tests. In this study, batch experiments were performed to evaluate desorption of hexadecyltrimethylammonium, a cationic surfactant, from zeolite mineral surfaces. The results indicate that the sorbed surfactant is subject to slow desorption (on the order of 0.0001–0.002 per pore volume), depending on initial surfactant loading, the type of mineral substrate, and the flow rate.

KEYWORDS:

HDTMA, Charged Mineral Surfaces, Modified Zeolite Minerals, cation exchange capacity

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INTRODUCTION

Surfactant modification in previous studies was limited to the levels corresponding to the cation exchange capacity (CEC) of the clay minerals [1,2,3]. Thus, sorption of the surfactant was attributed to cation exchange on negatively charged clays and zeolites, until the mid-1990s, when [4,5] found that hexadecyltrimethylammonium (HDTMA), sorbed onto vermiculitic soils, kaolinite, and smectite clays, could be as high as 200% of their CECs. Sorption beyond the CEC was attributed to hydrophobic interactions among surfactant tail groups [4,5]. Separately [6], found that surfactant-modified zeolite (SMZ) was able to sorb and retain chromate, an unexpected property, if the cationic surfactant molecules were held onto zeolite by cation exchange only. Detailed investigations showed that the sorption of chromate and other anionic contaminants and desorption of surfactant counter ions were stoichiometric, suggesting that anion exchange was responsible for the retention of anionic species on SMZ [7,8]. The positively charged surface was formed by a surfactant bilayer formation on the external surfaces of the zeolite, with the positively charged head groups of the outer surfactant layer balanced by counter ions such as Br^- [7]. Thereafter, it was found that surfactant-modified kaolinite, illite, and smectite, with surfactant loadings exceeding their CECs, were also able to sorb and retain chromate and nitrate [7]. Compared to studies on mechanisms of surfactant sorption, tests on the stabilities of the surfactant-modified minerals have been limited. Thus, the long-term retention of sorbed HDTMA, in particular, on the outer layer of the sorbed surfactant bilayer

responsible for the retention of anionic contaminants, has been questioned⁵, found that much of the HDTMA held beyond the CEC of a vermiculitic soil was readily desorbed. For soil modified to 1.95 times its CEC, about 30% of the HDTMA was desorbed after 13 wash cycles at a liquid-to-solid ratio of 10:1, corresponding to 600 pore volumes (PV) [5].

After 11 wash cycles corresponding to 110 PV, about 15% of the HDTMA desorbed from zeolite modified to 200% of the zeolite's external cation exchange capacity (ECEC) [9]. The only column study relevant to the stability of sorbed surfactant molecules on charged surfaces was performed on low organic carbon aquifer materials treated with dodecylpyridinium [10]. Their results showed that after flushing with 1000 PV of 0.01 M CaCl_2 solution, only about 16% of the original dodecylpyridinium remained on the soil. Thus, to further evaluate the feasibility of using surfactant-modified clays and zeolites for environmental remediation, the desorption of sorbed surfactant from these mineral surfaces needs further study, particularly from column flow-through desorption tests.

MATERIALS AND METHODS

Surfactant Loading

For batch desorption experiments, Erionite, Cowlesite, and Willhendersonite were prepared at various HDTMA loading levels using methods similar to those described above, with a liquid-to-solid ratio of 3:1. The Erionite was modified with HDTMA to 15, 30, and 60 mmol/kg, corresponding to 50, 100, and 200% of its CEC. The Cowlesite was modified to 240

mmol/kg, equivalent to 200% of the Cowlesite CEC, whereas the willhendersonite was modified to 50, 150, and 200 mmol/kg, corresponding to 50, 150, and 200% of the Willhendersonite's ECEC.

Desorption from Batch Experiments

Desorption of HDTMA from Erionite, Cowlesite, and Willhendersonite occurs almost instantaneously (Figure 3). In addition, higher initial HDTMA loadings resulted in higher amounts of HDTMA desorbed. Also noticed from Figure 3 is that the aqueous HDTMA concentration decreases as the equilibration time increases. This feature was attributed to a later rearrangement of sorbed HDTMA molecules from patchy bilayer to monolayer configuration (Li, 1999)[11].

DESORPTION BEHAVIOR OF LOADED MODIFIED ZEOLITE MINERALS

Desorption behaviour of loaded analogue of modified zeolites was studied by equilibrating loaded analogue of modified zeolite with distilled water, NaOH (0.01M) pH ~12, NaOH (0.1M) pH~13 and 0.28 M Na₂CO₃ / 0.5 M NaOH pH~13. Each mixture was equilibrating at 25 °C for 24 hour under the following conditions. 1. The whole specimen was exposed to leachant so that full surface of the specimen remained in contact with it. 2. Sealed polypropylene bottles were used as leachant or buffer containers. Leaching rate was studied for CrO₄²⁻, AsO₄³⁻ and SeO₄²⁻ oxoanions from loaded modified zeolite minerals and has been carried out with a view to explore the possibilities of its application for long term disposal of these toxic metal oxoanions. The

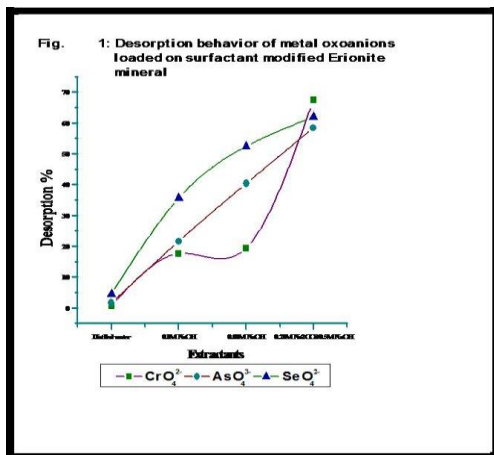
technique of extraction efficiency studies has been developed by Li (1998)[7].

Desorption behavior of loaded analogue of modified Erionite

The present desorption studies have been performed with Chromate, Arsenate and Selenate saturated powder sample in the presence of different extracts and distilled water. Loaded modified Erionite mineral (100mg) sorbed with respective metal oxoanions, CrO₄²⁻, AsO₄³⁻ and SeO₄²⁻ were placed in sealed polypropylene bottles with 25 ml of buffer solution NaOH (0.01M) pH ~12, NaOH (0.1 M) pH~13 and 0.28M Na₂CO₃/ 0.5 M NaOH pH ~13 and distilled water. The bottles were placed in reciprocating water bath shaker at room temperature. After the completion of predecided leaching time, the solution was centrifuged and the concentration of metal oxoanion leached out from modified Erionite mineral into the leachant is then estimated spectrophotometrically.

The results obtained from desorption study table 1 and fig.1 suggested that modified Erionite mineral loaded with CrO₄²⁻ shows 0.7% leaching with distilled water, 17.6% leaching with NaOH(0.1M), 19.4% leaching with 0.01M NaOH and 67.5% leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Erionite mineral loaded with AsO₄³⁻ shows 1.6 % leaching with distilled water, 21.6% leaching with NaOH (0.1M), 40.3% leaching with 0.01M NaOH and 58.4 % leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Erionite mineral loaded with SeO₄²⁻ shows 4.5 % leaching with distilled water, 35.6% leaching with NaOH (0.1M), 52.4% leaching with 0.01M NaOH and 61.9 % leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Maximum

percentage (67.5%) of CrO_4^{2-} ion leached out with 0.28M Na_2CO_3 / 0.5 M NaOH from the modified Erionite mineral.



Desorption behavior of loaded analogue of modified Cowlesite

The desorption studies have been performed with Chromate, Arsenate and Selenate saturated powder sample in the presence of different extracts and distilled water. Loaded modified Cowlesite (100mg) sorbed with respective metal oxoanions, CrO_4^{2-} , AsO_4^{3-} and SeO_4^{2-} were placed in sealed polypropylene bottles with 25 ml of buffer solution NaOH (0.01M) pH ~12, NaOH (0.1 M) pH~13 and 0.28 M Na_2CO_3 / 0.5 M NaOH pH ~13 and distilled water. The bottles were placed in reciprocating water bath shaker at room temperature. After the completion of predecided leaching time, the solution was centrifuged and the concentration of metal oxoanion leached out from modified Cowlesite mineral into the leachant is then estimated spectrophotometrically. The results obtained from desorption study fig.2 suggested that modified Cowlesite mineral loaded with

CrO_4^{2-} shows 2.8% leaching with distilled water, 61.9% leaching with NaOH (0.1M), 24.8% leaching with 0.01M NaOH and

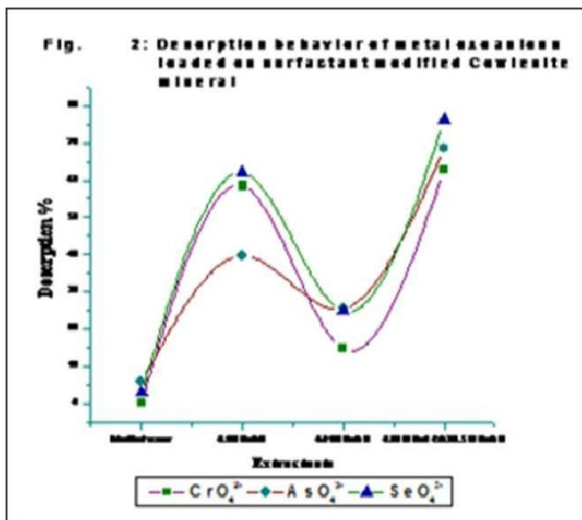
TABLE: 1 DESORPTION BEHAVIOR OF METAL OXOANIONS LOADED ON SURFACTANT MODIFIED ERIONITE MINERAL

Equilibration time: 24 hours.

Metal oxoanions	Extractants	Desorption %
CrO_4^{2-}	Distilled water	0.7
	0.1M NaOH	17.6
	0.01 M NaOH	19.4
	0.28 M Na_2CO_3 /0.5 M NaOH	67.5
	NaOH	67.5
AsO_4^{3-}	Distilled water	1.6
	0.1M NaOH	21.6
	0.01 M NaOH	40.3
	0.28 M Na_2CO_3 /0.5 M NaOH	58.4
	NaOH	58.4
SeO_4^{2-}	Distilled water	4.5
	0.1M NaOH	35.6
	0.01 M NaOH	52.4
	0.28 M Na_2CO_3 /0.5 M NaOH	61.9
	NaOH	61.9

76.1% leaching with 0.28M Na_2CO_3 / 0.5 M NaOH after 24 hours equilibration. Cowlesite mineral loaded with AsO_4^{3-} shows 0.09 % leaching with distilled water, 58.4% leaching with NaOH (0.1M), 14.7% leaching with 0.01M NaOH and 62.8% leaching with 0.28M Na_2CO_3 / 0.5 M NaOH after 24 hours equilibration. Cowlesite mineral loaded with SeO_4^{2-} shows 5.6 %

leaching with distilled water, 39.6% leaching with NaOH (0.1M), 25.4% leaching with 0.01M NaOH and 68.5% leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Maximum percentage (76.1%) of CrO₄²⁻ ion leached out with 0.28M Na₂CO₃/ 0.5 M NaOH from the modified Cowlesite mineral.



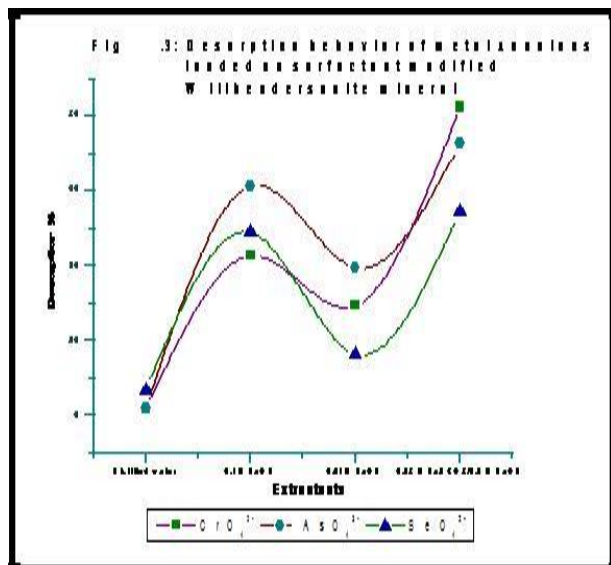
DESORPTION BEHAVIOR OF LOADED ANALOGUE OF MODIFIED WILLHENDERSONITE

This desorption studies have been performed with Chromate, Arsenate and Selenate saturated powder sample in the presence of different extracts and distilled water. Loaded modified Willhendersonite (100mg) sorbed with respective metal oxoanions, CrO₄²⁻, AsO₄³⁻ and SeO₄²⁻ were placed in sealed polypropylene bottles with 25 ml of buffer solution NaOH (0.01M) pH ~12, NaOH (0.1 M) pH~13 and 0.28 M Na₂CO₃/ 0.5 M NaOH pH ~13 and distilled water. The bottles were placed in reciprocating water bath shaker at room temperature. After the completion of predecided leaching time, the solution was

centrifuged and the concentration of metal oxoanion leached out from modified Willhendersonite mineral into the leachant is then estimated spectrophotometrically. The results obtained from desorption study and fig.3 suggested that modified Willhendersonite mineral loaded with CrO₄²⁻ shows 1.4% leaching with distilled water, 42.6% leaching with NaOH(0.1M), 29.1% leaching with 0.01M NaOH and 82.5% leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Willhendersonite mineral loaded with AsO₄³⁻ shows 1.5 % leaching with distilled water, 61.3% leaching with NaOH (0.1M), 39.4% leaching with 0.01M NaOH and 72.4% leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Willhendersonite mineral loaded with SeO₄²⁻ shows 6.7 % leaching with distilled water, 48.9% leaching with NaOH(0.1M), 16.3% leaching with 0.01M NaOH and 54.5% leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Maximum percentage (82.5%) of CrO₄²⁻ ion leached out with 0.28M Na₂CO₃/ 0.5 M NaOH from the modified Willhendersonite mineral.

In this research, desorption of HDTMA from charged surfaces of non expandable minerals (kaolinite, illite, and clinoptilolite) was determined in a series of batch and column tests. These three minerals were chosen because they possess high HDTMA sorption capacities, and the sorption of HDTMA was on their external surfaces only, and they have been studied in detail for their retention of anions after HDTMA modification.

Hexadecyltrimethylammonium was chosen because of its high affinity to the negatively charged mineral surfaces, and HDTMA-modified minerals have high anion sorption capacity.



Result and Discussion

Desorption behavior of loaded Modified Zeolite minerals

The results from this study show that HDTMA desorption follows different trends at different surface coverages. Desorption behaviour of loaded analogue of modified zeolites was studied by equilibrating loaded analogue of modified zeolite with distilled water, NaOH (0.01M) pH ~12, NaOH (0.1M) pH~13 and 0.28 M Na₂CO₃ / 0.5 M NaOH pH~13. Each mixture was equilibrating at 25⁰ C for 24 hour under the following conditions.

1. The whole specimen was exposed to leachant so that full surface of the specimen remained in contact with it.
2. Sealed polypropylene bottles were used as leachant or buffer containers.

Leaching rate was studied for CrO₄²⁻, AsO₄³⁻ and SeO₄²⁻ oxoanions from loaded modified zeolite minerals and has been carried out with a view to explore the possibilities of its application for long term disposal of these toxic metal oxoanions. The technique of extraction efficiency studies has been developed by Li (1998)[11].

Desorption behavior of loaded analogue of modified Erionite

The present desorption studies have been performed with Chromate, Arsenate and Selenate saturated powder sample in the presence of different extracts and distilled water. Loaded modified Erionite mineral (100mg) sorbed with respective metal oxoanions, CrO₄²⁻, AsO₄³⁻ and SeO₄²⁻ were placed in sealed polypropylene bottles with 25 ml of buffer solution NaOH (0.01M) pH ~12, NaOH (0.1 M) pH~13 and 0.28M Na₂CO₃/ 0.5 M NaOH pH ~13 and distilled water. The bottles were placed in reciprocating water bath shaker at room temperature. After the completion of predecided leaching time, the solution was centrifuged and the concentration of metal oxoanion leached out from modified Erionite mineral into the leachant is then estimated spectrophotometrically.

The results obtained from desorption study table.1 and fig.1 suggested that modified Erionite mineral loaded with CrO₄²⁻ shows 0.7% leaching with distilled water, 17.6% leaching with NaOH(0.1M), 19.4% leaching with 0.01M NaOH and 67.5% leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Erionite mineral loaded with AsO₄³⁻ shows 1.6 % leaching with distilled water, 21.6% leaching with NaOH (0.1M), 40.3% leaching with 0.01M NaOH and 58.4 %

leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration.

Erionite mineral loaded with SeO₄²⁻ shows 4.5 % leaching with distilled water, 35.6% leaching with NaOH (0.1M), 52.4% leaching with 0.01M NaOH and 61.9 % leaching with 0.28M Na₂CO₃/ 0.5 M NaOH after 24 hours equilibration. Maximum percentage (67.5%) of CrO₄²⁻ ion leached out with 0.28M Na₂CO₃/ 0.5 M NaOH from the modified Erionite mineral.

CONCLUSIONS

Cationic surfactants sorbed on charged mineral surfaces are subject to slow desorption. The rate of surfactant desorption depends on the initial surfactant loading level, the type of mineral substrate, and the flow rate. Higher desorption rates were found from sorbed surfactant bilayers than from monolayers. The slow desorption may not be a major drawback for particular applications of surfactant-modified minerals.

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