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Hybrid materials in the remediation of arsenic contaminated waters: a physico-chemical study

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ABSTRACT

Hybrid materials are obtained by the organic modification of sericite using the organic cations viz. tetramethylammonium chloride (TMA or T) and dimethyldioctadecylammonium chloride as (DDDMA or D) by a simple wet cation exchange process. Surface morphology of these solids is discussed with the Scanning Electron Microscopic images. Moreover, the materials are characterized by the X-ray diffraction and Fourier Transform-Infrared analytical techniques. Removal behavior of these organo-modified sericite samples is assessed for arsenite and arsenate from aqueous solutions under the batch and column reactor operations. The batch reactor experiments show that increasing the sorptive concentration (1–20 mg/L) and pH (2–10) is caused to decrease the percent uptake of arsenite and arsenate significantly. Increasing the background electrolyte concentrations from 0.0001 to 0.1 mol/L $NaNO_3$ causes a significant decrease in percent removal of As(III) which infers that As(III) is sorbed onto the solid surface, primarily, by weak electrostatic or by van der Waals forces hence, forming an outer-sphere complexes at the solid surface. On the other hand As(V) uptake is insignificantly affected in presence of background electrolyte concentrations. This indicates that As(V) is sorbed by a strong chemical force and forming an inner sphere complexes onto the solid surface. The equilibrium state modeling shows that the data is fitted well to the Freundlich and Langmuir adsorption isotherms. The sorption capacities of these solids are calculated under these equilibrium conditions which indicate that organo-modified-sericite samples possess significantly higher removal capacity comparing to the virgin sericite. The leaching of the organic molecules (T or D) are also conducted in the sorption process of As(III) or As(V) and shows that almost negligible amount of T or D leaches in the bulk solutions since the Total Organic Carbon value of the bulk solution is not increased. Further, the breakthrough curves are obtained for these oxyanions under the column experimentations and the data is fitted well to the Thomas equation hence, the maximum loading capacity for arsenic is estimated under the dynamic conditions.

Keywords: Hybrid materials; Arsenite; Arsenate; Batch operation; Fixed-bed column; Sorption

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1. Introduction

Arsenic is a ubiquitous element available in all segments of environment. It enters and mobilizes into the natural environment mainly through a combination of natural processes such as weathering reactions, biological activity and volcanic emission as well as through several anthropogenic activities. Additionally, the mining activities, combustion of fossil fuels, the use of arsenic containing pesticides, herbicides and crop desiccants are reportedly releasing the arsenic into the environment. Arsenic has received a greater concern in the South East Asia (major part of Bangladesh and West Bengal, India); where arsenic contaminated soil causes contamination of underground waters which is reported to be a major source of drinking water [1]. It is further reported that more than six million people are on great risk; drinking the water having arsenic level above 50 μg/L in that region [2,3]. Arsenic poisoning is associated with various biological disorders including with skin, lung, bladder and kidney cancer, pigmentation changes, skin thickening (hyperkeratosis), neurological disorder, muscular weakness, loss of appetite, nausea etc. [4,5]. The acute toxicity may cause even the mortality [6]. Keeping in view the World Health Organization (WHO) in 1993 and the United States Environmental Protection Agency (US-EPA) in 2001 have reduced the limit of arsenic in drinking water from 50 to 10 μg/L [7,8].

Various materials such as zeolites, clays, activated carbon, bio-materials, metal oxides, zero-valent iron and neutralized red mud are suggested, previously, a good sorbing materials to remove arsenic from the arsenic contaminated waters [9]. Clay and minerals are natural materials and perhaps viable materials for the arsenic decontamination. However, the sorption capacity of these materials is reportedly insignificant for arsenic. Additionally, these materials possess low settling capacities hence, limiting its practical implication in such purposes [10]. Initial studies of using surfactant-modified clays in the environmental remediation are mainly focused on removal of hydrophobic organic contaminants from water [11,12]. Moreover, it is reported that if the surfactant loading on clays and zeolite is exceeded to its cation exchange capacity (CEC) or external CEC, the modified mineral could reverse their surface charge and show strong affinities for anions such as chromate, nitrate, sulfate [13–15] and iodide [16]. Li and Bowman [17] used kaolinite intercalated with hexadecyltrimethylammonium bromide (HDTMA) as an effective adsorbent for arsenate removal, and reported that the adsorption capacity of As(V) onto the organo-kaolinite is at least two times greater than the un-modified kaolinite. Kaolinite and zeolite modified by HDTMA causes to enhance the As(V) adsorption significantly, whereas the As(III) adsorption is almost unaffected [18]. Organo-bentonites are prepared by modification of bentonite with various cationic surfactants, and are used to remove As(V) and As(III) from aqueous solutions [9]. The results show that the adsorption capacities of bentonite modified with octadecyl benzyl dimethyl ammonium is significantly higher than the un-modified bentonite. The adsorption kinetics is fitted well to the pseudo-second-order rate model. The adsorption of As(V) and As(III) is strongly dependent to solution pH. Moreover, the presence of anions could not affect, significantly, the adsorption of As (III), but it clearly suppresses the As(V) sorption. Hybrid zirconiumpolyacrylamide material (ZrPACM-43) is synthesized by the sol–gel pathway and further the materials are applied in the removal of arsenic(III) from aqueous solutions [19]. Similarly, amino functionalized magnetic graphene composites are synthesized using the graphene sheets and further the material is useful in decontamination of several heavy metal toxic ions from aqueous solutions [20].

Sericite is a mica based natural clay, having abundance in Korea is used in the removal/speciation of several inorganic cations viz. Cu(II), Pb(II), Ni(II), Cs(I) etc. from aqueous solutions [21–23] and possess reasonably a good sorption capacity for these cations. Further, organo-modified sericite is exploited in the removal of phenol from aqueous solutions under the batch reactor operations [24]. The sericite is modified by poly (hydroxo aluminium) ions (Al) and followed by hexadecyltrimetrylammonium or alkyldimethylbenzylammonium ions to obtain the hybrid materials viz. Al-HDTMA-sericite (AH) and Al-AMBA-sericite (AA) [25]. These inorgano-organo-sericite samples are then employed in the removal of As(III) and As(V) from aqueous solutions under the batch and column reactor operations. The simulated batch reactor data indicated that As(V) is adsorbed specifically onto the solid surface whereas As(III) is sorbed mainly through electrostatic or even by the van der Waals attraction. Moreover, the results obtained under dynamic conditions show that the materials are reasonably useful in the speciation/attenuation of these two ions from water bodies. Similarly, the sericite is modified with the HDTMA or AMBA and further utilized in the remediation of arsenic contaminated wasters [26]. The encouraging results obtained previously prompted us further to employ the organo-sericite in the attenuation and speciation of arsenic. The present paper deals to obtain and assess the applicability of two different hybrid materials precursor to

sericite i.e. tetramethylammonium-sericite (T) and dioctadecyldimethylammonium-sericite (D) in the remediation of arsenic contaminated waters under batch and column studies.

2. Materials and methods

2.1. Materials

Sericite is obtained from the Keuman deposit, Gagokmyun, Samcheok City, Kagwon province, Korea. It is crushed and sieved to obtain particle size 200–300 BSS (British Standard Sieve). The powder is washed with distilled water, dried and crushed in mortar for its further use. The CEC of sericite is obtained by the US-EPA method 9080 (http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/9080.pdf), which is found to be 37.22 meq/100 g of sericite. Sericite contained with various metal oxides primarily containing the silicon and aluminum oxides as reported elsewhere [23]. Tetramethylammonium chloride (TMA) and dioctadecyldimethylammonium bromide (DDDMA) are obtained respectively from Junsei Chemical Co. Ltd, Japan and Sigma Aldrich, USA. Sodium meta-arsenite and disodium hydrogen arsenate heptahydrate are obtained from Wako Pure Chemical Industries Ltd, Japan. The other chemicals are of AR grade. The deionized water is purified (18 MΩ-cm) using a Millipore water purification system (Milli-Q+).

The hybrid organo-sericite is obtained by incorporating the TMA/or DDDMA within the sericite network. Twenty grams of sericite powder is taken into 1.0 L of TMA or DDDMA solution containing the equivalent amount of 1.0 or 2.0 CEC of sericite; correspondingly named as T1 or D1 and T2 or D2 materials. The mixture is refluxed for 48 h at 60˚C under constant stirring. The slurries are filtered and washed with plenty of purified water. Soxhlet extraction is conducted to remove any excess of free surfactants. The sericite which is then loaded with organic surfactants i.e. T1, T2, D1 or D2 are dried at 90˚C and stored in the airtight polyethylene bottles for further experimentation.

2.2. Surface morphology of organo-modified-sericite materials

The surface morphology of sericite, T1 and D1 solids are obtained by the scanning electron microscope (SEM) images using a SEM (Model FE-SEM SU-70; Hitachi, Japan). X-ray diffraction (XRD) data is recorded using the XRD machine (PANalytical, Netherland; Model X'Pert PRO MPD). The Cu K_α radiation having wavelength 1.5418 Å is used for XRD. Fourier transform-infra red (FT-IR) data is obtained for these materials using a FT-IR machine (Bruker, Tensor 27, USA by KBR disk method).

2.3. Speciation studies of As(III) and As(V)

Speciation of arsenic(III) and arsenic(V) are conducted separately using the MINEQL+ (Version 4.5), a geochemical computer simulation program. The initial concentration of As(III) and As(V) is taken 2.0 mg/L at constant temperature 25˚C. The species distribution of As(III) and As(V) as a function of pH is obtained.

2.4. Batch reactor experiments

Stock solutions of As(III)/or As(V) 100 mg/L is prepared by dissolving an appropriate amount of respective arsenic salts in distilled water and the desired concentration is obtained by successive dilution of stock solution. 2.0 mg/L of As(III) /or As(V) solution (100 mL) is taken into polyethylene bottles and the pH is adjusted by a drop-wise addition of 0.1 mol/L HNO_3/or NaOH solutions. 0.2 g of solid i.e. organo-sericite is then added into these bottles. The bottles are kept in an automatic shaker (KUKJE, Shaking Incubator, Korea model 36-SIN-125) for 24 h at 25 ± 1˚C in order to achieve equilibrium between solid/solution interfaces. The samples are then taken out from shaker and filtered with 0.45 μm syringe filter and the pH is again checked and reported as final or equilibrium pH. The filtrates are subjected to its bulk sorptive concentration measurements using an AAS (Fast Sequential Atomic Absorption Spectrometer: Model AA240FS, Varian) as well to the TOC measurements using TOC analyzer (Shimadzu, Japan; Model: TOC-VCPH/CPN). The percent removal is calculated as stated elsewhere [23].

Sorptive concentration dependence data is collected taking arsenic concentrations from 1.0 to 20.0 mg/L at constant pH 4.5 and at constant temperature 25 ± 1˚C. A constant dose 0.2 g/L of solid is added into these solutions. The sorption process is carried out as described before. Further, the equilibrium concentration dependence sorption data are further employed in equilibrium modeling studies using the Freundlich and the Langmuir adsorption isotherms as discussed elsewhere [23,25].

The ionic strength dependence data is collected varying the background electrolyte concentrations of sorptive solutions from 0.0001 to 0.1 mol/L of $NaNO_3$. The sorptive pH (~4.5) and temperature (25 ± 1˚C) is kept constant throughout the experiments. Results are presented as percent removal as a function of background electrolyte concentrations.

2.5. Column reactor experiments

The column experiments are performed using a glass column (1 cm inner diameter) packed with 1.0 g of T1 or D1 (kept in the middle of the column); below and above to this, 2.0 g of virgin sand particles (14–16 BSS) are taken. It is then fully packed with glass beads. Sorptive solutions of As(III)/or As(V) 2.0 mg/L having a constant pH 4.5 is pumped upward from bottom of column using Acuflow Series II, High-Pressure liquid chromatographic pump, at a constant flow rate of 0.70 mL/min. Effluent samples are then collected using Spectra/Chrom CF-1 fraction collector. The liquid samples collected are filtered using a 0.45 μm syringe filter and the total bulk sorptive concentration is measured using an AAS. Further, the breakthrough data is utilized to optimize the removal capacity of these solids under the dynamic conditions using the Thomas Equation as described elsewhere [25,27,28].

3. Results and discussion

3.1. Characterization and surface morphology of organo-modified-sericite materials

SEM images are obtained for the solids sericite, T1 and D1 and shown in Fig. 1. Sericite sample possesses very compact and ordered layer structure which hardly has micro- or meso-pores on its surface. However, the organo-modified-sericite samples show heterogeneous and disordered surface structure having distinct visible pores on it. The layers are clearly propped-up in presence of organic cations. Moreover, at places, the organic molecules are aggregated onto the surface. It is assumed that the water molecules or even the potassium ions, which are present previously within the interspace of sericite, are replaced by the TMA or DDDMA organo cations. Hence, the surface of the sericite becomes more disordered. Similar results are obtained previously where sericite is pillared with aluminum and HDTMA or AMBA as to obtain the inorgano-organo-sericite [25].

The XRD data of these solids are recorded and presented graphically in Fig. 2. Characteristic peaks of sericite mineral is observed and marked in the XRD curve. The peaks are found at the 2θ values of 19.82, 20.83, 25.43, 26.62, 27.87, 36.00, 36.52, 42.41 and 50.12 assigned with the standards sericite mineral phase [27]. Samples T1 and Di showed almost an identical diffraction pattern with slight change in the d-spacings and intensities of peaks.

Further, the FT-IR data is collected for the sericite and modified sericite samples i.e. T1 and D1. The FT-IR results are presented graphically in Fig. 3.

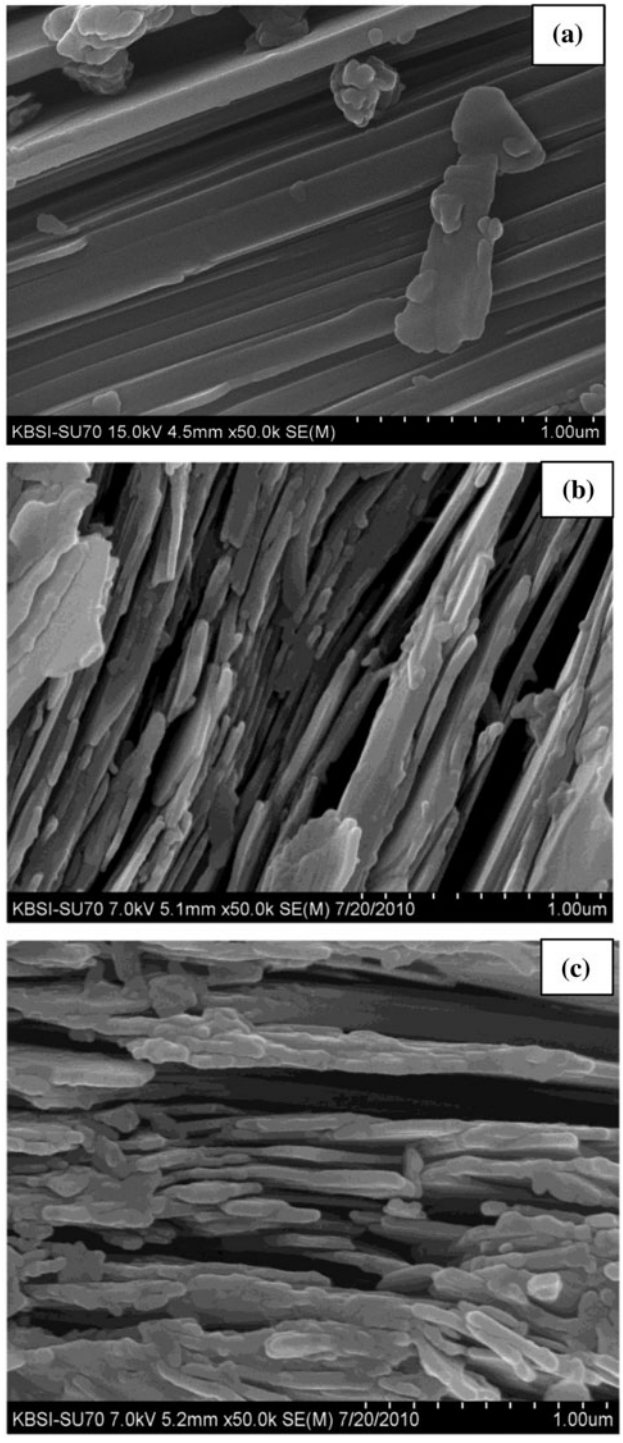

Fig. 1. SEM images of (a) Sericite, (b) T1 and (c) D1 solids.

Figure shows asymmetric and symmetric stretching vibrations of H-O-H are occurred around the wave number of 3,630 and 3,426 cm^{-1} (not much pronounced with sericite and D1). Similarly, H-O-H

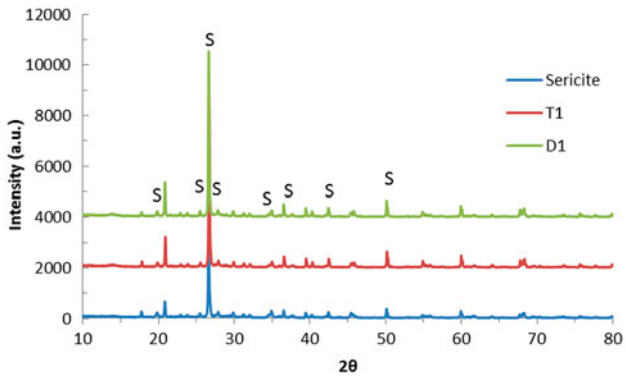

Fig. 2. XRD pattern of sericite, T1 and D1 solids.

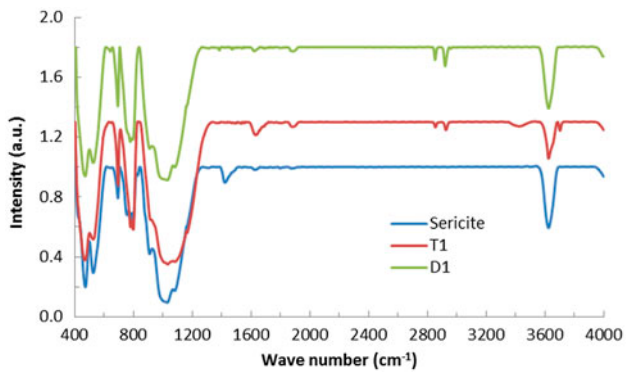

Fig. 3. FT-IR spectral data of sericite, T1 and D1 solids.

bending vibration is observed around the wavenumber of 1,625 cm^{-1} for these samples. This clearly indicates the presence of hydroxyl groups within the clay sheets and the water molecules present within the interlayer space of sericite [29–31]. A prominent IR peak centered around 1,030 cm^{-1} is an indicative of the Si–O stretching vibrations [32]. Moreover, couple of IR bands occurred around 690 and 790 cm^{-1} are assigned to the Si–O quartz vibrations [33]. Further, interesting to note that the modified samples T1 and D1 possessed prominent peaks centering around 2,930 cm^{-1} and 2,850 cm^{-1} are assigned as $–CH_2$ asymmetric stretching and $–CH_2$ symmetric vibrations, respectively [29]. This confirms the introduction of organo cations tetramethylammonium or dimethyldioctadecylammonium within the sericite network.

3.2. Speciation study of As(III) and Arsenic(V)

The speciation study of As(III) and As(V) is conducted at wide range of pH. Results are presented in Fig. 4(a) and (b), respectively for the As(III) and As (V). The Fig. 4(a) clearly demonstrates that uncharged H_3AsO_3 species is dominant below the pH 8 and above pH 8 the anionic species $H_2AsO_3^-$ is dominant. On the other hand, As(V) speciation data shows that at lower pH till pH 6.8, H_3AsO_4 and $H_2AsO_4^-$ species are dominated whereas above pH 7.0, $HAsO_4^{2-}$ anionic species are dominated (*cf* Fig. 4(b)).

3.3. Batch reactor studies

3.3.1. pH dependence study

Mechanism involved at solid/solution interfaces is, perhaps, better dealt with the pH dependence sorption studies. Therefore, the pH dependence sorption of As (III) or As(V) by these solids are obtained and presented graphically in Fig. 5(a) and (b) respectively for As(III) and As(V). In general, low to moderate pH values favor the percent uptake of As(III) or As(V) by these modified-sericite samples; whereas the high pH values greatly suppresses the uptake of these two sorbing species. On the other hand, very low percent uptake of As(III) and As(V) is obtained by the virgin sericite sample which is almost unaffected with the pH change. Quantitatively, increasing the pH from 2.0 to 10.0, the corresponding decrease in percent uptake of As(III) is found to be, respectively from 36.27 to 15.54% for T1; from 32.64 to 16.58% for T2; from 34.20 to 3.63% for D1 and from 18.13 to 1.04% for D2 samples. Similarly, the decrease in percent uptake of As (V) is recorded respectively from 56.44 to 23.11% for T1, from 39.11 to 20.89% for T2; 25.33 to 16.89% for D1. Unusually, very low percent uptake of As(V) by D2 sample is observed which is not affected significantly with pH. The values are found to be 24.89% and 26.22% at pH 1.94 and 9.34, respectively. It is clearly observed that increasing the dose of organic cations twice to CEC, i.e. the samples T2 and D2 show comparatively less percent removal of arsenic comparing to its corresponding samples of T1 and D1 having 1:1 CEC dose of organic cations. This is possibly due to the structural arrangements and number of monolayer formation of organic cations within the interspace of sericite having the basal spacing of *ca.* 8.0 Å. Possibly, the bilayer arrangement of organo cations within the interspace is not a suitable and stable arrangement and causing to decrease in As(III) or As (V) uptake. Earlier, however, it is reported that the HDTMA forms a stable bilayer within the interspace of zeolite when the surfactant addition is exceeded to the external CEC value [34,35]. Moreover, it is reported that the sorption of chromate on HDTMA-modified zeolite reached to its maximum value when modified to 200% to its external CEC [36]. However, the other studies, showed that 200% CEC loading of

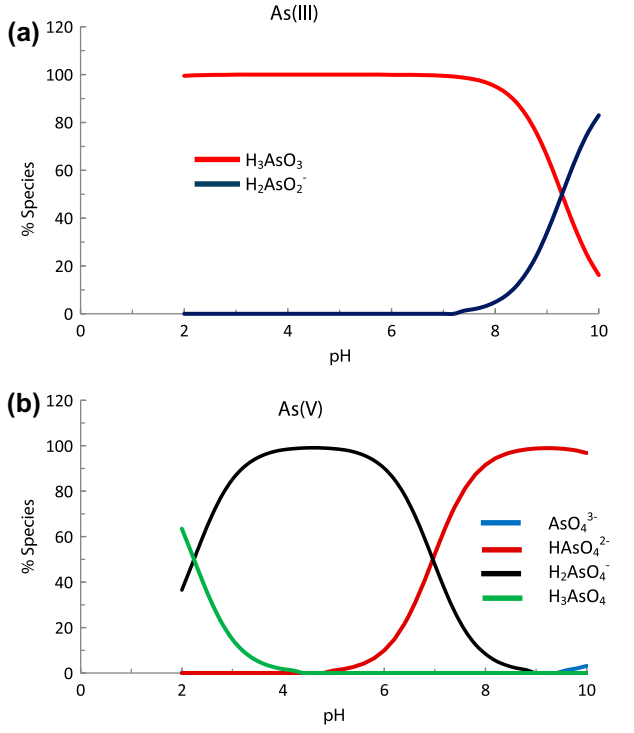

Fig. 4. Speciation of (a) As(III): 2 mg/L and (b) As(V): 2 mg/L as a function of pH.

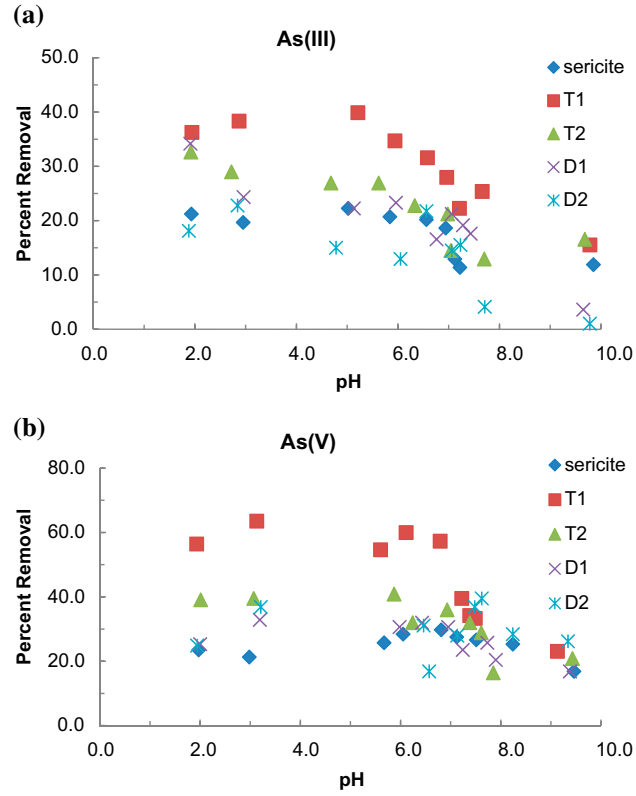

Fig. 5. Effect of pH in the removal of (a) As(III) and (b) As(V) using sericite and organo-modified sericite samples.

some quaternary ammonium cations (QAC) onto montmorillonite is suppressed significantly the removal capacity of methylene blue and they inferred that QAC's already occupied the cation-exchange sites of the precursor clays, making it difficult for methylene blue to occupy place within the interspace [37].

Relatively high and almost constant percent uptake of As(III) is occurred within the pH region 2–6. The high uptake of As(III) is possibly due to dominating van der Waals attractive forces operative in between the arsenic and solid surface and this possibly enables an enhanced uptake of arsenic(III) in this pH region. However, the uptake of As(III) is decreased gradually increasing the pH beyond ~6. This is because of the fact that the acidic dissociation of H_3AsO_3 species takes place and gradually the anionic species $H_2AsO_3^-$ (negatively charged) increases in solution as the speciation results also indicated (vide Fig. 4(a)). This indicates that both solid and sorbate ions carrying net positive charge hence repulsive forces causing for an apparent decrease in sorption of As(III) at higher pH values. Moreover, at extreme high pH condition i.e. pH 10 there could be a competition between the OH^- ion and the anion of As(III) i.e. $H_2AsO_3^-$, towards solid surface, and the OH^- ions may significantly compete for solid surface [38]. Similarly, the uptake of H_3AsO_3 species by iron modified sand is reported to be adsorbed by the van der Waals attraction [39]. However, an electrostatic attraction is reported previously for the sorption of As(III) by hybrid materials, modified activated carbon or soil samples etc. [25,40–42].

On the other hand, relatively high uptake of As(V) by T1 sample is almost unaffected up to the solution pH 6.7; beyond this it is greatly decreased. This could be explicable with the fact that at low pH values the surface carries net positive charge and mostly the As(V) present as anionic forms i.e. $H_2AsO_4^-$ or $HAsO_4^{2-}$ species (vide Fig. 4(b)), the electrostatic attraction favored the uptake of As(V) by these solids Eq. (1) [41].

$$(\text{Sericite-T/or D})^+ + H_2AsO_4^- \rightarrow (\text{Sericite-T/or D})^+ - H_2AsO_4^- \quad (1)$$

This is the driving force caused to attract the arsenic species within the interspace of the sericite network. In fact, the sericite is muscovite type mineral, possessed a layered structure. It possesses three sheet layers having the T:O ratio of 2:1 (where T: tetrahedral $[SiO_4]^{4-}$ and O: octahedral $[AlO_3(OH)_3]^{6-}$) and the apices of these sheets are having the oxygen atom from which some

are connected with protons (as –OH) and are perhaps taking part in surface complexation with the several heavy metal toxic ions including lead or copper [23]. However, it is assumed that the –OH group may be replaced with the arsenate and forming mono- or binuclear complexes with the Si or Al as demonstrated below Eq. (2) and (3):

$$> AlOH + H_2AsO_4^- \rightarrow \; > AlH_2AsO_4 + OH^- \quad (2)$$

$$2(> AlOH) + HAsO_4^- \rightarrow \; > Al_2HAsO_4 + 2OH^- \quad (3)$$

The specific sorption of As(V) by the modified sericite is again reaffirmed with the background electrolyte studies in later sections. Also the somewhat similar mechanism was suggested previously using the clay or aluminum hydroxide solids [43,44].

Further, increase in pH, there could possibly be a competition for the solid surface between the OH^- ions and the metal anions which seemingly restricts the uptake of As(V) by these solids [38].

3.3.2. Sorptive concentration dependence study

The sorptive concentration dependence data is collected for a wide range of initial arsenic concentration i.e. 1.0 to 20.0 mg/L. Results show that the organo-modified solids, at least T1 and D1, possess an enhanced amount of arsenic removal compared to the virgin sericite at all sorptive concentrations. Quantitatively, increasing the concentration from 1.0 to 20.0 mg/L of As(III), the corresponding decrease in percent removal is found to be, respectively from 30.21 to 1.68% for sericite; from 46.88 to 4.26% for T1; from 36.46 to 3.05% for T2; from 38.54 to 3.86% for D1 and from 33.33 to 2.39% for D2 samples. Similarly, the decrease in percent uptake of As(V) is found to be from 34.04 to 2.21% for sericite; from 47.87 to 7.39% for T1; from 42.55 to 5.70% for T2; from 43.62 to 6.31% for D1 and from 34.04 to 4.11% for D2 samples, respectively for an increase in sorptive concentration from 1.0 to 20.0 mg/L. This decrease in content of uptake is explained with the fact that at higher sorptive concentration of As(III)/or As(V); relatively lesser number of active sites are present whereas at lower concentrations less number of sorbing species are present for the same number of active sites available at the solid surface [45].

3.3.3. Equilibrium state modeling

The equilibrium state adsorption dependence data is further utilized to deduce various adsorption isotherm models viz. the Langmuir and the Freundlich models to its linear form. The equilibrium state concentration dependence data is fitted to these two models and hence, the Freundlich and Langmuir constants are estimated. These constants along with the R^2 values are returned in Table 1. The fitting data shows reasonably a good applicability of these two models is occurred for the systems studied. The difference in removal capacity estimated by these two models is attributing the different basic nature and assumptions of these two models. Further, organo-modified samples possess significantly higher adsorption capacity comparing to the virgin sericite; therefore shows its potential applicability in the remediation of waters contaminated with arsenic. Moreover, the sample T1 or D1 obtained by the 100% loading of surfactant to the sericite possess relatively higher adsorption capacity compared to its corresponding samples obtained by 200% loading of surfactant i.e. T2 or D2. These results again indicate the applicability of T1 and D1 samples with the stable monolayer structure of organo cation within the interlayer space of sericite. Among these two organo cations i.e. TMA and DDDMA; TMA-modified sericite shows relatively higher removal capacity than DDDMA-modified sericite at least towards the removal of As(III) or As(V) from aqueous solutions.

Further, the fractional values of Freundlich constant, i.e. $1/n$, obtained for these systems indicate a heterogeneous surface structure of solids with an exponential distribution of surface active sites [25]. Similarly, the Langmuir constant "b" reflected to the strength and affinity of these solids towards the adsorbing species [46].

3.3.4. Background electrolyte concentration study

The specific and non-specific adsorption of As(III) or As(V) onto the organo-modified-sericite, could be studied by carrying the ionic strength dependence study. It is reported previously that the specific adsorption is unaffected with the increase in ionic strength, whereas the non-specific adsorption is greatly influenced by the change of ionic strength because of the competitive adsorption with counter ions [47]. Hence keeping in view the study is conducted to observe the change in background electrolyte concentration i.e. $NaNO_3$ in the adsorption behavior of these solids in the removal of As(III)/or As(V)) at constant pH 4.5. The background concentration is increased from 0.0001 to 0.1 mol /L of $NaNO_3$ (1,000 times) and the corresponding percent removal of As(III)/or As(V) is obtained and

Table 1
Adsorption isotherm constants estimated for the sorption of As(III) and As(V) by sericite and organo-modified-sericite samples using linear adsorption equations

	Freundlich constants			Langmuir constants		
System	K_f (mg/g)	$1/n$	R^2	K_f (mg/g)	b	R^2
Sericite-As(III)	0.1942	0.314	0.829	0.4041	1.440	0.968
T1–As(III)	0.2986	0.454	0.959	1.0423	0.403	0.972
T2–As(III)	0.2162	0.488	0.972	0.8985	0.293	0.965
D1–As(III)	0.2342	0.513	0.937	0.9779	0.316	0.951
D2–As(III)	0.1891	0.467	0.887	0.6661	0.408	0.882
Sericite-As(V)	0.1941	0.579	0.969	1.1614	0.180	0.920
T1–As(V)	0.3381	0.577	0.988	1.9685	0.190	0.928
T2–As(V)	0.3006	0.519	0.978	1.3004	0.299	0.980
D1–As(V)	0.3006	0.536	0.966	1.3123	0.311	0.963
D2–As(V)	0.2377	0.477	0.767	0.6452	1.256	0.824

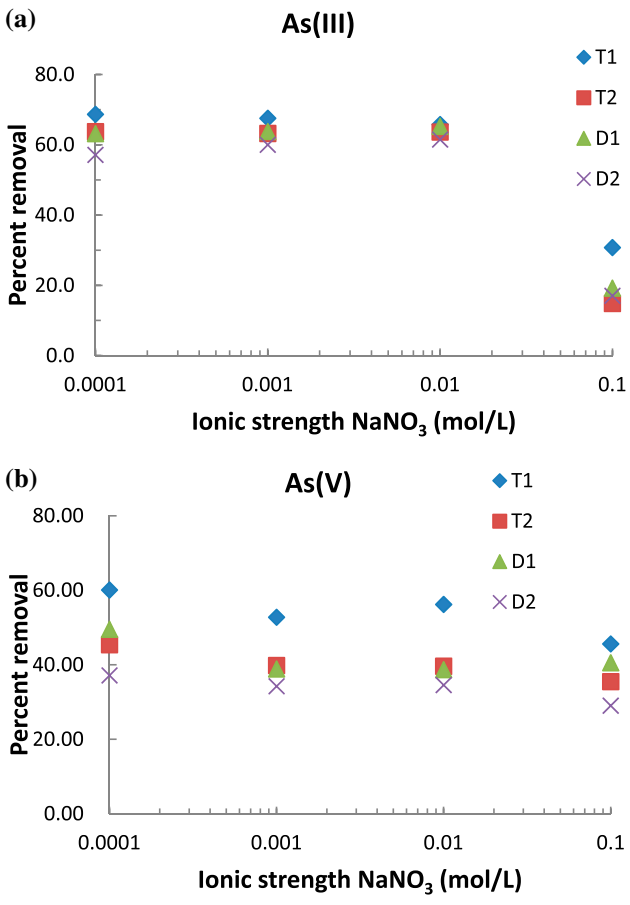

Fig. 6. Effect of ionic strength in the removal of (a) As(III) and (b) As(V) using organo-modified sericite.

represented graphically in Fig. 6(a) and (b) respectively for As(III) and As(V).

Quantitatively, increasing the background electrolyte concentration from 0.0001 to 0.1 mol/L $NaNO_3$ causes to decrease the As(III) uptake respectively from 68.68 to 30.77% for T1 i.e. 37.91% decrease; from 63.74 to 14.84% for T2 i.e. 49.9% decrease; 63.19 to 19.23% for D1 i.e. 43.96% decrease; and from 57.14 to 17.03% for D2 i.e. 40.11% decrease. Similarly, the uptake of As(V) is decreased from 60.09 to 45.62% for T1 i.e. 14.47% decrease; from 45.41 to 35.48% for T2 i.e. 10.03%; from 49.54 to 40.55% for D1 i.e. 8.99% decrease and from 37.16 to 29.03% for D2 i.e. 8.13% decrease. These results indicate that the 1,000 times increase of background electrolyte concentration causes significant decrease of As(III) by these solid materials. Therefore, it indicates that As(III) is adsorbed mostly with the weak attractive forces, perhaps van der Waals forces and forming an outer sphere complexes at the surface. On the other hand the uptake of As(V) is not significantly affected in presence of background electrolytes pointed it that As (V) is sorbed primarily by the strong chemical forces and forming an "inner sphere complexes" onto the solid surface of these modified sericite. As(III) sorption onto the zirconium(IV) oxide-ethanolamine is reported to be ion-exchange along with electrostatic attraction [48]. Vaisya and Gupta [39] also indicated that the major driving force in the sorption of As(III) onto the iron-modified sand was the van der Waals attraction.

3.4. Breakthrough curves for As(III) and As(V)

The applicability of the organo-sericite materials are further assessed in the removal of As(III) and As (V) under the dynamic conditions as performed with column experiments. The column data could be used for direct practical implication of these materials in the possible large scale or pilot scale treatment of water contaminated with arsenic. The column

conditions are maintained as mentioned before and the results are presented graphically in Fig. 7(a) and (b), respectively for As(III) and As(V). It is interesting to note that the complete breakthrough is obtained for As(III) at the throughput volume of 1.22 L for T1 and 0.64 L for D1 solids. Similarly, it is obtained for the As (V) at 0.96 L for T1 and 0.29 L for D1. Relatively high value of throughput volume for these solids indicates its potential applicability in the remediation of water contaminated with arsenic. Further, the breakthrough data is utilized for the non-linear fitting to the Thomas equation [27] in order to optimize the two unknown parameters viz. q_0 and K_T known as loading capacity and Thomas rate constant. Reasonably a good fitting of breakthrough data is obtained for these systems as shown in Fig. 7(a) and (b). The Thomas constants are

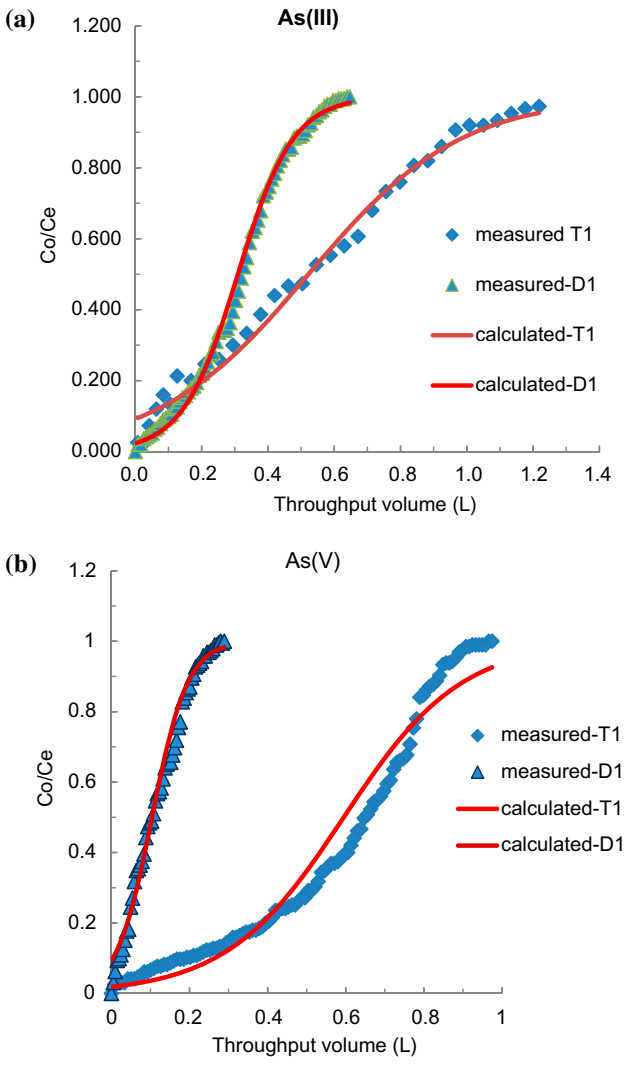

Fig. 7. Breakthrough curves for the removal of (a) As(III) and (b) As(V) by organo-modified-sericite fitted to the Thomas model.

Table 2
Thomas constants for the removal of As(III) and As(V) from aqueous solutions by organo-modified-sericite

Systems	q_0 (mg/g)	$K_T \times 10^{-3}$ (L/min/mg)
T1–As(III)	0.826	1.938
D1–(As(III)	0.589	4.427
T1–As(V)	1.160	2.388
D1–As(V)	0.199	7.998

evaluated for these solids and are returned in Table 2. The high loading capacity is obtained for TMA modified sericite comparing to the DDDMA modified sericite at least for both the arsenic species i.e. As(III) and As(V). This clearly pointing its applicability in the treatment of arsenic contaminated waters. These results are in a line to the batch reactor data. Similar results are also reported previously using the biosorbents or manganese and iron coated sands, etc. [25,45,49,50].

4. Conclusions

Four different TMA/or DDDMA-modified sericite samples are obtained (viz. T1 and T2 or D1 and D2 obtained by 100 and 200% CEC loading of TMA/or DDDMA onto sericite). The surface morphology of these solids indicates that the presence of organo cations significantly disordered the compact and layered structure of sericite. The XRD data enables the presence of sericite minerals with these solids and IR data indicates the introduction of organic cations within the sericite framework. Further, the suitability and applicability of TMA and DDDMA modified sericite is assessed for the decontamination of arsenic contaminated waters. The studies are performed under batch and column reactor operations. Various parametric batch studies show that lower pH and high sorptive concentration favors greatly the uptake of As(III) and As(V) by these solids. The equilibrium state concentration dependence data is fitted well to the Freundlich and Langmuir adsorption isotherms. Moreover, the estimated capacity for these solids indicates that samples T1 and D1 possesses significantly higher sorption capacity than that of virgin sericite or samples T2 and D2. The 1,000 times increase in background electrolyte concentrations ($NaNO_3$) causes significant decrease in As(III) removal which indicates the arsenic(III) is predominantly sorbed by weak van der Waals attractive forces. However, As(V) sorption is insignificantly decreased by the similar increase in background electrolyte concentrations pointing that As(V) is sorbed with strong chemical forces and forming an inner

sphere complexes at solid surface. Moreover, interesting to note that, no leaching of organic cations, i.e. TMA or DDDMA throughout the pH regions ~2–10, is occurred in the sorption of As(III) or As(V) by these organo-modified sericite sampels as obtained by bulk TOC data measurements. Further, the column reactor operations indicate very high value of breakthrough volume obtained for T1 and D1 solids. The breakthrough data is well fitted to the Thomas equation. Moreover, the T1 sample possesses significantly higher loading capacity than the sample D1.

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