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Abstract: The current research focuses on removal of arsenite ions from aqueous solutions by a new adsorbent, surfactant modified akaganeite (Ak_m), prepared after the adsorption of the cationic surfactant, hexadecyl trimethyl ammonium bromide (N-Cetyl-N,N,N-Trimethylammonium Bromide) onto akaganeite. The new adsorbent was investigated with Fourier transform infrared spectra and X-ray photoelectron spectroscopy methods for a better understanding of the effects of surface properties on arsenite adsorption. Surfactant modified akaganeite was found to be an effective adsorbent for the removal of arsenite ions from aqueous systems. It presented a significantly higher arsenite adsorption capacity than the pure nanocrystalline akaganeite. Kinetics of adsorption obeys a second-order rate equation. The maximum adsorption capacity was found to 328.3 mg g^{-1} over a wide pH range significantly higher than those of other adsorbents reported.

Keywords: Iron oxide hydroxide, surfactant-modified adsorbent, akaganeite, process mechanism, arsenite removal

INTRODUCTION

Arsenic is one of the most toxic contaminants found in the environment and has been recognized as a toxic element for centuries. Arsenic contamination

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has become a worldwide epidemic, especially in developing countries where a significant percentage of the population depends on groundwater for drinking. Chronic exposure to arsenic contaminated drinking water can result in serious health problems, such as skin lesions and cancers (1). To minimize the health impact of arsenic, the World Health Organization (WHO) in 1993 and the National Health and Medical Research Committee (NHMRC), Australia, in 1996 had recommended the maximum contaminant level (MCL) of arsenic in drinking water as 10 and 7 $\mu g\,L^{-1}$ respectively (2, 3). The MCL of arsenic in drinking water has also been reduced from 50 to 10 $\mu g\,L^{-1}$ by the European Commission in 2003 (4). Arsenic occurs in both organic and inorganic forms in natural water but organic arsenic is of little importance as it goes through bio transformation and detoxifies through methylation. Inorganic arsenic occurs in −3, 0, +3, and +5 oxidation states in aquatic systems. Under reducing environment As(III) is found primarily as H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} whereas different hydrolysis species of As(V) such as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-} can be present in water with dissolved oxygen/oxidizing environment (5). It is also well known from the chemistry of arsenic that As(III) is more toxic and mobile than As(V). Due to the presence of neutral ionic specie of As(III) in the pH range of most surface waters (6.5–7.5), this form of arsenic is very difficult to treat by different technologies.

Arsenic can be removed from contaminated water by physico-chemical (adsorption, ion exchange, precipitation–coagulation, membrane filtration, permeable reactive methods) as well as biological techniques (phytoremediation, biological treatment with living microbes/bio-filtration) (6). Recently, adsorption processes have attracted considerable attention owing to their ability to treat aqueous solutions contaminated with trace quantities of arsenic. So, different types of sorbents have been attempted for As(III) removal up to various degrees of success (Table 1).

Considering the affinity of arsenic towards iron, various iron-based media have been developed and effectively used as adsorbents for the removal of both As(III) and As(V) from water. According to previous studies, iron oxides, including oxyhydroxides and hydroxides, such as amorphous hydrous ferric oxide (FeOOH), goethite (a-FeOOH) and hematite (a-Fe_2O_3), are promising effective adsorptive materials for both arsenite and arsenate removal from water (7, 8). Iron oxide coating cement (9), iron oxide loading slag (10), amorphous or crystalline iron(III) phosphates (11), and iron(III) loaded orange waste (12) have also been proposed. Bang and his co-workers (13) proposed the use of zero-valent iron. Iron hydroxide phases have been also incorporated in various materials for improving maximum adsorption capacity, for example in MCM-41 type materials (14).

Recently, a novel adsorbent, nanocrystalline akaganeite, was examined for the removal of arsenites from aqueous solutions and it presented a high sorption capacity (q_{max} 135.2 mg As(III) g^{-1}) at a wide pH range of 4–9. The maximum sorption capacity was significantly higher than for most

Table 1. Comparison of certain arsenite Q_{max} values for various sorbents

Sorbent	Q_{max} (mg/g)	pH	Reference
Akaganéite	135.2	7.0	Current paper
Surfactant-modified akaganéite	328.3	7.0	Current paper
Granular titanium dioxide	32.4	7.0	(32)
Nanocrystalline titanium dioxide	67.4	7.0	(33)
Activated alumina	0.2	7.6	(5)
Activated alumina	3.5	6.9	(34)
Fresh biomass	120	7.0	(35)
Galena	8.1	7.0	(36)
Sphalerite	3.1	9.0	(36)
Red mud	0.3	9.5	(7)
Zr-loaded resin	88.4	9.0	(37)
Iron oxide coating cement	0.7	7.0	(9)
Amorphous $FePO_4$	21	—	(11)
Crystalline $FePO_4$	16	—	(11)
Iron(III) loaded orange waste	90.7	8.0	(12)

of the other adsorbents reported; meanwhile the preparation of the nanocrystalline akaganeite was simple and relative low cost. The purpose of the current work was the preparation and characterization of a new sorbent material- modified akaganeite – which was prepared by modification of pure akaganeite (β-FeOOH) with a cationic surfactant, (N-Cetyl-N,N,N-Trimethylammonium Bromide – HDTMA), as well as the study and evaluation of its ability to remove arsenites from aqueous solutions.

MATERIALS AND METHODS

Akaganeite Preparation

Akaganeite (denoted hereafter as Ak) was prepared by precipitation from an aqueous solution of iron(III) chloride ($FeCl_3 \cdot 6H_2O$ 0.506 M). For the hydrolysis process an aqueous solution of ammonium carbonate (0.23 g L^{-1}) was used (15). The preparation of the gel was carried out in a three-necked round-bottom flask, placed in a thermostat at 25°C. The precipitating agent was added dropwise, using a dosimetric pump at a constant flow rate. Vigorous mechanical stirring was applied in order to achieve good mixing. The starting pH of the hydrolysis process was 1.7, while the final one was 8.0. The precipitate was decanted in a dialysis cellulose membrane for the removal of chloride anions and subsequently was freeze-dried in a bench-scale instrument.

The produced material presented the following physical characteristics: surface area 330 $m^2\,g^{-1}$ (BET method), pore volume 0.35 $cm^3\,g^{-1}$, predominant pore diameter 2.5 nm. The crystallites of akaganeite had small size, 3–6 nm, i.e. in the order of nanocrystals.

Cationic Surfactant Adsorption onto Akaganeite

Effect of pH

For the examination of the effect of pH on the surfactant adsorption onto akaganeite, a quantity of 0.1 $g\,L^{-1}$ akaganeite was added into Erlenmeyer flasks containing 100 mL surfactant solutions of a constant initial concentration of (0.01 $mol\,L^{-1}$). The pH was adjusted with 0.1 M HNO_3 or 0.1 M NaOH at a range from 4 to 14. Next, the flasks were put in a shaker bath at 25 ± 1°C for 24 h, at a shaking rate of 160 rpm. The residual surfactant, i.e. that remaining in solution after the application of solid/liquid separation of suspended solids by 0.45-μm filtration membrane, was chemically analyzed (16).

Equilibrium Tests

For the equilibrium experiments a quantity of 1 $g\,L^{-1}$ akaganeite was added into Erlenmeyer flasks containing a series of surfactant solutions at varying initial concentrations (0–1000 $mg\,L^{-1}$). The pH was adjusted to approximately 11 with 0.1 M NaOH. Next, the flasks were put in a shaker bath at 25 ± 1°C for 24 h, at a shaking rate of 160 rpm. The residual surfactant, i.e. that remaining in solution after the application of solid/liquid separation of suspended solids by 0.45 μm filtration membrane, was chemically analyzed.

Modified Akaganeite Preparation

Modified akaganeite (denoted hereafter as Ak_m) was prepared after the adsorption of the cationic surfactant (HDTMA) on akaganeite. The surfactant used for the modification of akaganeite was hexadecyl – trimethyl ammonium bromide (N-Cetyl-N,N,N-Trimethylammonium Bromide) – HDTMA – of 98% purity and it was obtained from Panreac Chimica SA.

In Erlenmeyer flasks of total volume 250 mL, 100 mL of a solution of 0.01 M of surfactant was added. Each solution contained 1.0 g of akaganeite and the pH of the solution was adjusted to 11. The flasks were capped and equilibrated in a shaker bath at 25 ± 1°C for 24 h, at a shaking rate of 160 rpm, for 24 hours to allow akaganeite to adsorb HDTMA, until the solution reached equilibrium. After the application of solid/liquid separation of suspended solids by 0.45 μm membrane the sorbent was freezed-dried.

Arsenites Adsorption onto Surfactant – Modified Akaganeite

The arsenite stock solution was prepared from the dissolution of arsenic trioxide of 99.8% purity and it was obtained from AnalaR. To perform an arsenite adsorption experiment, arsenite solutions were prepared with 0.1 M KNO_3 ionic strength. A fixed mass of akaganeite (Ak) (0.5 g L^{-1}) was put into Erlenmeyer flasks containing a series of arsenite solutions at varying initial concentrations (0–300 mg L^{-1}). The final solution was adjusted to the desired pH with 0.1 M HCl or 0.1 M NaOH. The flasks were put in a shaker bath at 25 ± 1°C for 24 h, at a shaking rate of 160 rpm, until the solution reached equilibrium. Preliminary experiments verified that after 24 hours no measurable change occurred in the adsorbed amount. The pH was monitored at both the beginning and end of each of the adsorption experiments. Little variation in pH was observed during the course of an adsorption experiment. The residual arsenic, i.e. that remaining in solution after the application of solid/liquid separation of suspended solids by 0.45 μm membrane filtration, was chemically analyzed. The molybdenum blue method was followed, using a double-beam UV-visible spectrophotometer (Hitachi Model U-2000) according to the appropriate standard method (17).

Surface Characterization Methods

Surface Area Measurements

Porosity, surface area, pore volume and pore size distributions were obtained from nitrogen adsorption and desorption isotherms using a Micrometrics Tristar 3000 system at liquid nitrogen temperature after the sample was degassed at 70°C overnight. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method and the pore volume and pore size distribution was obtained from the N_2 desorption branch of isotherms using the Barrett-Joyner-Halenda (BJH) method.

FTIR Measurements

Fourier transform infrared (FT-IR) spectroscopy was performed from 4000 to 400 cm^{-1} with a Perkin-Elmer Spectrum 2000 spectrophotometer. Samples of the adsorbent, before and after arsenite adsorption, were ground with special grade KBr in a fixed ratio, in an agate mortar. The same amount of mixed powder was also used to prepare the pellet for FTIR. All measurements were carried out at room temperature.

XPS Measurements

The X-ray photoelectron spectroscopy (XPS) study was conducted by a SPECS LHS-10 UHV system at the Institute of Chemical Engineering and High Temperature Chemical Processes in Patras (Greece).

RESULTS AND DISCUSSION

Surfactant Adsorption onto Akaganeite

In Fig. 1a the adsorption of HDTMA on the surface of akaganeite, is presented over the pH range from 4 to 12. As it is shown the adsorption is a strong function of pH. There is an increase in surface potential with increasing pH. Therefore, surfactant cations are adsorbed at high pH values due to increased interactions between negatively charged akaganeite and positively charged HDTMA. From this figure it is depicted that at pH 11 the better results are presented, so the preparation of surfactant-modified akaganeite (Ak_m) was achieved at this pH value.

The equilibrium isotherm of HDTMA cation onto akaganeite is shown in Fig. 1b. The adsorption was carried out at pH 11. The equilibrium adsorption data were fitted to the Freundlich equation. Figure 1b shows that the adsorption of surfactant onto akaganeite (Ak) follows an adsorption isotherm, which satisfies an equation of the type

$$Q_{eq} = K_F \cdot C_{eq}^{1/n} \qquad (1)$$

where Q_{eq} is the quantity of solute (HDTMA) sorbed per unit weight of solid adsorbent (Ak), C_{eq} is the concentration of solute in the solution at

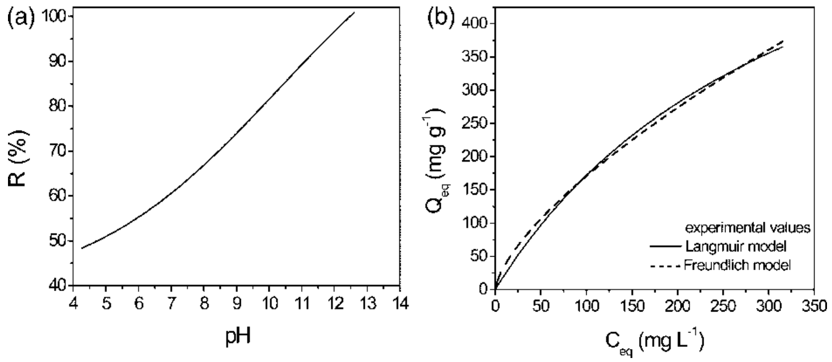

Figure 1. (a) Effect of pH value on the preparation of modified akaganeite; akaganeite dose 0.5 g L^{-1}, surfactant concentration 0.01 M, temperature 25°C, contact time 24 h. (b) Adsorption isotherms of HDTMA on akaganeite; akaganeite dose 0.5 g L^{-1}, pH = 11, temperature 25°C, contact time 24 h.

equilibrium, and K_F and $1/n$ are constants indicating the adsorption capacity and the adsorption intensity respectively. ($1/n < 1$). The values of these constants are listed in Table 2. The Freundlich equation applies very well for solids with heterogeneous surface properties and generally for heterogeneous solid surfaces. Generally, if the Freundlich constant $1/n$ is in the range 2 to 10 (7.376 in our case) it indicates a favorable sorption process.

Moreover, according to Rosen (18) the adsorption of cationic surfactants from solution onto solid surfaces can be described by the Langmuir isotherm, even though the assumptions of Langmuir sorption may not be completely satisfied:

$$Q_{eq} = \frac{Q_{max} K_L C_{eq}}{1 + K_L C_{eq}} \tag{2}$$

where K_L is an energy term which varies as a function of surface coverage strictly due to variations in the heat of adsorption and Q_{max} is the maximum loading capacity. The HDTMA adsorption was well described by the Langmuir isotherm with correlation coefficient (r^2) exceeding 0.99 and the Langmuir adsorption maximum loading capacity was 765 mg g^{-1}. The values of Q_{max} and K_L are presented in Table 2. The data clearly indicate that both the Langmuir and the Freundlich isotherm models give fairly good linear fits to the adsorption according to the resulting R^2 values.

Sorbent Characterization

N_2 adsorption-desorption isotherms of the synthesized Ak_m are shown in Fig. 2. The isotherms are of classical type IV, characteristic of mesoporous materials according to the JUPAC. The sample showed well-defined hysteresis loops with a steep desorption branch and a less steep adsorption branch, belonging to the H2 type, characteristic of mesoporous materials. A narrow pore size distribution was determined by BJH method from the desorption branch of the isotherm, centered at 4.6 nm (Fig. 2 inset). The specific

Table 2. Equilibrium parameters for Ak and Ak_m for various experimental conditions

		Langmuir constants			Freundlich constants		
Material	pH value (−)	R^2 (−)	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2 (−)	K_F (mg g^{-1})	$1/n$ (−)
HDTMA on Ak	11	0.994	765.0	0.003	0.998	0.7	7.376
As(III) on Ak	4	0.939	75.9	0.217	0.965	21.6	2.837
As(III) on Ak	7	0.994	135.2	0.063	0.989	12.7	1.686
As(III) on Ak_m	7	0.990	328.3	0.042	0.986	18.9	1.424
As(III) on Ak_m	4	0.866	169.6	0.104	0.766	33.8	2.510

(BET) surface area of the sample was 131.7 $m^2 g^{-1}$ with a pore volume of 0.116 $cm^3 g^{-1}$. The specific surface area of the pure nanocrystalline akaganeite previously found to be 330 $m^2 g^{-1}$. The decrease of surface area presented by surfactant-modified akaganeite can be attributed to the presence of the cationic surfactant.

SEM micrographs (Fig. 3) revealed that surfactant-modified akaganeite grains had all about similar morphology and an average size between 60 and 120 μm. Akaganeite grains previously found to have a size between 30 and 100 μm. The incensement of size can be attributed to the surfactant binded onto akaganeite.

Arsenites Adsorption onto Surfactant – Modified Akaganeite

Kinetics

The time dependence curve of As(III) removal is shown in Fig. 4a. It was found that the uptake of As(III) increase with the lapse of time. However, the adsorption of As(III) was rapid in the first 15 min after which the rate slowed down as the equilibrium approached. In order to investigate the mechanism of sorption and potential rate controlling step, such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. Over 25 models are reported in the literature (19), all attempting to describe quantitatively the kinetic behavior during the

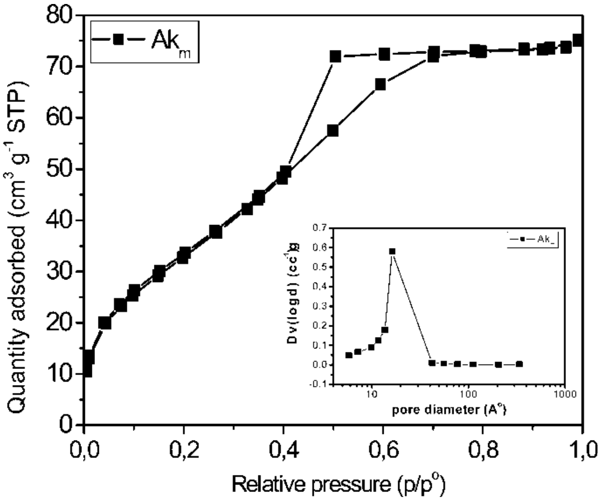

Figure 2. Nitrogen adsorption–desorption isotherm of surfactant-modified akaganeite. The inset displays the desorption (DV)logd graph of surfactant-modified akaganeite.

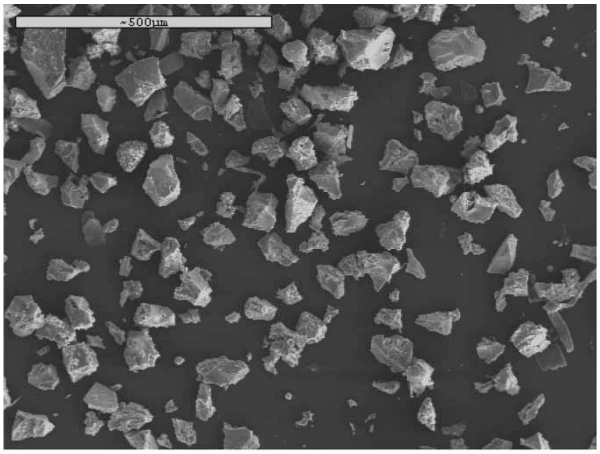

Figure 3. SEM image of surfactant-modified akaganeite.

adsorption process. Each adsorption kinetic model has its own limitation and is derived according to certain initial conditions based on certain experimental and theoretical assumptions. A number of these models assume linear equilibrium isotherms, while fewer models assume the equilibrium isotherms to be nonlinear. Figure 4a also illustrates the comparison of experimental uptake data with theoretical predictions (curves) based on Elovich, Lagergren, and Ritchie kinetic equations. The best fit for the experimental series ($R^2 = 0.999$) of this study was achieved by the application of Ritchie kinetic equation:

$$\frac{1}{q_t} = \frac{1}{k_2 q_{eq} t} + \frac{1}{q_{eq}} \tag{3}$$

where q_{eq} and q_t are the amount of As(III) adsorbed per unit mass of modified-akaganeite at equilibrium and time t, respectively, and k_2 is the rate constant of the second order adsorption. From Eq. (2), a plot of $1/q_t$ versus $1/t$ should give a straight line to confirm the applicability of the second-order kinetic model (Fig. 4b) (20). Besides, for adsorption on the outer surface of adsorbent, there is a possibility of transport of adsorbent ions from the solution to the pores of the adsorbent (5). This possibility was tested in terms of a graphical relationship between the amount of As(III) adsorbed and the square root of time (Fig. 4c). In order to show the existence of intraparticle diffusion in the adsorption process, the amount of As(III) sorbed per unit mass of adsorbent at time t, q_t was plotted as a function of square root of time, $t^{0.5}$. The rate constant for the intraparticle diffusion was obtained using the equation:

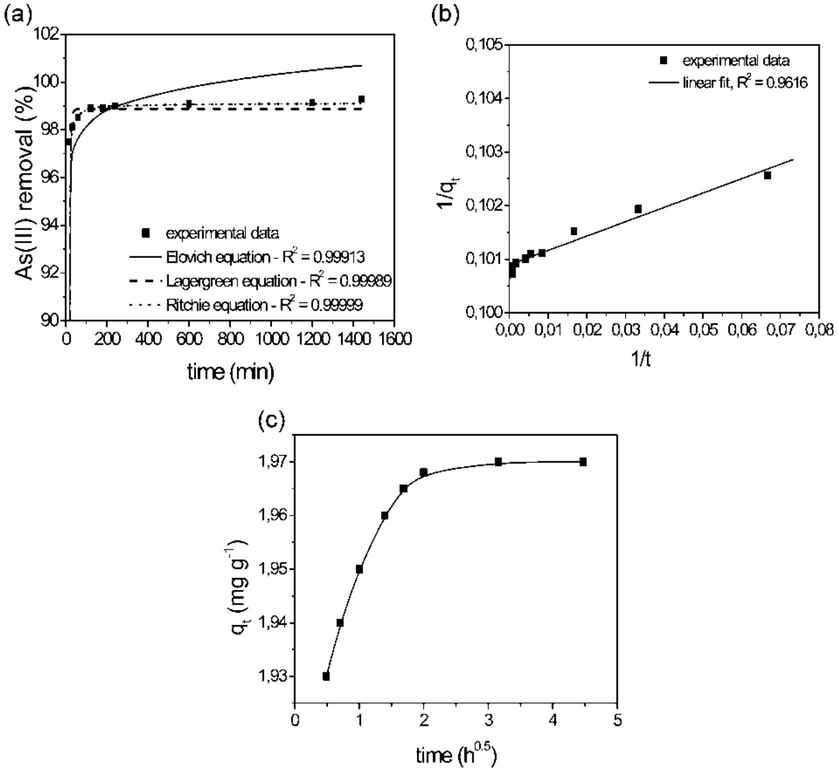

Figure 4. (a) Comparison of experimental uptake data with theoretical predictions (curves) based on the first-order kinetic equations of Elovich and Lagergren, at adsorbent dose 1 g L^{-1} modified-akaganeite, adsorbate concentration 10 mg L^{-1}, pH = 7.0 and temperature 25°C. (b) The second-order plot for As(III) adsorption on the modified-akaganeite; modified-akaganeite dose 1 g L^{-1}, adsorbate concentration 10 mg L^{-1}, pH = 7.0 and temperature 25°C. (c) Intraparticle mass transfer curve for adsorption of As(III) on modified-akaganeite; modified-akaganeite dose 1 g L^{-1}, adsorbate concentration 10 mg L^{-1}, pH = 7.0 and temperature 25°C.

$$q = K_p t^{1/2} \tag{4}$$

where K_p is the intraparticle diffusion rate constant. The plot for intraparticle diffusion shows that the initially curved portion reflects film or boundary layer diffusion effect and the subsequent linear portion attribute to the intraparticle diffusion effect. K_p value was obtained from the slope of the linear portion of the curve at each solute concentration, 0.033 mg g^{-1} $h^{-1/2}$ at initial As(III) concentration of 10 mg L^{-1}. This suggests that the adsorption is governed by the diffusion within pores of the adsorbent. The linear portions of the curves do not pass through the origin (Fig. 4c) (5). This indicates that the mechanism of As(III) removal on modified akaganeite is complex and both the surface adsorption as well as the intraparticle diffusion contribute to the rate determining step.

Effect of pH

The removal of arsenites from aqueous solutions by adsorption is highly dependent on pH of the media which affects the surface charge of the solid particles and the degree of ionization and speciation of adsorbate. The effect of pH on As(III) adsorption by modified akaganeite was studied in the pH range between 4 and 12 at the contact time 24 h (Fig. 5). The maximum adsorption of As(III) occurs from pH 6 to 8 and pH 7 was chosen for further studies. Adsorption decreases at both lower and higher pH values. Moreover, as it is evident from Fig. 6, the adsorption of As(III) over the pH range 4.0 – 9.0 is not strongly dependent on pH, which is highly advantageous for practical operation.

Adsorption Isotherm

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. In this study, Freundlich (Eq. (1)) and Langmuir (Eq. (2)) isotherms have been applied. Arsenite adsorption isotherms for pure and surfactant-modified akaganeite were obtained at pH 4 and pH 7 (Fig. 6). For each isotherm the initial As(III) concentrations were varied between 10 and 200 mg L^{-1}, whereas the sorbent concentration was kept constant at 0.5 g L^{-1}. From Fig. 6 it can be concluded that the sorption capacity of

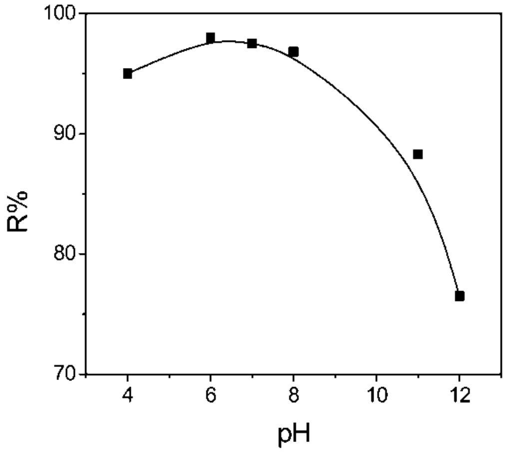

Figure 5. Influence of pH on arsenite removal (conditions: [sorbent] = 0.5 g L^{-1} modified-akaganeite, $[As(III)]_{initial}$ = 10 mg L^{-1}, contact time 24 h, temperature = 25°C).

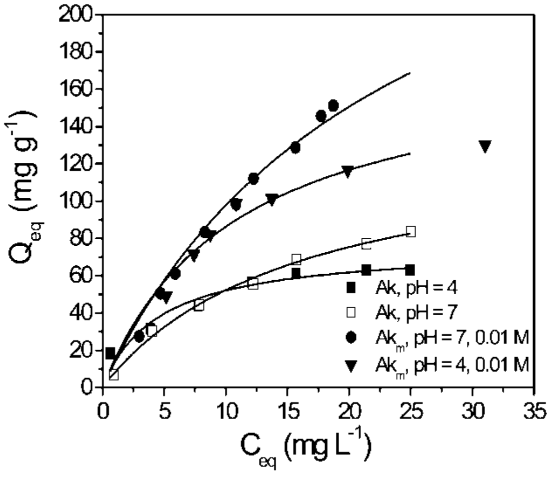

Figure 6. Sorption isotherms of arsenites for Ak and Ak_m for various experimental conditions; modified-akaganeite dose 0.5 g L^{-1}, temperature 25°C, contact time 24 h.

modified akaganeite was always higher than this of pure material, the better results were achieved at pH 7.

Each data series fitted employing non-linear regression analysis. The Langmuir and Freundlich adsorption constants evaluated from the isotherms at certain experimental conditions and their correlation coefficients are presented in Table 2. According to these coefficients, both models could adequately predict experimental data. This observation implies that monolayer sorption as well as heterogenous surface conditions may co-exist under the applied experimental conditions (21).

Regarding the Langmuir model the sorption capacity Q_{max} was found to decrease from 135.2 to 75.9 mg As(III) g^{-1} for akaganeite and from 328.3 to 169.6 mg As(III) g^{-1} for modified akaganeite, as the pH was decreased from 7 to 4. So, it is clear that the surfactant successfully modifies the surface causing an increased adsorption. It is useful to clarify that Q_{max} is the maximum value of Q_{eq} that is important to identify which sorbent and experimental conditions show the highest uptake capacity, and as such it is useful for scale-up considerations. The Langmuir constants can be used for calculating the dimensionless separation factor (r), which is defined as:

$$r = \frac{1}{1 + K_L C_o} \tag{5}$$

From the Langmuir constants in Table 2, the factor r can be calculated as 0.87 – 0.045 for surfactant-modified akaganeite, at the initial arsenite concentrations between 10 and 200 mg As(III) L^{-1}. The r values fall between 0 and

1, which is indicative of favorable adsorption of arsenites on pure and surfactant-modified akaganeite.

It is also mentioned that desorption experiments were carried out and showed that neither measurable amount of surfactant nor arsenite ions released to the solution in all pH range.

FTIR Studies Evaluation

FTIR Studies of Akaganeite

The infrared spectra of pure akaganeite (Ak), of surfactant modified akaganeite (Ak_m) and of surfactant modified akaganeite after the adsorption of As(III) ions, are presented in Figs. 7a and 7b. IR spectroscopy has been considered as a kind of direct means for investigating mechanisms of arsenic adsorption on iron oxides (22, 23).

The FTIR spectrum of akaganeite presents a broad absorption band near 3401 cm^{-1} due to the overlapping antisymmetric $\nu3$ and symmetric $\nu1$ (H-O-H) stretching vibrations of H-bonded water. The band at 1073 cm^{-1} corresponds to the bending vibration of hydroxyl group (M-OH) (24). In akaganeite, OH ··· Cl bonds are formed instead of OH ··· O bonds, so, there are two sets of librations, due to hydrogen bonds, i.e. those of OH librational R_{OH} 847 and 820 cm^{-1} and those of 698.4 due to the two OH ··· Cl hydrogen bonds present. In the nanocrystalline sample prepared in the laboratory the bands at 847 and 820 are diminished and mostly disappeared due to the washing of the chlorine ions. The band at 423 cm^{-1} corresponds to the energy translational mode of akaganeite due to the Fe-O stretches.

FTIR Studies of Surfactant Modified Akaganeite

In FTIR spectra of surfactant modified akaganeite (Ak_m), the band due to the OH^- stretching region of H_2O shifts to higher frequency (3412 cm^{-1}). These results are consistent to those in the literature in which it was reported that the position of the ν_2 mode of H_2O decreases and H_2O-stretching band shifts to higher wavenumber upon lowering the H_2O content. This could be explained by the reduction of water content due to its replacement by $HDTMA^+$ ions. The latter reflects that the amount of hydrogen bonded H_2O molecules present in surfactant-modified akaganeite (Ak_m) is less than that in the sample of Ak. This observation could also be attributed to the replacement by $HDTMA^+$ ions. The adsorption bands at 2918.2 and 2849.7 cm^{-1} can be attributed to the anti-symmetric and symmetric CH_2 stretching modes of amine, respectively. The frequencies of the CH_2 stretching absorption bands of amine chains are extremely sensitive to the conformational changes of the chains and only when the chains are highly ordered (all trans

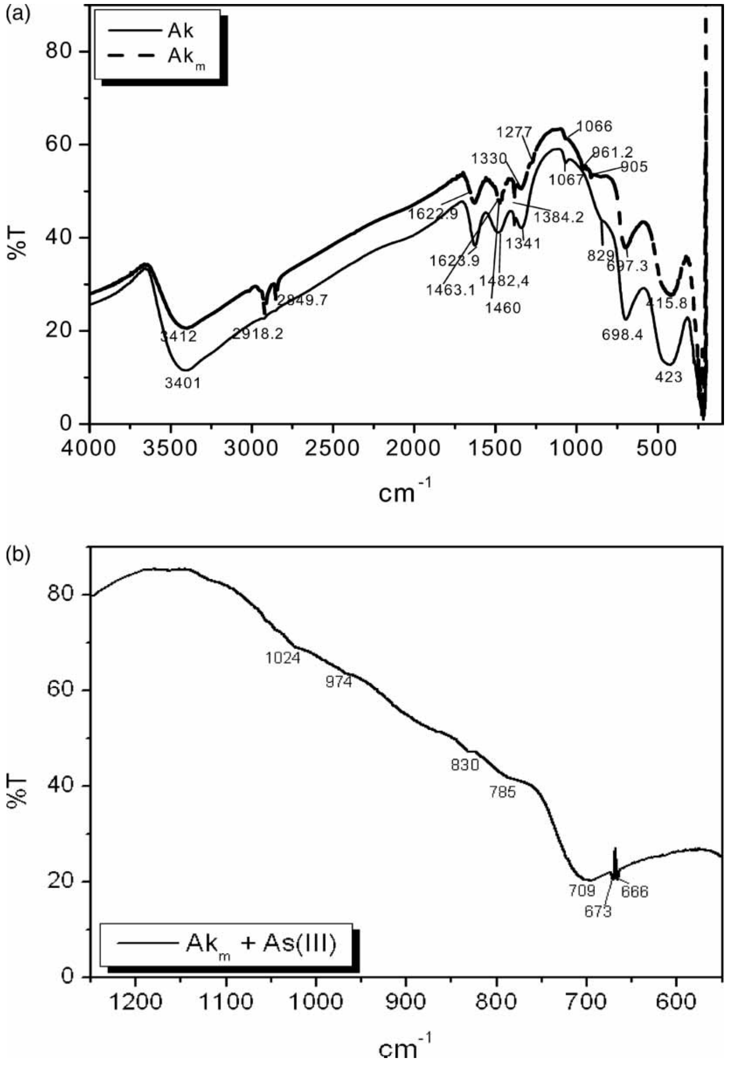

Figure 7. (a) FTIR spectra of Ak and Ak$_m$. (b) FTIR spectra of Ak$_m$ after arsenites sorption.

conformation), the narrow absorption bands appear around 2916 ($v_{as}(CH_2)$) and 2848.9 cm^{-1} ($v_s(CH_2)$) (25).

The infrared absorption bands at 1460 cm^{-1} can be attributed to the methylene scissoring modes. Doublets are observed in this region for the pure crystalline HDTMA (26). The splitting of the CH_2 scissoring bands is due to the intermolecular interaction between the two adjacent hydrocarbon chains and further requires an all-trans conformation for its detection. In the spectrum of surfactant modified akaganeite although exists a band due to the characteristic absorption band of akaganeite the splitting of the CH_2 scissoring band at 1463.1 is obvious. Assuming 35 Å^2 as the surface area per head group of a CTAB ion (27), a monolayer of vertically oriented ions is succeeded at a concentration of 8.8 10^{18} head groups. Since 1.7 10^{22} head groups was the calculated concentration of surfactant bonded to 1 mole of akaganeite (according to carbon elemental analysis), it was concluded that a bilayer was formed with the polar head groups oriented outward, toward the solution. This conclusion is consistent to our FTIR spectrum of hybrid surfactant-akaganeite that presented a splitting of the CH_2 scissoring band at 1463.1, indicative of an all-trans conformation.

The band at 1067, which corresponds to the bending vibration of hydroxyl group (M-OH), was still observed at the sample of surfactant modified akaganeite showing that the surfactant has not possibly reacted with OH functional groups. It is concluded from the above FTIR measurements that HDTMA is sorbed on the surface of akaganeite, replacing sorbed water, and that the surfactant chains are highly ordered (all trans conformation). The absorption band at 961.2 cm^{-1} can be attributed to CN^+ stretch (28).

FTIR Studies of Surfactant Modified Akaganeite after the Arsenite Adsorption

According to the surface complex model theory (STUM) (29) metal hydroxyl groups on the surface of many metal oxides, which can be detected by IR spectroscopy, are the most abundant and reactive adsorption sites for anions. From Fig. 7b where the FTIR spectra of the sample of surfactant modified akaganeite (Ak_m) after As(III) adsorption is presented, it is obvious that the M-OH bending bands disappeared (1067.1 cm^{-1}) indicating that the arsenite ions have substituted M-OH from the surface while the features assigned to H_2O remained unchanged.

In the FTIR spectrum for the sample of surfactant-modified akaganeite after arsenite sorption at pH 7, small bands are observed at 785 cm^{-1} that corresponds to the stretching vibration of the As-O bond, 830 cm^{-1} that corresponds to the stretching vibration of the Fe-O-As groups and 666 cm^{-1} that corresponds to the symmetric stretching vibration of the As-OH groups.

These results are in reasonable agreement with the earlier study of As(III) sorption to Fe and Al oxides by Suarez et al., and Goldberg and Johnston (23) who reported bands at 794 and 631 cm^{-1}. They concluded that the 783 cm^{-1} corresponds to the stretching vibration of the As-O bond resulted from the formation of an inner-sphere complex. They also assigned the 824 cm^{-1} band to the Fe-O-As groups.

From the changes in FTIR spectra it is speculated that arsenite ions reacted rather directly with Fe substituted surface OH^- functional groups of akaganeite than with surfactant molecules. This suggests that there is a specific adsorption between the arsenite anions and the adsorbent, thus the substitution of M-OH groups by As(III) ions plays an important role in the adsorption mechanism.

XPS Evaluation

XPS measurements were obtained for the samples of surfactant modified akaganeite (Ak_m) and of samples of surfactant modified akaganeite after the sorption of As(III) ions. In all the spectra there is an energy shift to higher binding energies of about +14 eV, which occurs due to the low conductivity of the samples. In the manuscript, the real (corrected) binding energy is given. In the y-axis of the figures the counts s^{-1} is given.

XPS Measurements of Surfactant-Modified Akaganeite

In Fig. 8a the wide scan for the sample of surfactant modified akaganeite (Ak_m) is presented. The main elements detected are Fe, O, C, and traces of N and Cl. The presence of C and N can be attributed to the existence of the surfactant. The orientation of the broad oxygen peak O1s, which has its center at a binding energy $BE = 530$ eV, indicates that it is formed from three components. The resultant components were one at $BE = 528.8$ eV corresponding to the oxygen of oxide after surfactant adsorption, the second at $BE = 530.9$ eV corresponding to the hydroxyl oxygen and the third at 533.2 corresponding to sorbed water. The peak of iron was located at a binding energy of 711.7 eV (data not shown).

XPS Measurements of Surfactant-Modified Akaganeite after the Sorption of As(III) Ions

In the wide scan of surfactant modified akaganeite after the sorption of As(III) ions, the elements detected are Fe, O, C, As, N, and Cl (Fig. 8b). In Fig. 8d the oxygen peak O1s is shown, which is broad. The orientation of this peak indicates that it is formed from two components, one at $BE = 530$ eV corresponding to the oxygen of oxide after some adsorption and the other, at $BE = 532$ eV corresponding to sorbed water. It is characteristic that the peak at 530.9 eV corresponding to hydroxyl oxygen does not exist suggesting that all hydroxyl oxygen atoms are occupied after sorption, which is in accordance with the results obtained by FTIR.

In the wide scan XPS spectra before and after As(III) adsorption there is only one peak N1s at 399.1 eV which is attributed to the N atom in the $-NH_2$ and/or the -NH- groups on the surface of the hybrid surfactant-akaganeite. If arsenate ions were binded to nitrogen atoms leading to the formation of $R-NH_2As$ complexes, a lone pair of electrons in the nitrogen atom would be donated to the shared bond between the N and the AsO_4^3, and as a consequence,

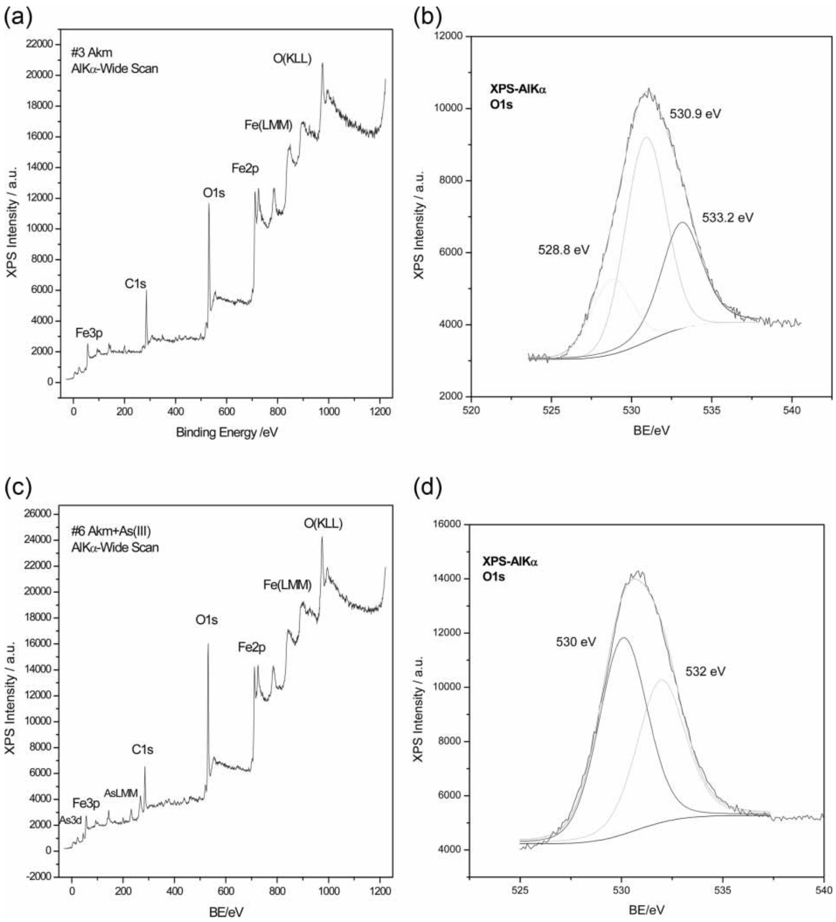

Figure 8. (a) Wide scan of surfactant-modified akaganeite. (b) Wide scan of surfactant modified akaganeite after arsenites adsorption. (c) O(1s) core level photoelectron spectra of anions and cations on surfactant modified akaganeite. (d) O(1s) core level photoelectron spectra of anions and cations on surfactant modified akaganeite after arsenites adsorption.

the electron cloud density of the nitrogen atom could be reduced and resulted in a higher BE peak (30). The lack of this new peak could be evidence that arsenate ions are not bounded to the surfactant but to the iron.

Our XPS results suggest that the adsorption of HDTMA onto akaganeite and As(III) onto surfactant modified akaganeite (Ak_m) affects the charge on the oxygen and the iron atoms indicating that during the adsorption of HDTMA on Ak and As(III) onto the surfactant modified akaganeite (Ak_m) electron transfer occurred between the surfactant and iron and oxygen atoms of akaganeite as well as between arsenite ions and iron and oxygen atoms of surfactant modified akaganeite. The electron transfer indicates that a strong interaction was expected to take place.

MECHANISMS OF ARSENITES SORPTION

A number of mechanisms may play a role in controlling the adsorption of arsenite ions onto surfactant modified akaganeite. Modifying akaganeite particles with a cationic surfactant will influence both specific chemical and electrostatic interactions between arsenite and akaganeite surface.

Although there is no universal agreement on how the sorption of surfactants occurs to the surfaces, it was speculated that at low concentrations, on polar surfaces, cationic surfactants adsorb with their polar moiety in contact with the surface due to interaction between the surfactant head group and the surface according the equation:

$$\equiv FeOH + RN(CH_3)_3^+ + Br^- \longleftrightarrow (\equiv FeO\text{-})[RN^+(CH_3)_3] + H^+ + Br^-$$

As surfactant concentration increased, monomer interactions occur on the surface resulting in a small lag in the sorbed mass. As a result of further increase of the surfactant concentration, aggregates (bilayer, hemimicelle, micelle like structures) form on the surface (31).

The adsorption of arsenite ions on surfactant-modified akaganeite was proved to be higher compared to the arsenite adsorption on pure akaganeite nanocrystals. The better adsorptive results of the surfactant-modified akaganeite can be attributed to the diffuse double layer theory. Decreased double layer thickness due to surfactant existence, allows the neutral at this pH region arsenite ions to approach closer to the available functional groups on the akaganeite surface, where they form inner-sphere complexes via ligand exchange mechanisms to discrete surface metal cations. The fact that arsenite ions are possibly not coordinated to the external polar groups of the surfactant but are coordinated to discrete surface iron cations is supported by our XPS and FTIR results.

CONCLUSIONS

It is concluded from XPS measurements and FTIR spectra that the surfactant is sorbed on the surface of akaganeite. In addition, arsenite ions react with surface OH^- functional groups suggesting that there is a specific adsorption between arsenite ions and the surfactant-modified akaganeite. The maximum adsorption capacity (328.3 mg g^{-1}) was higher enough than that of pure akaganeite (135.2 mg g^{-1}). This can be attributed to the presence of the surfactant. Since the adsorption of arsenite ions on surfactant-modified akaganeite was higher compared to the arsenite adsorption on pure akaganeite nanocrystals, it is concluded that the adsorption of the cationic surfactant HDTMA onto akaganeite led to a new effective adsorbent for removing arsenite ions.

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