

Removal of As (III) from Aqueous Solutions Using Montmorillonite

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ABSTRACT

Arsenic (III) adsorption has been studied as a function of concentration of arsenic (III) in the solution, pH of the solution, contact time during the batch extraction process using montmorillonite (MMT) and surfactant modified MMT (CPC-MMT and CTAB-MMT) from aqueous solution. It has been observed that up to 90% of arsenic (III) can be extracted from a solution containing 100 ppm of As (III) at pH 8.0, within a contact time of 10 minutes. The lowest level of As (III) that could be extracted was found to be 0.4 ppm.

Keywords: *Arsenic (III), MMT, Surfactant Modified MMT, Adsorption Isotherm*

1. Introduction

Arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel and zinc, etc. are the metals of major environmental concern in the present day world. Arsenic has been classified as one of the most toxic and carcinogenic metal and has therefore been recorded by the World Health Organization as a first priority issue [1].

Arsenic is ubiquitous and ranks 20th in natural abundance, comprising about 0.00005% of the earth's crust. Most environmental problems are due to the mobilization of arsenic under natural conditions (natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities).

Arsenic is known to exist in various oxidation states as arsenious acids, arsenic acids, arsenites, arsenates, methylarsenic acid, dimethylarsinic acid, etc., in water. Two forms that are commonly found in natural water are arsenite (AsO_3^{3-}), As (III) and arsenate (AsO_4^{3-}), As (V). Arsenic (V) dominates in oxic water, while arsenic (III) is more likely to occur in anoxic water [2]. Of both the forms As (III) is known to be more toxic than As (V) and is predominant in ground waters [3].

The occurrence of arsenic in natural water is a worldwide problem. Arsenic pollution has been reported in the Argentina, Bangladesh, Canada, China, India, Japan, Mexico, New Zealand, Taiwan and USA. Fifty districts of Bangladesh and nine in West Bengal (India) have been reported to have the concentration of arsenic above the World Health Organization's arsenic guideline value of

$10 \text{ mg}\cdot\text{L}^{-1}$ [4,5] in the drinking water.

Prolonged consumption of water containing arsenic is known to produce long term health effects, including dermal changes and respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic, and carcinogenic effects [6]. Long term exposure to arsenic via drinking water causes skin, lung, bladder, and kidney cancer, skin thickening (hyperkeratosis) neurological disorders, muscular weakness, loss of appetite, and nausea.

Various methods that have been reported for the removal of arsenic from aqueous solutions include coagulation and flocculation, precipitation, adsorption and ion exchange, membrane filtration, ozone oxidation, bioremediation and electrochemical treatments. Most of these methods involve production of high arsenic contaminated sludge [7], high maintenance cost and require relatively expensive mineral adsorbents which offset performance and efficiency advantages [8].

Of all the methods adsorption has been most extensively used as reported by Abhijit and Sunando [9]. As cited by Deliyanni, Peleka and Matis [10] selective adsorption utilizing biological materials, mineral oxides, clay minerals, zeolites, fly ash, activated carbons, or polymer resins, has generated increasing interest. In the present work, montmorillonite (a member of the smectite group of the clay mineral) has been selected as the host material for the removal of arsenic from aqueous solutions. MMT is known for its low cost, high surface area, high chemical stability, high sorption properties and rich intercalation chemistry. To the best of our knowledge, the best result

achieved so far accounts for the detection of 10 ppm of arsenic using montmorillonite [1].

2. Experimental

2.1. Materials and Methods

Montmorillonite (MMT-KSF) was obtained from Sigma Aldrich (USA). Cetylpyridinium chloride (CPC) and cetyl trimethylammonium bromide (CTAB) were obtained from Merck (Germany) and British Drug House respectively. Arsenious oxide and potassium antimonyl tartarate were obtained from British Drug House (England), Sodium hydroxide; hydrochloric acid and potassium iodate were obtained from Qualingens (India). Leuco crystal violet (LCV) was obtained from Sigma Aldrich Pvt. Ltd. (Germany). The AR grade chemicals/reagents and double distilled water was used throughout the experiment.

2.2. Synthesis of Organoclay

Surfactant modified clay (CPC-MMT and CTAB-MMT) were synthesized by the modification of the reported procedures by Khalaf, Bouras and Perrichon [11].

In order to facilitate intercalation, 5.0 g of dried (80°C) MMT was dispersed in 250 ml of double distilled water and was kept under constant stirring for a period of 24 hours. To this 1% aqueous surfactant (CPC and CTAB) solution was gradually added with constant stirring over a period of 3 hours at NTP. The clay suspension was separated by centrifugation and washed with double distilled water for the complete removal of unreacted surfactant. The residue thus obtained were dried at 80°C and was labelled as CPC-MMT and CTAB-MMT.

2.3. Characterization

X-ray diffractograms were recorded on X-ray Diffractometer (Philips PW3710) using CuK α radiations. The specific surface areas were measured by adsorption of nitrogen according to the BET method. UV-VIS studies were performed on Systronics UV/VIS spectrophotometer. pH was monitored using a pH meter (Eutech instruments, pH 510).

2.4. Experimental

2.4.1. Preparation of As (III) Solution

As (III) stock solution (1000 mg/L) was prepared by dissolving 1.320 g of arsenious oxide (As₂O₃) in 25 mL of 1 M NaOH in double distilled water. The solution was then diluted to about 100 mL with double distilled water and two drops of 0.2% phenolphthalein was added to this solution followed by neutralization of the solution using 1 M HCl. The volume of the solution was made up to 1 L in a volumetric standard flask.

2.4.2. Spectrophotometric Determination of As (III)

The concentration of arsenic (III) was determined spec-

trophotometrically procedure using LCV as reported [12].

The reagent blank gave negligible absorbance at the above wavelength. A rectilinear calibration graph was obtained by measuring the absorbance of the solution at 592 nm over a known concentration range and concentration of As (III) in the experimental solution was calculated from the calibration curve.

2.4.3. Behavior of As (III) Adsorption on Clay and Modified Clay

The adsorption experiments were carried out using MMT and CPC-MMT and CTAB-MMT as an adsorbent. The batch experiments were carried out with 0.1 g of the adsorbent and 50 mL of (100 ppm) As (III) solution, as a function of pH, contact time and concentration. The concentration of arsenic in the supernatant was estimated spectrophotometrically. The percentage of the metal adsorbed onto the adsorbent was calculated using the relation:

$$\% \text{As (III) adsorbed} = \left[\frac{C_i - C_e}{C_i} \right] * 100$$

Amount of metal adsorbed (q_e) was calculated from the relationship

$$q_e = \frac{(C_i - C_e) * V}{m}$$

where C_i was the initial As (III) concentration (mg/L), C_e was the final concentration of As (III) in the solution after equilibrium was attained (mg/L), V was the volume of the As (III) solution (L) and m was the mass of the adsorbent (g) used.

3. Results and Discussions

3.1. XRD Analysis

The X-ray diffraction pattern of the clay and the organo clay is shown in **Figure 1**. The decrease in the 2 theta value with respect to MMT was observed in case of CPC-MMT and CTAB-MMT. The interlayer (d_{001}) spacing of MMT, CPC-MMT and CTAB-MMT is 12 Å, 19.5 Å and

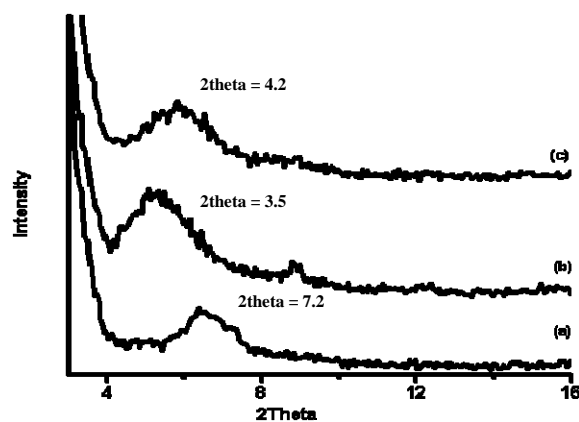


Figure 1. XRD pattern of (a) MMT; (b) CTAB-MMT; (c) CPC-MMT.

17.6 Å respectively. The increase in d spacing of CPC-MMT and CTAB-MMT with respect to MMT is 7.5 Å and 5.6 Å respectively. This increase in the basal spacing is attributed to intercalation of the surfactants into the interlayer region of the host clay, MMT.

Generally, there are two most important mechanisms of the cationic surfactant adsorption on solids: 1) ion exchange and 2) hydrophobic interactions [13]. Thus, there are two well-distinguished phases of CPC and CTAB adsorption on MMT, first can be ascribed to incomplete monolayer formation. After the monolayer onset of the surfactant is completed bilayers are formed. The CPC adsorption arrangements are illustrated in **Figure (2)**. **Figures 2(a)-(c)** illustrates the CPC adsorption on external MMT surface and **Figures 2(d) and (e)** simply manifest the intercalation, as also observed by the X-ray diffraction analysis. Similar adsorption mechanism is also followed by the CTAB on MMT surface. The alkyl ammonium bilayer structure (**Figure 2(c)**) is positively charged, which makes possible the adsorption of arsenite ions [14].

3.2. Surface Area Analysis

The Nitrogen BET adsorption method indicates that the

surface area of MMT, CPC-MMT and CTAB-MMT are 28,700 cm²/g, 82,000 cm²/g and 98,200 cm²/g, respectively. This increase in surface area of CPC-MMT and CTAB-MMT clays with respect to MMT is 53,000 cm²/g and 69,500 cm²/g respectively. The increase in surface area is due to an increase in the interlayer spacing.

3.3. Effect of pH on As (III) Adsorption

The effect of pH on the amount of arsenic uptake by clay and organo clay (CPC-MMT and CTAB-MMT) was studied in the pH range of 1 - 12, using 0.1 gram of the adsorbent and 100 ppm at As (III) solution with contact time of 60 minutes (**Figure 3**).

The percentage of As (III) adsorbed increased from 47.5% (23.5 mg/g) to 70.25% (35.15 mg/g) in the pH range of 1 - 8, and then decreased to 56.88% (28.45 mg/g) at pH 12 in MMT. A similar behaviour was observed for CPC-MMT and CTAB-MMT where the percentage of As (III) adsorbed in the pH range of 1 - 8, increased from 89% (44.5 mg/g) to 94.4% (47.20 mg/g) in case of CPC-MMT and 88% (44 mg/g) to 92.6% (46.32 mg/g) in case of CTAB-MMT, followed by a decrease in As (III) adsorption up to pH 12 in both the cases.

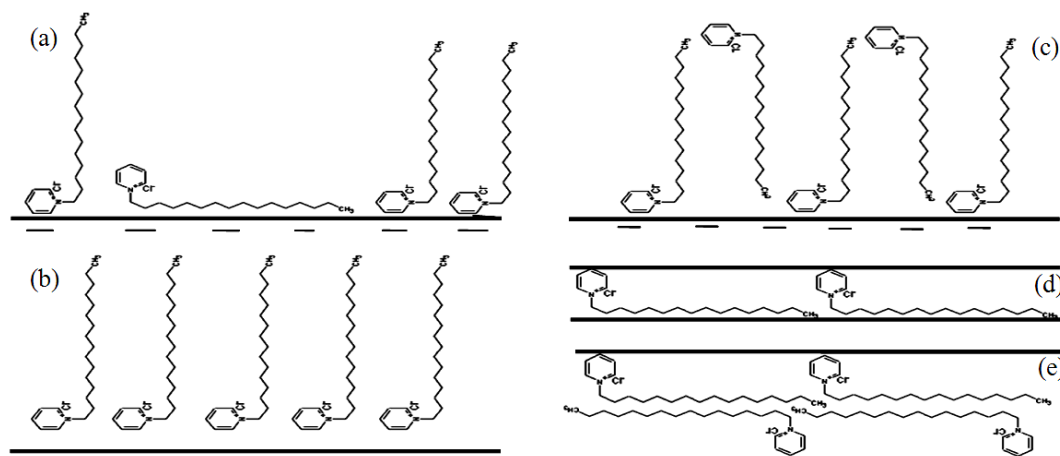


Figure 2. Arrangement of CPC adsorbed onto MMT (a) incomplete monolayer (b) monolayer (c) bilayer (d) monolayer intercalated (e) bilayer intercalated.

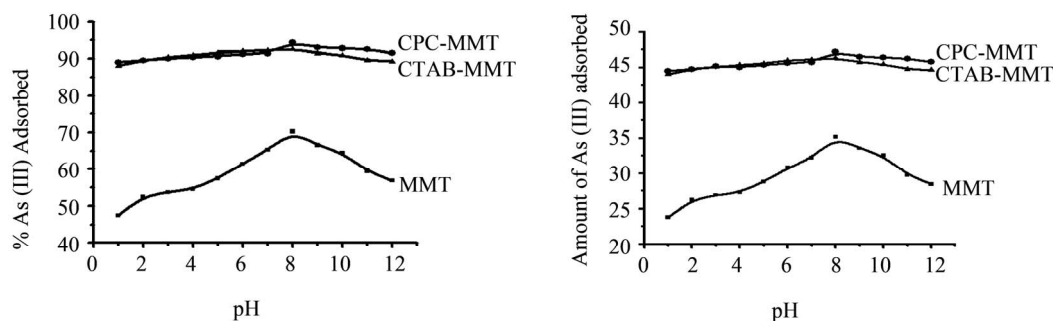


Figure 3. Adsorption as a function of pH. Conc. of As (III) solution = 100 ppm, mass of adsorbent = 0.1 gm, pH 1 - 12, contact time = 60 minutes.

These results show that in a highly acidic medium, where the adsorbent surfaces are highly protonated and As (III) mainly exists in the form of neutral H_3AsO_3 species, adsorption of As (III) is not favorable. This is due to the weak interaction that occurs between the adsorbent and H_3AsO_3 . Therefore, the only driving force between H_3AsO_3 and the adsorbent is the physical adsorption, thereby resulting in less adsorption. At near neutral pH values (7 - 9), slow dissociation of H_3AsO_3 producing arsenite ions begins and it reaches a maximum at pH 8.0. These partially neutral and partially negatively charged arsenite ions are attracted to the positively charged surface of the adsorbent thereby resulting in high As (III) uptake by the adsorbent in this pH range. At pH 10 and above, the adsorbent surfaces become negatively charged. Hence, the interaction between the adsorbent and arsenite ions decreases leading to low As (III) uptake by the adsorbent.

The As (III) uptake by CPC-MMT and CTAB-MMT was observed to be higher than MMT. This is because, the surface of the organo clay composites is highly positively charged than MMT, as indicated by the zeta potential values (MMT = 12.9 mV, CPC-MMT = 17.2 mV, CTAB-MMT = 22.6 mV). This in turn facilitates stronger interaction between the positively charged clay surface and the existing species of arsenite ions in the solution, thereby leading to a higher As (III) uptake.

Therefore pH (8.0) was fixed as the pH at which maximum As (III) adsorption on the clay and organoclay had occurred.

3.4. Effect of Contact Time on As (III) Adsorption

The effect of contact time on the amount of arsenic uptake

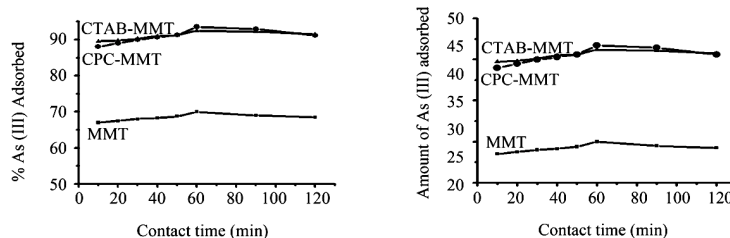


Figure 4. Adsorption as a function of contact time. Conc. of As (III) solution = 100 ppm, mass of adsorbent = 0.1 gm, pH 8.0, contact time = 10 – 120 minutes.

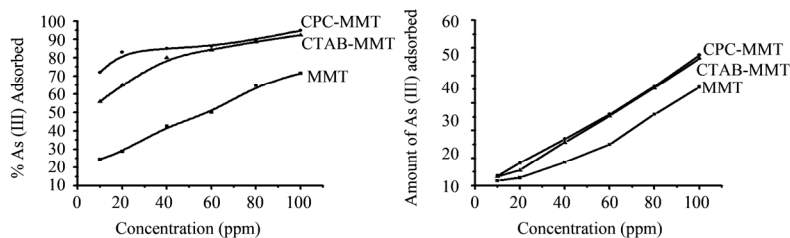


Figure 5. Adsorption as a function of As (III) concentration. Conc. of As (III) solution = 10 ppm – 100 ppm, mass of adsorbent = 0.1 gm, pH 8.0, contact time = 60 minutes.

by clay (MMT) and organoclay (CPC-MMT and CTAB-MMT) was studied as a function of time in the range of 10 - 120 minutes, using 0.1 gram of the adsorbent, at pH 8.0 with initial concentration of As (III) at 100 ppm (Figure 4).

The percentage of As (III) adsorbed increased from 67% (33.5 mg/g) at 10 minutes to 70% (35 mg/g) at 60 minutes on MMT and decreases thereafter. A similar behaviour was observed for CPC-MMT and CTAB-MMT where the percentage of As (III) adsorbed increased from 88% (44 mg/g) at 10 minutes to 94% (47.44 mg/g) at 60 minutes in the former and 89% (44.75 mg/g) at 10 minutes to 92.5% (46.25 mg/g) at 60 minutes in the latter.

The adsorption of As (III) on the clay and organoclay occurred very quickly in the initial phase of the experiment. This could be due to the availability of a large number of adsorption sites on the clay surface. Maximum adsorption of the As (III) was observed in the time duration of 60 minutes and beyond this no further increase in adsorption was observed. Therefore, 60 minutes was fixed as the time at which maximum As (III) adsorption on the clay and modified clay had occurred.

3.5. Effect of Initial Concentration on As (III) Adsorption

The effect of initial concentration on the amount of arsenic uptake by clay (MMT) and organoclay (CPC-MMT and CTAB-MMT) was studied using 0.1 gram of the adsorbent and by varying the concentration of As (III) solution from 0.2 - 100 ppm and maintaining pH 8.0 and a contact time of 60 minutes. (Figure 5)

An increase in the percentage of As (III) adsorbed was observed from 24% to 71% in MMT on varying the metal

concentration from 10 - 100 ppm. The percentage of As (III) adsorbed increased from 21% to 94.4% in CPC-MMT and 21% to 92.3% in CTAB-MMT on varying the metal concentration from 0.2 - 100 ppm. The amount of As (III) adsorbed increased from 0.066 mg/g to 47.43 mg/g in case of CPC-MMT and 0.065 mg/g to 46.25 mg/g in CTAB-MMT composites. Whereas, in case of MMT the amount of As (III) adsorbed increases from 1.85 mg/g to 35.75 mg/g on varying concentration from 10 - 100 ppm.

The increase in As (III) adsorption on all the three adsorbents in the given concentration range indicates a heterogeneous system where adsorption is not restricted to monolayer formation. The percentage of As (III) adsorbed in case of surfactant organoclay was observed to be higher than that of the host clay. This can be explained on the basis of zeta potential studies. The zeta potential values of CPC-MMT and CTAB-MMT were found to be +22.6 mV and +17.2 mV respectively. The zeta potential values suggest that the adsorption is therefore due to the electrostatic attraction between the positively charged adsorbent (organoclay) and the negatively charged adsorbate (arsenite). In case of MMT, the zeta potential value is +12.9 mV and is therefore less positively charged as compared to CPC-MMT and CTAB-MMT. Therefore, the interaction between the adsorbent and arsenite ions is less, thereby leading to a low uptake.

3.6. Adsorption Isotherms

The Freundlich isotherm is one of the widely used mathematical descriptions and it usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. It describes a heterogeneous system and reversible adsorption process that is not restricted to the monolayer formation. This model predicts that adsorption of arsenic on the organoclay increases with increase in arsenic concentration in the solution.

The Freundlich equation is as follows: $q_e = K_f C_e^{1/n}$

The linear form of the above equation is given as:

$$\log q_e = \log K_f + 1/n \log C_e$$

where K_f is the Freundlich constant (mg/g) and $1/n$ is the heterogeneity factor. A plot of $\log q_e$ and $\log C_e$ gives a straight line and the values of K_f and n can be calculated from the intercept and slope of the plots respectively (**Figure 6**).

The linear equation obtained for CPC-MMT and CTAB-MMT were $y = 1.25689x + 1.67829$ ($R^2 = 0.9992$) and $y = 1.48656x + 1.66462$ ($R^2 = 0.9951$) respectively. The K_f values obtained from the equation were 47.74 mg/g and 46.19 mg/g respectively.

The value of n obtained from the above equation was 0.7956 and 0.6727 respectively. These values indicate a favorable adsorption process.

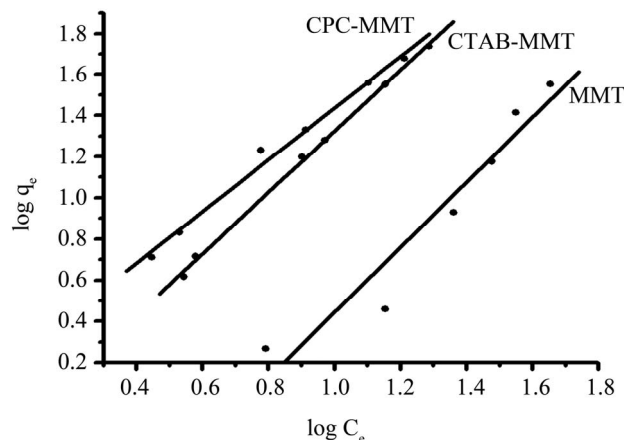


Figure 6. Freundlich plot for the adsorption of As (III) on MMT, CPC-MMT and CTAB-MMT.

4. Conclusions

The results obtained indicate that the maximum As (III) uptake on MMT, CPC-MMT and CTAB-MMT was found to be 35.75 mg/g (71%), 47.43 mg/g (95%) and 46.15 mg/g (92%) respectively. The adsorption capacity of CPC-MMT and CTAB-MMT was observed to be higher than that of MMT. This is because of the higher positively charged organoclay surface which facilitates stronger interaction between the adsorbent and the adsorbate, thereby leading to a higher As (III) uptake. The lowest level of detection of As (III) from aqueous solutions was found to be 0.4 ppm using both the clay composites (CPC-MMT and CTAB-MMT). This process was found to be highly effective over a wide range of concentration and pH. Thus, these composites can be successfully employed for the removal of As (III) from aqueous solutions.

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