Synthesis, characterization and trivalent arsenic sorption potential of Ce-Al nanostructured mixed oxide

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Abstract. Arsenic contamination in the ground water has serious health consequences in many parts of the world. The surface sorption method for arsenic mitigation has been widely investigated due to its simple method, inexpensive operation, highly efficient and low content of by-products. In the present study, nanostructured hydrated cerium aluminum oxide (NHCAO) was synthesized and characterized and its arsenic (III) sorption behavior from the aqueous solution was studied. The material was characterized in SEM, FE-SEM, TEM, AFM, XRD, and FT-IR. Batch method was used for the kinetics of As (III) sorption on nanoparticles at 303 (± 1.6) K and at pH 7.0 (± 0.2). The experiments on isotherm subject were performed individually at 288K, 303K, 318K temperatures at pH 7.0 (± 0.2) using the batch sorption method. In the kinetics study of arsenic (III) sorption, the sorption percentage was observed to remain nearly unchanged up to pH 9.0, thereafter only slight reduction in sorption percentage. The equilibrium sorption results were tested using the models of Langmuir and the Freundlich isotherm. The Langmuir model is the most fitted model for the sorption reaction. NHCAO was highly efficient in As(III) removal out of the water in the extensive range of pH and could be used for arsenic removal from contaminated water.

1. Introduction

Arsenic contamination in ground water has been denounced in Bangladesh, India, China, Taiwan, Vietnam, USA, Argentina, Chile, and Mexico [1]. In many of these countries, the concentration has surpassed the allowed value of 10 ppb. The Bengal basin is considered to have the highest contamination of arsenic makes it the most affected geological place in the world [2]. Arsenic contamination of ground water and ingestion of contaminated water has long term consequences like social disorders, health hazards and socioeconomic dissolution. Long-term arsenic exposure can lead to cancer and many non-cancerous diseases [1]. In 1993, the World Health Organization (WHO) has amended the directive for the quality of drinking water in which the permissible limit of arsenic was lowered from 50 to 10 ppb so that to minimize the hazardous impact of arsenic on health [3].

Various technologies have been used for arsenic removal, and the effectiveness of these techniques is dependent on the physical and chemical characteristics of the arsenic content in water. Commonly used techniques are (i) oxidation followed by precipitation, (ii) coagulation/electro-coagulation/co-precipitation, (iii) adsorption onto sorptive media, (iv) ion-exchange, and (v) membrane technique, (vi) foam floatation, (vii) solvent extraction, and (viii) bioremediation.

Nanomaterials are quickly came forth as strong candidates for water treatment in the countries with conventional technologies. Two interesting properties make nanoparticles highly usable as sorbents [4]. The nanoparticles have much larger surface areas on a mass basic in contrast to macro particles. They also can be extended using certain reactor groups to improve their chemical affinity against the target
compounds. The researchers are exploiting these properties to promote exceptionally selective and effective sorbents to remove the organic and inorganic pollutants out of the contaminated water. Among the available methods, adsorption is highly useful because of its easy treatment, highly efficient, and can be applied to develop a filter for household purpose. The mixed oxides nano-agglomerates, namely iron–cerium, iron–manganese, iron–zirconium, iron–titanium, iron–chromium, cerium–manganese etc. were prepared, characterized and effectively used to remove the pollutant (i.e. arsenic, fluoride etc.) from aqueous solutions [5-8].

An attempt has been made to synthesize a mixed oxide nanoparticles for observing its capacity in arsenic adsorption. As many previous works have revealed immense potential in nanoparticles in pollutant adsorption, effort was given to develop a material which will be cheap, and at the same time will be very much efficient in arsenic adsorption, so that the material can be easily used for contaminated water purification for household purpose and in large scales as well. This manuscript reports herein the synthesis and characterization of Nanostructured Hydrous Cerium Aluminium Oxide (NHCAO) with arsenic (III) sorption properties from the aqueous solution.

2. Materials and methods

2.1. Synthesis of Ce(IV)-Al(III) binary oxide
Ammonium ceric nitrate and aluminum chloride solutions were mixed in mole ratio of 1:1. The mixed solution was heated at 80°C and 0.1M Na$_2$CO$_3$ solution was added to the mixture drop wise under vigorous stirring condition. With the addition of Na$_2$CO$_3$, pH of the solution mixture gradually increased. The final pH of the solution was maintained at 9.0. A yellowish precipitate was obtained which was then filtered, washed thoroughly with distilled water. The solid mass was then dried at 90°C. The Nanostructured Hydrous Cerium Aluminium Oxide (NHCAO) thus resulted was then meshed and applied for arsenic sorption study.

2.2. Arsenic solutions
Stock standard solution of As(III) (1000 mgL$^{-1}$) was made by dissolving 0.1320 gm. As$_2$O$_3$ (99.9% Aldrich, USA) in 10 mL 4% (w/v) NaOH, adjusted to acid condition with 2.0 mL concentrated HCl, and diluted with arsenic free de-ionized water to 100 mL. The working solutions of required As(III) concentrations were prepared by diluting the stock with 0.2% (v/v) HCl. The stock solution was freshly made every other three days and frozen to avoid oxidation.

2.3. Analytical methods
The arsenic in samples was determined by hydride generation atomic absorption spectrophotometer (Perkin Elmer-3100) and UV-VIS spectrophotometer (Systronics UV-VIS spectrophotometer 117) using the methods as described by the standard methods [9]. The X-ray diffraction (XRD) patterns of NHCAO were determined by power diffractometer (Philips Analytical PW-1710) utilizing Cu Kα radiation source. The voltage and applied potential current were 40 kV and 30 mA, respectively. The Atomic Force Microscopic (AFM) images for surface topography of the samples were carried out in non-contact mode using multimode scanning probe microscope (Agilent AFM 5500 series, USA) equipped with multipurpose small scanner using low coherence laser (1 mW power, 670 nm wavelength, coherence length (< 50 µm), scan range: XY: 0–10 µm; Z: 0–2 µm, noise level: XY < 0.1 nm RMS, Z < 0.02 nm RMS). The mixed oxide’s Fourier Transform Infrared (FTIR) spectra and the associated pure oxides were individually noted by a Perkin Elmer (U.S.) system 2000 spectrophotometer in 2 cm$^{-1}$ resolution. Scanning electron microscopic (SEM) images with EDS (Tescan Vega, U.K.; model LSU+) spectra were recorded spraying the sample on a carbon tape. Transmission electron micrograph (TEM) image was recorded on a H800 transmission electron micrograph (Hitachi, Japan) operating at 200 kV.

2.4. Batch experiments
Batch method was applied for the As(III) sorption kinetics on NHCAO at 303 (±1.6)K and at pH 7.0 (± 0.2). In this experiment, 500.0 mL of As(III) solution [concentrations (mgL$^{-1}$); 5.0 and 10.0] taking into
one liter glass vessel, was positioned in a thermostatic bath to achieve the desired temperature. 1 g NHCAO was added to that thermostatic solution and the reaction mixture was stirred (280 ± 5 rpm) using a speed adjustable agitator. A pH-meter electrode was fitted for frequent on line pH checking of the reaction mixture. Any change of pH noted was adjusted by the addition the small amount of 0.1 (M) NaOH or 0.1(M) HCl, as necessary. A certain volume of the reaction mixture, 2.0 mL at initial successive three steps and 5.0 mL in the later stages, was sampled time to time. The sample solutions were filtered by 0.45 µm-membrane filter and, the filtrates were tested for arsenic content.

The isotherm experiments were performed individually at temperatures 288K, 303K, 318K at pH 7.0 (± 0.2) by batch sorption method. Here, the As(III)-solutions of concentration (mgL⁻¹) ranged from 5.0 to 350.0 were used. The sorbent dose used was 2.0 g per L of solute solution. The agitation (speed: 280 ± 5 rpm) time applied was 2.5 h. The pH solution was adjusted twice throughout the experimental process (at 1.0 h and 2 h of agitation from zero time) with the addition of 0.1 M HCl and/or 0.1 M NaOH as necessary. Residual arsenic was analyzed in the filtered sample [9].

3. Results and discussion

3.1. XRD analysis

Figure 1 shows the NHCAO’s XRD pattern. Presence of sharp peaks indicates the crystalline nature of the binary oxide. Peaks at 2θ values 28.6, 47.6, 56.4 and 69.5 correspond to the cubic antifluorite ceria phase. However peak characteristics of alumina phases are absent in the XRD pattern, indicating complete incorporation of Al³⁺ ions within the unit cells of ceria.

3.2. AFM analysis

Figure 2 shows the AFM image (surface topography) of NHCAO. The image shows small differences in contrast indicating presence of smooth surface. The difference between peak height and average baseline is 8.5 nm indicates the height of the particle.

3.3. SEM analysis

Figure 3a and 3b show SEM images of NHCAO in two different magnifications. From both the images it is clear that there is no particular surface morphology present in the material. The EDAX spectra indicate presence of both Ce and Al on the material surface (figure 4).

![Figure 1. XRD pattern of NHCAO.](image_url)
**Figure 2.** AFM analysis of NHCAO.

**Figure 3.** SEM analysis of NHCAO.

**Figure 4.** The EDAX spectra of cerium-aluminium binary oxide.
3.4. TEM analysis
Figure 5a and 5b show TEM images of NHCAO in two different magnifications. The black spots indicate presence of agglomerated particles. The particle size ranged between 8-10nm, which indicates that the synthesized mixed oxide is nanostructured in nature.

3.5. FT-IR analysis
Figure 6 shows FTIR spectra of all the three samples indicated. The FTIR spectra of cerium oxide contain a sharp peak at 1145 cm$^{-1}$, indicating the stretching vibration of Ce-O bond. The FTIR spectra of pure aluminum oxide contain sharp peaks at ~ 1415 cm$^{-1}$ and 3150 cm$^{-1}$ which represent the –OH stretching and bending mode of vibration of surface hydroxyl groups. The peak 660 cm$^{-1}$ might be associated to the stretching vibration of Al-O bond. The FTIR spectrum of Ce-Al binary oxide shows peaks at 1390 and 3450 cm$^{-1}$ which are due to the availability of surface –OH groups. The peak at 1065
cm\(^{-1}\) indicates presence of Ce-O bonds. The value of this wave number and also the peak intensity is somewhat lower compared to the wave number of pure cerium oxide (1145 cm\(^{-1}\)) indicating weakening of Ce-O bond due to the formation of Ce-O-Al bond.

3.6. Effect of pH on As(III) sorption

Figure 7 shows the variation of As (III) sorption percentage at initial pH solution. It was found from the plot that the sorption percentage stayed nearly unchanged up to pH = 9.0. Then, a slight reduction in sorption percentage was noted. The As(III) species contained in the solution as As(OH)\(_3\) up to pH = 9.0, because the pK\(_{a1}\) value of As(OH)\(_3\) is 9.2. As a result of the fact a small change in the sorption capacity was observed upto pH = 9.0 although the surface charge of the oxide gradually varied with the variation of the solution pH. Above pH 9.0 As(OH)\(_3\) dissociated to produce As(OH)\(_2\)O\(^-\) and the surface of the oxide also became predominantly negatively charged. As a result columbic repulsion was produce between the solute and sorbent which decreased down the sorption perntage.

3.7. Kinetics of arsenic (III) sorption

Figure 8 shows the variation of As(III) sorption by the increase contact time at T= 303 K and pH\(_i\)=7.0. The plot showed that a plateau was reached after the contact time of ~ 50 min., which means that the equilibrium was obtained in the sorption reaction within 50 min. of contact time. The obtained were analyzed by two well known kinetic equations the pseudo first order (1) and the pseudo second order model equations (2) as follows

\[
q_t = q_e \left[1 - \exp(-k_1t)\right] \quad (1)
\]

\[
q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \quad (2)
\]

where \(q_e\) and \(q_t\) are the amount (mg . g\(^{-1}\)) of arsenic(III) sorption at equilibrium and at time, t (min.), respectively; and \(k_1\) (min\(^{-1}\)) and \(k_2\) (g . mg\(^{-1}\).min\(^{-1}\)) are the rate constants for the respective equations (2, 3). The parametres obtained are summarized in the table 1. Comparison of either \(\chi^2\) or \(R^2\) values indicates that the sorption reaction followed the pseudo second order kinetics.

![Figure 7](image_url)

**Figure 7.** The plots of sorption percentage of arsenic (III) by NHCAO against pH\(_i\) at T = 303K.
Figure 8. The plots of time dependent sorption capacity ($q_t$, mg.g$^{-1}$) of As(III) by NHCAO at T = (303 ± 1.0) K, pH$_i$ = (7.0 ± 0.2).

Table 1. The parameters of kinetic model evaluated for the sorption of arsenic(III) on NHCAO at pH$_i$ = (7.0 ± 0.1) and T = 303 (± 1.0K) for Arsenic (III) concentration 10.0 mgL$^{-1}$

| Pseudo-first order parameters | Pseudo-second order parameters |
|-------------------------------|--------------------------------|
| $k_1$                         | $q_e$                          |
| $q_e$                         | $R^2$                          |
| $\chi^2$                     | $k_2$                          |
| $q_e$                         | $R^2$                          |
| $\chi^2$                     |                                |
| 0.22 (±0.03)                  | 8.56 (± 0.21)                  |
| 0.74                          | 0.26                           |
| 0.04 (± 0.01)                 | 9.12 (± 0.09)                  |
| 0.97                          | 0.03                           |

3.8. Isotherm analysis of As(III) sorption

Figure 9 shows the equilibrium capacity ($q_e$, mg.g$^{-1}$) of As(III) sorption on NHCAO at 303K and pH=7.0 against equilibrium arsenic(III) concentrations, ($C_e$, mgL$^{-1}$). The equilibrium data were analyzed by the models of Langmuir (eq. 3) and the Freundlich (eq.4) isotherm [5], normally applied to express the equilibrium sorption result.

Langmuir equation: $q_e = (q_mK_aC_e) / (1+K_aC_e)$

Freundlich equation: $q_e = K_F C_e^{1/n}$

where $q_m$ and $K_a$ are the Langmuir constants associated to monolayer sorption capacity (mg.g$^{-1}$) and sorption equilibrium constant (L.g$^{-1}$), respectively. $K_F$ and $n$ are the Freundlich constants attributed to the sorption capacity (mg.g$^{-1}$) and sorption intensity, respectively. The isotherm parameters obtained after non linear fit of these model equations to the experimental data were summarized in table 2. From the $\chi^2$ or $R^2$ values it is discovered that the model of Langmuir is the most fitted model for this sorption reaction. The maximum monolayer sorption capacity value shows that NHCAO is very much effective in As(III) removal.
Figure 9. The plot of q_e (mg g⁻¹) versus C_e (mg L⁻¹) on As(III) sorption by NHCAO at T = 303 (± 1.0) K, pHᵢ = 7.0 (± 0.2).

Table 2. The isotherm parameters estimated using the non-linear analysis of equilibrium arsenic (III) sorption result on NHCAO at pHᵢ = (7.0 ± 0.1) and T = 303 ± 1.0K).

|           | Langmuir | Freundlich |
|-----------|----------|------------|
| q_m       | 20.99 ± 1.05 | 5.91 (± 0.75) |
| K_a       | 0.21 ± 0.04   | 0.96 |
| R²        | 0.98        | 1.48 |
| χ²        | 0.70        | |
| n         | 2.93 ± 0.38  | |

4. Conclusions
The Ce-Al binary oxide (NHCAO) synthesized by a simple precipitation method is highly efficient in As(III) removal out of the contaminated water in the wide range of pH. Kinetic study revealed that maximum adsorption happened in the first 50 minutes of contact time. The monolayer sorption capacity of NHCAO is rather proportional toward the other As(III) adsorbents reported earlier [5, 6, 8, 10-13]. Cerium aluminum mixed oxide particle prepared in this study can be regarded as the effective adsorbent for arsenic. Previous study reported the effectiveness of Aluminium-Cerium mixed oxide nanoparticles in deflourination of water [14]. Our study further shows the utility of NHCAO in inorganic remediation of arsenic from drinking water.

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