Chapter-5
Arsenic sorption in presence of co-occurring ions on nano-structured cerium(IV) associated iron(III) bimetal mixed oxide sorbent (NICMO): role of surface properties in guiding sorption mechanism

5.1. Introduction

Nano-particles usually exhibit remarkable physical properties, rapid chemical reactivity, and high sorption capacity for inorganic compounds. Studies of the fate and transport of nano-particles were largely concerned with their properties and behavior change over time, whether they would interact with toxic contaminants after being released into the environment or would change the anticipated impact of nano-particles themselves and the toxic contaminants when they interact with one another.

Arsenic is one of the most toxic elements and is found virtually in all environmental systems as a result of both geological processes and anthropogenic activities [1, 2]. Sorption of arsenic with metal oxides had been widely used because of its effectiveness and simplicity for point-of-use applications.

As already discussed in section 3.1 of chapter-3 that different forms of iron(III) oxide like oxy hydroxide, hydroxide, goethite, and hematite were promising for removing both As(III) and As(V) from aqueous solution [3-6].

On the other hand, ceria nano-particles [7] were considered to be a representative member of an industrially important class of metal oxide nano-particles [8, 9]; they could be used as automotive catalytic converters [10], UV-blocking agents [11], and single, nanowire-based gas sensors [12]. Hydrous cerium oxide (HCO) nano-particles were synthesized by a simple precipitation process, and their arsenic sorption performances were investigated. Due to the
presence of high affinity surface hydroxyl groups, HCO nano-particles demonstrated exceptional sorption properties in terms of sorption capacity and kinetics on both As(III) and As(V). Such exceptional arsenic sorption properties by HCO nano-particles were shown to derive from the strong inner-sphere complex ion [13].

However, other reports showed that ceria nano-particles were able to rescue HT22 cells from oxidative stress-induced cell death [14] and protect against the progression of cardiac disfunction [15]. All these facts encouraged in attempting to synthesize nano-structured ceria(IV) associated iron(III) bimetal mixed oxide nano-particle for scavenging contaminant like arsenic.

In the sorption test, bimetal mixed oxide sorbent showed a significantly higher As-(V) sorption capacity than the referenced cerium(IV) and iron(III) oxides prepared by the same procedure [16].

Thus, this chapter systematically represented the synthesis, characterization and physicochemical interpretation of arsenic sorption over nano-structured cerium(IV) associated iron(III) oxide in presence of common groundwater occurring ions.

This chapter has been divided into four sections. Section-A described the characterization of synthetic nano-structured cerium(IV) associated iron(III) bimetal mixed oxide (NICMO). Section-B and section-C have shown, respectively, As(V) and As(III) sorption behavior from aqueous medium in the absence/ presence of groundwater occurring ions. Finally, section-D illustrated fixed bed NICMO column analysis systematically for sorptive removal of arsenic from the contaminated ground water system.
5.2 Materials and Methods

5.2.1 Chemicals

Disodium hydrogen arsenate heptahydrate (Na$_2$HAsO$_4$.7H$_2$O, Merck, Germany) was used for the preparation of stock As(V) solution. Analar reagent (A. R.) grade As$_2$O$_5$ (BDH, England) was used for preparation of the stock As(III) solution. Laboratory grade reagents used were ferric chloride hexahydrate (FeCl$_3$.6H$_2$O, Merck, India), sodium hydroxide (NaOH, SD Fine Chemicals, India) and ammonium cerium(IV) nitrate, (NH$_4$)$_2$Ce(NO$_3$)$_6$, (Merck-India). Ferric chloride hexahydrate and ammonium cerium(IV) nitrate (ACN) were laboratory grade reagent (Merck, India) and used for the synthesis of the nano-structured cerium(IV) associated iron(III) bimetal mixed oxide. The chemicals used for the analysis of arsenic were guaranteed reagent (Merck, Germany) described in sub-section 4.2.1.

5.2.2 Synthesis of Nano-structured cerium(IV) associated iron(III) bimetal mixed oxide (NICMO) by co-precipitation, hydrothermal process

At first, 100 ml 0.1(M) ammonium cerium(IV) nitrate solution (ACN) in 0.1(M) HCl and 100 ml 0.1(M) ferric chloride solutions in 0.1(M) HCl were prepared separately in two different beakers and stirred continuously for its complete dissolution. Then, Ce(IV) solution was added slowly to Fe(III) solution with vigorous stirring to give rise to an intermediate deep orange coloured solution. At this point, pH of the mixed solution was in the acidic range. To it 5(M) NaOH solution was added drop wise with continuous stirring to raise the pH from acidic range to alkaline range (pH=9–9.5) which was initially checked with pH paper and finally with pH meter.
Finally, precipitation starts and pH at this point abruptly jumps up from neutral range to highly alkaline range with few drops of alkali. The gel like precipitate was allowed to stand for 48hrs without disturbing. The suspension was repeatedly washed with distilled water and then dried at 100°C for hrs. The dried product was grounded in a mortar and pestle and sieved to separate the agglomerates having dimension in the range 140-290 nm. The material was homogenized at pH-7.0.

5.2.3. Analytical instruments

All the analytical instruments used here are already described in chapter-3 under sub-section 3.3. Electrochemical behavior of the samples through cyclic voltammetry measurement was investigated using AUTOLAB-30 potentiostat/galvanostat. A platinum electrode and a saturated Ag/ AgCl electrode were used as counter and the reference electrodes, respectively. Cyclic voltammograms were carried out between -0.5 and 0.5 V with respect to reference electrode in 1(M) KCl solution at a scan rate of 5 mV. s⁻¹.

5.3. Experimental procedures

5.3.1. Batch sorption experiment

Batch experimental procedure adopted for arsenic sorption reaction has been described in ‘Material and Methods’ section (Chapter-2).

For the effect of calcined temperature, NICMO calcined (1.0 hour) at 100°, 150°, 200°, 250°, 300°, 350°, 400 and 500 °C respectively was used separately with arsenic solution.

Influence of pH on arsenic sorption reaction between NICMO calcined at 200°C (NICMO) and arsenic solution was conducted separately for 2.0 hours at initial solution pH (pHᵢ) = 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 respectively.
Kinetics of As(V) and As(III) sorption reactions with NICMO were conducted at pH 7.0 (±0.1) and T = 30 (±1)° C separately in the absence and presence of groundwater occurring ions at background. The concentration (mg. L⁻¹) of each ion added respectively to As(V) or As(III) aqueous system had been noted in Table-5.1. Concentration of the externally doped ions added to arsenic aqueous system were considered taking a close consultation with the upper limit of WHO recommended values and whose final concentration in the system might lay an impact on our main stream experiment. Set-up and other conditions of the experiments remain the same as described in the experimental procedures.

Isotherm experiments of As(V) and As(III) sorption reaction were conducted at T = 30 (±1.0)° C and pH 7.0 (±0.1). Initial As(III) or As(V) concentrations (C₀) used were ranged in 10.0 to 250.0 mg. L⁻¹ with NICMO in the absence/presence of ions shown in Table 5.1.

The amount of sorbed arsenic per gram of NICMO at any time, t (qₜ) or at equilibrium (qₑ) were calculated using the mass balance equation (2.1) given in the experimental sub-section (2.5) of chapter-2.

Table- 5.1: Concentration of different ions added to aqueous solution of As(V) (C₀ = 6.5 and 4.5 mg. L⁻¹)/As(III) (C₀ = 4.8 mg. L⁻¹) at T = 30 (±1.0)° C and pH 7.0 (±0.1)

<table>
<thead>
<tr>
<th>Different Ions</th>
<th>Sulphate (SO₄²⁻)</th>
<th>Chloride (Cl⁻)</th>
<th>Phosphate (PO₄³⁻)</th>
<th>Bicarbonate (HCO₃⁻)</th>
<th>Silicate (SiO₂²⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mg. L⁻¹)</td>
<td>200.0</td>
<td>400.0</td>
<td>50.0</td>
<td>300.0</td>
<td>50.0</td>
</tr>
</tbody>
</table>
5.3.2. Thermodynamic parameter

For estimation of thermodynamic parameters of both As(V) and As(III), equilibrium experiment described above in sub-section 5.3.1 were conducted separately at \( T (\pm 1, K) = 283, 293, 303, 313 \) and 323, \( pH_i = 7.0 (\pm 0.1) \) taking 100 mg NICMO dose in the absence/presence of background ions listed in Table 5.1 for determining the equilibrium constants.

5.3.3. Desorption study

For desorption experiment, 2.0 g of the bimetal mixed oxide was agitated for two hours with 50 ml of 1000 mg. L\(^{-1}\) As(V) and As(III) solution, respectively taken inside polyethylene (PET) bottles. After agitation, the reaction mixture was filtered and washed three times with distilled water. Then, the solid arsenic adsorbed oxide was dried in an air oven maintained at 100°C. 100 mg of this arsenic adsorbed oxide was again agitated with varying strength of alkali solution and finally filtered after 2.0 hours of agitation. The filtrate was analyzed for the desorbed arsenic.

5.4. Results and Discussion

Section-A: Characterization of synthetic NICMO

5.4.1. Physicochemical characterization of NICMO

5.4.1.1. XRD pattern analysis

Fig. 5.1(i) shows the Photoshop compiled and edited x-ray diffraction (XRD) patterns of \( \text{Fe}_2\text{O}_3 \) (a), \( \text{CeO}_2 \) (b) and NICMO (c) samples. It indicated that the samples were crystalline. Comparison of the broadness of the individual peaks of the three synthetic materials revealed that the crystallite size of NICMO was smaller to that of the individual oxides (\( \text{Fe}_2\text{O}_3 \) and \( \text{CeO}_2 \)) prepared by calcinations of their respective amorphous hydroxides. Values of the peak positions at \( ^\circ 2\theta \) for NICMO were 28.5°, 33.1°, 47.5°, 56.6° and 58.28° while those for...
Fe₂O₃ were 24.21 (0 1 2), 33.25 (1 0 4), 35.72 (1 1 0), 40.97 (1 1 3), 49.6 (0 2 4), 54.22 (1 1 6), 57.78 (1 2 2/0 1 8), 62.61 (2 1 4), 64.17 (3 0 0), 72.18 (1 1 9) and 75.67 (2 2 0) and for CeO₂ were 33.0 (2 0 0), 56.3 (3 1 1), 69.43 (4 0 0), 76.69 (3 3 1) and 79.04 (4 2 0) respectively.

Figure 5.1(i): X-ray diffraction patterns of synthetic (a) Fe₂O₃, (b) CeO₂ and (c) NICMO

It was found that two peaks of NICMO out of five were identical in position with CeO₂ phase having cubic structures corresponding to reflection from (1 1 1) and (2 2 0) planes, and one common with Ce₂O₃ phase having hexagonal structures corresponding to reflection from (2 0 1) plane, respectively (Table-5.2). Only one XRD peak of NICMO were found to be close to α-Fe₂O₃, indicating incorporation of some Fe³⁺ ion in to the crystal structure of cerium oxide by either replacement or occupying void space.
Table-5.2: Comparison of x-ray diffraction data of NICMO with relevant JCPDS

International Centre for Diffraction data.

<table>
<thead>
<tr>
<th>Incineration temperature (°C)</th>
<th>°2θ (exp)</th>
<th>°2θ (JCPD)</th>
<th>Intensity h k l</th>
<th>Incineration temperature (°C)</th>
<th>°2θ (exp)</th>
<th>°2θ (JCPD)</th>
<th>Intensity h k l</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>28.5</td>
<td>28.54</td>
<td>999 1 1 1</td>
<td>100</td>
<td>33.1</td>
<td>33.18</td>
<td>999 1 0</td>
</tr>
<tr>
<td>100</td>
<td>47.49</td>
<td>47.48</td>
<td>458 2 2 0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Again, the sharpness of XRD peaks of CeO₂ [pattern-b, Fig. 5.1(i)] was greater than that of NICMO, which was due to the incorporation of Fe³⁺ ions into the well defined crystallites of CeO₂.

Thus, the degree of crystallinity of NICMO was lowered than that of CeO₂ and Fe₂O₃.

Broadening of the XRD peak patterns of NICMO with respect to CeO₂ and Fe₂O₃ indicated that some strain was present in the oxide. The crystal strain arises from the substitution of some of Ce⁴⁺ (0.97 Å) ions by smaller Fe³⁺ (0.65 Å) ions in the unit cell.

Fig. 5.1(ii) demonstrates the XRD pattern of NICMO samples prepared by incinerating at temperature (°C) 100, 200, 300, 400 and 500, respectively. The peaks obtained at 28.5°, 33.1°, 47.5°, 56.6° and 58.28°, respectively, in the XRD patterns of all the incinerated samples of NICMO were compared with the standard JCPDS- International Centre for Diffraction Data (Table-5.2). The peak found at 33.1° in the XRD patterns of NICMO samples is common which was due to α-Fe₂O₃ phase of hematite variety having rhombohedra structures corresponding to reflection from (1 0 4) planes. The peaks obtained at 28.5° and 47.5° in the XRD patterns of the samples are due to CeO₂ phase with cubic structures corresponding to
reflection from (1 1 1) and (2 2 0) planes, respectively. The distinct and well-defined peak at 56.6° present in the XRD pattern of NICMO sample dried at 100°C was due to Ce₂O₃ phase with hexagonal structures corresponding to reflection from (2 0 1) plane. The intensity of this peak had reduced and almost got overshadowed by its adjacent peak when the sample got incinerated at 200°C, and finally disappeared at further higher temperatures (~ 500°C) which might be due to the oxidation of Ce(III) to Ce(IV) in the presence of oxygen at higher temperature.

Figure 5.1(ii): X-ray diffraction patterns of NICMO calcined at (°C) (a) 100, (b) 200, (c) 300, (d) 400, (e) 500.

Another XRD peak obtained at 58.28° in the incinerated samples was probably due to the formation of some mixed phase of the prepared oxide that developed at 100°C only but became more distinct and prominent with rise of incineration temperature. This observation clearly indicated that the mixed oxide had well-defined Ce₂O₃ phase when prepared and dried at ~70°C that gradually vanished allowing equilibrium inter-conversion to perhaps more thermodynamically stable CeO₂ with rise of incineration temperature.
With increase of incineration temperature, no segregation or aggregation occurred in NICMO as evidenced from different temperature (Photoshop edited, not to scale) compiled XRD patterns. The average particle size calculated from the Gaussian fit of the distinct peaks and then computing its modeled data into Scherrer’s equation followed by averaging the data found it to be approximately 3.56 nm.

The nature of XRD pattern and its concurrent particle size calculation were almost consistent at different incinerated temperatures emphasizing the thermal stability of the synthesized NICMO. Thus, the XRD pattern confirmed the heat-treated synthesized NICMO to be thermally stable crystalline bimetal mixed oxide ranging in nano dimension.

<table>
<thead>
<tr>
<th>Incineration temperature (°C) of NICMO</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3.65</td>
</tr>
<tr>
<td>200</td>
<td>3.78</td>
</tr>
<tr>
<td>300</td>
<td>3.45</td>
</tr>
<tr>
<td>400</td>
<td>3.68</td>
</tr>
<tr>
<td>500</td>
<td>3.50</td>
</tr>
</tbody>
</table>

5.4.1.2. Thermo gravimetric (TG) and differential thermal (DT) analysis

Fig. 5.2 demonstrates the TG-DT spectra of NICMO. Amount of the sample taken was 9.855 mg that was subjected to 40 to 45 mins of TG scan in the temperature range 30.6°C to 450°C.
It was found that the percentage of weight loss was 24.32 corresponding to 2.396 mg at the temperature range 30°-75° obtained within 5 mins of TG scan.

Figure 5.2: Thermogravimetric (TG) and differential thermal (DT) spectra of NICMO

The single sharp endothermic peak obtained in the temperature range 60°-90°C in DT spectrum was due to the elimination of physically attached water molecules. The thermal stability of the sample at higher temperature also supported and agreed well with the XRD patterns obtained at higher temperature.

5.4.1.3. Fourier transform infra-red spectroscopy (FTIR)

Fig. 5.3 demonstrates FTIR spectra of pure iron(III) oxide (spectrum-a), pure cerium oxide (spectrum-b) and NICMO (spectrum-c). Absorbance bands (spectrum- a to c, Fig. 5.3) at wave number (\(\nu, \text{ cm}^{-1}\)) values ranging between 3700-3300 and 1750-1600 were for the symmetrical and asymmetrical stretching and bending vibration modes of O-H bonds of hydroxyl groups, respectively. Additionally, the absorption band around 870 cm\(^{-1}\) in pure iron(III) oxide (spectrum-a, Fig. 5.3) and 860 cm\(^{-1}\) in pure Ce(III) oxide (spectrum-b, Fig. 5.3) were for Fe-O
and Ce-O bonds, respectively. Additional wave number ($\nu$, cm$^{-1}$) values, presumably for the symmetrical and asymmetrical bending vibration of metal bonded hydroxyl group (M-OH) [17] in the bimetal mixed oxide were at 1385 and 1060, respectively (spectrum-c, Fig. 5.3).

Figure 5.3: FTIR analysis of (a) Synthetic Iron(III) oxide, (b) Synthetic Cerium(IV) oxide, and (c) Iron(III)-Cerium (IV) bimetal mixed oxide formed by chemical precipitation (NICMO)

Thus, it can be concluded that the oxide as-prepared by chemical precipitation method was characterized to be bimetal mixed oxide whose inherent nature was totally different from the individual oxides analyzed. Appearance of a weak peak at 534 cm$^{-1}$ in NICMO (spectrum-c, Fig. 5.3) was presumably due to the formation of hetero metal oxygen bond.

5.4.1.4. Zero-point surface charge pH ($pH_{ZPC}$)

According to Stumm [18], $pH_{ZPC}$ of a composite oxide is approximately the weighted average of the values of its components. However, $pH_{ZPC}$ of Fe-Ce sorbent (7.13 ± 0.10) was higher than that of the reported values of pure iron(III) oxide (6.2) and pure cerium(IV) oxide (6.8)
indicating the bimetal oxide to be just not the physical mixture of the individual pure synthetic oxides estimated by the procedure described by Babic et al. [19].

Figure 5.4: Analysis of zero-point surface charge (pH_{ZPC}) of NICMO

Thus, the surface of NICMO was positively charged at pH < 7.13 (Fig. 5.4) that was favorable for non-specific attraction of As(V) through Columbic attraction between anions and sorbent surface.

5.4.1.5. Scanning electron microscopic (SEM) image of NICMO

Fig. 5.5 (a) shows SEM image of NICMO, which established the agglomerated surface morphology with irregular shape that was unevenly dispersed over a base matrix of oxide surface almost covering up its porous nature. SEM image of NICMO with EDAX analyzed data at marked site [(Fig. 5.5 (b)) shows that the surface mean percentage (parenthesis) composition of NICMO sample was O (37.39), Ce (47.52) and Fe (17.06), indicating Fe: Ce mole ratio to 1: 1.1 and empirical composition FeCe_{1.1} O_{7.6}. 

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Figure 5.5: Scanning electron microscopic (SEM) image of (a) NICMO (b) Scanning electron microscopic (SEM) image with EDAX data of NICMO

5.4.1.6. Transmission electron microscopic (TEM) image of NICMO

Fig. 5.6 shows the transmission electron microscopic (TEM) image of NICMO with $4.3 \times 10^4$ fold magnification. Dimensions estimated for the crystallite particles from the TEM image were ranged in 10 to 20 nm under crystal packing force. However, the calculated crystallites
size of NICMO obtained inserting the data of XRD peaks into Scherrer's equation were 3.56 nm.

Figure 5.6: Transmission electron microscopic image of NICMO

5.4.1.7. BET surface area analysis of NICMO

Fig. 5.7 represents the plots of (a) N₂ adsorption-desorption and (b) pore size distribution of NICMO. The isotherm clearly showed the gradual increase of adsorption from P/P₀ 0.1 to 0.2 followed by a large and two small inflections at P/P₀ ranged in 0.1 to 0.35, 0.55 to 0.65 and 0.65 to 0.75.

The location of the hysteresis loop in N₂ isotherm can be used to determine the nature of pores, i.e., a regular framework pore or interparticle voids (such as textual pore). The framework porosity lying between 0.4-0.7 P/P₀ in N₂ isotherm indicates itself to be contained within the uniform channels of the templated framework, while the textural porosity at 0.8-1.0 P/P₀ arises from the non-crystalline intra-aggregate voids and spaces formed by inter-particle contacts. [16, 20]. So, our is a case of porosity arising out of channels of the template framework but surely with non uniformity in pore size distribution as evidenced from decreasing sharpness of inflexion points.

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The latter isotherm is associated with an irregular desorption hysteresis. The BET surface area (m$^2$. g$^{-1}$) of NICMO had been found to be 104, that was lower compared to the specific surface area of pure cerium(IV) oxide (122) and higher than that of pure iron(III) oxide (98) [16]. It was found from Fig. 5.7 (b) that the pore volume of the sample was 0.132 cm$^3$. g$^{-1}$. The narrow pore size distribution of NICMO shown in Fig. 5.7 (b) suggested that the sample has a maximum pore size 5.68 nm.

5.4.1.8. Raman Effect

Fig. 5.8 shows the Raman spectra of cerium(IV) associated iron(III) bimetal mixed oxide (NICMO). No characteristic peaks of either synthetic iron(III) oxide or cerium(III) oxide were observed in the spectra which indicated that the bimetal mixed oxide is not just a physical mixture of the two. Sharp peaks are observed within the range 2000-2300 cm$^{-1}$ which might be due to the presence of hetero-metal bonding via oxygen linkage (i.e, Fe-O-Ce). Peaks at ~ 3500 cm$^{-1}$ are due to surface hydroxyl (O-H) groups present on the oxide surface.
Figure 5.8: Raman spectra of cerium(IV) associated iron(III) bimetal mixed oxide sorbent (NICMO)

Table 5.4: Summarized physical characteristic features of NICMO sample

<table>
<thead>
<tr>
<th>Physical Characteristic Parameters of NICMO</th>
<th>Physical Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average particle size (XRD Analysis) (nm)</td>
<td>3.56</td>
</tr>
<tr>
<td>Band Assignment in FTIR Spectra (cm(^{-1}))</td>
<td>Hetero-metal bridging at 534.</td>
</tr>
<tr>
<td>(\text{pH}_{zpc})</td>
<td>7.13 (± 0.1)</td>
</tr>
<tr>
<td>Empirical formula derived from SEM Analysis</td>
<td>FeCe(<em>{1.1}) O(</em>{7.6})</td>
</tr>
<tr>
<td>Particle size (TEM) Analysis (nm)</td>
<td>10 to 20</td>
</tr>
<tr>
<td>BET Surface Area (m(^2). g(^{-1}))</td>
<td>104</td>
</tr>
</tbody>
</table>
5.4.2. Section-B: Studies on As(V) sorption behaviour on NICMO surface from its aqueous solution in the presence of some major groundwater occurring ions

5.4.2.1. Effect of calcination temperature on NICMO and As(V) sorption

Removal capacity \( (q_e, \text{mg. g}^{-1}) \) of As(V) by sorption on calcined NICMO samples obtained from solutions of initial concentration \( (C_0) = 4.5 \) and \( 9.0 \text{ mg. L}^{-1} \), respectively, at pH \( 7.0 \) \((\pm0.1)\) and \( T = 30 (\pm1.0)\text{°C} \) versus temperature of calcinations employed on NICMO. Fig. 5.9 showed that the sorption capacity \( (q_e) \) increased with increasing temperature of calcinations from \( 100\text{°C} \) to \( 200\text{°C} \) and decreased above \( 200 \text{ °C} \). This indicated that the active sites available for sorption presumably enhanced due to the elimination of physically bound (H-bonded) water molecules (R-5.1) from the solid surfaces with increasing calcination temperature from \( 100\text{°C} \) to \( 200\text{°C} \) that was confirmed from the single sharp endothermic peak obtained in the range \( 60\text{°}-90\text{°C} \) in DT spectrum.

![Figure 5.9: Variations of As(V) removal capacity (mg. g\(^{-1}\)) at pH 7.0 (±0.2) versus calcination temperature on synthetic NICMO](image)

Figure 5.9: Variations of As(V) removal capacity (mg. g\(^{-1}\)) at pH 7.0 (±0.2) versus calcination temperature on synthetic NICMO
The decrease of $q_e$ at calcined temperature above 200° C is due to the dehydroxylation of exposed M-OH groups from NICMO surfaces (R-5.2). The increase or decrease in values is very low and gradual due to the thermal stability of NICMO that does not undergo any transition or phase change.

\[ \text{M-OH} \rightarrow \text{OH}_2 \rightarrow \text{M-OH} + \text{H}_2\text{O} \uparrow \]  

(R-5.1)

\[ 2 \text{M(OH)}_3 \rightarrow \text{M}_2\text{O}_3 + 3\text{H}_2\text{O} \uparrow \]  

(R-5.2)

The results obtained were found to be similar with that reported previously for crystalline hydrous ferric oxide [21] but differed slightly from that of hydrous stannic oxide [22] and crystalline hydrous titanium oxide [23].

5.4.2.2. Effect of pH

Fig. 5.10 demonstrates As(V) removal capacity ($q_e$, mg. g$^{-1}$) of NICMO versus pH$_i$. It was found that the nature of the plots remain similar with respect to the slow decrease of $q_e$ values with increasing pH$_i$ for both the concentrations of As(V). Interpretation on the observed variation could be given based on the nature of the surface of the solid and pH dependent As(V) species in solution. As(V) ion occurs mainly in the form of H$_2$AsO$_4$ in the pH range 3 to 6, while divalent anion HAsO$_4^{2-}$ dominates at higher pH values (between pH 8 to 10.5). In the intermediate region (6 to 8), both species coexist with one another [24, 25].
As evident from the plot (Fig. 5.10) that theoretically sorption experiments should be set at pH 2 to 3 to get high removal capacity but the practical application shows dissolution of the iron component of the bimetal mixed oxide. Thus, the resulting sorption experiments can be set at neutral pH without sacrificing much of sorption capacity [26].

The slight decrease of $q_e$ in the pH range 5.0 to 7.0 is due to the fact that the equilibrium pH (pH$_e$) of said pH$_i$ range was near to pH$_{zpc}$, indicating neutral NICMO surface to bind to As(V) species via weak dipole-ion interaction.

5.4.2.3. Solubility test of NICMO

The solubility products of ceric hydroxide [Ce(OH)$_4$] is much lower of the order $10^{-40}$ [27] than most other insoluble cerium salts. Low solubility product of Fe(OH)$_3$ is also well known (K$_{sp}$ of Fe(OH)$_3$ = $5 \times 10^{-38}$ at 25° C). Hence, the tests for the presence of iron(III) and Ce(IV) ions at working pH range were found to be negative.
So, it can be safely used without its chances of dissolution in the filtrate, leading to solubility loss of the material at the experimental conditions.

Thus, NICMO calcined at 200°C could safely be used as a filtrating medium for upgrading high arsenic contaminated groundwater to the potable standard.

5.4.2.4. Kinetic analysis

Fig. 5.11 (a, b) shows the time dependent As(V) sorption amounts \( q_t \) by NICMO at \( \text{pH}_i = 7.0 \pm 0.1 \) and \( T = 30 \pm 1.0 \)°C from As(V) solution of \( C_0 = 4.5 \) mg L\(^{-1} \) in the presence of either background ion such as Cl\(^-\), SO\(_4^{2-}\), HCO\(_3^-\), PO\(_4^{3-}\) and SiO\(_3^{2-}\).

Figure 5.11: Plots of \( q_t \) (mg. g\(^{-1}\)) versus contact time, t (min.) with non-linear fits of data with (a) pseudo-first order and (b) pseudo-second order equations. \( C_0 = 4.5 \) mg As (V). L\(^{-1}\), NICMO dose = 2.0 g.L\(^{-1}\), T= 30 (±1.0)°C and pH\(_i\) = 7.0 (±0.2). Ions added with As (V) solution: ■ no ion, ● SO\(_4^{2-}\), ▲ Cl\(^-\), ▼ HCO\(_3^-\), ◄ PO\(_4^{3-}\), ◆ SiO\(_3^{2-}\).
Despite the equilibrium time for the present reaction was seen to be 90 minutes, almost 90% of the sorption took place within 60 minutes of reaction time.

To ascertain the kinetics, the estimated $q_t$ data were analyzed with non-linear least square fit method by pseudo-first order (eq. 2.5) and pseudo-second order (eq. 2.8) model equations.

Table-5.5: Kinetic model parameters for As(V) sorption by NICMO at pH 7.0 ($\pm 0.1$) and temperature $T= 30 (\pm 1.0) ^{\circ}C$ in the presence of some co-occurring ions [$C_0 = 4.5$ mg As (V) L$^{-1}$].

<table>
<thead>
<tr>
<th>Ion present with As(V)</th>
<th>Pseudo-first order, $q_t = q_e(1-e^{-kt})$, kinetic parameters</th>
<th>Ion present with As(V)</th>
<th>Pseudo-second order, $q_t = \frac{k_2q_e^2}{1+kt_2q_e}$, kinetic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1 \times 10^{-1}$ min$^{-1}$</td>
<td>$q_e$ mg.g$^{-1}$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>$PO_4^{3-}$</td>
<td>0.599 ± 0.009</td>
<td>1.14</td>
<td>0.966</td>
</tr>
<tr>
<td>$HCO_3^-$</td>
<td>1.041 ± 0.01</td>
<td>1.382</td>
<td>0.986</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>1.702 ± 0.025</td>
<td>1.622</td>
<td>0.968</td>
</tr>
<tr>
<td>$SiO_3^{2-}$</td>
<td>1.258 ± 0.02</td>
<td>1.765</td>
<td>0.960</td>
</tr>
<tr>
<td>$Cl^-$</td>
<td>3.274 ± 0.027</td>
<td>1.871</td>
<td>0.98</td>
</tr>
<tr>
<td>No other ions</td>
<td>1.926 ± 0.027</td>
<td>1.969</td>
<td>0.973</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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These observations established that the kinetics of As (V) sorption reaction with NICMO in the presence of tested ions at background was pseudo-second order type. The modeled $q_t$ value was highest in the absence of any tested ion at background, indicating different degrees of competitive influence of the ions added to As(V) solution.

Again, the results revealed (Table- 5.5) that the adverse influence of chloride (Cl') and silicate ($\text{SiO}_3^{2-}$) ions were poorer to that of sulphate ($\text{SO}_4^{2-}$), phosphate ($\text{PO}_4^{3-}$) and bicarbonate ($\text{HCO}_3^-$) ions on As(V) removal by NICMO.

### 5.4.2.5. Diffusion kinetics

Theoretical treatment of the intra-particle diffusion of a solute into the interior of the solid yields rather a complex mathematical relationship, which differs in form as a function of geometry of the solid particles. The functional relationship described in chapter-2 applied to predict the rate-controlling step (RCS) of the sorption reaction is given by equation (2.9).

If intra-particle diffusion be RCS, the plot of $q_t$ versus $t^{0.5}$ should be a straight line and must pass through the origin. Any deviation of the plot from linearity should indicate RCS to be either boundary layer (film) diffusion or multistage controlled phenomenon.

Weber and Morris plot describing non-linear nature of $q_t$ versus $t^{0.5}$ [Fig. 5.12 (a)] over the range of contact time indicated that RCS was not intra-particle (pore) diffusion; instead it might be considered as the boundary layer (film) diffusion or multistage process.

When the values of $q_t$ before attaining equilibrium (limited up to 40 minutes) were modeled with Weber and Morris equation (2.9) on origin spread sheet, a number of linear curve...
fittings corresponding to the data set of different single as well as binary system were obtained as given in [Fig. 5.12 (b)].

To confirm the nature of RCS, the coefficients of intra-particle (pore) diffusion ($D_p$, cm$^2$. s$^{-1}$) and film diffusion ($D_f$, cm$^2$. s$^{-1}$) were calculated using equations (2.10, 2.11) of chapter-2.

It is known that if the calculated value of $D_p$ is ranged between $10^{-11}$ and $10^{-13}$ cm$^2$. s$^{-1}$, RCS should be intra-particle (pore) diffusion and that if ranged between $10^{-6}$ to $10^{-8}$ cm$^2$. s$^{-1}$, then RCS should be boundary layer (film) diffusion [chapter-2].

![Weber-Morris plots](image)

**Figure 5.12:** Weber-Morris plots for (a) intra-particle diffusion taken over the total time interval, (b) modeled linear plots taken up to 40 minutes of As(V) removal reaction with NICMO at $C_0 = 4.5$ mg As(V). L$^{-1}$. Ions added with As(V) solution at background: ■ no ion, • SO$_4^{2-}$, ▲ Cl$^-$, ▼ HCO$_3^-$, ◇ PO$_4^{3-}$, ▼ SiO$_2^{2-}$.

Taking the rate constant values from pseudo-second order model (best fit) equation (2.8), time for 50 % sorption reaction ($t_{0.5}$) was calculated, and used to determine the values of diffusion
coefficients. Values \((cm^2, s^{-1})\) of \(D_p\) and \(D_f\) calculated were \((0.45 \text{ to } 2.80) \times 10^{-9}\) and \((2.27 \text{ to } 8.88) \times 10^{-9}\) (Table-5.6) in the absence or presence of ground water occurring ions at background, respectively.

Values of \(D_p\) were of the order \(10^{-9}\) \(cm^2, s^{-1}\), which was about 100 times greater than \(10^{-11}\) \(cm^2, s^{-1}\) irrespective of the tested ion added to As(V) solution. Again, the values of \(D_f\) were found to be of the order \(10^{-9}\) \(cm^2, s^{-1}\), which was also outside the range.

Thus, RCS for As(V) sorption reactions with NICMO in the absence/presence of investigated groundwater occurring ions at background were neither controlled by intra-particle nor by boundary-layer diffusion phenomenon. Therefore, it can be concluded that the present reaction was a multi-stage process, which was found to be different from the result reported by Zhang [28] but similar to that reported by Gupta and Ghosh [29] and Gupta etal [30].

Table-5.6: Pore and Film diffusion coefficients calculated for As(V) adsorption reaction with NICMO at \(pH_i = 7.0 \pm 0.2\) and \(T = 30(\pm1) \, ^\circ C\).

<table>
<thead>
<tr>
<th>Ion added</th>
<th>(t_{0.5}) ((\times 10^2)) (sec)</th>
<th>(D_p) ((\times 10^{-9})) (cm^2.s^{-1})</th>
<th>(D_f) ((\times 10^{-9})) (cm^2.s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>0.371</td>
<td>2.802</td>
<td>8.882</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>0.868</td>
<td>1.198</td>
<td>6.58</td>
</tr>
<tr>
<td>No ion</td>
<td>0.871</td>
<td>1.194</td>
<td>2.27</td>
</tr>
<tr>
<td>HCO(_3^{-})</td>
<td>1.444</td>
<td>0.720</td>
<td>6.087</td>
</tr>
<tr>
<td>SiO(_3^{2-})</td>
<td>1.458</td>
<td>0.713</td>
<td>2.487</td>
</tr>
<tr>
<td>PO(_4^{3-})</td>
<td>2.309</td>
<td>0.450</td>
<td>4.949</td>
</tr>
</tbody>
</table>
5.4.2.6. Equilibrium modeling

A more systematic and quantitative way of judging and comparing sorption performance is through sorption isotherm analysis. Fig. 5.13(a, b) demonstrates equilibrium As(V) sorption capacity (\(q_e, \text{mg. g}^{-1}\)) of NICMO versus equilibrium As(V) concentration (\(C_e, \text{mg. L}^{-1}\)) obtained at pH = 7.0 (±0.1) and T = 30 (±1.0)°C, respectively. To understand the sorption mechanism, the equilibrium data shown as points were analyzed by isotherm model equations [31] namely Langmuir equation (eq. 2.12) and Freundlich equation (eq. 2.13) with non-linear regression fit method on origin spread sheet.

The parameters related to the isotherm equations were estimated and shown in Table-5.7 with regression coefficient (\(R^2\)) and statistical error chi-square (\(\chi^2\)) values. Based on the values of \(\chi^2\) and \(R^2\) (Table-5.7), it was found that goodness of the data fit with Langmuir model (\(R^2 \geq 0.99\)) was comparatively better than that of Freundlich model (\(R^2 = 0.93-0.98\)). Well fits of the equilibrium data with the Langmuir model indicated that the sorption sites of NICMO surface were homogeneous and equally accessible to all As(V) species. Values of the dimensionless Freundlich constant (n) laid between 1.9 and 2.9, indicating moderate affinity of the solid surface for As(V) species. It was concluded that the present result was similar with other researchers [32-35]. The value of monolayer sorption capacity, \(q_m (55.513 \pm 2.235 \text{mg.g}^{-1})\) (Table-5.7) of As(V) in the absence of any ion was about 15 -35 % higher than that in the presence of any background ion, indicating adverse influence of the background ions on As(V) removal by NICMO. Notably lower \(q_m\) values were found in the presence of \(\text{PO}_4^{3-}\), \(\text{SO}_4^{2-}\) and \(\text{HCO}_3^{-}\), indicating strong adverse effect of those ions on As(V) sorption by NICMO.
Figure 5.13: Plot of equilibrium sorption data on As(V) removal by NICMO at pH = 7.0 (± 0.2) and T = 303 (± 1.0) K in presence of some ions, and non-linear fits of the data with (a) Langmuir and (b) Freundlich, model equations. Ion added with As(V) solution at background: ■ no ion, ● SO$_4^{2-}$, ▲ Cl$^-$, ▼ HCO$_3^-$, • PO$_4^{3-}$, ◄ SiO$_3^{2-}$.

Decrease in removal efficiency of As(V) in the presence of ion like SO$_4^{2-}$ had been reported by Wijnja and Schulthess [36]. They confirmed the formation of both inner and outer-sphere surface complexes of SO$_4^{2-}$ on the oxide surface in the presence of As(V) using Raman and ATR-FTIR spectroscopy. As PO$_4^{3-}$ has close chemical and structural similarity with As(V), it competes well with As(V) [37, 38] for occupying sorption sites. It is also true that the constant of binding affinity value of As(V) is about seven times greater than that of PO$_4^{3-}$ on oxide surface. So, the reaction is generally physiosorption type but definitely hinders As(V) sorption causing decrease in the removal efficiency. The strong interaction of HCO$_3^-$ occurs at lower pH and is related to the pH dependency of the carbonate adsorption [39]. Analysis of
The sorption data obtained for As(V) in the presence of bicarbonate revealed the formation of a bi-dentate surface complex as confirmed from ATR-FTIR spectroscopy.

Table-5.7: Isotherm parameters estimated by the non-linear fit method of equilibrium As(V) sorption data on NICMO at pHt=7.0 (± 0.2) and T = 30(±1) °C.

<table>
<thead>
<tr>
<th>Ions present</th>
<th>Freundlich Isotherm Parameters.</th>
<th>Langmuir Isotherm Parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$\chi^2$</td>
</tr>
<tr>
<td>$PO_4^{3-}$</td>
<td>0.955</td>
<td>4.236</td>
</tr>
<tr>
<td>$HCO_3^-$</td>
<td>0.974</td>
<td>3.283</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>0.936</td>
<td>14.543</td>
</tr>
<tr>
<td>$SiO_3^{2-}$</td>
<td>0.924</td>
<td>22.518</td>
</tr>
<tr>
<td>$Cl^-$</td>
<td>0.925</td>
<td>26.749</td>
</tr>
<tr>
<td>No other ions</td>
<td>0.946</td>
<td>23.455</td>
</tr>
</tbody>
</table>

The negligible change of sorption capacity obtained in case of chloride doping compared to that in the absence of any ion was due to the fact that complexes of chloride with the bimetal oxide was much weaker than those between arsenate and the sorbent [37]. Although the formation of $S_{Fe-CaH}_2SiO_4$ $Na^+$ is quite evident that reduces surface potential, thereby increasing electrostatic repulsion between As(V) and the negatively charged surface sites [40]causing decrease of sorption capacity. But this observation prevails only when the final pH of the system was far greater than 7.0 in the range 9.0. Since, the experimental pH 302
final pH of the system was far greater than 7.0 in the range 9.0. Since, the experimental pH was set below 7.0 so, As(V) removal was not affected noticeably by silicate addition from external sources.

5.4.2.7. Mean adsorption energy

Mean sorption energy \( (E_{\text{DR}}, \text{kJ. mol}^{-1}) \), which helps to predict the nature of the reaction is defined as the free energy of transfer of one mole solute from infinity (in solution) to the surface of the sorbent. Value of \( E_{\text{DR}} \) is related to the Dubinin-Radushkevich (D-R) constant, which could be computed from the analysis of equilibrium data of a sorption reaction with D-R isotherm equation (2.14) and Polanyi potential \( (e) \) expressed by equation (2.15).

![Dubinin-Radushkevich (D-R) isotherm plot of As(V) sorption on NICMO at pH 7.0 ± 0.1 and at T = 30(±1)°C in the presence of different ions at background: □ no ion, ● SO₄²⁻, ▲ Cl⁻, ▼ HCO₃⁻, ◆ PO₄³⁻, ▲ SiO₃²⁻.](image)

Values of \( K_{D-R} \) \((\text{mol}^2 \cdot \text{kJ}^{-2})\) were given by equation (2.16) and calculated from the slope of each linear plot of \( \ln Q_e \) versus \( e^2 \) (Fig. 5.14) and the corresponding \( E_{\text{DR}} \) values were also
computed (Table-5.8). It was found that the experimental data fit were well with D-R isotherm \( (R^2 = 0.978-0.996) \) [41]. Values of \( E_{DR} \) for sorption reaction of As(V) with NICMO in the absence/presence of investigated background ions laid between 8.98 and 11.99 kJ.mol\(^{-1}\) (Table-5.8), indicating hypothetical borderline between physio-sorption or ion-exchange sorption mechanism [33, 42] that can be further confirmed from the values of enthalpy (\( \Delta H^\circ \)) and extent of desorption.

**Table- 5.8: Dubinin-Radushkevich (D-R) isotherm parameters evaluated for As(V) sorption by NICMO at pH = 7.0 (± 0.2) and at T = 30 (±1) °C**

<table>
<thead>
<tr>
<th>Ion with As solution</th>
<th>D-R isotherm parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R^2 )</td>
</tr>
<tr>
<td>SiO(_2^\cdot)</td>
<td>0.995</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.995</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>0.978</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>0.994</td>
</tr>
<tr>
<td>PO(_4^{3-})</td>
<td>0.993</td>
</tr>
<tr>
<td>No ion</td>
<td>0.996</td>
</tr>
</tbody>
</table>

### 5.4.2.8 Thermodynamic parameters

Thermodynamic parameters for As(V) removal reaction with NICMO were estimated using standard equations described in chapter-2 based on the assumption that the activity coefficient of the solutes added in solution was unity.
The thermodynamic constant \( (K_c) \) was calculated using equation (2.20) taking the experimental data of equilibrium \( q_e \) and \( C_e \) obtained at initial As(V) concentration 4.5 mg. L\(^{-1}\), \( T (\pm 1.0) K = 283, 293, 303, 313 \) and 323 and \( \text{pH}_i = 7.0 \), respectively.

Values of the changes of entropy and enthalpy at standard conditions \( (\Delta S^0 \text{ and } \Delta H^0) \) were calculated from the slope and intercept of the plot of \( \log (q_e/C_e) \) versus \( (1/T) \) (Fig. 5.15) of the linear relation given by equation (2.19) in sub-section 2.5.3 (chapter-2).

Figure 5.15: Plot of \( \ln (q_e/C_e) \) versus \( (1/T) \) of 4.5 mg. L\(^{-1}\) As (V) sorption by NICMO at pH 7.0 (± 0.1) and at 303 (± 1.0) K in presence of different ions: ■ no ion, ● SO\(_4^{2-}\), ▲ Cl\(^{-}\), ▼ HCO\(_3^{-}\), ♦ PO\(_4^{3-}\), ◄ SiO\(_3^{2-}\).

Taking the values of \( \Delta S^0 \) and \( \Delta H^0 \), the standard Gibb’s free energy \( (\Delta G^0) \) for As(V) sorption reaction with NICMO in the absence/presence of some groundwater occurring ions were calculated and summarized in Table-5.9. Increase of entropy was due to the increase of randomness at solid-liquid interface due to the release of aqua molecules when aquatic As(V) species got distributed on to the solid surface. Range of \( \Delta H^0 \) values indicate physio-sorption...
type of reactions actually occurring in all the systems under investigation. Values of $\Delta G^o$ were found to be progressively negative with increasing temperature on the reactions in all the binary systems developed indicating considerable increase of spontaneity of the reactions as evidenced from the change of Gibb’s free energy values. The results obtained were found to be similar to those single systems free from any groundwater occurring ions as reported earlier by various authors [29-30, 33, 41]

Table-5.9: Thermodynamic parameters estimated for As(V) sorption by NICMO at different reaction temperatures (K) at pH 7.0 (± 0.2) in presence of some co-occurring ions [$C_0 = 4.5$ mg As (V) L⁻¹]

<table>
<thead>
<tr>
<th>+ Ion added</th>
<th>+ ΔS° (kJ.mol⁻¹ K⁻¹)</th>
<th>+ ΔH° (kJ.mol⁻¹)</th>
<th>(-ΔG°) (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>283 K</td>
<td>293 K</td>
<td>303 K</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.084</td>
<td>10.923</td>
<td>12.850</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.101</td>
<td>15.067</td>
<td>13.613</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.104</td>
<td>15.138</td>
<td>14.190</td>
</tr>
<tr>
<td>SiO₃²⁻</td>
<td>0.100</td>
<td>13.623</td>
<td>14.627</td>
</tr>
<tr>
<td>No ion</td>
<td>0.098</td>
<td>12.800</td>
<td>15.045</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.107</td>
<td>15.900</td>
<td>14.428</td>
</tr>
</tbody>
</table>

5.4.2.9. Arsenic desorption

Percentages of arsenic desorption from As⁵⁺—NICMO versus concentrations of alkalis employed (Fig. 5.16) showed that the desorption percentage of arsenic from the solid was
very good. It was found that As(V) desorption efficiency of KOH from NICMO surface was better than that of NaOH. The desorption percentage increased with increasing alkali concentration. However, highest 82.69% of adsorbed arsenic could be desorbed from the solid surface with 2.0 M KOH solution. High desorption of adsorbed As(V) implied physio-sorption type of reactions actually occurring in the systems leading to weak interaction of As(V) over NICMO surface.

Figure 5.16: Plots of desorption percentage of As(V) from solid surface with variation of alkali concentrations.

5.4.2.10. Experimental evidences of As(V) sorption over adsorbent surface.

5.4.2.10.1. X-ray diffraction pattern of synthetic As(V) sorbed NICMO

X-Ray diffraction pattern of As(V) sorbed synthetic NICMO (AsV-NICMO) shown in (Fig. 5.17) was almost similar to NICMO [Fig. 5.1(a)]. With the decrease of the sharpness of the
peaks of NICMO, the degree of crystallinity reduced in As\textsuperscript{V}-NICMO presumably due to the surface of NICMO strongly interacting with As(V) species.

After As(V) adsorption, peak positions changed so also, the crystal structure of the material and the peak intensity almost reduced to half. However, the peaks observed in As(V) sorbed sample (As\textsuperscript{V}-NICMO, Fig. 5.17) were at 28.59°, 32.88°, 48.42°, 57.63° respectively. Comparing the peak data with standard JCPDS file, suggested that the peaks at 32.85°, 48.42° and 57.63° in As\textsuperscript{V}-NICMO are due to As(V)-O phase with orthorhombic structure corresponding to reflection from (3 1 0), (1 4 1) and (3 4 1) planes, respectively. The peak with double intensity at 28.59 was due to the overlap of two peaks at exactly same 2\textdegree angle: one arising from CeO\textsubscript{2} phase with cubic structure and other peak was that from As\textsubscript{2}O\textsubscript{5} phase with orthorhombic structure corresponding to reflection from (1 1 1) and (1 4 1) planes respectively.

Figure 5.17: X-Ray diffraction patterns of synthetic As(V) sorbed NICMO (As\textsuperscript{V}-NICMO).
5.4.2.10.2. Interpretation of spectral (FTIR) data followed by analysis of NICMO and As(V) sorbed NICMO: an overview of probable mechanism

Comparison of FTIR spectra of NICMO (spectrum-a) and As(V)-NICMO (spectrum-b) [Fig. 5.18 (i)] showed that

➢ Broad stretching band of O-H in spectrum-a of NICMO became exceedingly weak in spectrum-b at wave number (ν) 3670 to 3300 cm\(^{-1}\) of As(V)-NICMO.

➢ Area occupied by the stretching band of O-H group in NICMO (spectrum-a) was significantly reduced indicating disappearance of some O-H group from the solid surface on As(V) sorption in As(V)-NICMO (spectrum-b).

➢ Two additional bands at wave number 1060 and 1385 cm\(^{-1}\) presumably due to the symmetrical and asymmetrical bending of MOH group in spectrum-a of NICMO almost disappeared in As(V) sorbed material (spectrum-b).

➢ Band at wave number 534 cm\(^{-1}\) of spectrum-a indicated hetero- metal bridging of MOM\(\square\) bond which almost disappeared in spectrum-b suggesting considerable reduction of metal-oxygen character at the substrate surface after As(V) sorption. This concluded that As(V) species had strongly interacted with the surface of the mixed metal oxide.

➢ Appearance of band at wave number \(\sim 820\) cm\(^{-1}\) in spectrum-b corresponds to As\(^V\)-O stretching vibration mode in AsO\(_4\)^{3-} which supported the incorporation of As\(^V\)-O bond on to the material surface.
Figure 5.18 (i): FTIR spectra of (a) NICMO and (b) As(V) adsorbed NICMO (As$^V$-NICMO).

FTIR spectrum-a when compared with FTIR spectra-(b-d) of As$^V$-NICMO (shown in Fig. 5.18 ii) are found to be identical with one another.

Figure 5.18 (ii): FTIR spectra of (a) As$^V$–NICMO, (b) As$^V$–NICMO in the presence of $\text{SO}_4^{2-}$ , (c) As$^V$–NICMO in the presence of $\text{HCO}_3^-$ and (d) As$^V$–NICMO in the presence of $\text{PO}_4^{3-}$. 

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Absence of any notable difference of spectrum-a with spectra-(b to d) indicated that the ground water occurring tested ions had no influence on As(V) sorption mechanism over NICMO.

Additionally, solution pH after As(V) sorption reaction with NICMO almost remained unchanged indicating the release of aqua molecules on to the system.

Slight shifting and well splitting of band in FTIR spectrum suggested the dominance of mono protonated monodentate complex [S-OAsO₂(OH)] on the oxide surface.

Based on the experimental results, the mechanism for arsenic sorption could be suggested as

\[
S_{\text{Fe-Ce}} - \text{OH} + \text{H}_2\text{AsO}_4^{-} \rightarrow S_{\text{Fe-Ce}} - \text{OAs(OH)O}_2 + \text{H}_2\text{O}
\]

5.4.3.11 Conclusion

1. Synthetic iron(III)-cerium(IV) bimetal mixed oxide (NICMO) was agglomerated nanoparticles (10-20 nm) with zero-point surface charge pH (pH_{ZPC}) at 7.13 (± 0.05).

2. Incinerated NICMO at 200° C had highest As(V) removal capability at optimized pH (7.0 ± 0.1) and temperature 303K.

3. Reaction kinetics for As(V) removal by NICMO obeyed pseudo-second order equation better than pseudo-first order equation.

4. Equilibrium data for the sorption reactions in the absence/presence of background ions described Langmuir isotherm model \((R^2 \geq 0.98)\) and D-R isotherm model \((R^2 \geq 0.98)\) relatively better than Freundlich model \((R^2 \geq 0.92)\) with Langmuir monolayer sorption capacity of NICMO to be 55.513 (± 2.235) mg. g⁻¹ in the absence of any co-occurring ion at background.
5. Range of values of standard enthalpy ($\Delta H^\circ$) indicated physio-sorption to be the actual nature of the reactions and the negative values of Gibb's free energy ($\Delta G^\circ$) confirmed the overall spontaneity of the reactions in the given direction.

6. Excellent desorption established weak interaction of As(V) over the given oxide surface.

7. Interpretation of X-ray diffraction pattern and spectral data confirmed the incorporation of As(V)-O bond in the adsorbed sample.

5.4.3. Section-C: Studies on As(III) sorption behaviour on NICMO surface from the aqueous solution in the presence of some major groundwater occurring ions

**5.4.3.1. Effect of heat treatment temperature on NICMO and As(III) sorption**

Fig. 5.19 shows the variation of As(III) sorption amount per gram of NICMO ($q_e, \text{ mg. g}^{-1}$) against heat treatment temperature on the material. It was found that the values of sorption capacity ($q_e$) increased with enhancement of calcined temperature on NICMO from 100° C to 200° C, and that decreased steadily from 200° C to 500° C. The increase in $q_e$ was due to the elimination of the physically attached (H-bonded) and coordinated water molecules from the solid surfaces with increasing temperature of calcination from 100° C to 200° C. This led to the increase of surface active M-OH sites per unit area causing increase of $q_e$ with increasing temperature on NICMO till 200° C.
Figure 5.19: Variation of As(III) removal capacity at pH$_i$ 7.0 ± 0.2 with increasing incineration temperature on NICMO.

Further increase of temperature beyond 200° C caused decrease in the value of $q_e$ due to the decrease of surface active M-OH sites with elimination of water by dehydroxylation reactions.

$\text{-M-OH-OH} \rightarrow \text{-M-OH} + \text{H}_2\text{O}^\uparrow$ (M-OH sites available for sorption increased with elimination of physically attached water incinerating up to 200° C)

$2\text{M(OH)}_3 \rightarrow \text{M}_2\text{O}_3 + 3\text{H}_2\text{O}^\uparrow$ (M-OH sites available for sorption decreased incinerating above 200° C).

5.4.3.2 Effect of pH on As(III) sorption

Fig. 5.20 shows the variation of As(III) adsorption amount ($q_e$, mg. g$^{-1}$) by NICMO versus initial pH (pH$_i$) of As(III) solution. It showed that $q_e$ increased with increasing pH$_i$ from 3.0 to 7.0, and decreased at pH$_i$ above 7.0 showing a maxima at pH 7.0 from As(III) solutions of initial concentration ($C_0$) 4.8 and 9.6 mg .L$^{-1}$ at 303 K. Thus, the pH$_i$ optimized was 7.0 for conducting the kinetics and equilibrium experiments for As(III) removal by NICMO.
Figure 5.20: As(III) removal capacity of NICMO versus pH$_j$ at 30 °C.

Lower percentage of As(III) removal at pH$_j$ below 7.0 and above 7.0 than at pH$_j$ 7.0 was due to the Columbic repulsion between like charges of solute and solid surface, and solubility loss of the material. Mechanism of pH dependent As(III) removal by NICMO was proposed that was found to be similar to that suggested by Sverjensky and Fukshi [43] as given in subsection 3.4.3.3 of chapter-3.

5.4.3.3 Kinetic analysis of As(III) sorption

Fig. 5.21 (a, b) demonstrates the variation of time dependent As(III) adsorption amount ($q_t$, mg. g$^{-1}$) of NICMO versus reaction time ($t$, mins) at pH$_j$ = (7.0 ± 0.2) and T = (303 ± 1.0) K from As(III) solution of $C_0 = 4.8$ mg.L$^{-1}$ in the absence/presence of background ions such as Cl$^-$, SO$_4^{2-}$, HCO$_3^-$, PO$_4^{3-}$ and SiO$_3^{2-}$. It had indicated that the time required to reach the plateau was ~ 1.5 hours and, about 90 % of the adsorbed amount ($q_e$, mg. g$^{-1}$) took place within 40 minutes of the reaction time.
The pH dependence on As(III) removal was due to the differences in arsenic adsorption in terms of ionization of both adsorbates and adsorbents.[43, 44]

Aqueous As(III) protonation equilibria can be probably represented as

\[
\text{As(OH)}_3^0 = \text{AsO(OH)}_2^- + \text{H}^+; \quad \log K = -9.17
\]

So, fast initial reaction up to time, \( t = 40 \text{ min} \) was due to the rapid diffusion of As(OH)_3 through the boundary surface of liquid-solid interface by Columbic attraction.

Figure 5.21: Plot of \( q_t \) (mg.g\(^{-1}\)) against time, \( t \) (min.) and non linear fit of kinetic data with (a) pseudo-first order and (b) pseudo-second order equations. \( C_0 = 4.8 \text{ mg As(III). L}^{-1} \), NICMO dose = 2.0 g.L\(^{-1} \), \( T = 303 \text{ K} \) and \( pH_f = 7.0 \pm 0.2 \). Ions added with As(III) solution: ■ no ion, • SO\(_4\)^{2-}, ▲ Cl\(^-\), ▼ HC\(_3\)O\(_3\)^-, ● PO\(_4\)^{3-}, ◄ SiO\(_3\)^{2-}.

The slow reaction at \( t > 40 \text{ min} \) was presumably due to the columbic and steric hindrance between the solute species sorbed at initial stages over NICMO surface and the remaining
solute in solution or the liquid phase reduced concentration of solute that failed to cross over the diffusion barrier at solid-liquid boundary layer similar to the result obtained by Gupta et al. [45]

Table 5.10: Kinetic model parameters for As(III) sorption by NICMO at pH 7.0 (± 0.1) and temperature (T) = 30 (±1) °C in the presence of some co-occurring ions [C₀ = 4.8 mg As (III) L⁻¹].

<table>
<thead>
<tr>
<th>Ion present</th>
<th>Pseudo-first order, ( q_t = q_e (1-e^{-k_1 t}) ), kinetic parameters</th>
<th></th>
<th>Pseudo-second order, ( q_t = k_2 q_e^2 (1+t.k_2.q_t) ), kinetic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>with As(III)</td>
<td>( k_1 \times 10^{-1} )</td>
<td>( q_e )</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>PO₄²⁻</td>
<td>2.92±0.066</td>
<td>2.117</td>
<td>0.955</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>2.903±0.046</td>
<td>2.200</td>
<td>0.977</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3.089±0.048</td>
<td>2.221</td>
<td>0.980</td>
</tr>
<tr>
<td>SiO₃²⁻</td>
<td>3.146±0.033</td>
<td>2.298</td>
<td>0.991</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.695±0.024</td>
<td>2.286</td>
<td>0.992</td>
</tr>
<tr>
<td>No other ions</td>
<td>2.394±0.031</td>
<td>2.297</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The values of experimental \( q_t \) were found to be more close to the modeled \( q_t \) of pseudo-second order kinetics, indicating pseudo-second order type of adsorption reaction actually taking place. Again, the values of \( q_t \) obtained in the absence of either ion were higher than

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that in the presence of any competing ion added at background, indicating adverse influence of the ions on As(III) adsorption by NICMO (Table-5.10).

However, the results indicated that the adverse effects of Cl\(^-\) and SiO\(_3^{2-}\) were poor to that of SO\(_4^{2-}\), PO\(_4^{3-}\) and HCO\(_3^-\) given in Table-5.10.

### 5.4.2.4. Diffusion Kinetics

Theoretical aspects of the used functional relationship for the diffusion kinetics have already been discussed in sub-section 5.4.2.4 of chapter 5.

![Figure 5.22: Modeled Weber-Morris plots over the range of contact time for intra-particle diffusion kinetics of As(V)-sorption by NICMO in presence of some background ions. Ions added with As(III) solution: ■ no ion, • SO\(_4^{2-}\), ▲ Cl\(^-\), ▼ HCO\(_3^-\), ♦ PO\(_4^{3-}\), ◄ SiO\(_3^{2-}\).](image)

Fig. 5.22 shows the variations of \(q_t\) (mg. g\(^-1\)) against \(t^{0.5}\) (Weber and Morris plot) for removal of As(III) by sorption on NICMO. It was found that the plots were not straight lines with zero
intercept. Instead, they could be described by joining 'two straight lines. Thus, RCS of As(III) sorption reactions might be controlled by either boundary layer (film) diffusion or multistage phenomenon.

Taking the rate constant values from pseudo-second order model (best fit) equation (2.8), time for 50 % sorption reaction \( t_{0.5} \) was calculated, and used to calculate the values of diffusion coefficients. Values \( (\text{cm}^2 \cdot \text{s}^{-1}) \) of \( D_p \) and \( D_f \) calculated were \( (1.58 \text{ to } 2.43) \times 10^{-9} \) and \( (0.48 \text{ to } 2.27) \times 10^{-9} \) (Table 5.2.5) in the absence or presence of ground water occurring ions at background, respectively. Values of \( D_p \) were of the order \( 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1} \), which was about 100 times greater than \( 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1} \) irrespective of the tested ion added to As(V) solution. Again, the values of \( D_f \) were found to be of the order \( 10^{-9} \text{ cm}^2 \cdot \text{s}^{-1} \), which was also outside the range.

**Table-5.11: Pore and Film diffusion coefficients calculated for As(III) sorption reaction with NICMO at \( pH_i = 7.0 \pm 0.2 \) and \( T = 30(\pm 1) \degree C. \)

<table>
<thead>
<tr>
<th>As(III) + Ion added</th>
<th>Half life time for each Ion, ( t_{0.5} (\times10^3) ) (sec)</th>
<th>Pore diffusion coefficients, ( D_p \ (\times10^{-9}) )</th>
<th>Film diffusion coefficients, ( D_f \ (\times10^{-9}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_3)(^-)</td>
<td>4.28</td>
<td>2.43</td>
<td>0.482</td>
</tr>
<tr>
<td>SO(_4)(^2-)</td>
<td>4.609</td>
<td>2.257</td>
<td>1.341</td>
</tr>
<tr>
<td>HCO(_3)(^-)</td>
<td>5.063</td>
<td>2.054</td>
<td>1.73</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>5.261</td>
<td>1.977</td>
<td>1.175</td>
</tr>
<tr>
<td>PO(_4)(^3-)</td>
<td>5.447</td>
<td>1.909</td>
<td>2.27</td>
</tr>
<tr>
<td>No ion</td>
<td>6.601</td>
<td>1.576</td>
<td>0.624</td>
</tr>
</tbody>
</table>

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Thus, RCS for As(V) sorption reactions with NICMO in the absence/presence of investigated groundwater occurring ions at background were neither controlled by intra-particle nor by boundary-layer diffusion phenomenon. Therefore, it can be concluded that the present reaction was a multi-stage process, which was found to be different from the result reported by Zhang [46] but similar to that reported by Gupta and Ghosh [29] and Gupta et al [30].

5.4.3.5. Equilibrium Modeling

A more systematic and quantitative way of performance judgement of reaction can be ascertained via isotherm analysis of equilibrium data.

Fig. 5.23 (a, b) show the variations of equilibrium capacity, $q_e$ (mg.g$^{-1}$) versus equilibrium concentration, $C_e$ (mg.L$^{-1}$) of As(III) sorption by NICMO at pH$_i$ = 7.0 ± 0.2 and T = (303 ± 1.0) K in the absence/presence of ions at background specified elsewhere. To ascertain the mechanism, the equilibrium data were analyzed by Langmuir (eq. 3) and Freundlich (eq. 4) isotherm model equations with non-linear regression fit method and model parameters are estimated (Table-5.12).

Well fits of the equilibrium data with Langmuir model indicated that the adsorption sites on NICMO surface were homogeneous, and equally accessible to all the solute species at 303 K.
Figure 5.23: Plot of equilibrium sorption data of As(III) removal by NICMO at pH = 7.0 (± 0.2) and T = 303 (± 1.0) K in presence of some ions, and non-linear fits of the data with (a) Langmuir and (b) Freundlich, model equations. Ion added with As(III) solution at background: ■ no ion, • SO$_4^{2-}$, ▲ Cl$^-$, ▼ HCO$_3^-$, ● PO$_4^{3-}$, ◄ SiO$_3^{2-}$.

It is clear that doping of cerium largely enhanced the adsorption capacity of iron oxide, which is in accordance with the enhanced specific surface area (SSA) of this binary system. Besides the increase of surface area, cerium doping also increases the amount of sorption active sites on iron oxides which will contribute to the enhancement of As(III) sorption performance. According to the surface complex model theory, hydroxyl groups on the surface of metal oxides are the active sorption sites for arsenite as suggested by Li et al [47].
### Table-5.12: Isotherm parameters estimated by the non-linear fit method of equilibrium As(III) sorption data on NICMO at pH_t=7.0 (± 0.2) and T = 30 (±1) °C.

<table>
<thead>
<tr>
<th>Ions present</th>
<th>Freundlich Isotherm Parameters.</th>
<th>Langmuir Isotherm Parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R^2 ) ( x^2 ) ( K_f ) (mg. g(^{-1})) ( n )</td>
<td>( R^2 ) ( x^2 ) ( q_m ) (mg.g(^{-1})) ( K_L ) (×10(^{-2}))</td>
</tr>
<tr>
<td>As(III) with</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO(_4^{3-})</td>
<td>0.943 29.157 10.150±0.846 2.469</td>
<td>0.993 3.381 64.851±8.419 7.219±0.032</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>0.951 35.273 17.293±2.722 3.322</td>
<td>0.991 6.547 67.303±2.018 17.660±0.023</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>0.971 20.583 12.339±1.890 2.663</td>
<td>0.98 14.541 71.347±4.097 8.760±0.020</td>
</tr>
<tr>
<td>SiO(_3^{2-})</td>
<td>0.975 15.913 9.129±1.559 2.373</td>
<td>0.984 10.032 75.053±4.710 4.497±0.009</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.923 66.451 15.778±3.481 2.445</td>
<td>0.99 8.291 83.061±0.967 14.141±0.020</td>
</tr>
<tr>
<td>No other ions</td>
<td>0.963 28.884 9.470±1.987 2.237</td>
<td>0.980 16.017 86.293±6.884 4.268±0.010</td>
</tr>
</tbody>
</table>

#### 5.4.3.6. Mean sorption energy

Mean sorption energy (\( E_{DR} \), kJ. mol\(^{-1}\)), which could help to predict the type of sorption reaction, has been defined elsewhere including the parameters which are related to Dubinin-Radushkevich (D-R) equations (2.14-2.16). Values of D-R constant (\( K_{D-R} \)) were calculated from the slope of linear plots of \( \ln Q_e \) versus \( \varepsilon^2 \) (Fig. 5.24). Using the estimated values of \( K_{D-R} \), the values of \( E_{DR} \) were calculated and presented in Table-5.13.
Figure 5.24: Dubinin-Radushkevich (D-R) isotherm plot of As(III) sorption on NICMO at pH 7.0 ± 0.1 and at 303 ± 1.0 K in the presence of different ions at background: ■ no ion, ● SO₄²⁻, ▲ Cl⁻, ▼ HCO₃⁻, ♦ PO₄³⁻, ◄ SiO₃²⁻.

Table 5.13: Dubinin-Radushkevich (D-R) isotherm parameters evaluated for As(III) sorption by NICMO at pH = 7.0 (± 0.2) and at T = 30 (±1) °C.

<table>
<thead>
<tr>
<th>Ion with As(V) in solution</th>
<th>R²</th>
<th>SD</th>
<th>E_DR / (kJ. mol⁻¹)</th>
<th>-K_{D-R} (×10⁻³) / (mol².kJ⁻²)</th>
<th>Q_m / (mol.Kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No ion</td>
<td>0.964</td>
<td>0.209</td>
<td>10.325</td>
<td>4.69</td>
<td>3.695</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.955</td>
<td>0.246</td>
<td>10.588</td>
<td>4.46</td>
<td>4.928</td>
</tr>
<tr>
<td>SiO₃²⁻</td>
<td>0.988</td>
<td>0.111</td>
<td>10.403</td>
<td>4.62</td>
<td>3.143</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.972</td>
<td>0.142</td>
<td>12.347</td>
<td>3.28</td>
<td>2.413</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.968</td>
<td>0.185</td>
<td>12.004</td>
<td>3.47</td>
<td>2.113</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.967</td>
<td>0.194</td>
<td>11.07</td>
<td>4.08</td>
<td>3.041</td>
</tr>
</tbody>
</table>
It had been seen that the values of $E_{dr}$ ranged within 10.0 to 12.5 kJ.mol$^{-1}$ for As(III) sorption by NICMO in the absence/presence of background ions (given in Table-5.13), indicating borderline of ion exchange/chemisorption phenomena of As(III) over NICMO.

5.4.3.7. Thermodynamic parameters

Thermodynamic parameters for As(III) sorption reaction over NICMO were estimated using standard relations shown in chapter-2.

Thermodynamic constant ($K_a$) was calculated inserting experimental $q_e$ and $C_e$ values at $T = (283, 293, 303, 313$ and $323)$ K and pH$_t = (7.0 \pm 0.1)$, respectively, in equation (2.20).

According to equation (2.21), the plots of $\log_{10} (q_e/C_e)$ against $(1/T)$ (Fig. 5.25) were a straight line with positive intercepts.

Figure 5.25: Plot of $\ln (q_e/C_e)$ versus $(1/T/ K^{-1})$ for As (III) sorption by NICMO from $C_0 = 4.8$ mg. L$^{-1}$ at pH $7.0 \pm 0.1$ and $T = 303$ K in the presence of different ions: ■ no ion, • SO$_4^{2-}$, ▲ Cl$^-$, ▼ HCO$_3^-$, ◆ PO$_4^{3-}$, ◀ SiO$_3^{2-}$
From the slope and intercept of the plots, the parameters such as entropy and enthalpy changes ($\Delta S^0$ and $\Delta H^0$) were calculated and summarized in (Table-5.14). Taking the values of $\Delta S^0$ and $\Delta H^0$, standard free energy change ($\Delta G^0$) were calculated (Table-5.14) using literature available standard relation.

**Table-5.14: Thermodynamic parameters estimated for As(III) sorption by NICMO at different reaction temperatures (K) at pH, 7.0 (± 0.2) in presence of some co-occurring ions [C₀ = 4.8 mg As (III) L⁻¹]**

<table>
<thead>
<tr>
<th>Ion added</th>
<th>$+\Delta S^0$ (kJ.mol⁻¹ K⁻¹)</th>
<th>$+\Delta H^0$ (kJ.mol⁻¹)</th>
<th>(-$\Delta G^0$) (kJ.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)+</td>
<td>283 K</td>
<td>293 K</td>
<td>303 K</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.148</td>
<td>21.059</td>
<td>20.826</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.170</td>
<td>25.501</td>
<td>22.694</td>
</tr>
<tr>
<td>SiO₃²⁻</td>
<td>0.169</td>
<td>26.114</td>
<td>21.810</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.177</td>
<td>28.493</td>
<td>21.485</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.175</td>
<td>28.771</td>
<td>20.725</td>
</tr>
<tr>
<td>No ion</td>
<td>0.204</td>
<td>35.435</td>
<td>22.354</td>
</tr>
</tbody>
</table>

It was found that the reactions in the absence or presence of ions at background were endothermic ($\Delta H^0$ = positive) and $\Delta H^0$ was maximum in the absence of any ion in the system.
Values of $\Delta H^\circ$ (kJ.mol$^{-1}$) ranged from 21.059 to 35.435 that indicated chemo-sorption type of reaction actually occurring in all the systems under study. Sorption process gets more favorable with increase of temperature as evidenced from the Gibb's free energy values with various ions playing its role in the reaction.

5.4.3.8. Desorption study

Fig. 5.26 represents the percentage of arsenic desorption of As$^{\text{III}}$-NICMO versus different alkali concentrations. It was found that the desorption efficiency of KOH was better than that of NaOH and the desorption percentage increased with increasing concentration. However, highest 63.41% of sorbed arsenic was desorbed by 2.0 (M) KOH solutions. Average desorption of sorbed As(III) from the oxide surface indicated strong binding of As(III) to oxide surface as already explained by chemo-sorption concept taking place in the experimental system. More than fifty percent desorption of NICMO indicated another cycle of reuse of this fixed bed packed column for field application.

![Figure 5.26: Desorption study arsenic with variation of alkali solutions](image)

Figure 5.26: Desorption study arsenic with variation of alkali solutions
Values of $E_{DR}$ that ranged within 10.0 to 12.5 kJ mol$^{-1}$ for As(III) sorption by NICMO in absence/presence of background ions also established the degree of strong binding of As(III) by the material surface.

5.4.3.9. Experimental evidences of As(III) sorption over NICMO surface.

5.4.3.9.1 Scanning and transmission electron microscopic images of As$^{III}$-NICMO.

A slight morphological change visible in the images at microscopic level indicated uneven distribution of large sized agglomerates over the entire surface partially suppressing the small scale agglomeration [Fig. 5.27 (i)].

![SEM images of As(III) sorbed NICMO](image1.png)

![SEM images of As(III) sorbed NICMO with EDAX data](image2.png)

Figure 5.27: Scanning electron microscopic (SEM) image of (i) As(III) sorbed NICMO (As$^{III}$-NICMO) and (ii) As(III) sorbed NICMO (As$^{III}$-NICMO) with EDAX data.
Demonstration of SEM image with EDAX analyzed data [Fig. 5.27 (ii)] showed an irregular surface morphology of As\textsuperscript{III}-NICMO. EDAX analyzed data showed that the mean percentages of oxygen, iron, cerium and arsenic at the marked sites of As\textsuperscript{III}-NICMO surface were 21.58, 17.17, 54.6 and 6.66, respectively, indicating the empirical composition to be \( \text{Fe}_{3.4}\text{Ce}_{4.3}\text{As}_{1.0}\text{O}_{15} \). The changes of composition and morphology of As(III) sorbed NICMO had been revealed by comparing with that of NICMO (Fe\textsubscript{1.1}Ce\textsubscript{0.7}O\textsubscript{7.6}) [Fig. 5.5 (b)], which was due to the incorporation of As(III) as (HO\textsubscript{3})\textsubscript{2}As at pH ~ 7.0.

Agglomeration of the crystallite particles in NICMO (Fig. 5.6) was not distinctly visible in As\textsuperscript{III}-NICMO sample (Fig. 5.28). In fact, the concept of particle agglomeration was not evident here but an overall smearing of arsenic over the adsorbent surface almost covering up the pictorially dark adsorbent sites.
5.4.3.9.2 X-ray diffraction analysis of synthetic $\text{As}^{\text{III}}$-NICMO

The sharpness of the peaks of $\text{As}^{\text{III}}$-NICMO considerably reduced and large background noise became evident, causing decrease of degree of crystallinity in $\text{As(III)}$ adsorbed material presumably due to the surface of NICMO strongly interacting with $\text{As(III)}$ species.

After $\text{As(III)}$ sorption, peak positions got shifted so also the crystal structure of the material and the peak intensity almost reduced to half. However, the peaks observed in $\text{As(III)}$ sorbed sample [$\text{As}^{\text{III}}$-NICMO, Fig. 5.29] were at 29.4°, 33.14°, 34.37°, 48.42°, 57.63° and 78.9° respectively, which were compared with the standard diffraction data base of JCPDS files. Surprisingly, some unexpected and interesting results were obtained while assigning and rationalizing the peaks. The peak at 33.14° was retained in the XRD pattern of $\text{As}^{\text{III}}$-NICMO sample which was due to $\alpha$-$\text{Fe}_2\text{O}_3$ phase of Hematite variety having rhombohedra structures corresponding to reflection from (1 0 4)
planes. The peak at 34.37° developed due to As$_2$O$_3$ phase of monoclinic variety having Claudetite II structures corresponding to reflection from (1 0 3) plane.

Contrary to our expectation, the peaks at 48.42° and 57.63° developed due to As$_2$O$_5$ phase with orthorhombic structure corresponding to reflection from (1 4 1) and (3 4 1) planes respectively. The peaks at 29.4° and 78.9° were due to the presence of Ce$_2$O$_3$ phase with hexagonal structure corresponding to reflection from (0 0 2) and (0 0 5), respectively.

5.4.3.9.3. Interpretation of the spectral (FTIR) data and analysis of NICMO and As (III) sorbed NICMO (As$^{\text{III}}$-NICMO). Overview of probable mechanism.

From the analysis of FTIR spectra of (a) NICMO and (b) As$^{\text{III}}$—NICMO [Fig. 5.30], it was found that

- The broad stretching adsorption bands of O-H at wave number 3650 to 3250 cm$^{-1}$ of pure mixed oxide (spectrum-a) became somewhat weak in As$^{\text{III}}$-NICMO (spectrum-b).
The area occupied by the stretching and bending absorption bands of O-H group in spectrum-a of NICMO slightly reduced in Fig. 5.30 indicating proportionate disappearance of some O-H group from the solid surface on As(III) adsorption as seen from spectrum-b of As$^{III}$-NICMO.

Two additional well-defined sharp band at $\nu \sim 1375$ and $1060 \text{ cm}^{-1}$ presumably due to the symmetrical and asymmetrical bending of MOH group in spectrum-a of NICMO completely disappeared in As(III) sorbed material (spectrum-b).

Surprisingly, the appearance of distinct and well-defined band at $\nu \sim 821 \text{ cm}^{-1}$ in spectrum-b does not correspond to As(III)-O stretching vibration mode in AsO$_3^2-$ contrary to our expectation. This anomalous spectral behavior was probably due to the incorporation of As(III)-O bond in the adsorbed sample that had been partially oxidized to As(V)-O.

Figure 5.30: FTIR spectra of (a) NICMO and (b) As(III) sorbed NICMO (As$^{III}$-NICMO).
5.43.9.4. Cyclic voltammetry

Cyclic voltammetry is a versatile electrochemical technique for a quick search of redox couples present in a system. During the forward scan starting from negative to positive (-0.5 V to +0.5 V), if the potential of the working electrode is more positive than that of any redox couple present in the solution, then, the corresponding species in the couple is likely to be oxidized (i.e., electrons flowing away from the electrode) and under such circumstances the potential is referred as $E_{ox}$.

Similarly, if the reverse scan of the potential (+0.5 V to -0.5 V) indicates working electrode potential to be more negative compared to the reduction potential of the redox couple, then, reduction (i.e., electrons flowing away from the electrode) is likely to take place and the corresponding potential is referred as $E_{red}$.

It is quite interesting to note that the potential of pure NICMO ($E_{ox}/E_{red} = 0.158V/-0.261V$) shifted to lower potential ($E_{ox}/E_{red} = 0.038V/-0.156V$) after 10 minutes of sorption reaction with As(III) solution. Finally, equilibration with As(III) solution after a time interval of two hours cause further depression of redox couple potential to a lower value ($E_{ox}/E_{red} = 0.023V/-0.141V$) creating a small potential difference of $\Delta E = 0.164$ V between $E_{ox}$ and $E_{red}$ compared to the relative high potential difference of pure NICMO state ($\Delta E = 0.419$ V) indicating rapid, spontaneous electron transfer kinetics.

Thus, more positive $\Delta E$ value of pure NICMO relative to the redox couple in the system accounts for the oxidation of equilibrated As(III) present in the reaction medium.
Higher positive fractional value of transferred electron (n) in the redox reaction estimated from the relation ($\Delta E = 59/n$ mV) undoubtedly added weightage to the prediction of oxidation of As(III) to its higher oxidation state As(V).

Figure 5.31: Current (A) against potential (Volt) of (a) pure NICMO, (b) 10 min reaction of NICMO with As(III) and (c) 2 hour equilibration of NICMO with As(III).

Thus, from the above observations, it can be concluded that Cerium(IV) itself being a good oxidizing agent ($\text{Ce}^{4+}/\text{Ce}^{3+} = 1.72$) in acidic medium oxidizes the surface sorbed As(III) to As(V) ($\text{As}^{3+}/\text{As}^{5+} = 0.56$) itself getting reduced to $\text{Ce}^{3+}$ according to the underlying redox reaction.

$$\text{As}^{3+} + 2\text{Ce}^{4+} = \text{As}^{5+} + 2\text{Ce}^{3+}$$
5.4.3.10 Probable mechanism

The comparative less disappearance of OH group from NICMO on As(III) sorption supports two facts. The expected disappearance of some O-H group from the solid surface on As(III) sorption with the further introduction of O-H group into the system at the later stages of the reaction. This agreed well with the increase of pHf over pHi during sorption of As(III) over the sorbent surface.

Thus, As (III)-sorption mechanism taking place under sufficient time lag is explained by the increase of pH, XRD, FTIR and cyclic voltammetry analysis as described below.

\[
\begin{align*}
S_{\text{Fe-Ce}} + \text{OH} + &\text{As(OH)}_3 \rightarrow S_{\text{Fe-Ce}} - \text{O} - \text{As(OH)}_2 + \text{H}_2\text{O} \\
S_{\text{Fe-Ce(OO)}} + &\text{As(III)} \rightarrow S_{\text{Fe-Ce(OO)}} - \text{As(III)} \\
S_{\text{Fe-Ce(OO)}} - &\text{As(III)} + \text{H}_2\text{O} \rightarrow S_{\text{Fe-Ce(OO)}} - \text{As(V)} + \text{OH}^- \\
S_{\text{Fe-Ce}} + &\text{As(V)} \rightarrow S_{\text{Fe-Ce}} - \text{As(V)}
\end{align*}
\]

5.4.3.11 Conclusion

1. pHi optimized was 7.0 for conducting the kinetics and equilibrium experiments for As(III) removal by NICMO and pH dependent As(III) removal mechanism was similar to that apprehended by Sverjensky and Fukshi model.

2. Values of experimental q_i were found to be more close to the modeled q_i of pseudo-second order kinetics, indicating pseudo-second order type of sorption reaction actually taking place in single as well as binary systems taken into consideration.
3. Well fits of the equilibrium data with Langmuir model indicated that the sorption sites on NICMO surface were homogeneous, and equally accessible to all the solute species at 30°C.

4. Chemo-sorption is the actual nature of the reaction taking place with the sorption process getting more favorable with the increase of temperature.

5. Microscopic images prove to be quite handy in quantifying the degree of change of morphology and composition of the sorbent surface after As(III) binding.

6. Interpretation of experimental evidences of As(III) sorption over NICMO surface confirmed oxidation of surface adsorbed As(III) to As(V) in a thermodynamically controlled sorption reaction.

7. Average desorption of adsorbed As(III) from the oxide surface and the values of $E_{DR}$ obtained in absence/ presence of background ions established the degree of strong binding of As(III) to the given sorbent surface.

Section-D: Application of synthetic nano-structured cerium(IV) associated iron(III) bimetal mixed oxide (NICMO) packed fixed-bed column for arsenic removal from natural ground water system.

5.4.4 Application of NICMO to fixed bed column in the removal of arsenic from ground water: prediction of column performance.

5.4.4.1 Source of the field sample

Ground water collected from a tap in College Street near Presidency College Campus and analyzed for arsenic. After reproducing the data thrice, the value of arsenic was confirmed to
be $1.5 \times 10^{-3}$ mg.L$^{-1}$. The ground water sample was then, spiked with arsenic solution until the initial concentration reached $1.3 \times 10^{-1}$ mg.L$^{-1}$.

Fixed-bed column experiments were conducted using uniformly packed NICMO in glass tubes of internal diameter (i. d.) 0.7 cm and length 25.0 cm up to the depth, as desired, over glass wool sheet. Here, packing of NICMO was done with proper precaution to avoid void spaces, channels and cracks in beds.

This water sample was passed through NICMO packed fixed bed for filtration (flow rate: 1.0 mL. min$^{-1}$). The filtered water was collected in 100 mL fractions and analyzed for the residual concentration of arsenic.

5.4.4.2. Application of NICMO to column experiment.

5.4.4.2.1. Effect of bed depth (absorbent mass) on breakthrough curve

Dependence of bed depth on the breakthrough curve had been investigated by passing arsenic spiked ($0.13$ mg. L$^{-1}$) ground water through three NICMO columns made by packing with 3.0, 4.0 and 5.0 g of the material. The column heights became 4.0, 5.0 and 6.0 cm, respectively, at a flow rate of 1 ml. min$^{-1}$. The breakthrough curve was shown in Fig. 5.32
Figure 5.32: Effect of bed-depth on breakthrough curve for arsenic sorption by NICMO at pH 7.0

It was observed from Fig. 5.32 that the shape and the gradient of the curves were somewhat similar with varying bed depth. The breakpoint (arsenic concentration: 0.01 mg. L$^{-1}$) reached faster in the columns with lower bed depth. The higher uptake and gradual increase in the slope of the breakthrough curves were observed at the initial stage of the curves. This gradual increase continued till the break point of the curve, followed which there was a rapid increase in effluent concentration of arsenic after break point. The columns with lower bed depth got saturated faster than the higher ones. The break through volumes for the columns with bed depth 4.0, 5.0 and 6.0 cm were 1200, 2000 and 3000 ml, respectively. This was due to the increase in the empty bed contact time (EBCT) with increasing bed depth. EBCT for columns with bed depth 4.0, 5.0 and 6.0 cm were 1.54, 1.925 and 2.31 min, respectively.

With increased EBCT, the diffusion process became more effective and, the breakthrough volume ($V_b$) or breakthrough time ($t_b$) reached later. With increasing EBCT, the contact time
between adsorbate and adsorbent increased and a higher amount of adsorbate got adsorbed to the bed and hence, \( V_b \) increased with the increase of bed depth.

5.4.4.2.2. Effect of flow rate on the breakthrough curve

The results demonstrated in Fig. 5.33 showed the influence of the effluent flow rate on the breakthrough curve of arsenic removal at a fixed bed depth (5.0 cm) of NICMO column.

![Graph showing the effect of flow rate on breakthrough curves for arsenic sorption by NICMO at pH 7.0](image)

Figure 5.33: Effect of flow-rate on the breakthrough curves for arsenic sorption by NICMO at pH 7.0

It was found that the breakthrough volumes \( V_b \) (ml) for the effluent flow rate (ml.min\(^{-1}\)) 1.0, 2.0 and 4.0 were 2000, 1500 and 1000 respectively. Results showed that the decrease of flow rate increased the breakthrough volume or the breakthrough time \( (t_b) \) which was due to the decrease of EBCT (min) from 1.925, 0.963 and 0.481 respectively. Lower the EBCT, less effective is the diffusion process resulting in lower sorption capacity. Thus, the adsorbent needs more time to bind to the metals effectively. The results also showed that the plateau of the breakthrough curve reached faster with decreasing flow rate. This was due to the fact that
the solute in the mobile phase spent more contact time with the adsorbent surface with decreasing flow rate in the stationary phase and, thus the adsorption front delayed in reaching the bottom of the column

5.4.4.2.3 Effect of input feed solution concentration on the break through curve

Effect of input concentration (C₀) of As(III) on the breakthrough curves showed that (Fig. 5.34) the break volume (Vₜ) reduced (3.5, 2.0 and 1.0 L) with increasing C₀ (65.0, 130.0 and 260.0 µg.L⁻¹) despite EBCT value (1.925 min) remaining constant for the fixed bed depth 5.0 cm.

![Breakthrough curve graph](image)

Figure 5.34: Effect of arsenic concentration in input feed solution on the breakthrough curves for arsenic sorption by NICMO at pH 7.0

This observation was due to the appearance of fresher solute per unit surface area of the stationary bed at an effluent rate 1.0 mL.min⁻¹ [48-52]. As the rate of diffusion of solute into the interior of the fixed solid bed should not theoretically vary for a given EBCT, so the plateau in the breakthrough curves should attain identical position despite the increase of
solute load per unit surface. The plateau of the breakthrough curve reached earliest for the
lowest concentration \(C_0\), because of the fast attainment of output concentration \(C_t\) to the
input \(C_0\) value. The unexpected late attainment of the plateau at higher loading of solute per
unit area on the stationary phase was due to the delayed equality of \(C_t\) with \(C_0\) \((C_t/C_0 = 1.0)\).

5.4.4.3. Fitting of different models on the breakthrough curves

The breakthrough curves \([48]\) obtained by plotting \(C_t/C_0\) values against time (min), were
subjected to analysis using two common models, viz. Thomas model and Adams-Bohart
model given by equation 2.17 and 2.18 to get an insight of the sorptive behaviour of arsenic
used in this study. Non-linear fitting of the breakthrough curves for the effect of variation of
bed depth, flow rate and arsenic concentration in feed solution were shown in Fig. 5.32 to
5.34. Some parameters for the water quality were analyzed and summarized in Table-5.15 (a).
Also, their corresponding values after filtration through fixed column bed of different bed
heights, flow rate and input solution concentration at breakpoint were collectively
summarized in Table-5.15 (b). The model parameters were evaluated using non-linear
regression analysis and presented in Table-5.15(c).

Table-5.15(a): Some observed water quality parameters (mg.L\(^{-1}\), except pH) of the field sample
before treatment through the fixed bed of NICMO packed column.

<table>
<thead>
<tr>
<th>As (total)</th>
<th>pH</th>
<th>Fe(^{2+})</th>
<th>F(^-)</th>
<th>HCO(_3)(^-)</th>
<th>Hardness</th>
<th>Ca(^{2+})</th>
<th>Cl(^-)</th>
<th>TDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.002</td>
<td>7.22</td>
<td>0.108</td>
<td>0.245</td>
<td>498</td>
<td>112</td>
<td>68</td>
<td>376</td>
<td>628</td>
</tr>
</tbody>
</table>
Table-5.15(b): Some analyzed water quality parameters (mg. L⁻¹) of arsenic spiked field sample after filtration through the fixed bed of NICMO packed column at breakthrough point. (arsenic concentration: 0.01 mg. L⁻¹)

<table>
<thead>
<tr>
<th>Water quality Parameters</th>
<th>Depth (cm) of fixed bed NICMO packed column</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>Fe²⁺ (×10⁻²)</td>
<td>1.30</td>
</tr>
<tr>
<td>F⁻ (×10⁻¹)</td>
<td>1.90</td>
</tr>
<tr>
<td>HCO₃⁻ (×10⁻³)</td>
<td>2.66</td>
</tr>
<tr>
<td>Hardness (×10⁻¹)</td>
<td>5.42</td>
</tr>
<tr>
<td>Ca²⁺ (×10⁻¹)</td>
<td>1.81</td>
</tr>
<tr>
<td>Cl⁻ (×10⁻²)</td>
<td>1.69</td>
</tr>
<tr>
<td>TDS (×10⁻¹)</td>
<td>2.79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water Quality Parameters</th>
<th>Effluent rate (mL.min⁻¹) through NICMO packed fixed bed (6.0 cm) column</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Fe²⁺ (×10⁻²)</td>
<td>0.7</td>
</tr>
<tr>
<td>F⁻ (×10⁻¹)</td>
<td>1.1</td>
</tr>
<tr>
<td>HCO₃⁻ (×10⁻²)</td>
<td>1.68</td>
</tr>
<tr>
<td>Hardness (×10⁻¹)</td>
<td>2.98</td>
</tr>
<tr>
<td>Ca²⁺ (×10⁻¹)</td>
<td>1.05</td>
</tr>
<tr>
<td>Cl⁻ (×10⁻²)</td>
<td>1.03</td>
</tr>
<tr>
<td>TDS (×10⁻¹)</td>
<td>2.41</td>
</tr>
</tbody>
</table>

Table-5.15(b) Continued in next page

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### Table 5.14

<table>
<thead>
<tr>
<th>Water parameters</th>
<th>Spiked As(III) concentration (µg.L⁻¹) in groundwater sample passed through NICMO packed fixed-bed (6.0 cm) column</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>65</td>
</tr>
<tr>
<td>Fe²⁺ (∙10⁻²)</td>
<td>0.43</td>
</tr>
<tr>
<td>F⁻ (∙10⁻¹)</td>
<td>0.42</td>
</tr>
<tr>
<td>HCO₃⁻ (∙10⁻²)</td>
<td>1.14</td>
</tr>
<tr>
<td>Hardness (∙10⁻¹)</td>
<td>0.89</td>
</tr>
<tr>
<td>Ca²⁺ (∙10⁻¹)</td>
<td>0.78</td>
</tr>
<tr>
<td>Cl⁻ (∙10⁻²)</td>
<td>0.73</td>
</tr>
<tr>
<td>TDS (∙10⁻²)</td>
<td>0.82</td>
</tr>
</tbody>
</table>

5.4.4.3.1 Modeling of breakthrough curves for variation of bed depth/adsorbent mass

Fig. 5.32 showed the non-linear fit of the breakthrough data for the variation of bed-depth with (a) Thomas model and (b) Adams-Bohart model. The modeled parameters predicted are demonstrated in Table5.15 (c). It was found that the Thomas model fit described ($R^2 = 0.992$-$0.998$) the breakthrough data better than Adams-Bohart model ($R^2 = 0.83$-$0.926$). Values of the Thomas model rate constant ($k_{TH}$, mL.min⁻¹.mg⁻¹) decreased and the column sorption capacity ($q_0$, mg. g⁻¹) increased with increasing bed depth/adsorbent mass.
Figure 5.32: Model analysis fits of the breakthrough curves having different bed depth/adsorbent mass using (a) Thomas (b) Adams-Bohart model.

Decrease of the Thomas model rate constant ($k_{TH}$) was due to the increase of the mass transport resistance with increasing depth of fixed stationary bed [48-52].

Again, the mass transport resistance is proportional to the axial dispersion and thickness of the liquid film on the particle surface. Thus, the solute in mobile phase came across more available sorption sites with increasing bed height/adsorbent mass, which caused the increase of $q_0$-values of NICMO packed columns.

Fig. 5.32 (b) showed the Adams-Bohart model prediction fits, which satisfactorily obeyed only the later portion of the breakthrough curves. Adams-Bohart model approach was more focused in estimating the characteristic parameters like maximum adsorption capacity ($N_0$) and the kinetic constant ($k_{AB}$) [Table-5.15 (c)].
Analysis showed that there lied a good agreement between the experimental and the modeled values at the particular concentration attained in this experiment. Thus, Adams-Bohart model could only be safely used to describe the later portion of the breakthrough curve, which was limited to the range of the conditions used.

5.4.4.3.2 Modeling of breakthrough curves for the variation of effluent flow rate

Fig. 5.33 demonstrates the model fit of the column performance data with (a) Thomas model and (b) Adams-Bohart model, respectively, with variation of the effluent flow rate/ EBCT for As(III) removal from spiked groundwater. It was found that the fits of the data were better with Thomas model \((R^2 = 0.996-0.997, \chi^2 \times 10^{-3} = 0.4-0.7)\) than Adams-Bohart model \((R^2 = 0.83-0.89, \chi^2 \times 10^{-3} =0.01-0.03)\). The parameters estimated from the model fits were shown in Table-5.15 (c). It had been found that the values of kinetic rate constant \((k_{TH})\) (mL.min\(^{-1}\).mg\(^{-1}\)) for As(III) removal were 7.54, 18.77 and 43.69, respectively, with increasing effluent flow rates from 1.0 to 4.0 mL.min\(^{-1}\). Again, the values of column sorption capacity \((q_0)\) (mg.g\(^{-1}\)) for As(III) removal decreased with increasing flow-rate. The increase of \(k_{TH}\) and the decrease of \(q_0\) were due to the decrease of the mass-transport resistance and EBCT of the solute with the available active sites on the adsorbent surface [48-52]. The low effluent rates of the present investigation suggested negligible effect on the increase of axial dispersion, which was confirmed from the increase of the rate constant \((k_{TH})\) values. Thus, the decrease of EBCT with increasing effluent flow rate enhanced the driving force of mass transfer in the liquid film.
Figure 5.33: Model analysis fits of the breakthrough curves with variation of effluent flow rate using (a) Thomas (b) Adams-Bohart model.

The kinetic constant ($k_{AB}$) and the saturation concentration ($N_0$) values estimated from the non-linear fits of the breakthrough curves with Adams-Bohart model [Fig. 5.33 (b)] were presented in Table-5.15 (c). Despite the overall fits of the breakthrough data with the Adams-Bohart model were comparatively weaker ($R^2 = 0.83-0.89, \chi^2 \times 10^{-3} =0.01-0.03$) than the Thomas model ($R^2 = 0.996- 0.997, \chi^2 \times 10^{-3} =0.4-0.7$) yet the saturation concentration ($N_0$) like column capacity ($q_0$) significantly decreased with the increase of effluent flow rate or decrease of EBCT.

5.4.4.3.3 Modeling of breakthrough curves with the variation of input feed solution concentration

Fig. 5.34 demonstrates the fits of the breakthrough data with the variation of input ($C_0$) feed solution concentration with (a) Thomas model and (b) Adams-Bohart model. The parameters
estimated from the model fits were shown in Table-5.15 (c). It had been seen that the fits of the data with Thomas model \((R^2 = 0.98-0.99, \chi^2 \times 10^3 = 0.68-2.7)\) were better than Adams-Bohart model \((R^2 = 0.89 - 0.96, \chi^2 \times 10^3 = 3.9-16.8)\). Both \(K_{Th}\) and \(k_{AB}\) values [Table-5.15(c)] decreased with increasing \(C_0\) of the feed solution at a fixed EBCT (1.925 min).

![Figure 5.34: Model analysis fits of the breakthrough curves with variation of input feed solution concentration of As(III) using (a) Thomas (b) Adams-Bohart model.](image)

It indicated that NICMO could be an effective material in removing arsenic from the groundwater. It can be rationalized that arsenic removal from groundwater was only possible by surface reaction that reduced the chance of precipitation at this experimental conditions. From the kinetic plots, it was evident that the sorption reactions at the initial stages were very rapid at \(pH \sim 7.0\) and room temperature, making the surface of the adsorbent negative. This hindered anion sorption due to Columbic repulsion at the later stages of the surface reactions and thus, increased the resistance of mass-transportation. The highest \(K_{Th}\) value was obtained
for the lowest input concentration (65.0 µg. L⁻¹), indicating kinetically favorable arsenic removal by NICMO packed fixed bed column from contaminated groundwater [48-52].

Table-5.15(c): Thomas and Adams-Bohart model parameters from non-linear analysis of breakthrough curves

A. Bed depth (cm) variation

<table>
<thead>
<tr>
<th>Bed depth (cm)</th>
<th>EBCT (min)</th>
<th>Thomas Model</th>
<th>Adams-Bohart Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>$\chi^2$</td>
</tr>
<tr>
<td>4.0</td>
<td>1.54</td>
<td>0.998 4.1</td>
<td>10.385</td>
</tr>
<tr>
<td>5.0</td>
<td>1.925</td>
<td>0.996 7.0</td>
<td>7.538</td>
</tr>
<tr>
<td>6.0</td>
<td>2.31</td>
<td>0.992 11.8</td>
<td>5.154</td>
</tr>
</tbody>
</table>

B. Flow rate (ml.min⁻¹) variation

<table>
<thead>
<tr>
<th>Flow rate (ml/min)</th>
<th>EBCT (min)</th>
<th>Thomas Model</th>
<th>Adams-Bohart Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>$\chi^2$</td>
</tr>
<tr>
<td>1.0</td>
<td>1.925</td>
<td>0.996 7.0</td>
<td>7.538</td>
</tr>
<tr>
<td>2.0</td>
<td>0.963</td>
<td>0.997 4.7</td>
<td>18.769</td>
</tr>
<tr>
<td>4.0</td>
<td>0.481</td>
<td>0.996 6.6</td>
<td>43.692</td>
</tr>
</tbody>
</table>

Table-5.15(c) continued in next page

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C. Input feed solution concentration (µg.L⁻¹) variation

<table>
<thead>
<tr>
<th>Concentration (µg.L⁻¹)</th>
<th>EBCT (min)</th>
<th>Thomas Model</th>
<th>Adams-Bohart Model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R²</td>
<td>χ²</td>
<td>kₜh (mL)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(× 10⁻⁴) min⁻¹</td>
<td></td>
</tr>
<tr>
<td>65.0</td>
<td>0.996</td>
<td>7.4</td>
<td>57.538</td>
</tr>
<tr>
<td>130.0</td>
<td>0.996</td>
<td>7.0</td>
<td>7.538</td>
</tr>
<tr>
<td>260.0</td>
<td>0.994</td>
<td>6.6</td>
<td>1.231</td>
</tr>
</tbody>
</table>

5.4.5. Arsenic sorption on synthetic NICMO: role of surface properties in controlling varying degree of natural ground water filtration efficiency.

5.4.5.1 Source of the field sample

Same ground water sample that was collected from a tube well (depth: 40-45 m) at College Street near Presidency College Campus, was used to design fixed-bed packed column and analyzed for some water quality parameters. Fixed-bed column experiments were conducted using uniformly packed NICMO up to a height of 6.0 cm in glass tubes of internal diameter (i. d.) 1.4 cm and length 25.0 cm up to the depth, as desired, over glass wool sheet taking care of all possible precautions. After reproducing the data thrice, the arsenic concentration was confirmed to be 1.3×10⁻³ mg.L⁻¹. The ground water sample was then spiked with As(III) solution until the initial concentration reached 1.9×10⁻¹ mg.L⁻¹. Groundwater sample was also analyzed for some water quality parameters [(Table- 5.16 (a)] and passed through NICMO.
packed fixed bed column for filtration (flow rate: 1.0 mL·min⁻¹). The filtered water was collected in 100 mL fractions and analyzed for arsenic concentration.

**5.4.5.2. Design of Fixed-Bed packed Column**

Fig. 5.35 demonstrates the result obtained by filtering the collected groundwater sample of arsenic concentration (0.19 mg·L⁻¹). To estimate the rate of attainment of equilibrium between mobile and stationary phases, the breakthrough curve obtained from the treatment of field sample was analyzed as shown in idealized curve (Fig. 5.35). The curves were idealized by the assumption that removal of the solute was complete over the initial stages of operation. The break-point was so chosen where arsenic concentration (Cᵦ) crossed over 0.01 mg·L⁻¹ in the effluent. At an arbitrarily selected effluent concentration, Cₓ, closely approaching C₀, the sorbent was considered to be essentially exhausted.

**5.4.5.3. NICMO packed fixed bed column experiment**

A fixed-bed column was made by uniform packing NICMO up to a height of 6.0 cm into a glass tube of internal diameter (i. d.) 1.4 cm and length 25.0 cm. Based on the theories and description given in sub-section 2.6.2, the experimental and calculated parameters for the stationary fixed bed sorption of arsenic by NICMO bed were calculated and summarized along with its observed values, respectively in Table-5.16 (a, b).

It was found that the stationary fixed-bed column of NICMO filtered 3.2 L water with outlet water volume (Vᵦ) at breakthrough point (As concentration = 10 μg·L⁻¹) to be 2.0 L and EBCT value 9.24 minute.

The column saturation at exhaustion point estimated to be 70.34 %.
Figure 5.35: Breakthrough curve for the filtration of groundwater sample by NICMO packed fixed bed column.

Table 5.16 (a): Observed parameters for the stationary fixed-bed As (III) removal by NICMO column.

<table>
<thead>
<tr>
<th>Co</th>
<th>Cx</th>
<th>Cb</th>
<th>Vx</th>
<th>Vb</th>
<th>(Vx-Vb)</th>
<th>Fm</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mg.L⁻¹)</td>
<td>(×10⁻¹)</td>
<td>(×10⁻²)</td>
<td>(g.cm⁻²)</td>
<td>(×10⁻³)</td>
<td>(g.cm⁻²)</td>
<td>(×10⁻¹)</td>
<td>(cm)</td>
</tr>
<tr>
<td>1.0</td>
<td>1.875</td>
<td>1.69</td>
<td>1.0</td>
<td>1.883</td>
<td>1.298</td>
<td>5.844</td>
<td>6.494</td>
</tr>
</tbody>
</table>

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Table- 5.16 (b): Calculated parameters for the stationary fixed-bed As (III) removal by NICMO column.

<table>
<thead>
<tr>
<th>Flow rate (ml.min⁻¹)</th>
<th>tₐ(×10³) (min)</th>
<th>tₙ(×10³) (min)</th>
<th>f(×10⁻¹)</th>
<th>tᵢ(×10⁴) (min)</th>
<th>δ (cm)</th>
<th>% saturation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.9</td>
<td>8.999</td>
<td>9.372</td>
<td>2.789</td>
<td>1.899</td>
<td>70.336</td>
</tr>
</tbody>
</table>

5.4.5.4 Conclusion

1. Water quality parameters analyzed at breakpoint after filtration through fixed bed stationary column showed considerable improvement of quality of drinking water.

2. Break-through curves obtained for As(III) removal from the spiked groundwater were described well by the Thomas model better than that of Adam-Bohart model.

3. Natural ground water filtration efficiency can be estimated from the fixed bed column saturation at exhaustion point that was found to be 70.34 %.

4. This study demonstrated that NICMO could be an effective media for arsenic removal from contaminated water in a fixed stationary bed column.

Literature cited


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