INTRODUCTION
Arsenic in water has become a global threat as pollutants in drinking water and ground water due to its toxic, carcinogenic and omnipresent nature. Arsenic is mobilized into water bodies both by natural processes and anthropogenic activities. Arsenic exists in two predominant inorganic species; arsenite [As(III)] under reducing condition and arsenate [As(V)] under oxidizing condition in a water environment. Long-term uptake of arsenic contaminated water even at low level, can cause arsenicosis, a disease leading to serious health effects like respiratory, pulmonary, cardiovascular, hematological, gastrointestinal, hepatic, dermal, renal, neurological, mutagenic, immunologic, diabetes mellitus, and so on.

As an effect of arsenic, WHO and USEPA have reinforced guideline value of 10-µg/L. Arsenic poisoning episode in natural ground water has been reported from several countries like Taiwan, West Bengal-India, Chile, Argentina, Mexico, Hungary, Canada, Vitenam, China, USA, Sri Lanka etc.

A variety of treatment technologies have been reported for the removal of arsenic from arsenic contaminated water such as precipitation, co-precipitation, ultrafiltration, ion exchange and reverse osmosis. Among all these technologies, adsorption method is found efficient, simple and economical. Different types of adsorbents; goethite, low cost ferruginous manganese ore, polyaluminium granulate, zeolitimicidazolate frameworks, multi-wall carbon nanotubes (MWCNTs), ferrihydrite, copper oxide nanoparticles, ferricyanide, granular schwertmannite and soon have been applied for the adsorption of arsenic.

Mobility and adsorption behavior of arsenic is dependent on its oxidation state and As(V) is found to be easily removed than As(III). So, conversion of As (III) to As (V) and simultaneous adsorption of As(V) is required for the complete removal of arsenic from contaminated water. The objective of this study was to prepare and characterize Fe-Mn oxide adsorbents which can be applied to arsenic (III) removal from water. The prepared adsorbents were characterized by XRD and SEM. Efficiency of arsenic adsorption on the adsorbent was assessed by an arsenic kinetic (R^2 =0.99) for both adsorbents. Removal efficiency of the adsorbents decreased with increase in the pH value and increased with increase in the concentration of adsorbent in the suspension.

Based on the result, the synthesized Fe-Mn oxides have significant potential applications in the inorganic arsenic treatment in the water.

Keywords: Arsenite; Adsorption; Amorphous; Fe-Mn oxide.

2. EXPERIMENTAL SECTION

2.1 Materials
All the chemicals used throughout this study were of analytical grade reagent. Arsenite (As(III)) stock solutions were prepared by dissolving sodium arsenite (NaAsO2) (LOBA CHEMIE PVT.LTD, India) in deionized water. Working solution of As (III) were freshly prepared by diluting the As(III) stock solution with deionized water.

2.2 Synthesis of adsorbent
Two different iron-manganese oxides (Fe-Mn oxide-1 and Fe-Mn oxide-2) were synthesized by oxidation and co-precipitation methods followed the procedure reported with slight modifications.

Fe-Mn oxide-1 and Fe-Mn Oxide-2
Solution 1 was prepared by dissolving Potassium permanganate (KMnO4, 0.015 M) in 200 mL of deionized water. For Fe-Mn oxide-1, solution 2 was prepared by dissolving ferric chloride hexahydrate (FeCl3.6H2O, 0.045 M) in 200 mL of deionized water. For Fe-Mn oxide-2, the solution 2 was prepared by dissolving ferrous sulphate...
heptahydrate (FeSO\(_4\).7H\(_2\)O, 0.045 M) in 200 mL of deionized water. Under the magnetic stirring, solution 1 and respective solution 2 for Fe-Mn oxide-1 and Fe-Mn oxide-2, separately were mixed and 5 M NaOH solutions were added to make the solution pH in the range between 7.0 and 8.0. Then formed suspension was stirred for 1 hour and aged at room temperature for 24 hours and repeatedly washed with deionized water. The suspension was filtered and finally dried at 105 °C for 4 hours in an oven. The dried material was crushed with a mortar and pestle into fine powders, then sieved to obtain a particle size less than 100-µm and stored in vacuum desiccators until further use.

### 2.3 Structural characterization

The basic properties such as degree of crystallinity and the morphology of the adsorbents were examined using powder X-ray diffraction studies (XRD) and Scanning electron microscopy (SEM). Powdered X-Ray Diffract meter, X’Pert 3040-PRO (PAN analytical Co.) with copper as anode material and 0.5 Kα1/ Kα2 radiation was used. Powdered adsorbents were dried to constant weight and ground. Data were collected at 40 Kev and 40 mA in Goniio scan axis between 10° and 90° 2θ in 0.026° steps. The surface morphology of the adsorbents were observed using Scanning electron microscopy (SEM) (Hitachi S-3500N, Japan).

### 2.4 Adsorption Experiments

#### 2.4.1 Adsorption kinetics

Definite volume of the arsenite stock solution was added to definite volume of deionized water to make a definite concentration of the arsenite in which ionic strength was maintained by the addition of 0.001 M sodium nitrate (NaNO\(_3\)). pH of the solution was adjusted to 7.0 by the addition of 0.1 M HCl and 0.1 M NaOH. Prepared Fe-Mn oxides were added to obtain 0.2 g/L suspension. The suspension was mixed in the shaker with speed of 150 rpm for 24 hours at 25 °C. Approximately, 1.5 mL aliquots from the suspension at the intervals of 0.5, 1.0, 2.0, 4.0, and 24 hours of reaction were taken.

The adsorption capacity of arsenite (q, mg/g) was calculated using the following equations:

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]  \hspace{1cm} (1)

Where, \(C_0\) and \(C_e\) are the initial and the remaining concentrations of arsenite solution (mg/L), \(V\) is the initial solution volume (L), and \(m\) is the adsorbent weight (g).

The removal rate (%) was calculated according to eq. (2):

\[
\text{Removal \%} = \frac{C_0 - C_e}{C_0} \times 100
\]  \hspace{1cm} (2)

Where, \(C_0\) and \(C_e\) are the initial solution and remaining concentrations of arsenite solution (mg/L), respectively.

#### 2.4.2 Effect of pH

To find out the effect of pH, solutions containing defined concentration of arsenite were prepared to form solutions with 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 pH values throughout the experiment by adding 0.1 M HCl or 0.1 M NaOH. Prepared Fe-Mn oxides were added to obtain 0.2 g/L suspension. The suspension was mixed in the shaker with speed of 150 rpm for 24 hours at 25 °C. 1.5 mL aliquots were taken after 24 hours of reaction time.

#### 2.4.3 Effect of adsorbent dose

For observing the effect of concentration of adsorbents, in the solutions containing definite amount of arsenite, different amount of adsorbents were added to make suspensions 0.05 g/L, 0.1 g/L, 0.15 g/L and 0.2 g/L and pH was adjusted to 7.0 by the addition of 0.1 M HCl and 0.1 M NaOH. The suspensions were mixed in the shaker with speed of 150 rpm for 24 hours at 25 °C. 1.5 mL aliquots from the each suspension were taken after 24 hours of reaction time.

### 2.5 Analysis of arsenic

After adsorption, samples were filtered through 0.45-µm membrane filters for the analysis of arsenic As(III). The concentrations of As(III) were determined by Graphite Tube Atomizer (GTA), 240FSAA (Agilent Technologies).

### 3. RESULTS AND DISCUSSION

#### 3.1 Characterization of adsorbents

#### 3.1.1 XRD

Crystalline peak was not detected in X-ray powder diffraction pattern (XRD) of both Fe-Mn oxides. This indicates that both oxides exist mainly in amorphous form (Fig 1a and b), which increases the surface area of the adsorbent for the adsorption16.

Figure: 1. X-ray diffraction (XRD) pattern of (a) Fe-Mn oxide-1 and (b) Fe-Mn oxide-2.
3.1.2 SEM

Particle shape of the adsorbents studied by Scanning electron microscopy (SEM) showed the presence of many aggregated small particles in both prepared Fe-Mn oxide-1 (Fig 2a and b) and Fe-Mn oxide-2 (Fig 3a and b). Particles size was found to be smaller in Fe-Mn oxide-1 than in Fe-Mn oxide-2. So, surface of both oxides were rough.

![SEM images of Fe-Mn oxide-1 in different magnification. Scale bars are 1.00-µm and 500 nm.](image1)

![SEM image of Fe-Mn oxide-2 in different magnification. Scale bars are 1.00-µm and 500 nm.](image2)

3.2 Removal efficiency of adsorbents

3.2.1 Adsorption kinetic

The adsorption kinetics of arsenic (III) onto Fe-Mn oxides were determined through the curves of adsorption capacity as a function of time. Fig 4a shows that the adsorption of As(III) on Fe-Mn oxide-1 and Fe-Mn oxide-2 was fast during the initial stage in 30 minutes and gradually slowed with increasing reaction time. The optimum time to attain the equilibrium was 4 hours. The maximum adsorption capacity of As(III), i.e., $q_{t,\text{max}}$, was observed to be 43.9 mg/g and 39.45 mg/g for Fe-Mn oxide-1 and Fe-Mn oxide-2 and its removal rate was determined to be 97% and 94%, respectively (Fig 4b). To gain insight into the adsorption mechanism, Pseudo-first-order and Pseudo-second-order kinetic models were applied to fit experimental data as shown in Table 1. Pseudo-second order model was observed fitted well to describe adsorption of As(III) on both oxides as indicated by higher correlation coefficient values ($R^2=0.99$ for both oxides, which indicated that the adsorption process might be chemisorption).

The mathematical equations are used to fit experimental data are given as,

- **Pseudo-first order equation**, $q_t = q_e (1-e^{-kt})$ (3)
- **Pseudo-second order equation**, $q_t = \frac{q_e^2 k_1 t}{1+q_e k_2 t}$ (4)

In eqs. (3) and (4), $q_t$ (mg/g) is the adsorption amount at a given time $t$ (h) and $q_e$ (mg/g) is the adsorption equilibrium capacity at the terminal experimental time. In the equations, $K_1$ (1/h) and $K_2$ (g/mg h) indicate the adsorption rate constants of the pseudo-first order and pseudo-second-order model.

![Adsorption kinetics of As (III) onto Fe-Mn oxide-1 and Fe-Mn oxide-2 at pH 7.0± 0.1](image3)
3.2.2 Effect of pH

pH is one of the main influencing factors that affect the adsorptive interaction on the adsorbents. To gain more insight into the adsorption process, the effects of initial pH on adsorption capacity of arsenic (III) on adsorbents were examined over a wide range of pH (4.0-9.0), respectively as demonstrated in Fig 5. Adsorption of As (III) was decreased with increase in pH in both Fe-Mn oxide-1 and Fe-Mn oxide-2 as shown in Fig 5. About 99% of As (III) was removed by both Fe-Mn oxide-1 and Fe-Mn oxide-2 at pH 4.0±0.1. The removal efficiency was gradually decreased with increase in pH value and decreases up to about 93% and 89% by Fe-Mn oxide-1 and Fe-Mn oxide-2, respectively at pH value 9.0±0.1. With increase in pH, positive charge density of the adsorbent decreases and turns into negative charge density resulting in electrostatic force of repulsion. At Lower pH, positive charge increases as a result of protonation of the adsorbent surface and attract negatively charged arsenic anion easily but with increase in the pH negative charge on adsorbent increases which causes the electrostatic force of repulsion between adsorbent and arsenic anion thus lowering adsorption capacity. However, adsorption of As (III) was not measured below pH 4 in this study.

3.2.3 Effect of the dose of adsorbent

Adsorbent amount is an essential factor for arsenic(III) removal by adsorption process is demonstrated in Fig 6. It was found that arsenic removal increased with increasing adsorbent dose up to 0.2 g/L. With the increase in the concentration of the adsorbent dose from 0.05 to 0.2 g/L, the removal efficiency of the As (III) increases. The increase in the removal of As(III) may be attributed to increase in the surface area of adsorbent available for mass transfer. Removal efficiency reaches up to 95.97% and 96.73% at 0.2 g/L dose of Fe-Mn oxide-1 and Fe-Mn oxide-2 respectively.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Initial concentration of As(III) mg/L</th>
<th>Pseudo-first-order model</th>
<th>Pseudo-second order model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$Q_{max}$</td>
<td>$K_1$</td>
</tr>
<tr>
<td>Fe-Mn oxide-1</td>
<td>8.96</td>
<td>41.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Fe-Mn oxide-2</td>
<td>8.35</td>
<td>37.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

4. CONCLUSION

In this study, As (III) adsorption was studied under batch experiments as an adsorption kinetics, isotherms, and effect of pH. Iron-Manganese oxides were prepared by oxidation and co-precipitation. Fe-Mn oxides were amorphous with many small aggregated particles which increases roughness of the adsorbents. Prepared adsorbents were highly efficient in the removal of As(III), 97% and 94% of As(III) was removed by Fe-Mn oxide-1 and Fe-Mn oxide-2 respectively within 24 hours of reaction time. Pseudo-second order model describe well the adsorption mechanism ($R^2=0.99$). Adsorption decreases with increase in the pH value. 99% adsorption of As(III) was observed at pH 4.0 by both oxides. 93% and 89% adsorption of As(III) was observed at pH 9.0 by Fe-Mn oxide-1 and Fe-Mn oxide-2 respectively. Adsorption of As (III) increases with increase in the adsorbent dosage. Maximum adsorption was found at 0.2 g/L adsorbent dose in both oxides. The Fe–Mn oxides system exhibits an obvious synergistic effect for the removal of As(III) in an aqueous solutions.

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REFERENCES