Solvothermal Synthesis of Diethylamine Functionalized and Yeast Cross-Linked $\text{Fe}_3\text{O}_4$ Nanoadsorbents for Heavy Arsenate Removal

This chapter includes:

- Introduction
- Structural characterization of $\text{Fe}_3\text{O}_4$ nanoparticles
- Morphological analysis
- Surface charge analysis
- Magnetic characterization
- Arsenate removal
- Langmuir and Freundlich Isotherm
- Pseudo First-order and Second-order Kinetics
- Desorption
- Discussion
- Conclusion
- References
5.1 Introduction

Arsenic is one of the most dangerous heavy metals present in the water and it produces biological toxicity to humans [1]. Occurrence of arsenic contamination in drinking water is very high and its leads to negative health effects. Nearly 144 million people were affected worldwide for this problem [2]. Depending on the environmental conditions, arsenic can occur in different oxidation (-3, 0, +3 and +5) states. But mostly trivalent and pentavalent ions of arsenic are more toxic [3]. Therefore, the recovery and purification of the arsenic from aqueous solution is important to restrict the environmental problems. World health organization’s (WHO) recommended levels of arsenic in drinking water should not be more than 10 µg/l [4]. However in day-to-day life, arsenic contamination levels are increasing in drinking water due to anthropological activities. The complete removal of arsenate from drinking water is the major challenge prevailing worldwide. If the contamination level increases above 10 µg/l, then the toxicity of drinking water induces many diseases such as blackfoot disease, gastrointestinal problems, keratosis, nerve tissue injuries, as well as cancer in skin, lungs, bladder and kidney [5,6]. A lot of arsenic remediation technologies have already been tested and in routine use. But cost effectiveness and ecological competiveness are the major drawbacks of the existing technologies [7]. Various types of nanomaterials are being developed for arsenic removal but the efficiency is still challengeable. Diverse environmental challenges such as wastewater treatment, heavy metal removal and remediation have been resolved using engineered magnetic nanoparticles. However, compared to other types of nanoparticles, the zerovalent iron or di/tri-valent iron oxide nanoparticles offers high arsenic adsorption capacity including both arsenite As(III) and arsenate As(V) respectively [1]. The adsorption of these metal ions occurs either by electrostatic or surface complexation or the combination of both mechanisms [6]. Afterwards, it can be easily removed or collected in the presence of a strong external magnetic field. So, further recovery of the adsorbent by filtering, settling and centrifugation process is not necessary. In conventional adsorption technologies, the adsorbent recovery process is time consuming, hazardous and not cost effective [8]. The high surface to volume ratio and surface charge along with superparamagnetic behavior of the nanoparticles are important for high arsenic removal efficiency, strong reactivity and fast kinetic reactions [9].
In recent years, the development of magnetite nanoparticles with desirable physicochemical properties has been widely investigated for dynamic research in the field of engineering, medicine and the potential environmental abatement [10]. The magnetite nanoparticles with unique superparamagnetic properties could be highly desirable owing to an eco-friendly, non-hazardous, low material cost, high reproducibility, recyclable and environmental stability [11]. Generally, the pristine nanoparticles tend to aggregate owing to strong Van der Waals and magnetic dipole-dipole attraction which limits their desirable properties [12]. So, the surface of the Fe₃O₄ nanoparticles can be modified with either inorganic or organic materials to overcome the aggregation and increase the stability. Different inorganic materials such as gold, silver, silica etc. and the organic materials such as polyethylene glycol, polyvinyl pyridilone, polyvinyl alcohol, dextran, citric acid etc. have been used to coat or modify the surface of the magnetic nanoparticles for suitable applications. The functional chemicals such as amine, thiol, hydroxyl, carboxyl, aldehyde, ketone groups etc have been used to cross-link the magnetic nanoparticles for appropriate surface modifications [13]. Compared to inorganic materials, organic functionalization with amino groups is easy to bind or attach the biomolecules like enzymes or proteins easily for suitable environmental applications [14]. Recently, the amine-rich magnetite/bacterial cellulose nanocomposite has been used as effective adsorbents for the removal of arsenic metal from aqueous solution [15]. Therefore, significant efforts have been made to select the appropriate surface modification agents to acquire more binding efficiency and enhanced stability.

In the present study, the surface modified Fe₃O₄ nanoparticles were prepared by two-step process using facile solvothermal and nanoprecipitation method. The surface of the Fe₃O₄ nanoparticles was altered by functionalization with diethylamine and cross-linked with yeast cells. The monodispersed shape of the Fe₃O₄ nanoparticles along with high negative surface charge assists the arsenate removal from polluted water. The removal of As(V) was studied with respect to contact time, adsorbent dosage, adsorbate concentration, and pH. The Langmuir and Freundlich isotherms were used to calculate the precise absorption co-efficient of the As(V) ions. The surface functionalized Fe₃O₄ nanoparticles could be very easily recovered from arsenic contaminated water using external strong magnet.
5.2 Results and Discussion

5.2.1 Structural analysis

The crystal structure and phase purity of the various concentrations of diethylamine functionalized Fe$_3$O$_4$ nanoparticles (DMNPs) was studied by using XRD pattern. Figure 5.1(a-c) shows the X-ray diffraction pattern for the three different concentrations of DMNPs. All the diffraction peaks were attributed to the cubic structure of Fe$_3$O$_4$ nanoparticles and very well matches with the standards without any impurities (JCPDS#:89-3854). The average grain size of the magnetite nanoparticles was estimated using Scherrer formula. The strong diffraction peak along (311) plane was used to calculate the FWHM for estimating the average grain size. The estimated average grain size was 20 nm for 3 ml diethylamine functionalized Fe$_3$O$_4$ nanoparticles. Further increase the diethylamine concentration to 6 and 9 ml increases the average grain size to 24 and 35 nm respectively. The diethylamine interacts with Fe$^{3+}$ ions and endow with the required nucleation growth to increases the grain size [16]. The sharp and strong diffraction peaks confirms the high crystalline behavior. Also, the diffraction peaks doesn’t shift and it may be confirmed that the diethylamine functionalized Fe$_3$O$_4$ nanoparticles did not affect the crystalline structure but it only influences the average grain size.

The FTIR spectra were acquired in an effort to study the interaction between the magnetite nanoparticles and surfactants. Figure 5.2 (a-c) shows the FTIR spectra for the diethylamine functionalized Fe$_3$O$_4$, pure yeast and yeast cross-linked Fe$_3$O$_4$ nanoparticles respectively. In Fig. 5.2a, the broad and strong spectroscopic band at 455 and 578 cm$^{-1}$ corresponds to the symmetric Fe-O-Fe stretching vibration and it indicates that the Fe ions are distributed in both tetrahedral and octahedral sites [17]. The corresponding bands further confirm the formation of magnetite nanoparticles as observed in XRD analysis. The peak at 788 cm$^{-1}$ represents the N-H wagging which confirms the presence of primary and secondary amine group. Also, the broad peak at 1074 cm$^{-1}$ indicates the strong stretching vibration of the N-H molecules and confirms the successful wrapping of diethylamine in Fe$_3$O$_4$ nanoparticles. The peak at 1632 cm$^{-1}$ represents the carboxyl group from ethylene glycol molecule during the preparation of magnetic nanoparticles.
Fig 5.1. XRD pattern for the (a) 3, (b) 6 and (c) 9 ml of diethylamine functionalized Fe$_3$O$_4$ nanoparticles

Fig 5.2. FTIR spectra for (a) DMNPs, (b) pure yeast and (c) YcMNPs
No other additional peaks were observed and it confirms the high purity of the diethylamine functionalized \( \text{Fe}_3\text{O}_4 \) nanoparticles. In the case of pure yeast cells as shown in Fig 5.2b, the broad band at 3412 cm\(^{-1}\) can be ascribed to N-H asymmetric stretching due to the presence of amino group in proteins on the cell wall of yeast cells. The broad band at 1670 cm\(^{-1}\) is assigned to C=O stretching vibrations that represent the keto groups present in the yeast cell walls. The characteristic peak at 1545 cm\(^{-1}\) corresponds to stretching vibrations of -C=C- that confirms the inherent structure of yeast cells. These characterized peaks can be attributed to the presence of pure yeast cells [18]. Figure 5.2c shows the cross-linking between the host magnetite nanoparticles and the guest yeast cell. If the yeast cells were cross-linked with \( \text{Fe}_3\text{O}_4 \) nanoparticles, the corresponding Fe-O bond was slightly shifted ~10 cm\(^{-1}\) due to change in the bond length. The band at 1160 cm\(^{-1}\) corresponds to the C-O stretching vibrations. Other peaks at 1480 and 1120 cm\(^{-1}\) were assigned to C=O stretching due to the presence of ketones in yeast cell wall. The two weak peaks at 2850 and 2950 cm\(^{-1}\) represents the symmetric and asymmetric stretching vibrations of \(-\text{CH}_2\) molecules. Another broad absorption peak arising from N–H stretching vibrations of the amino group could be located at about 3415 cm\(^{-1}\) and also this peak might overlap with vibration bands associated with water or surface -OH groups. The amine groups strongly imply the occurrence of proteins on yeast cell walls. All the corresponding peaks were well matched with pure yeast. The results clearly reveal that yeast cells were successfully cross-linked to \( \text{Fe}_3\text{O}_4 \) nanoparticles and form a magnetite nanobiocomposite.

5.2.2 Morphological analysis

The electron microscopic images for the pristine and various concentrations of diethylamine functionalized \( \text{Fe}_3\text{O}_4 \) nanoparticles were recorded using FESEM and the images are shown in Fig 5.3(a-j). To reveal the in-depth structure of the various morphologies, higher magnification images were also recorded for all the samples. FESEM images in Fig 5.3(a,b) for the pristine \( \text{Fe}_3\text{O}_4 \) nanoparticles shows the monodispersed spherical shape and size in the range of < 50 nm. The rearrangement of the smaller particles was due to the slow diffusion process of homogeneous nucleation and it leads to a formation of the spherical magnetite nanoparticles. When 3 ml of diethylamine was added in the reaction, the monodispersed spherical particles adheres together to form chain-like structure through magnetic dipoles and the size increases as
Fig 5.3: High and low magnification FESEM micrographs for the (a,b) pristine, (c,d) 3, (e,f) 6, (g,h) 9 and (i,j) 12 ml diethylamine functionalized Fe₃O₄ nanoparticles
Fig 5.4. Low and high magnification FESEM micrographs for pure yeast cells (Live cells)

Fig 5.5. Low and high magnification FESEM micrographs of the Yeast cross-linked Fe₃O₄ nanoparticles with different magnifications
>75 nm as shown in Fig 5.3c. The higher magnification image in Fig 5.3d shows the primary nanoparticles were aggregated to form a non-uniform distribution of larger rigid particles in addition to the chain-like structure. Further increasing the concentration of diethylamine to 6 ml, the spherical cabbage like shape with central pores was obtained due to the internal arrangement of the smaller cluster particles with a mean diameter of 300 nm as shown in Fig 5.3e. The central porous structure was clearly observed in magnified FESEM image as shown in Fig 5.3f. However, the pores was disappears and form a uniform distribution of cabbage shaped structures with identical diameter during the 9 ml of diethylamine functionalization as shown in Fig 5.3g. The rough surface of the cabbage shaped nanoparticles was fashioned by packing of several nanocrystals observed in higher magnification image as in Fig 5.3h [19]. Further increasing the concentration of diethylamine to 12 ml, the tightly arranged layers were compressed to form irregular shaped aggregated nanocrystals as shown in Fig 5.3(i,j). The inter-particle dipolar energy between the surface layers creates the recrystallization mechanism to generate aggregated nanocrystals [20]. So, the various concentration of diethylamine plays a significant function to influence on the nucleation and growth of monodispersed shape and size of the magnetite nanoparticles. Figure 5.4(a-d) shows the low and higher magnification micrographs of the pure yeast cells. The pure yeast cells have monodispersed ellipsoidal shape with smooth surface in the size range of > 5µm. Figure 5.5 (a-d) reveals the yeast cross-linked magnetite nanoparticles with different magnifications. The Fe$_3$O$_4$ nanoparticles were adhered on the surface of the yeast and formed an irregular shape of aggregation. The van der Waals interaction or attractive magnetic force between the particles and yeast cells produces this aggregation effect [21]. Moreover, the number of free sites [22] on the surface of cabbage shaped nanoparticles could serve as cross-linking sites to produce YcMNPs nanobiocomposites. Similar results have been analyzed for the preparation of the TiO$_2$@yeast carbon microsphere [18]. The results clearly demonstrate that Fe$_3$O$_4$ nanoparticles were kinetically adsorbed or cross-linked yeast cells.

The EDX spectrum of the diethylamine and yeast functionalized magnetite nanoparticles are shown in Fig 5.6(a,b). The spectrum of diethylamine functionalized Fe$_3$O$_4$ nanoparticles originates from the point scans designate that the particles contain only Fe and O elements. It shows further evidence for the formation of magnetite nanoparticles.
CHAPTER - 5

Solvothermal Synthesis of Diethylamine Functionalized and Yeast Cross-Linked Fe₃O₄ Nanoadsorbents for Heavy Arsenate Removal

Fig 5.6. EDX spectra for (a) DMNPs and (b) YcMNPs

as observed from XRD analysis. The atomic percentage of Fe ion lies high in DMNPs when compared to YcMNPs and the corresponding values were shown in Fig 5.6(a,b). The low value of the Fe percentage in YcMNPs may result from the presence of yeast cell or any other contamination in the magnetite nanoparticles.

5.2.3 Possible growth mechanism

Systematic analysis of the samples were performed to understand the growth mechanism by using FESEM by varying the concentrations of diethylamine in the range of 3-12 ml. Based on the understanding from the FESEM images the possible formation mechanism was proposed for the pristine and functionalized Fe₃O₄ nanoparticles as shown in Fig 5.7. All the solvothermal reactions were carried at a constant temperature of 200 °C and time 12 h respectively. The permittivity of the ethylene glycol (EG) permits to suspend highly polar organic and inorganic compounds which make highly viscous and an effective medium. Ethylene glycol would slow down the diffusion of metal ions and assist in the formation of new nucleus to induce the homogeneous growth of
micro/nanoparticles [23]. Because, EG does not act only as a solvent but also as a strong reducing agent for Fe$^{2+}$/Fe$^{3+}$ ions. At the earlier stage, the complex becomes unstable due to the reaction between EG and both OH$^{-}$ and Fe$^{3+}$ ions to form FeOOH particles. This may happen due to the Fe$^{3+}$ ions does not reduced by EG at room temperature [24]. After increasing the reaction time and temperature, the FeOOH ions react with Fe$^{2+}$ ions to form agglomeration free spherical shaped pristine Fe$_3$O$_4$ nanoparticles. The growth direction was not restricted in all the three dimensions which lead to the formation of monodispersed spherical shape. It is understood that the primary driving force could reduce the surface energy during the particle growth [25]. The surface of the pristine magnetite nanoparticles shows fairly smooth morphology with more number of particles visible as shown in Fig 5.3b and the particle size distribution is in range of < 50 nm.

Fig 5.7. Schematic illustration for the proposed formation mechanism of pristine, diethylamine functionalized and yeast cross linked Fe$_3$O$_4$ nanoparticles
Interestingly, hundreds of spherical nanoparticles are combined to attain chain-like structure and larger nanocrystals due to the strong interaction of magnetic dipoles. This interaction happens when there is a crucial interaction between the spherical nanoparticles due to the addition of 3 ml of diethylamine. The diethylamine acts as strong molecular co-ordinates with many metal cations to form the stable complex of the magnetite nanoparticles and structure directing agents [26]. Figure 5.3d clearly demonstrates the primary assembly of spontaneous nucleation to induce shape modification via diethylamine [27]. When increasing the concentration to 6 ml of diethylamine, the chain-like nanoparticles were combined to form the thick layers and create a non-uniform distribution of cabbage shaped structure. Further on observation of the central part of the nanoparticle, the cabbage shape depicts that number of nanolayers interweave together to form an open porous structure, as shown in higher magnified image in Fig 5.3f. The possible reason for dissimilarity in the morphology obtained is due to the various binding forces between the Fe$^{2+}$ or Fe$^{3+}$ ions, which affects the reaction system [14]. Ostwald ripening mechanism plays an active role to produce number of sub-layers that are densely-packed into cabbage shape by trapping of smaller particles [28]. Further increasing the concentration to 9 ml of diethylamine, the monodispersed cabbage shape was obtained. But, the boundaries of the cabbage structures were not uniform for all the nanoparticles. The multifaceted surface of the magnetite nanoparticles was obtained due to the dissimilar radial growth of the internal crystals and packing of many nanocrystals [29]. This type of multi-faceted particles was used to absorb the arsenic contamination efficiently compared to smooth surface of the magnetite nanoparticles. The exact mechanism of the assembled cabbage structure is still unclear due to lack of available literature reports. When the reaction was prolonged to 12 ml of diethylamine, the multi-facet layers were tightly packed to form the non-uniform distribution of aggregated diverse nanocrystal shapes. The possible mechanism for the generation of diverse nanocrystals is that the diethylamine could be selectively adsorbed on the surface layer of Fe ions due to reducing interfacial energy [30]. Also, the change in viscosity of the reaction solution via high concentration of diethylamine may influence the nucleated diverse nanocrystals [31]. The FESEM analysis, it is clearly visible that the addition of
Fig 5.8. Room temperature magnetic hysteresis loops for the (a) pristine, (b) DMNPs and (c) YcMNPs

Fig 5.9. Zeta potential graph for (a) DMNPs, (b) pure Yeast and (c) YcMNPs
diethylamine in the solvothermal reaction is an efficient way to regulate the monodispersed shape and size of the Fe$_3$O$_4$ nanostructure.

### 5.2.4 Magnetic properties

The magnetic properties of surface functionalized Fe$_3$O$_4$ nanoparticles were studied by vibrating sample magnetometer. The superparamagnetic behavior of the pristine, diethylamine (9 ml) functionalized and yeast cross-linked magnetite nanoparticles were confirmed by measuring the hysteresis loop at room temperature as shown in the Fig 5.8(a-c). The negligible hysteresis shows immeasurable remanance and coercivity due to nanosized magnetite particles. An interesting phenomenon is the existence of superparamagnetic behavior in various nanostructures which could be attributed to the thermal energy which can overcome the anisotropy energy barriers of a single particle. So, the net magnetization of the particle assemblies in the absence of an external magnetic field is zero [32]. The superparamagnetism occurs due to the thermal activation process making a quicker relaxation of the net magnetization [33]. The saturation magnetization (M$_s$) value of pristine nanoparticles was found to be 52 emu/g. It is slightly less compared to the bulk materials (92 emu/g) [34] due to the pinning of surface spins, shape and smaller size of the nanoparticles [35]. Also, a noteworthy fraction of surface atoms creates crystalline disorder within the surface layer, which may lead to a decrease in saturation magnetization [16]. The magnetization value was decreases to 40 emu/g for diethylamine functionalized magnetite nanoparticles. The decrease in the saturation magnetization values is not only due to the decreasing particle size but also due to diamagnetic materials present on the surface of the magnetite nanoparticles. Moreover, the quenching of magnetic moment is intrinsically related to magnetite nanoparticles which means the diethylamine incorporation significantly traps the magnetization [36]. The YcMNPs have the saturation magnetization of 23 emu/g and it is relatively high compared to the already reported value of 17.87 emu/g [37]. The surface dead layer or magnetically inactive layer of yeast molecule reduces the magnetization value. But, this magnetization value is enough for the magnetic separation [38]. The obtained magnetization values were relatively high in both DMNPs and YcMNPs and it is very much sufficient to separate the adsorbed arsenate from aqueous solution.
5.2.5 Surface charge analysis

The surface charges and colloidal stability of the magnetite nanoparticles are most essential in absorption kinetic studies. Diethylamine was used as a stabilizing agent to enhance the colloidal stability of the magnetite nanoparticles. The colloidal stability is directly correlated to the surface charge of the magnetite nanoparticles and it was measured by zeta potential analyzer and the corresponding graphs were shown in Fig 5.9 (a-c). Generally, the surface charge of the magnetite nanoparticles was varied by the addition of surfactant or bio-molecules. The obtained superficial charge value of diethylamine functionalized magnetite nanoparticles (DMNPs) has negative surface charge of -3.6 mV and it is almost close to neutral charge. The number of amine groups conjugated on the surface molecules contributes to low negative charge and improves the colloidal stability after the addition of diethylamine. The pure yeast cells also has negative surface charge of -19.1 mV due to the presence of the proteins and amino acids as shown in Fig 5.9b. Subsequently, the interaction of arsenate and DMNPs were far more superior compared to pure yeast cells due to strong electrostatic interaction of DMNPs than pure yeast cells. Figure 5.9c shows the yeast cross-linked magnetite nanoparticles (YcMNPs) has better colloidal stability due to the high negative surface charge of -33.4 mV due to the deprotonated amino groups from yeast cells. The highly negative surface charges assists in rapid interaction with arsenate molecules via Fe$^{2+}$/Fe$^{3+}$ ions and yeast cells. The obvious change in the zeta potential value further confirms the different surface agents were used to functionalize or cross-link the magnetite nanoparticles.

5.3 Adsorption of Arsenate using DMNPs and YcMNPs

5.3.1 Effects of adsorbent dosage with contact time

The percentage of the arsenate removal using DMNPs and YcMNPs depends on varying the adsorbent dosage as shown in Fig 5.10(a,b). However, the binding of arsenate with nanoadsorbants of DMNPs or YcMNPs increases with increasing time from 0-180 min. In the case of DMNPs, there was no removal of arsenate in the initial concentration of 50 mg. Whereas, by increasing the DMNPs concentration of 100, 150 and 200 mg, it reaches the maximum removal of 16.66, 66 and 76.66 % at 15 min as shown in Fig 5.10a.
Fig 5.10. Effect of contact time and various nanoparticles concentration for As(V) removal using (a) DMNPs and (b) YcMNPs
When increasing the adsorbent time gradually up to 180 min, the arsenate removal reached a maximum value of 56.66 to 83.33% for various concentrations. The maximum arsenate removal was observed within 45 min and saturated at 200 mg adsorbent dosage. From the crystal structure of the Fe$_3$O$_4$, the tetrahedral occupation of Fe$^{2+}$ ions located at the surface of phase may exchange ions to As tetrahedron site. So, the Fe$^{2+}$ ions may be operating via diethylamine as counter ions in the magnetite nanoadsorbants [39]. In the case of the YcMNPs, the complete removal of arsenate (99%) was observed within 180 min with 200 mg as shown in Fig 5.10b. It is mainly attributed to the surface complexation or ion exchange and chemical adsorption through strong electrostatic interaction between the yeast and magnetite nanoparticles [40]. The mechanism of the binding efficiency strongly depends on the redox reaction occurring on the surface of the nanoadsorbant system as reported in the literature [41]. The observed result shows that the arsenate adsorption kinetics was very fast at initial stage and slowly acquires equilibrium at 180 min. In comparison, the fast kinetics of arsenate adsorption occurs in YcMNPS rather than DMNPs with same contact time. The efficiency of arsenate removal percentage was compared with the existing literature as shown in Table 5.1.

5.3.2 Effects of adsorbate dosage with contact Time

Figure 5.11(a,b) shows the effect of arsenate removal by varying arsenate concentrations from 0.5 to 2.5 ppm with different contact time using 150 mg of DMNPs and YcMNPs respectively. It was observed that the arsenate removal was rapidly increases by decreasing the arsenate (ppm) concentrations. In 2.5 ppm of arsenate, the higher percentage (99%) removal of arsenate occurs at 160 min for DMNPs as shown in Fig 5.11a. Similarly, the same arsenate concentration for YcMNPs, 99% of arsenate was removed within 120 min as shown in Fig 5.11b. These results confirm the fast arsenate removal in YcMNPs compared to DMNPs due to the high negative surface charge as observed in zeta potential. However decreasing the arsenate concentration from 2.5 to 0.5 ppm, the maximum arsenate removal percentage (99%) was reaches within 30 min. It might happen that adsorption should be associated with the fast diffusion of species at the liquid-solid interfacial boundary [46]. Therefore, the removal efficiency was slowed down in higher As(V) concentration whereas fast kinetics was obtained at lower concentration. It may be attributed to the reality that at higher As(V) concentration, the
Table 5.1: Comparison of As(V) adsorption capacity with previously reported adsorbents

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbent Weight (mg/l)</th>
<th>Adsorption Time</th>
<th>As(V) Removal Percentage (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-FeOOH</td>
<td>100</td>
<td>12 hrs</td>
<td>90</td>
<td>42</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>200</td>
<td>12 hrs</td>
<td>51</td>
<td>43</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>50</td>
<td>7 hrs</td>
<td>85</td>
<td>65</td>
</tr>
<tr>
<td>Fe₃O₄-MnO₂</td>
<td>200</td>
<td>2 hrs</td>
<td>80</td>
<td>64</td>
</tr>
<tr>
<td>GO-Fe₃O₄</td>
<td>400</td>
<td>24 hrs</td>
<td>&gt;95</td>
<td>44</td>
</tr>
<tr>
<td>Bacteria-cellulose@Fe₃O₄</td>
<td>50</td>
<td>7 hrs</td>
<td>85</td>
<td>20</td>
</tr>
<tr>
<td>cellulose@Fe₂O₃</td>
<td>1000</td>
<td>1 hrs</td>
<td>90</td>
<td>45</td>
</tr>
<tr>
<td>DMNPs</td>
<td>150</td>
<td>160 min</td>
<td>99</td>
<td>Present work</td>
</tr>
<tr>
<td>YcMNPs</td>
<td>150</td>
<td>105 min</td>
<td>99</td>
<td>Present work</td>
</tr>
</tbody>
</table>

number of active sites on adsorbent surface is not enough to accommodate the magnetite nanoparticles. Conversely, at lower concentration of As(V) ions, the ratio of surface active sites are more in magnetite nanoparticles and it could be completely adsorbed on the adsorbent surface sufficiently [47].

5.3.3 Effects of pH dependent adsorption and desorption for As(V) ions

The influence of pH in the range of 3 to 11 for the removal of arsenate from aqueous solution using DMNPs and YcMNPs were also investigated and the results were shown in Fig 5.12(a,b). Generally, the surface complexation, electrostatic interaction and ion-exchange mechanisms may be recognized as the major adsorption and desorption mechanisms used for pristine or functionalized metal or metal oxide ions [48]. In the present case, both DMNPs and YcMNPs shows there was no significant arsenate removal
Fig 5.11. Effect of contact time and various Arsenate concentration for As(V) removal using (a) DMNPs and (b) YcMNPs
Fig 5.12. Effect of adsorption and desorption of As(V) ions by varying pH in (a) DMNPs and (b) YcMNPs
in the alkaline pH range of 11. When decreasing the pH range to 9 to 3, the adsorption takes place there by 45 to 99% of arsenate was removed. Therefore, the acidic pH condition could remove more arsenate from aqueous solution due to strong electrostatic attraction between DMNPs or YcMNPs. Therefore, the adsorption percentage was varied in alkaline and acidic pH due to change in surface charges. Moreover, the adsorption efficiency was dramatically changed due to the presence of oxygen atoms on the surface of Fe$_3$O$_4$ nanoparticles and it can be polarized under different pH conditions. Consequently, the surface charge was changed from positive to negative or vice-versa when the pH value lying below or above zero point of charge due to surface complexation model [9]. Therefore decreasing the pH from 11 to 3, the surface amine groups in DMNPs or protein molecules in YcMNPs becomes more deprotonated and increasing the net negative charges which directs to high arsenate adsorption. The surface charge mechanism of the present results was well agreeable with the literature report [49].

The regenerating use of DMNPs and YcMNPs are the essential feature in water research. So, the desorption experimentation was carried out for the adsorbent after As(V) adsorption as shown in Fig 5.12(a,b). Attempts were made to desorb As(V) from DMNPs or YcMNPs surface using acid or alkali (0.1 N HCl or NaOH). The maximum desorption of arsenate in DMNPs was found as 20% whereas 40% of desorption was observed in YcMNPS. The maximum efficiency was observed in alkaline pH than acidic conditions. The results confirm that surface modified magnetite nanoparticles could be used repeatedly in an adsorption–desorption cycle. This is very much essential to expose the DMNPs and YcMNPs to remove arsenic in the cost effective and economically viable way.

5.3.4 Batch adsorption isotherms

The non-linear forms of the Freundlich and Langmuir isotherm models have been used to interpret the accurate experimental isotherm data. The Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on the adsorbent surface containing a finite number of identical sites [50]. This model assumes uniform energies of adsorption without transmigration of adsorbate in the plane of the surface [51]. The non-linearized form of the Langmuir isotherm was applied to calculate the arsenate adsorption using the following equation [52]:

$$$$
Fig 5.13. Langmuir adsorption isotherm of As(V) ions using DMNPs and YcMNPs

Fig 5.14. Freundlich adsorption isotherm of As(V) ions using DMNPs and YcMNPs
\[ q_e = \frac{Q_0 b C_e}{1 + b C_e} \]  

(1)

Where, \( C_e (\text{mg/l}) \) is the equilibrium concentration of the arsenate adsorbate, \( q_e (\text{mg/g}) \) is the amount of arsenate adsorbate adsorbed per unit mass after adsorption equilibrium.

The Langmuir constant, \( Q_0 (\text{mg/g}) \) represents the maximum adsorption capacity of the adsorbent and \( b (\text{l/mg}) \) is the Langmuir constant term related to the energy of adsorption.

The Freundlich isotherm model of the arsenate adsorption can be expressed by the following equation:

\[ q_e = k_F C_e^{1/n} \]  

(2)

Where, the Freundlich constant \( k_F (\text{mg/g (l/mg)^n}) \) represents the relative adsorption capacity of the arsenate adsorbent, \( 1/n \) giving indication on the adsorption intensity. It is an empirical model representing multilayer adsorption sites and heterogeneous adsorption energies.

Both Langmuir and Freundlich models were regressively evaluated to fit experimental values of arsenate adsorption using DMNPs and YcMNPs as shown in Fig 5.13 and 5.14 respectively. The calculated relative coefficient and non-linear \( R^2 \) values for the Langmuir and Freundlich are listed in Table 5.2. The experimental values of both DMNPs and YcMNPs were well fit to the Langmuir isothermal model (\( R^2 = 0.99 \& 0.95 \)) and Freundlich isotherm model (\( R^2 = 0.97 \& 0.93 \)) as shown in Table 5.2. The fitting of Langmuir isotherm was just a little better than the Freundlich isotherm model due to relative surface complexation. The result confirms that the interaction between arsenate and adsorbent have monolayer adsorption rather than multi-layer adsorption process [53].

In Langmuir model, the constant \( Q_0 \) measures the maximum adsorption capacity of arsenate on the adsorbents. The value of \( Q_0 \) (2.870) is relatively high in YcMNPs than DMNPs (\( Q_0 = 2.333 \)). Based on the Freundlich parameters, the adsorption on adsorbent can be calculated from ‘n’ values. If the ‘n’ value lies below 1, it represents poor adsorption, above 1-2 shows moderately complicate and 2-10 corresponds to the good adsorption behavior [54]. The ‘n’ value of YcMNPs is 3.92 which show good specificity.
Table 5.2: Fitted parameters from Langmuir and Freundlich plots for adsorption of As(V) ions

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir plot</th>
<th>Freundlich plot</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_0 ) (mg/g)</td>
<td>( b ) (l/mg)</td>
</tr>
<tr>
<td>DMNPs</td>
<td>2.333</td>
<td>94.225</td>
</tr>
<tr>
<td>YcMNPs</td>
<td>2.870</td>
<td>91.258</td>
</tr>
</tbody>
</table>

when compared to the DMNPs value of 2.90. In the present case, there is significant improvement in the absorption capacity of arsenate from aqueous solution compared to the existing literatures [42-46].

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, \( R_L \) [55], which is given by the equation

\[
R_L = \frac{1}{1 + bC_0}
\]

where, \( C_0 \) represents the initial metal ion concentration (mg/l), \( b \) represents the Langmuir constant, \( R_L \) represents the favorable adsorption for all the initial concentration. The adsorption efficiency was analyzed by measuring \( R_L \) (dimensionless) factor and can be used for interpretation of the sorption type as shown in Table 5.3 [56].

It is essential to study whether a Langmuir adsorption system is favorable or not by calculating the \( R_L \). The value of \( R_L \) in the present study has less than one and more than zero for different concentrations. It indicates the favorable adsorption of As(V) on the DMNPs and YcMNPs (Table 5.4).

5.3.5 Adsorption kinetics

Adsorption kinetics is important in predicting the mechanisms (chemical reaction or mass transport process) that control the rate of the pollutant removal and retention time of adsorbed species at the solid-liquid interface [57]. In order to find the most fitting model for the experimental data, two different kinetic models such as pseudo-first-order
Fig 5.15. Pseudo second-order kinetic plot for the removal of As(V) ions using (a) DMNPs and (b) YcMNPs from aqueous solution
Table 5.3: Equilibrium parameter ($R_L$) for adsorption of As(V) ions

<table>
<thead>
<tr>
<th>$R_L$</th>
<th>Types of isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>unfavorable</td>
</tr>
<tr>
<td>$R_L &lt; 0$</td>
<td>unfavorable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favorable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

Table 5.4: Equilibrium parameter of dimensionless constant ($R_L$) for adsorption of As(V) ions

<table>
<thead>
<tr>
<th>Adsorbate concentration (mg L$^{-1}$)</th>
<th>$R_L$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMNPs</td>
</tr>
<tr>
<td>0.5</td>
<td>0.331</td>
</tr>
<tr>
<td>1.0</td>
<td>0.495</td>
</tr>
<tr>
<td>1.5</td>
<td>0.594</td>
</tr>
<tr>
<td>2.0</td>
<td>0.661</td>
</tr>
<tr>
<td>2.5</td>
<td>0.709</td>
</tr>
</tbody>
</table>

Rate (Lagergren) and pseudo second-order rate fittings were also analyzed. The pseudo-first-order rate equation is qualified as follows:

$$q_t = q_e (1 - e^{-k_1 t})$$  \hspace{1cm} (4)

Where, $q_t$ represents the amount of adsorbate adsorbed at time $t$ (mg/g), $q_e$ represents the amount of arsenate adsorbed per unit mass of adsorbent at equilibrium (mg/g), and $k_1$ is the equilibrium rate constant of the pseudo-first-order (min$^{-1}$). The calculated kinetics parameters of DMNPs and YcMNPs were fitted with the experimental
Table 5.5: Fitted parameters for the Pseudo first-order and pseudo second order kinetics for the adsorption of As(V) ions by DMNPs and YcMNPs

<table>
<thead>
<tr>
<th>Initial As(V) Conc. (mg L⁻¹)</th>
<th>qₑ(Exp) (mg g⁻¹)</th>
<th>DMNPs</th>
<th>YcMNPs</th>
<th>DMNPs</th>
<th>YcMNPs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>k₁ (L min⁻¹ mg⁻¹)</td>
<td>R²</td>
<td>k₂ (g mg⁻¹ min⁻¹)</td>
<td>qₑ(Cal) (mg g⁻¹)</td>
<td>R²</td>
</tr>
<tr>
<td>0.5</td>
<td>0.49</td>
<td>ND</td>
<td>ND</td>
<td>17.80</td>
<td>5.060</td>
</tr>
<tr>
<td>1.0</td>
<td>0.99</td>
<td>ND</td>
<td>ND</td>
<td>0.040</td>
<td>0.750</td>
</tr>
<tr>
<td>1.5</td>
<td>1.47</td>
<td>1.48</td>
<td>0.0405</td>
<td>0.800</td>
<td>0.933</td>
</tr>
<tr>
<td>2.0</td>
<td>1.93</td>
<td>1.97</td>
<td>0.0405</td>
<td>2.685</td>
<td>0.964</td>
</tr>
<tr>
<td>2.5</td>
<td>2.25</td>
<td>2.45</td>
<td>0.0405</td>
<td>3.639</td>
<td>3.690</td>
</tr>
</tbody>
</table>

Please purchase PDF Split-Merge on www.verypdf.com to remove this watermark.
data as shown in Fig 5.15a. The experimental results did not agree with the calculated \( q_e \) values obtained from pseudo-first-order rate model and summarized in Table 5.5. The \( R^2 \) values are relatively low and it indicates the adsorption dynamics was not efficient. It indicates that the adsorption of arsenate on the DMNPs or YcMNPs did not follow the pseudo-first-order kinetics. In many cases the first order equation of Lagergren does not fit well to the whole range of contact time and generally show highly varied \( q_e \) values and also applicable only over the initial stage of the adsorption process [58].

Therefore, the pseudo-second-order kinetic model was used to study the adsorption kinetics of the present system. The pseudo second order model is based on the sorption capacity on the solid phase. Contrary to other well established models, it predicts the behavior over the whole range of studies. The pseudo second-order model is expressed as follows:

\[
q_t = \frac{q^2_k t}{1 + q_e k_2 t}
\]

(5)

Where, \( q_e \) represents the adsorption capacity on the solid phase and \( k_2 \) is the pseudo second-order rate constant (g/mg min). The experimental and calculated fitting graph of DMNPs and YcMNPs were shown in Fig 5.15b. The applicability of the pseudo second-order kinetics model is calculated for various initial As(V) concentrations and the proximity of \( R^2 \) to 1 designates the model fitting is in good agreement with experimental data as shown in Table 5.5. The value of \( R^2 \) fitting was superior in YcMNPs rather than DMNPS. The observed deviation can be attributed to the sharp fall in the adsorbent by vacant binding sites. Moreover, the sharing of electrons between the As(V) ions and DMNPs/YcMNPS through valence force induces the chemisorptions and rate-limiting of arsenate adsorption [59]. Therefore, the obtained result follows the pseudo-second-order kinetics rather than pseudo-first-order kinetics model. Thus, it shows that the pseudo-second-order kinetics model was appropriate for the entire adsorption process.

5.4 Discussion

The diethylamine plays a vital role in the formation of spherical to cabbage shaped \( \text{Fe}_3\text{O}_4 \) nanoparticles in the present solvothermal process and the corresponding schematic illustration is shown in Fig 5.7. Initially, the surface of the magnetite
nanoparticles was modified with diethylamine because it has to increase the stability, shape directing agents and surface capping that resulting in the formation of the amine functionalized Fe$_3$O$_4$ nanoparticles. Also, the diethylamine induces the crystal growth by increasing the concentration and it was confirmed from the XRD analysis. In addition, the amine group performs active molecule for nucleophilic substitution or electrophilic addition to the targeted host materials [60]. The different concentration of diethylamine induces the monodispersed cabbage shape that was already discussed in the growth mechanism observed from FESEM analysis. The driving force from the primary particle dipoles remarkably adjoined to induce the anisotropic growth of surface layer which leads to the cabbage shape [61]. After getting cabbage shaped Fe$_3$O$_4$ nanoparticles, the yeast cells were cross-linked through nanoprecipitation method. The successful cross-linking was confirmed from FTIR spectra and the corresponding peaks were very well matches with pure yeast spectrum. Both DMNPs and YcMNPs have superparamagnetic behavior with negligible coercivity and remanance as observed in magnetic measurements. The saturation magnetization of YcMNPs was higher than DMNPs due to the presence of surface dead layers and these values could be enough for magnetic separation. It has been seen that the surface charge of the DMNPs and YcMNPs were found to be -3.6 and -33.4 mV respectively. The negatively charged magnetite nanoparticles interact with the cationic As(V) ions to increase the percentage efficiency of the arsenate adsorption by varying the pH. The higher percentages of arsenate removal kinetics were attained due to the strong electrostatic attraction between the arsenate and DMNPs or YcMNPs [4].

The capacity of the DMNPs or YcMNPS to adsorb As(V) ions from aqueous solutions depends on many factors such as number of available active sites on its surface (protonation or deprotonation), the attraction of adsorbate for each site (depends on electrostatic conditions) and the amount of adsorbate available near the surface [62]. The monodispersed shape and size could efficiently adsorb guest molecules due to internal steric hindrance of irregular arrangement and tightly packed surface layer leads to efficient arsenic adsorption [63]. The present work shows high adsorption capacity of arsenate than those of reported literature [18,42-46,64-65]. The time dependent adsorption shows that 99% of arsenate removed from aqueous solution at 160 min for
DMNPs and at 120 min for YcMNPs in 2.5 ppm of arsenate concentration. The YcMNPs have short time interval for arsenate adsorption than DMNPs. It might happen that the yeast cells can prevent Fe$_3$O$_4$ nanoparticles from aggregating in the composites, and then increase the effective adsorption process, resulting in the high arsenate adsorption [64]. Also, the high negative surface charge of the YcMNPs induces strong electrostatic interaction and more exchange of ions. Another factor to influence the arsenate adsorption depends on varying the pH. The pH was increased from 3 to 11, the arsenate adsorption decreases due to two possible reasons. First, increasing ionic strength could decrease the electrostatic monolayer around the surface of adsorbent leading to particle aggregation and decrease the surface active sites. The other reason may be the increase in pH alters the positive charged As(V) to negative charged ions. The surface charge modification induces the steric repulsive force between As(V) ions and DMNPs or YcMNPs leading to decrease adsorption [65]. The adsorption isotherms of the As(V) on DMNPs and YcMNPs could be well fitted with the Langmuir model than the Freundlich model which indicates the monolayer along with high adsorption affinity favours desirable saturation capacities [66]. Similarly, the adsorption kinetics shows that pseudo second order is favourable rather than first order kinetics. This shows that the rate-limiting step may be chemisorbed and involving valence forces through sharing or exchange of electrons between the adsorbent and As(V) ions [67]. The combination of a highly selective ion exchange with magnetic separation provides a promising approach for the processes to remove arsenate in wastewater and recover in solutions, which can be further processed to recycle the substance to a manufacturing process. The schematic diagram in Fig 5.16 shows the understanding mechanism of how the magnetite nanoparticles manipulate the arsenate separation using external magnetic field. In the first cyclic process, the DMNPs or YcMNPs were mixed with polluted (arsenate) aqueous solution. Afterwards, shaking at various time intervals (0-180 min), the DMNPs or YcMNPs could absorb the arsenate from polluted water. After adsorption, part of the magnetite nanoparticles were dispersed or settled at the bottom of the aqueous solution. The strong external magnetic field was applied to the surface of the solution container, the adsorbed arsenate in adsorbent were attracted by strong magnet. Then, 99 % of arsenate free aqueous solution was separated and the solution was used for further
Fig 5.16: Schematic illustration for the proposed mechanism of removal of As(V) ions using magnetic separation method

process. Therefore, the magnetic separation using Fe₃O₄ nanoparticles could be a feasible way to remove the arsenate from water, which is more convenient than conventional approaches of centrifugation or filtration.

Generally, the involved magnetic force \( F_m \) for magnetic separation can be expressed as \[ 2\]

\[
F_m = \mu_0 V_p M_p \Delta H
\]

(6)

Where, \( M_p \) represents the sample magnetization, \( \mu_0 \) symbolizes the permeability of free space, \( V_p \) describes the particle volume and \( \Delta H \) represents the gradient of magnetic field strength at the position of the nanoparticles. The nanoparticle magnetization may be expressed as

\[
M_p = \chi H
\]

(7)
Where $H$ represents the external magnetic field strength and $\chi$ represents the magnetic volume susceptibility. During magnetic separation, the gravitational force also plays an important role and it can be expressed as

$$F_g = (\rho_p - \rho_g)V_p g$$ \hspace{1cm} (8)

Where $g$ represents the acceleration due to gravity, $\rho_p$ describes the particle density and $\rho_g$ represents the density of fluids. According to the Stokes’ law, the hydrodynamic drag force $F_d$ can be expressed as

$$F_d = 6\pi\eta b(\nu_f - \nu_p)$$ \hspace{1cm} (9)

Where $b$ is a constant depending on the fluids and dimension of the particles, $\eta$ is the dynamic viscosity of the fluid, $\nu_p$ and $\nu_f$ represents the velocities of the particles and fluids respectively. From the above equations, the adsorbed arsenate containing magnetic nanoparticles depends on the particle scan be successfully separated from the aqueous solutions, even with a hand-held magnet.

5.5 Conclusion

The diethylamine functionalized Fe$_3$O$_4$ nanoparticles was successfully prepared via facile solvothermal process. The yeast cells were cross-linked with Fe$_3$O$_4$ nanoparticles by simple nanoprecipitation method. The presence of the diethylamine and cross-linked yeast cells in Fe$_3$O$_4$ nanoparticles were confirmed by FTIR analysis. The growth mechanism of the cabbage shaped nanostructures was proposed by self-assembly of primary layers via diethylamine. The negative surface charge of the magnetite nanoparticles was confirmed from zeta potential analysis which was required to adsorb the arsenate fast. The prepared magnetite nanoparticles were successfully applied as an effective adsorbent material for the removal of As(V) ions from the aqueous solution. In comparison, the YcMNPs have high arsenate removal efficiency than DMNPs. The removal efficiency were depends on adsorbent dosage, contact time and pH respectively. The experimental data were well fitted with Langmuir rather than Freundlich isothermal models due to monolayer surface homogeneity and accurate percentage of the arsenate adsorption. The dimensionless parameter $R_L$ provides the adsorption capacity and it confirm the present process is a favorable process. The future
direction of this work not only based on arsenic removal but also leads to remove other heavy toxic metal ions to make commercial products for multi functional environmental remediations.

In addition, the negative surface charge, high chemical and physical stability and the rich surface functionalization of amine or Fe₃O₄@yeast nanocomposites will also find other potential applications such as in the fields of targeted drug delivery, enzyme immobilization, magnetic separation and catalysis.
Reference


