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Synthesis and characterization of chitosan-magnetic iron nanoparticles

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ABSTRACT

Absorption is a common technology used for water and wastewater treatment since it is often fast and efficient, while costly at the same time. Therefore, the development of low-cost and efficient adsorbents has led to the rapid growth of research interest in this regard. Chitosan is a natural polyaminosaccharide with effective adsorption properties, which is applied to remove various pollutants. However, it has low efficiency in the adsorption of some pollutants, and its separation from aqueous solutions is difficult as well. Therefore, modification of chitosan has been recommended to address this issue. The present study aimed to synthesize nanosized chitosan-magnetic iron particles and determine their properties. Magnetic iron nanoparticles were fabricated using the chemical precipitation method, and magnetic chitosan was prepared. Several methods were applied to assess the properties of the synthesized adsorbent, including scanning electron microscopy, X-ray diffraction, atomic force microscopy, Fourier-transform infrared spectroscopy, dynamic light scattering, and zeta potential. Chitosan-magnetic iron nanoparticles had higher surface roughness and irregular pores, and the magnetic iron nanoparticles were successfully embedded in chitosan. Due to the surface charge of the chitosan-magnetic iron nanoparticles, it could be used as an effective adsorbent for the removal of contaminants with negative charge and their complete separation from aqueous solutions using magnets.

Keywords: Adsorbent, Chitosan, Magnetic iron nanoparticles, Modification

Introduction

Several methods are available for the removal of pollutants from aqueous environments, which could be classified as coagulation and flocculation,[1] chemical oxidation,[2] ion exchange, advanced oxidation,[3] fenton,[4] adsorption,[5] photocatalysis,[6] and membrane.[7] Among these methods, the absorption process has been extensively investigated by researchers due to its initial cost, simplicity, high flexibility, easy operation, insensitivity to toxic compounds, and ability to remove organic and inorganic compounds.[8]

Absorption is a separation process, in which solid particles are transferred from the liquid phase to the surface of a solid adsorbent. Previously, the use of adsorbents was based on

trial and error, while the current basis of absorption methods is the determination of pore structure, porosity, surface energy, functional groups, and operational parameters.[9] Natural polysaccharide polymers, such as chitosan and its derivatives, are considered to be effective adsorbents owing to their easy access, high absorption capacity, non-toxicity, environmental compatibility, cost-efficiency, and lack of sludge production.[10]

Chitosan is a natural polyaminosaccharide synthesized from the deacetylation of chitin, which is a polysaccharide predominantly consisting of unbranched chains of β-(1→4)-2-acetamido-2-deoxy-d-glucose.[11]

Natural chitosan has a low absorption capacity, and chemical modification is performed to enhance its absorption capacity.[12] This process is mainly carried out using magnetic iron. The correction of chitosan absorption capacity using magnetic iron is due to the fact that these metal compounds are chemically stable and have a high absorption

capacity.[13] Chitosan-iron complex is formed from chitosan polymer chains with iron via the amine group (-NH2) and hydroxyl group (-OH), thereby improving its absorption capability and facilitating its collection. This is considered to be a major advantage since the separation could be easily achieved using an external magnetic field.[12, 14] Furthermore, these particles will be reusable after retrieval. As such, numerous studies have been focused on the use of modified chitosan to remove various contaminants. For instance, Ekhlasi used chitosan to adsorb lead from aqueous solutions, reporting the elimination efficiency of 86%.[15] On the other hand, Raeiatbin applied magnetic chitosan for the adsorption of tetracycline from hospital wastewater.[16]

Although chitosan modification has improved its absorption properties, the findings in this regard have denoted that the modification conditions play a pivotal role in the adsorbent properties of this compound. Therefore, several studies have been conducted to identify the effective modification methods and operation conditions for the optimization of chitosan.

The present study aimed to synthesize nanosized chitosan-magnetic iron particles and determine their properties.

Materials and Methods

This applied research was conducted on a laboratory scale. All the chemicals were purchased from reputable enterprises and were of a standard laboratory grade. The adsorbent was prepared in two steps. The first stage involved the synthesis of magnetic iron nanoparticles using the chemical precipitation method as the most common approach to producing magnetic iron nanoparticles. In this method, bivalent and trivalent iron is mixed with an alkaline agent (e.g., ammonia), and a magnetic solution with negative charge is obtained by controlling the conditions of the experiment. To this end, 4.1 g of $FeCl_3$ and 2.5 g of $FeCl_2$ were placed in an ultrasonic transducer until the homogenization process was completed. Afterwards, the two compounds were combined and placed on a magnetic stirrer at the temperature of 80 ºC. Following that, 20

ml of ammonia solution was added, and the black solution was placed on the agitator for one hour at the temperature of 80 ºC. The prepared nanoparticles were washed repeatedly with distilled water and ethanol, separated with a neodymium magnet, and dried in an oven at the temperature of 70 ºC.

At the second stage, magnetic chitosan was prepared. Initially, five g of chitosan was added to 100 ml of carboxylic acid (0.5 N), and pH was increased to eight by adding a few drops of ammonia. The prepared solution was placed on the stirrer for 24 hours at room temperature. Following that, 0.3 g of ferromagnetic nanoparticles was added, nitrogen gas was injected into the solution, and the solution was placed on the stirrer for 60 minutes. Afterwards, 25 ml of ammonia (1 M) was gently added to the adsorbent. After 60 minutes, the solution was washed repeatedly, dried at the laboratory temperature, and used as the carboxylated chitosan modified with ferromagnetic nanoparticles (modified sorbent) in the experiments.[17]

Several methods were used to assess the properties of the synthesized adsorbent, bare chitosan, and iron nanoparticles. Moreover, the morphology of the synthesized adsorbent was evaluated via scanning electron microscopy (SEM; TESCAN, Czech Republic). The structural properties of the nanoparticles were also investigated using powder X-ray diffraction (XRD; INEL-Equinox-3000, France). In addition, surface topography and roughness were analyzed using atomic force microscopy (AFM; Ara-Research, model: Advance, Iran). A Fourier-transform infrared (FTIR) spectrometer (Bruker, model: Tensor 27, Germany) was also used to determine the functional groups.

Results and Discussion

Fig. 1 shows the SEM images of the magnetic iron nanoparticles and chitosan-magnetic iron nanoparticles with the magnification of 200 and 500 nanometers, respectively. The investigation of the images indicated that the outer surface of the chitosan-magnetic iron nanoparticles had higher roughness and more irregular pores

compared to the magnetic iron nanoparticles, which resulted in more reactive regions and
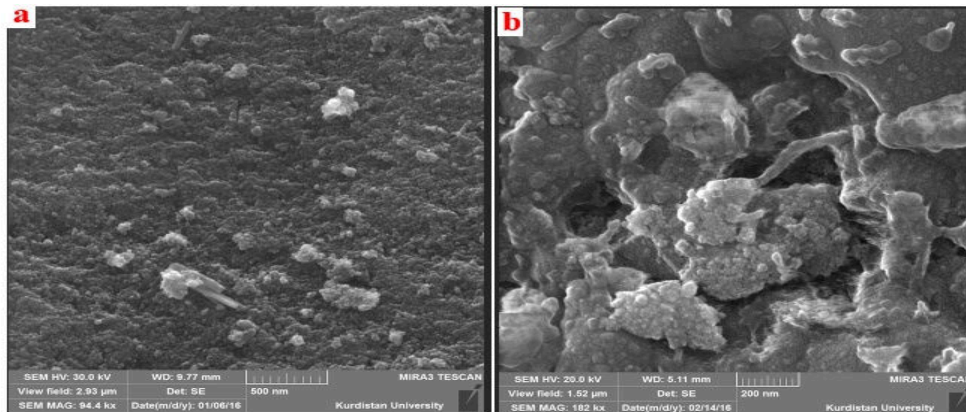
higher adsorption capacity.

Fig. 1. SEM image of a) Fe_3O_4 and b) chitosan-magnetic iron nanoparticles

In the present study, XRD images were used to verify the crystalline structure, measure the mean distance between the layers and atomic series, and determine the position of single crystals or grains.[18] Figure 2 depicts the XRD images of the magnetic iron nanoparticles and chitosan-magnetic iron nanoparticles within the 2θ range of 10-90°. As can be seen, the formed peak at 23.2° belonged to chitosan. Furthermore, the synthesized adsorbent was

relatively similar to pure magnetite. The main peaks (2θ) observed at 62.5°, 56.9°, 53.4°, 43.1°, 35.4°, and 30.1° corresponded to 220, 311, 400, 422, 511, 440, which were consistent with Fe_3O_4 based on the JCPDS card No. 19-0629.[19] Therefore, it could be concluded that the magnetic iron nanoparticles were successfully located onto the chitosan surface, and chitosan-magnetic iron nanoparticles could be separated from aqueous solutions using magnets.[19]
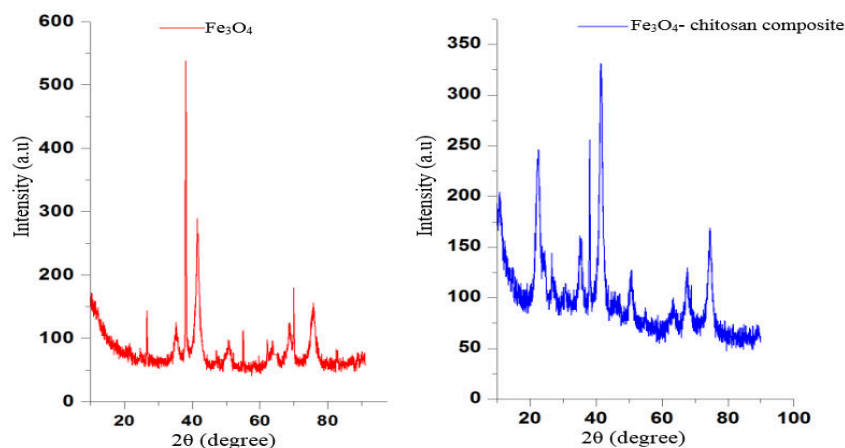

Fig. 2. XRD patterns of a) Fe_3O_4 and b) chitosan-magnetic iron nanoparticles

Fig. 3 shows the FTIR results regarding raw chitosan, carboxylated and modified chitosan, and magnetic iron nanoparticles. The

band observed at 578.6 cm^{-1} for the magnetic iron nanoparticles and chitosan-magnetic iron nanoparticles was attributed to the Fe-O tensile

bond of Fe_3O_4.[17,20] In addition, the bands observed at 3,413-3,440 cm^{-1} were attributed to 3,440 cm^{-1} in raw chitosan, carboxylated and modified chitosan, and magnetic iron nanoparticles were attributed to the tensile frequency of O-H and N-H.[20,22] A weak band was also observed at 2900 cm^{-1} for all the chitosan samples, which could be attributed to the –CH bond to carbon compounds. Another band was observed at 1,657 cm-1 for the ferromagnetic nanoparticles, as well as raw and carboxylated chitosan, which was more intensive in case of the carboxylated chitosan-

the tensile frequency of O-H and N-H.[20,21] The observed bands within the range of 3 ,413-ferromagnetic nanoparticle composite and could be attributed to the C=O tensile bond.

In the current research, the FTIR spectrum clearly confirmed the composition of the chitosan and magnetic iron nanoparticles. Similar results have been reported in the previous studies in this regard. For instance, Mohseni claimed that the band was observed at 578 cm^{-1} for iron nanoparticles and 3,440-3,413 cm^{-1} for the tensile strength of O-H and N-H.[17]
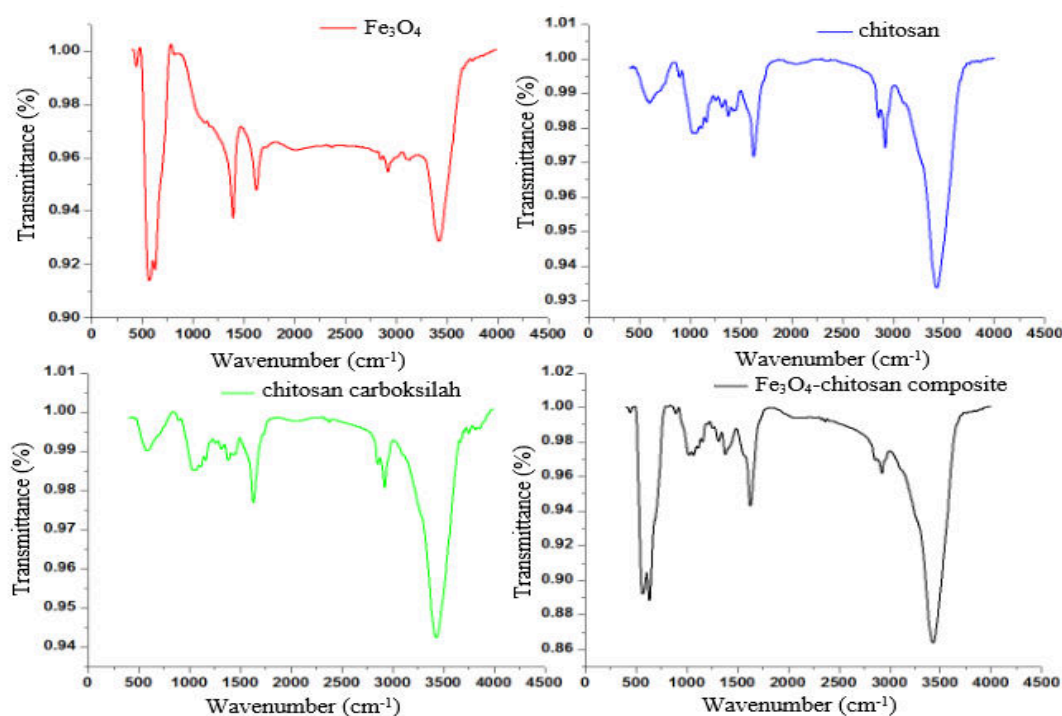

Fig. 3. FTIR spectra of Fe_3O_4, chitosan and chitosan-magnetic iron nanoparticles

Fig. 3 shows the FTIR spectra of Fe_3O_4, chitosan, and chitosan-magnetic iron nanoparticles. In the present study, the zeta potential method was also applied to recognize the electrical conditions of the colloidal suspensions. In addition, the zeta potential measurements were performed for the magnetic iron nanoparticles and chitosan-magnetic iron nanoparticles at the optimal pH. To this end, 0.01 g of the adsorbent was added to five ml of distilled water and placed under ultrasonic wave for 15 minutes. Afterwards, the zeta potential was

determined, and the results are presented in Table 1. According to the information in this table, the zeta potential of the magnetic iron nanoparticles and chitosan-magnetic iron nanoparticles was -8.45 and 6.46 mV, respectively.

Table 1. Zeta potential of Fe_3O_4 and Fe_3O_4-chitosan composite Nanoparticles

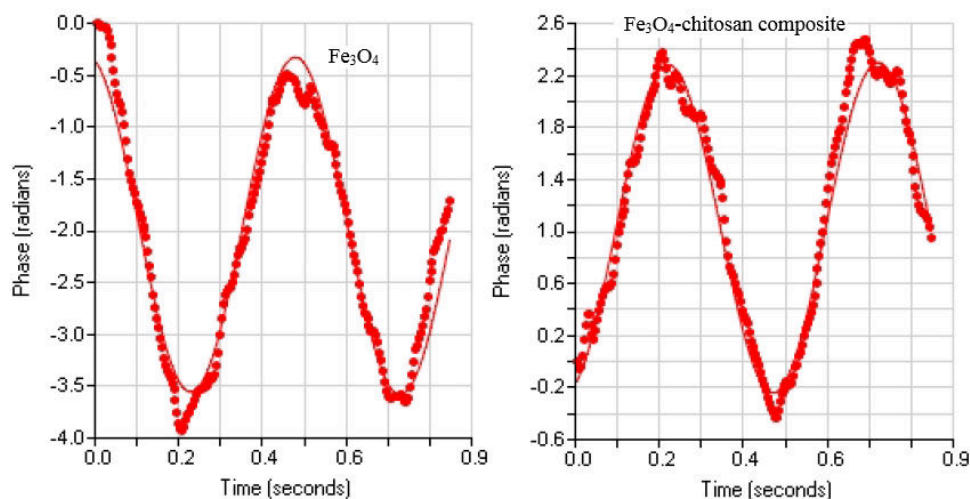|	Zeta Potential (mV)	Mobility (μ/s)/(V/cm)
Fe_3O_4	-8.45	-0.66
Fe_3O_4-chitosan composite	6.46	0.5

Fig. 4. Zeta potential of Fe$_3$O$_4$ and chitosan-magnetic iron nanoparticles

Fig. 5 depicts the results of dynamic light scattering (DLS) for the magnetic iron nanoparticles and chitosan-magnetic iron nanoparticles. As can be seen, the addition of iron reduced the size and uniform distribution of chitosan. The particle size was estimated to be within the range of 120-200 nanometers. In a similar study, Mohseni reported the particle size of magnetic chitosan to be within the range of 20-50 nanometers.[17] Furthermore, Hritcu reported the size of chitosan particles to be approximately 0.7 micrometers.[23]
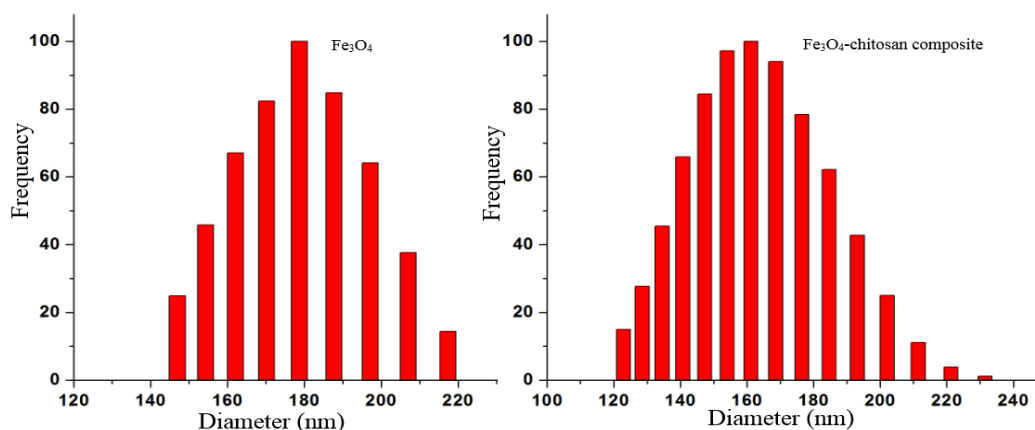

Fig. 5. DLS results of Fe$_3$O$_4$ and chitosan-magnetic iron nanoparticles

Conclusion

This study aimed to investigate the synthesis and characterization of magnetic iron nanoparticles and chitosan-magnetic iron nanoparticles. Morphological and specification analyses were performed for the magnetic iron nanoparticles and chitosan-magnetic iron nanoparticles, including SEM, FTIR, XRD, zeta potential, and DLS. The SEM results indicated that the chitosan-magnetic iron nanoparticles had higher surface roughness and more irregular pores compared to the magnetic iron nanoparticles. On the other hand, the XRD spectrum of the chitosan-magnetic iron nanoparticles was relatively similar to pure magnetite. Therefore, it could be concluded that the magnetic iron nanoparticles were successfully embedded in chitosan. According to the FTIR spectrum and based on the presence of Fe-O tensile bond at 578.6 cm^{-1} in the chitosan composite, modification was carried out successfully, resulting in the production of magnetic chitosan; this finding could explain the presence of the iron nanoparticles in the chitosan-magnetic iron nanoparticles. Due to the surface charge of the chitosan-magnetic iron

nanoparticles, this adsorbent could be used for the removal of contaminants with negative charge and their complete separation from aqueous solutions using magnets.

Acknowledgements

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