

Application of Magnetite Nanoparticles in Phenylalanine Removal from Water Samples

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Abstract

The purpose of the current research is investigating the phenylalanine removal by using magnetic nanoparticles (Fe_3O_4) from water samples. The effect of pH, contact time and phenylalanine concentration on phenylalanine adsorption efficiency by magnetite nanoparticles are studied in a batch system. Transmission electron microscopy (TEM), X-ray Diffraction Patterns (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the synthesized magnetite nanoparticles.

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1. Introduction

Nanostructured materials have unique properties which make them applicable for a variety of applications [1]. The nanomaterial level is the most advanced at present, both in scientific knowledge and in commercial applications. The majority of commercial nanoparticles are used in medicine. This application in medicine includes: bio detection, detection of proteins, separation and purification of biological molecules and cells. Moreover, the metal oxide nanoparticles are widely used in industrial, and cosmetic [2]. Different

chemical methods such as solvothermal, microwave, and co-precipitation have been used to prepare these materials [3-6]. Nonfunctional iron oxide has been previously used as metal adsorbent [7, 8]. The purpose of the present work was to investigate the phenylalanine removal from aqueous solutions by employing iron oxide as magnetic nanoparticle. The effect of important parameters such as pH, contact time and concentration of phenylalanine on adsorption efficiency were investigated. Phenylalanine is an amino acid that is widely used in many industries,

such as food, chemical, pharmaceutical, agricultural, medicine, and cosmetic [9]. To improve the efficiency of separation of amino acids from wastewater coming from fermentations broths, several techniques have been already employed [10-13]. For this aim, many studies have been reported for adsorption of amino acids on various materials including activated carbon, silica, ion exchangers, alumina, and polymeric resins [14-18]. A common mode of adsorption between amino acids and metal oxide surfaces is by electrostatic forces of attraction, since both amino acids and metal oxides are amphoteric in nature i.e. they can exist in different charged conditions, positive or negative, under different environmental conditions. The study of adsorption of amino acids on metal oxide particles has received increasing attention due to its practical importance and potential in the biochemical industries [19-25]. Notably, amino acids as the basic constituents of proteins and biological macromolecules have critical importance to the body. Drug delivery [26-28] and surface coating [29-33] are other fields in which the possibility of adsorption of amino acids on magnetic surfaces is of interest. The present investigation deals with adsorptive behavior of phenylalanine on nano-sized magnetic particles.

2. Experimental

2.1. Materials

Anhydrous Ferric chloride (FeCl_3), Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), methanol, L-Phenylalanine and ammonia were all analytical grade from Merck Chemical Co. and the water used in this study was double distilled.

2.2. Equipment

The morphology and dimension of the Fe_3O_4 were obtained from transmission electron microscopy

(TEM) using a (Philips, CM10) Model at a voltage of 100 kV. The phase purity was characterized by X-ray powder diffraction (XRD) (D8-Advance) using $\text{Cu-K}\alpha$ radiation ($\lambda=1.54056 \text{ \AA}$). The Phenylalanine concentrations were determined using a HPLC (JASCO, 100 Micro liters, USA). The pH measurements were performed with a (Metrohm 780) pH meter. FTIR spectra were obtained using a (Bruker Optics Ft Tensor 27, Germany) spectrophotometer to identify the functional groups and chemical bonding of the coated materials. The Rotator (Speed 220 R.P.M, Weight 32 kg, PARS AZMA Co. IRAN) was used to shake the test tubes.

2.3. Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 magnetic nanoparticles were prepared according to Maity et al. procedure with only minor modification [34]. Magnetic nanoparticles were prepared by chemical precipitation method. A complete precipitation of Fe_3O_4 was achieved under alkaline condition by maintaining a molar ratio of $\text{Fe}^{2+} : \text{Fe}^{3+} = 1:2$ under an inert environment. To obtain magnetic nanoparticles, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and FeCl_3 were dissolved under inert atmosphere in double distilled water with vigorous stirring (1000rpm). While the solution was heated to 80°C , ammonium hydroxide solution (25%) was added. To ensure the complete growth of the nanoparticle crystals, the reaction was carried out for 30 min at 80°C under constant stirring. The resulting suspension was cooled down to room temperature and it was repeatedly washed with double distilled water to remove unreacted chemicals. Finally, the wet magnetic particles were obtained by dewatering in a magnetic field.

2.4. Phenylalanine adsorption procedure

Phenylalanine adsorption by Fe_3O_4 has been studied in batch experiments. A known amount of

sorbent was mixed with 10 ml aqueous solution of phenylalanine and then a rotator was applied to shake the nanoparticles over a period of time. The phenylalanine concentration of aqueous phase was calculated according to Eq. (1):

$$\text{Phenylalanine removal efficiency (\%)} = \left[\frac{C_i - C_f}{C_i} \right] \times 100 \quad (1)$$

Where C_i and C_f are the initial and final concentrations of phenylalanine before and after the sorption, respectively.

The obtained Fe_3O_4 /Phenylalanine nanoparticles were separated afterwards by centrifuging the solution at 1000 rpm.

3. Results and discussion

3. 1. Characterization of nanoparticles

The identity and the phase purity of the synthesized nanoparticle were confirmed by XRD (Fig.1). As can be seen, the XRD pattern of magnetite nanoparticles was in good agreement with that of the standard Fe_3O_4 structure. The XRD spectrum of iron oxide nanoparticles exhibited peaks at 35.5, 43.1, 57 and 62.6 which correspond to magnetite (Fe_3O_4).

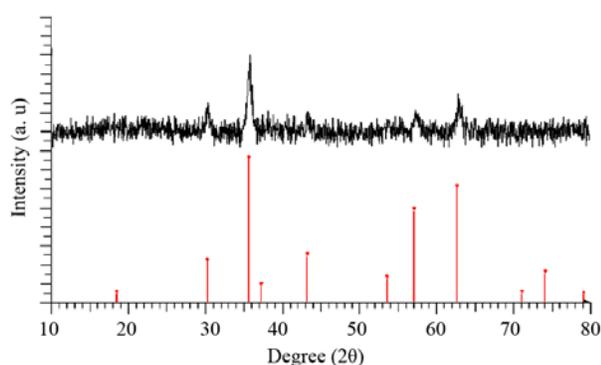


Fig. 1. XRD patterns of Fe_3O_4 nanoparticles.

The FT-IR spectrum is a helpful analysis in identifying the surface chemical composition of nanoparticles. The FT-IR spectra of Fe_3O_4

nanoparticles, Phenylalanine, and Phenylalanine / Fe_3O_4 nanoparticles are shown in Fig. 2a, 2b, and 2c, respectively. The peak appeared at 587cm^{-1} in Fig. 2a, is assigned to Fe-O bonds of Fe_3O_4 lattice. According to Ishii et al, there are two bands in FT-IR spectrum of Fe_3O_4 which the band at 570cm^{-1} can be assigned to the Fe^{3+} -O stretching mode of the tetrahedral and octahedral sites and the band at 390cm^{-1} is related to the Fe^{2+} -O stretching mode of the octahedral sites [35]. The peak at around 3390cm^{-1} as well as the appeared peak at 1630cm^{-1} are due to the stretching and bending vibration of water molecules present in KBr, respectively. The FT-IR spectrum of phenylalanine shown in Fig. 2b shows a series of bands recorded at 1074 and 700cm^{-1} which are ascribed to vibration modes of phenyl groups. The small appeared peak at around 3600cm^{-1} is ascribed to the stretching vibration of N-H of amide group. Moreover, the strong absorption at 1680cm^{-1} is assigned to the stretching vibration of C=O in amino acid. Other peaks from 500-1600 are due to the bending vibrations of either C=C, C=O, C=C, and C=N bonds. In Fig. 2c, it can be clearly observed that there is an interaction between phenylalanine and Fe_3O_4 so that some of the aromatic bending vibrations at around 600cm^{-1} are covered with the dominant Fe-O vibration. Moreover, it can be seen that the C=O stretching vibration of phenylalanine which is appeared at around 1680cm^{-1} (Fig. 2b) is shifted to the lower frequencies (Fig. 2c). It is an evidence for adsorption of phenylalanine onto the magnetite nanoparticles.

TEM micrograph for the prepared magnetic nanoparticles is shown in Fig.3. From the figure it is observed that the size of the magnetic nanoparticles is about 50 nm. The formed particles tend to cluster as they are hygroscopic in nature.

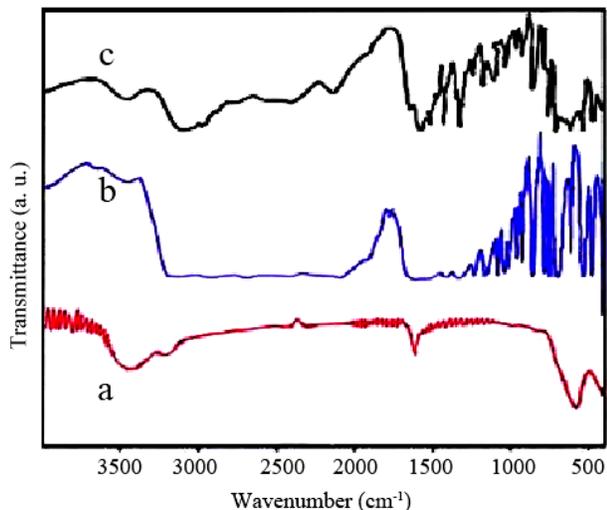


Fig. 2. FTIR spectra of (a) Fe₃O₄ nanoparticles (b) Phenylalanine and (c) Fe₃O₄/ Phenylalanine.

3.2. Adsorption of phenylalanine on Fe₃O₄ nanoparticles

Adsorption experiments were carried out in order to optimize of the main factors affecting the adsorption such as pH of the solution, contact time and concentration.

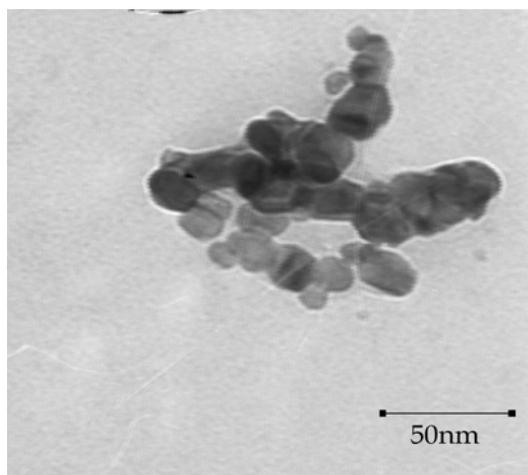


Fig. 3. TEM images of Fe₃O₄ nanoparticles.

Since pH played a key role in the adsorption process, the performance of the nanoparticle was studied in the pH range of 4.0–10.0 (Fig. 4). It is

shown that the sorption of phenylalanine onto nano-Fe₃O₄ is initially increased with pH and a plateau occurred at pH 9 onwards. As can be seen, under acidic pH conditions, the nanoparticles have lower adsorption tendencies.

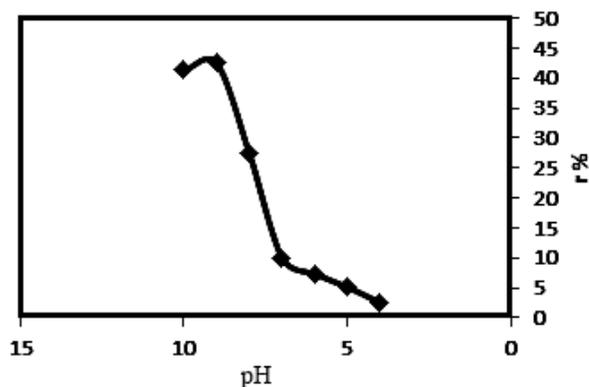


Fig. 4. The pH effect on the adsorption efficiency of phenylalanine on Fe₃O₄ nanoparticles.

The time dependent of phenylalanine removal from aqueous solutions was monitored for 12 hours (Fig.5). It could be seen that the maximum phenylalanine removal was obtained within 10 h, and then gradually reached to equilibrium in 12 h and no significant change was observed after that.

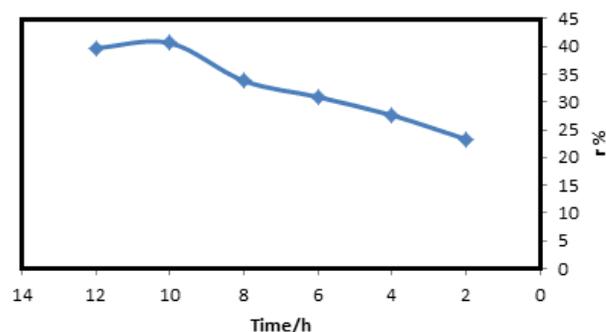


Fig. 5. Effect of contact time on the adsorption of phenylalanine by Fe₃O₄ nanoparticles.

As seen in Fig.6 the removal percentage of phenylalanine reached to a maximum value in 1.2mM concentration of phenylalanine.

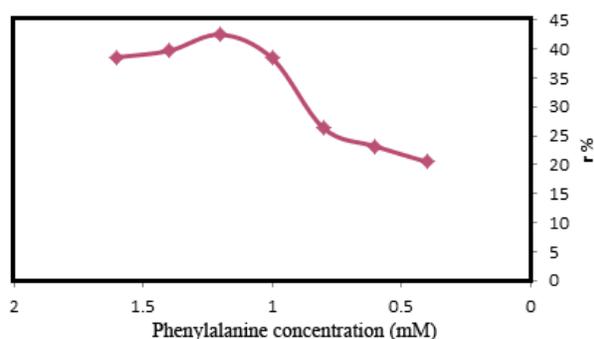


Fig. 6. Effect of phenylalanine concentration on the adsorption of phenylalanine by Fe_3O_4 nanoparticles

4. Conclusion

Magnetic nanoparticles were synthesized by chemical co-precipitation method. From XRD and FTIR analysis it is clear that the particles formed correspond to Fe_3O_4 . From the TEM analysis it is clear that the magnetic particles formed has a size less of 50 nm. The present study indicates that the prepared magnetite nanoparticles are potential adsorbent with relatively high efficiency to remove phenylalanine from aqueous solutions. The sorption process was found to be pH dependent and the maximum adsorption was observed at pH 9.0. The maximum adsorption capacity of the applied nano- Fe_3O_4 was measured to be 17.25 mg/g. Accordingly, the prepared sample can be a promising candidate for further studies.

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