

RESEARCH PAPER

Phenylalanine Removal from Water by Fe₃O₄ Nanoparticles Functionalized with Two Different Surfactants

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ABSTRACT

In the present study, the application for the removal of phenylalanine by using two nano sorbents, namely, cetyltrimethylammonium bromide - Coated and BKC (benzalkonium chloride)-Coated Fe₃O₄ nanoparticles was investigated. Solid-phase extraction (SPE) and ultra violet-visible spectroscopy were used for studying the removal ability of each nano-sorbent in this study. Scanning Electron Microscopy, X-ray diffraction and Fourier infrared were used to characterize the synthesized magnetite nanoparticles. Batch adsorption studies were carried out to study the effect of various parameters, such as contact time, solution pH and concentration of phenylalanine. The equilibrium adsorption data of phenylalanine onto Fe₃O₄ nanoparticles (non-functionalized sample), cetyltrimethylammonium bromide -Coated and BKC -Coated were analyzed using Freundlich and Langmuir adsorption isotherms. The results indicated that adsorption of phenylalanine increased with increasing solution pH and maximum removal of phenylalanine was obtained at pH=9.0. Correlation coefficient were determined by analyzing each isotherm. It was found that the Freundlich equation showed better correlation with the experimental data than the Langmuir.

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INTRODUCTION

Iron oxide magnetite (Fe₃O₄) has been intensively researched in recent years bearing to its special properties in chemistry as well as wide application in biology and catalysis areas [1–6]. Magnetic nanoparticles (MNPs) have attracted much attention because of their remarkable properties in the fields of medicine and biology such as cell isolation, [8] targeted drug delivery, [9, 10] enzyme immobilization, [11, 12] immuno assays, [13] and food analyses [14–16]. There are some industrial methods to synthesize MNPs including ball milling [17], chemical precipitation [18–21], thermal decomposition [22, 23], and

sonochemical synthesis [24].

Among the mentioned methods, chemical precipitation is commonly the simplest and is often used to produce Fe₃O₄ nanoparticles. Fe₃O₄ nanoparticles tend to aggregate due to strong magnetic dipole-dipole attractions and therefore, modification of the surface of the Fe₃O₄ nanoparticles during synthesis with various biodegradable polymers like xerogels [25], hydrogels [26], and organic surfactants was prevented from aggregation in solution [27].

Firstly, the aim of this study was to synthesize Fe₃O₄ nanoparticles with and without surfactants as coating materials in order to investigate the

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size modification of Fe₃O₄ nanoparticles. We choose microemulsion method for nanoparticles preparation that it has been used to synthesize various kinds of nanomaterials in recent years, such as catalytic and magnetic materials [28, 29–32]. Amino acids are essential for human beings and have many functions in metabolism. Phenylalanine (Phe) is a non-polar aromatic amino acid and has been extensively used as ingredient in the pharmaceutical and nutrition industries [33,34,35]. Phenylketonuria is a disease in which the oxidation of phenylalanine is impaired due to a deficiency of the phenylalanine hydroxylase enzyme, resulting in several problems including mental retardation and reduction of life expectancy [36,37]. The production of protein hydrolysates which is consumed by phenylketonuria patients depends on Phenylalanine removal. Adsorption of phenylalanine on materials such as activated carbons, zeolites, ion exchangers and polymeric resins have been reported in the scientific literature [38–42].

In this work, adsorption of Phe by using these three nanosorbents were compared and discussed. A common mode of adsorption between amino acids such as phenylalanine and metal oxide surfaces is by electrostatic forces of attraction, because both amino acids and metal oxides are amphoteric in nature, so they can exist in positive or negative charged conditions, under different ambient conditions. Benzalkonium chloride solutions are fast-acting biocidal agents with a moderately long duration of action. They are active against bacteria and some viruses, fungi, and protozoa. Benzalkonium chloride is also used as a preservative in nasal pharmaceuticals [43].

Materials and Methods

Anhydrous Ferric chloride (FeCl₃), Ferrous sulfate (FeSO₄·7H₂O), Methanol, Phenylalanine and ammonia were all of analytical grade from Merck (Germany), Chemical Co. and Surfactants [BKC and CTAB (C₁₉H₄₂BrN)] was purchased from Sigma. The water used in this study was double distilled.

Equipment

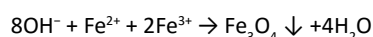
The phase purity was characterized by X-ray powder diffraction (XRD) (X Pert Prompd, Philips, Netherland) using Cu-Kα radiation (λ=1.54 Å). Scanning Electron Microscopy (SEM) micrographs were taken on a KYKY—EM3200 microscope. The Phenylalanine concentrations were determined

using a UV spectrometer (Beijing Rayleigh Analytical Instrument corp UV-2100). 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.

Preparation of uncoated nanomagnetic particles

First, uncoated nanomagnetic particles were prepared by chemical precipitation method. FeSO₄·7H₂O and FeCl₃ 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 was repeatedly washed with double distilled water to remove unreacted chemicals. Finally, the wet magnetic particles were obtained by dewatering in a magnetic field.

The Fe₃O₄ nanoparticles were prepared via the following reaction equation:



Preparation of coated nanomagnetic particles

To prepare coated nanomagnetic particles, 2.0 g surfactant (CTAB or BKC) was dissolved in 20 ml n-heptane and 12 ml n-hexanol to reach a transparent solution by stirring. The above solution was then put into a three-necked flask and stirred for 20 min at 40 under a nitrogen atmosphere. 0.5 mol/L of freshly prepared aqueous iron (II) sulfate in 0.6 mL double distilled water was then injected rapidly. After 2 min, 1.0 ml aqueous ferric chloride solution (0.5 mol/L) was added. The solution turned into light brown color. The emulsion containing 2 ml ammonia water (25% NH₃) as the water phase was also prepared using the same oil and surfactant phase. After 20 min, the emulsion containing ammonia was injected drop wise into the above three-necked flask with vigorous stirring at 70. The color of the solution quickly turned from light brown to black. The entire solution was heated at 70°C for 3 h. The whole procedure was carried out under an inert atmosphere to prevent the oxidation of

ferrous ions. Finally, the crude product was aged for 2 h at room temperature before being repeatedly washed with ethanol and water. The crude product was then retrieved by centrifugation and dried in a vacuum oven at 80 °C for 8 h.

Phenylalanine removal procedure

Phenylalanine adsorption by Fe₃O₄ 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 them over a period of time. The phenylalanine concentration of aqueous phase was calculated according to Eq. (1):

$$R = \left[\frac{C_0 - C_e}{C_0} \right] \times 100 \quad (1)$$

Where *R* is the removal efficiency of the Phenylalanine, *C*₀ and *C*_e are the initial and final concentrations of phenylalanine before and after the sorption, respectively.

Equilibrium adsorption study

The equilibrium adsorption capacity of adsorbents were calculated by the following equation (2):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where *q_e* is the equilibrium adsorption capacity of adsorbent in mmol/g adsorbent, *C*₀ is the initial concentration of the Phe (mmol/L), *C*_e is the equilibrium concentration of metal ions (mmol/L), *V* is the volume of Phe solution (L), and *W* is the weight of the adsorbent (g). The equilibrium adsorption of Phe solutions by CTAB and BKC were measured (100 ml of 10–70 mmol/l) after 10 h contact time.

Adsorption isotherms

The equilibrium adsorption data of Phenylalanine by Fe₃O₄ nanoparticles, CTAB -Coated and BKC-Coated were fitted into both the Freundlich and Langmuir isotherm equations. In the Langmuir model, it is assumed that the adsorption surface sites have identical energy and each adsorbate molecule has been located on a single site and hence this model predicts the formation of monolayer of a adsorbate on the adsorbent surface [44,45]. The Langmuir isotherm is given as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where *q_e* is the equilibrium sorption capacity of

sorbent in mmol/g sorbent, *C_e* is the equilibrium concentration of Phe (mmol/L), *q_m* is the maximum amount of Phe adsorbed (mmol/g) on sorbent, and *b* is the constant that refers to the bonding energy of sorption i ln/mg.

The Freundlich model describes a reversible heterogeneous adsorption since it does not restrict itself to a monolayer of adsorbent covering [46]. Actually, the Freundlich isotherm predicts that the Phenylalanine concentration on the adsorbent will increase as long as there is an increase of the ion concentration in the liquid solution. The Freundlich isotherm is given as:

$$q_e = K_f C_e^{1/n} \quad (4)$$

where *q_e* is the equilibrium adsorption capacity of the adsorbent (mmol/g) on adsorbent, *C_e* is the equilibrium concentration of Phe (mmol/L), *K_f* is the constant related to the adsorption capacity of the adsorbent (mmol/L), and *n* is the constant related to the adsorption intensity of the adsorbent. The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log q_e = \log K_f + 1/n \log C_e \quad (5)$$

RESULTS AND DISCUSSION

Characterization

The identity and the phase purity of the synthesized nanosorbents were confirmed by

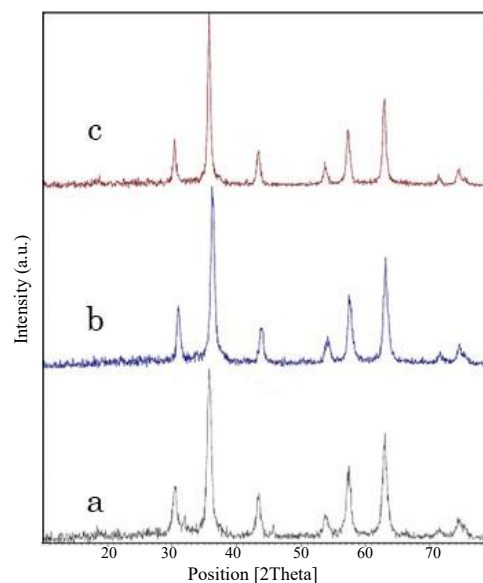


Fig. 1. XRD patterns of synthesized nano-sized Fe₃O₄ (a) uncoated-Fe₃O₄ (b) BKC-coated Fe₃O₄, (c) CTAB-coated Fe₃O₄.

XRD (Fig.1). As can be seen, the XRD pattern of magnetite nanoparticles was in good agreement with that of the standard Fe₃O₄ structure. The XRD spectra of iron oxide nanoparticles exhibited peaks at 30.5, 35.5, 43.4, 53.8, 57.3, 62.9 and 74.5 which correspond to magnetite (Fe₃O₄).

The FT-IR spectrum is a helpful analysis for identifying the surface chemical composition of nanoparticles. The FT-IR spectra of uncoated Fe₃O₄ nanoparticles, BKC-coated, and CTAB-coated Fe₃O₄ nanoparticles are shown in Fig. 2a, 2b, and 2c, respectively. The peaks appeared near at 570 cm⁻¹ in Fig. 2, is peak assigned to Fe-O bonds of Fe₃O₄ lattice. The peaks at around 3430 cm⁻¹ as well as the appeared peaks at 1633 cm⁻¹ are due to the stretching and bending vibration of water molecules present in KBr, respectively. It is observed that in Fig. 2b and 2c there are vibrations around 2800 and 2900 cm⁻¹ which can be attributed to the C-H stretching bands of the surfactants.

SEM micrograph for the prepared nanomagnetic particles is shown in Fig.3. From the figure, it is observed that the size of the nanomagnetic particles is about 45 nm. The formed particles tend to cluster as they are hygroscopic in nature.

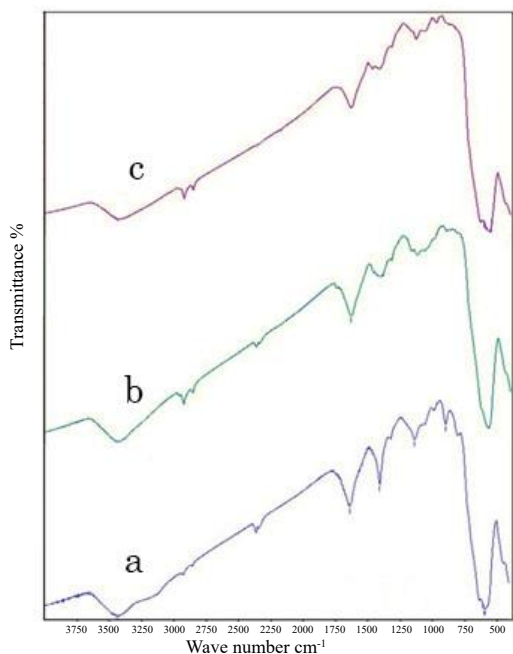


Fig. 2. FTIR spectra of (a) uncoated Fe₃O₄ nanosorbents (b) BKC-coated Fe₃O₄ nanosorbents and (c) CTAB-coated Fe₃O₄ nanosorbents

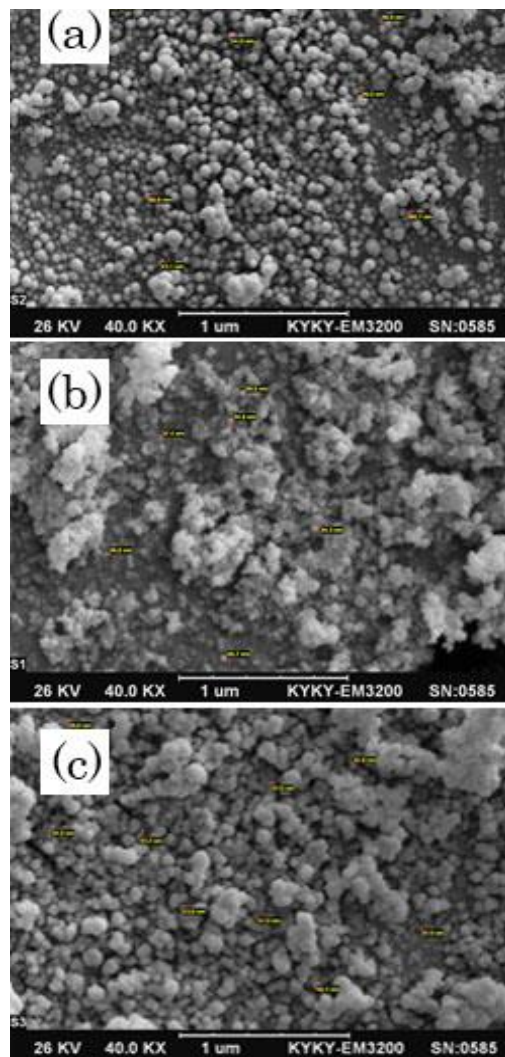


Fig. 3. SEM images of (a) uncoated Fe₃O₄ nanosorbents (b) BKC-coated Fe₃O₄ nanosorbents and (c) CTAB-coated Fe₃O₄ nanosorbents.

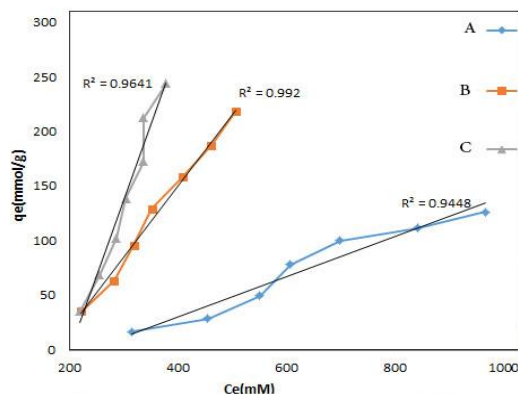


Fig. 4. Langmuir isotherms:(A) uncoated Fe₃O₄ nanosorbent, (B) BKC-coated Fe₃O₄ nanosorbent and (C) CTAB-coated Fe₃O₄ nanosorbent

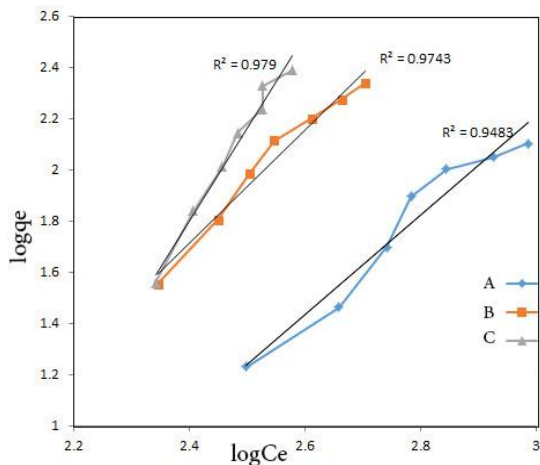


Fig. 5. Freundlich isotherms: (A) uncoated Fe₃O₄ nanosorbent, (B) BKC-coated Fe₃O₄ nanosorbent and (C) CTAB-coated Fe₃O₄ nanosorbent

Table 1. Langmuir and Freundlich isotherm data: (A) uncoated Fe₃O₄ nanosorbent, (B) BKC-coated Fe₃O₄ nanosorbent and (C) CTAB-coated Fe₃O₄ nanosorbent

	Freundlich Isotherm			Langmuir Isotherm		
	K _f	1/n	R ²	q _m (mmol/g)	b(1/mmol)	R ²
A	2.39	1.94	0.9483	51.81	0.1028	0.9448
B	2.68	2.203	0.9743	80.85	0.1259	0.992
C	5.43	3.62	0.979	85.48	0.3629	0.9641

Batch removal experiments for adsorption of phenylalanine

The adsorption of phenylalanine was studied by a batch operation at room temperature. The batch mode adsorption was selected due to its simplicity. In order to predict the adsorption behaviors of phenylalanine solution on uncoated Fe₃O₄ nanosorbents, BKC-coated and CTAB-coated Fe₃O₄ nanosorbent, Langmuir and Freundlich isotherm are used (Fig. 4,5). *b*, *q_m*, *n*, *K_f* values and the nonlinear regression correlations for Langmuir (*R*²) and Freundlich (*R*²) are given in Table 1.

Effect of pH on adsorption of phenylalanine

The adsorption experiments were carried out in a series of test tubes containing 0.05 g nanosorbents and 10 ml of phenylalanine solution at pH values (4-10). The prepared samples were shaken with mechanical shaker for 6 and 10 hours. Then solid/liquid phases were separated by filtration. The concentrations of phenylalanine before and after adsorption were determined using UV spectrometry.

It is shown that the sorption of phenylalanine

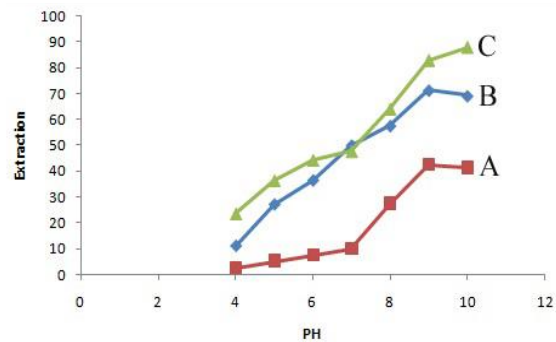


Fig. 6. The pH effect on the adsorption efficiency of phenylalanine: (A) uncoated Fe₃O₄ nanosorbent, (B) BKC-coated Fe₃O₄ nanosorbent and (C) CTAB-coated Fe₃O₄ nanosorbent

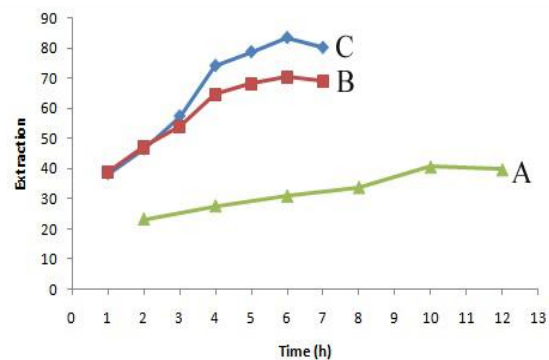


Fig. 7. Effect of contact time on the adsorption of phenylalanine: (A) uncoated Fe₃O₄ nanosorbent, (B) BKC-coated Fe₃O₄ nanosorbent and (C) CTAB-coated Fe₃O₄ nanosorbent

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 sorbents have lower adsorption tendencies (Fig 6).

Effect of contact time on adsorption of phenylalanine

Typically, 0.05 g nanosorbents were added into test tubes containing 10 ml of phenylalanine solution at a pH value of 9.0. The prepared samples were shaken with mechanical shaker for different time intervals (from 1 to 12 h). After desired shaking time, the nanosorbent was removed from the solution by filtration. The residual phenylalanine concentration was determined by UV spectrophotometer. The time dependent of phenylalanine removal from aqueous solutions was monitored for 12 hours (Fig.7). It could be seen that the maximum phenylalanine removal was obtained within 10 h, and then gradually reached equilibrium in 12 h and no significant

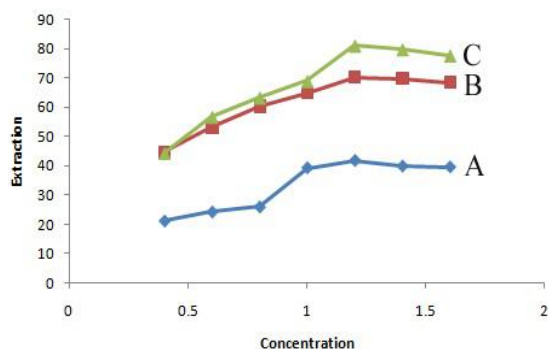


Fig. 8. Effect of phenylalanine concentration on its removal by: (A) uncoated Fe_3O_4 nanosorbents, (B) BKC-coated Fe_3O_4 nanosorbents and (C) CTAB-coated Fe_3O_4 nanosorbents

change was observed after that.

Effect of phenylalanine concentration on adsorption

Typically, 0.05 g nanosorbents were added into test tubes containing 10 ml of phenylalanine solution with various initial concentrations (from 0.4 mM to 1.6 mM) at pH 9.0. All of them were shaken with mechanical shaker. At the end of the equilibrium period, the nanosorbent was removed from the solution by filtration. As seen in Fig. 8 the removal percentage of phenylalanine reached to a maximum value in 1.2 mM concentration of phenylalanine.

CONCLUSION

The synthesis of magnetic nanoparticles (Fe_3O_4) and their coating with cetyltrimethyl ammonium bromide (CTAB) and benzal-conium chloride (BKC) has been reported in this study. The results obtained revealed that the CTAB and BKC modification effectively decreased the particle size and enhanced the dispersion of the particles in solution.

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 SEM analysis it is clear that the magnetic particles formed has a size near of 45 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. This study demonstrates that all the considered sorbents can be used as an alternative emerging technology for water treatment without any side effect or treatment process alteration. Table 2 show that the Langmuir and Freundlich

equation gives also a fairly good fit to the sorption isotherms. The sorption capacities of phenylalanine at pH 9.0 for uncoated Fe_3O_4 nanosorbents, BKC-coated Fe_3O_4 nanosorbents and CTAB-coated Fe_3O_4 nanosorbents were 51.81, 80.85 and 85.48 respectively.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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