ADSORPTION AND DESORPTION OF L-PHENYLALANINE ON NANO-SIZED MAGNETIC PARTICLES

N. Balaji[1], K. M. Meera Sheriffa Begum[1], N. Anantharaman[1] and M. S. Uddin[2]
[1]Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli, India
[2]Department of Chemical and Bio-Molecular Engineering, National University Singapore, Singapore
E-Mail: meera@nitt.edu, drkmmeera@yahoo.com

ABSTRACT

Nano magnetic particles play an important role in the field of bio-separations and biomedical applications. Due to their size, nanoparticles provide large specific surface area for adsorption of solutes and this coupled with the magnetic properties of these particles offer an excellent tool to handle these particles in suspension by using magnetic field. The present work deals with the synthesis, characterization and adsorption studies on nanomagnetic particles. The nanomagnetic particles (Fe_3O_4) were synthesized by chemical precipitation of Fe^{2+} and Fe^{3+} salts with alkaline medium under inert atmosphere. Characterization of magnetic particles were carried out using scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and vibrating sample magnetometer (VSM). Subsequently, the adsorption studies were carried out using L-phenylalanine amino acid at different ionic strengths and from the adsorption isotherms observed, different isotherm patterns were established. The desorption of L-phenylalanine from nano magnetic particles were also performed under acidic medium.

Keywords: nano-sized magnetic particles, L-phenylalanine, adsorption, desorption, isotherms.

1. INTRODUCTION

With the advent of improved technology in the recent years, more emphasis has been placed in the research (field) towards the invention and contraption of micro and nanotechnology. For example, recent drug delivery techniques for chemotherapy have engaged the use of nano-sized particles as a delivery tool. Lab-on-a-chip has been made possible by the application of nanotechnology [1-3]. Nanotechnology is also involved in the removal of toxic metal pollutants from waste water. Industrialization has brought about an ever-increasing exposure to toxic heavy metals such as lead, mercury or arsenic where they are irresponsibly dumped into rivers and oceans. A process using iron oxide nano particles as adsorbent to attract these heavy metals has been developed.

In view of its high efficiency, the quality of wastewater improved tremendously after treatment. Compared to other modes of removal of such heavy metals, this process has proven to be much more cost effective [4-7].

Many studies have been made on the adsorptive behavior of molecules on different surfaces because of their large potential for isolating components of interest.

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. Among other things, ionic strength of a solution can be varied to selectively adsorb targeted molecules while allowing other impurities to be separated. The study of adsorption of amino acids on metal oxide particles has received increasing attention because of its practical importance and potential in the biochemical industries [8-15]. Notably, amino acids are the basic constituents of proteins and biological macromolecules of critical importance to the human body. Drug delivery [16-19] and surface coatings [20-24] are other fields which are inspired by nano-technology and the possibility of adsorption of amino acids on magnetic surfaces. The present investigation deals with adsorptive and desorptive behavior of phenylalanine (aromatic) on nano-sized magnetic particles.

2. MATERIALS AND METHODS

2.1 Materials

Iron (II) chloride tetra hydrate (99%) and Iron (III) chloride hexa hydrate (98%) were obtained from Sigma-Aldrich (USA). Ammonium hydroxide (25%) solution and L-Phenylalanine were obtained from Fisher. All the chemicals were of AR grade and the water used in this study was double distilled.

2.2 METHODS

2.2.1 Preparation of Fe_30_4 magnetic particles

Magnetic particles were prepared by chemical precipitation method. A complete precipitation of Fe_3O_4 was achieved under alkaline condition, while maintaining a molar ratio of Fe^{2+}: Fe^{3+}=1:2 under an inert environment. To obtain 2 g of magnetic particles, 1.72 g of $FeCl_2{\cdot}4H_2O$ and 4.72 g $FeCl_3{\cdot}6H_2O$ were dissolved under inert atmosphere in 80 ml of double distilled water with vigorous stirring (1000rpm). While the solution was heated to 80ºC, 10 ml of ammonium hydroxide solution (25%) was added. To ensure the complete growth of the nanoparticle crystals, the reaction was carried out for 30 min at 80ºC under constant stirring. The resulting suspension was cooled down to room temperature and these repeatedly washed with double distilled water to remove unreacted chemicals. Finally, the wet magnetic particles were obtained by dewatering in a magnetic field. The wet solid particles thus obtained were dried by freeze-drying and subsequently charcterized. The reaction involved is as shown in eq. (1)

$FeCl_2.4H_2O + 2FeCl_3.6H2O + 8NH_4OH \rightarrow$

$Fe_3O_4(s) + 8NH_4Cl + 20H_2O$ ----- (1)

2.2.2 Characterization

The prepared magnetic particles were freeze dried for 24 hours using a Yamato- Neocool freeze-dryer and XRD measurements were performed using X'Pert- XRD Spectrometer (Cu target/40kV/30mA) to analyse the structural properties of magnetic particles. FTIR measurements were performed using a Perkin-Elmer infrared spectrometer (Model 1600) with KBr as background over the range of 4000-400 cm^{-1} to identify the magnetic materials in the sample. The magnetization for the super paramagnetic property was recorded using Vibrating Sample Magnetometer (VSM)

2.2.3 Adsorption Studies

Solutions of L-phenylalanine (M.W = 165) at various concentrations of 4, 3.2, 2.4, 2, 1.6, 1, 0.8, 0.4 mM were prepared at various values of pH (5.7, 7, 9.2). A desired amount of wet magnetic particles were added to various concentrations of L-phenylalanine solution at a particular pH and the samples were kept in a rotary shaker for predetermined equilibrium time of 6 hours and at a predetermined speed of 120 rpm. With the help of the magnetic field, the particles were allowed to settle completely. Supernatant liquid was analyzed to determine the concentration of L-phenylalanine using Jasco UV/Vis spectrophotometer. As the assays are found to be dependent on pH, calibration curves were prepared at different pH values.

. The adsorption studies were carried out similarly for various pH values. The amount of amino acid adsorbed is determined as the difference between the feed concentration and the supernatant liquid concentration after attaining equilibrium. The isotherms were then established for comparison.

2.2.4 Desorption studies

Desorption studies of L-phenylalanine from magnetic particles were carried out separately by using acidic buffer at a pH value of 4.0. Once the equilibrium was reached for the adsorption, using a particular feed concentration, the supernatant liquid was separated from the magnetic particles with the application of magnetic field. The particles were then repeatedly washed with double distilled water. Magnetic particles containing l-phenylalanine were then mixed with acidic buffer solution and the mixture was kept in the rotary shaker at 120 rpm for 2 hours. The supernatant liquid was then collected and analyzed using UV/Vis Spectrometer.

3. RESULTS AND DISCUSSIONS

3.1 Characterization

Fourier transform infrared spectroscopy (FTIR)

Infrared spectra obtained via FTIR can help in identifying the chemical composition and / or bonding present in an unknown molecule. The advantage of infrared spectroscopy is that the tool provides structural information about the presence of certain functional groups that are present in the sample.

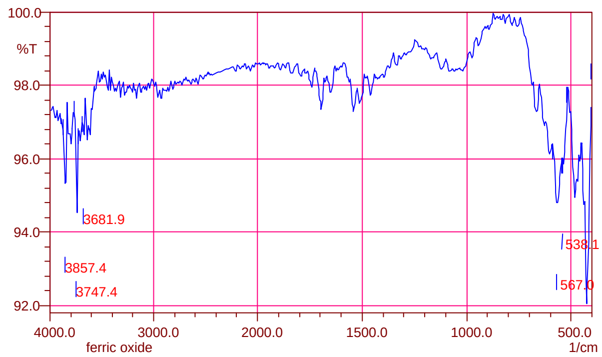

Figure-1. FTIR Spectra of Fe_3O_4 magnetic nano particles.

FT-Raman spectrometry was carried out using Perkin Elmer (Model 1600) FTIR with KBr as background over the range of 4000-400 cm^{-1}. The appearance of peaks at 3747.4 cm^{-1} and 587.0 cm^{-1} in the FTIR spectroscopy, as shown in Figure-1, indicated that the peak at 587 cm^{-1} is peak assigned to Fe_3O_4 group. The peak at 3390.77 cm^{-1} is due to the moisture present in KBr. Some small peaks reveal about the presence of impurities in nano magnetic particles. In literature, the characteristic peak for Fe_3O_4 (group) is at 600 cm^{-1} which is consistent with our results [7].

X-Ray diffraction (XRD)

XRD is a technique used to study the nature and chemical composition of the crystalline substances in the magnetic particles. The XRD spectra, as shown in Figure-2, of iron oxide nanoparticles exhibited peaks at 35.5, 43.1, 57 and 62.6 which correspond to magnetite (Fe_3O_4).

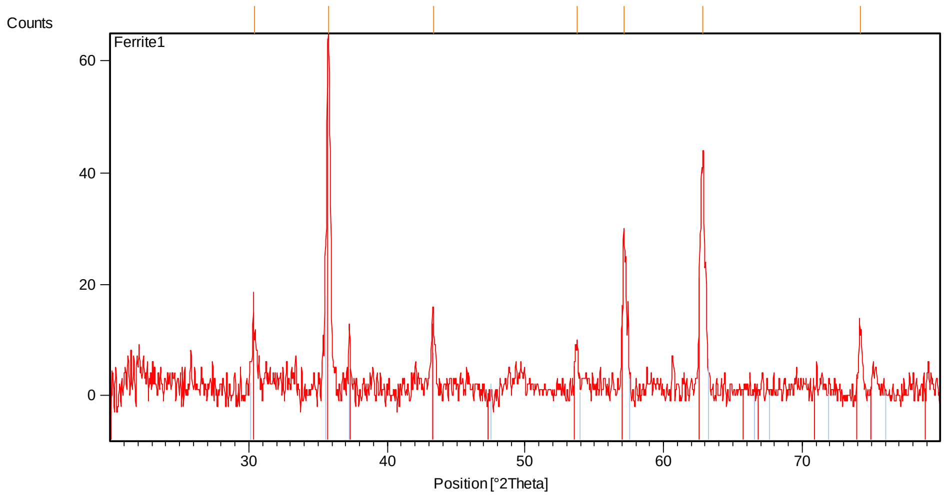

Figure-2. XRD Spectra of Fe_3O_4 magnetic nano particles.

TEM studies

TEM micrograph for the prepared nano magnetic particles is shown in Figure-3. From the figure it is observed that the particle size of the nano magnetic particles lie in the range of 10 to 15 nm. The particles formed tend to cluster as they are hygroscopic in nature.

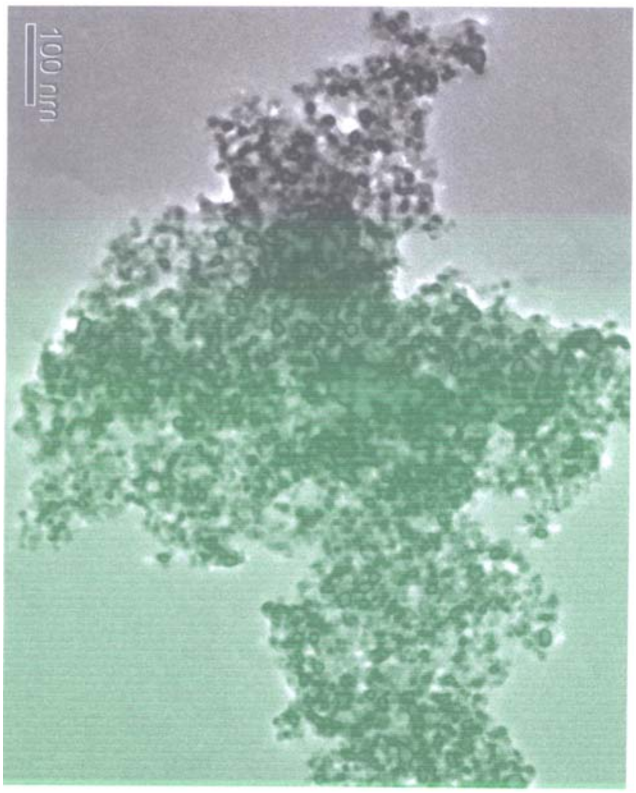

Figure-3. TEM micrograph.

Vibrating sample magnetometer (VSM)

The Superparamagnetic properties of the magnetic particles were also verified by the magnetization curve measured by Vibrating Sample Magnetometer (VSM). A typical plot of magnetization versus applied magnetic field (M-H loop) at 393 K is shown in Figure-4. The magnetization curve exhibits zero resonance and coercivity and also follows Langevin function, which proves that magnetic particle has the superparamagnetic properties. The saturation magnetization value of the obtained Fe_3O_4 magnetic particles is found to be 55.347 emu/g of bulk Fe_3O_4, which is comparable to the reported magnetization of 76 emu/g of bulk Fe_3O_4 [12]. This large saturation magnetization of magnetic particles makes them very susceptible to magnetic field, and therefore makes the solid and liquid separation easier.

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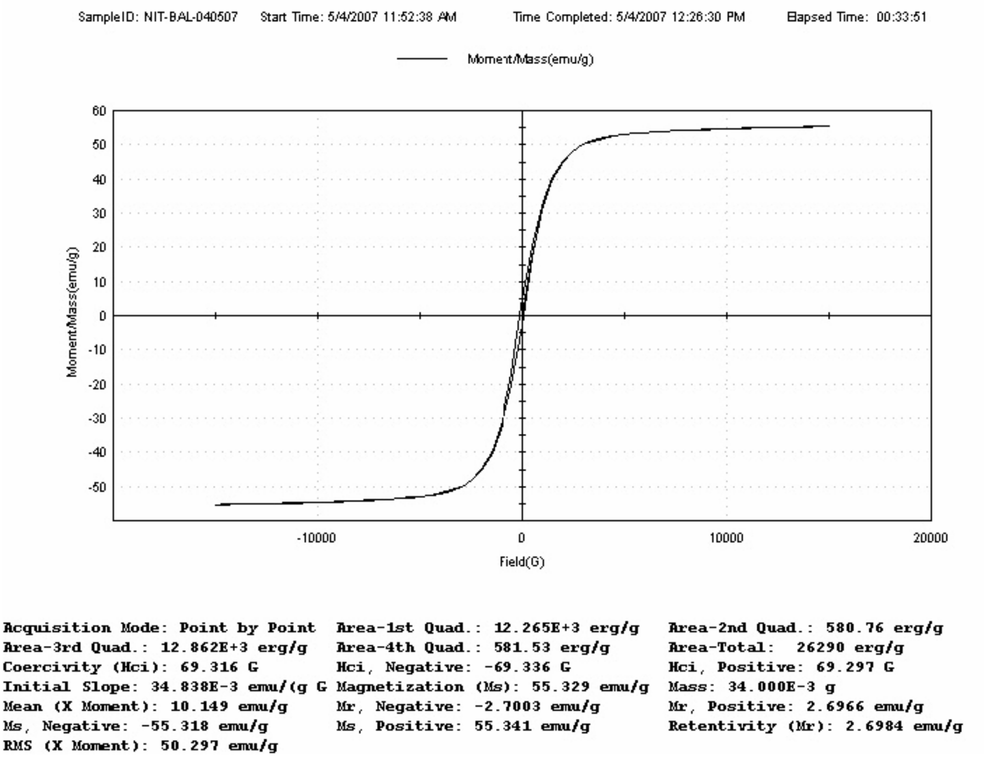

Figure-4. Magnetization curve of Fe_3O_4 magnetic nano particles at 393 K.

3.2 Adsorption on nano-sized magnetic particles

Adsorption equilibrium of L-phenylalanine was studied at different pH values and the results are shown in Figure-5. It indicates that pH has a significant effect on the adsorption of L-phenylalanine on magnetic particles. The maximum adsorption of l-phenylalanine occurred at an initial pH of 9.2, which is above the isoelectric point of L-phenylalanine (pI = 5).

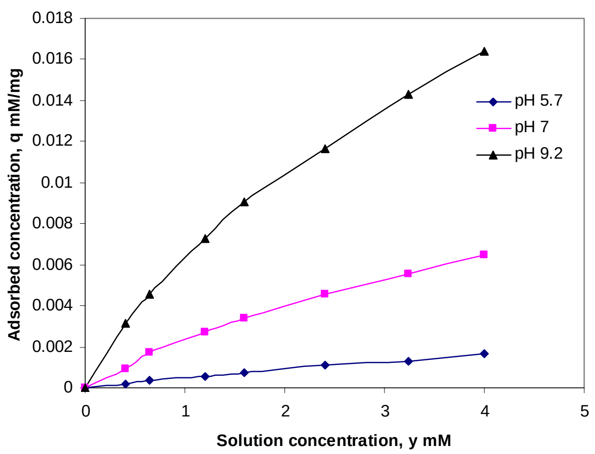

Figure-5. Linear adsorption isotherm at different pH values.

3.3 Summary of equilibrium parameters of the adsorption isotherms

From the adsorption isotherms observed, different isotherm patterns were established from the experiments performed and shown in Figures 6 and 7.

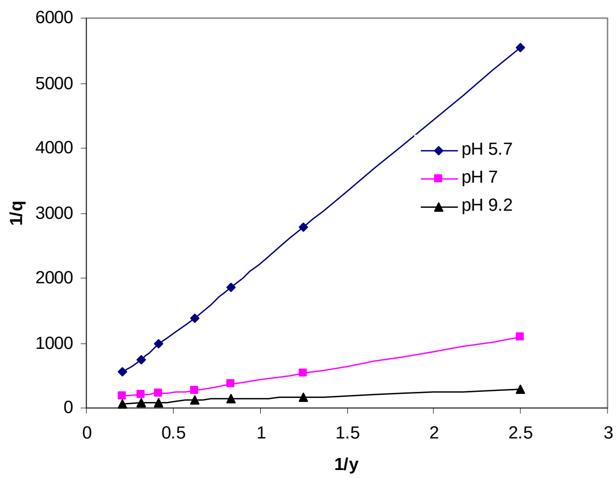

Figure-6. Langmuir adsorption isotherm at different pH values.

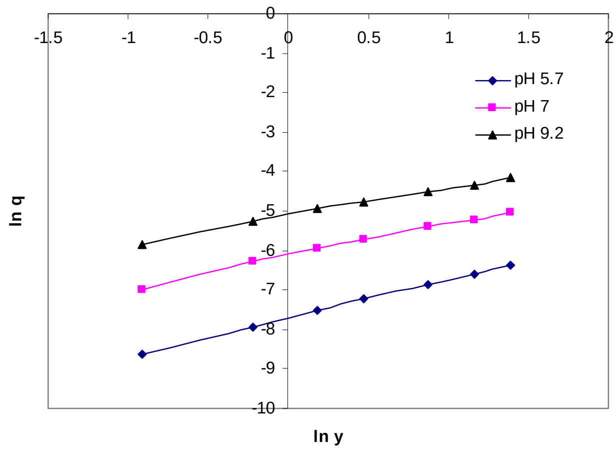

Figure-7. Freundlich adsorption isotherm at different pH values.

In principle, convex isotherms are favourable, as greater amounts of adsorbate can be obtained with low solute concentrations. On the other hand, concave isotherms are unfavourable. For L-phenylalanine, the amount adsorbed was minimal; hence the isotherm is apparently linear and follows the Henry's Law [9]. It is evident from the results shown in Table-1, that there is no clear indication to suggest that the main mode of adsorption between amino acids and magnetic particles are by the electrostatic forces of attraction. In addition, the extent of adsorption of aromatic amino acids such as L-phenylalanine would have been improved to further changes in pH.

Table-1. Adsorption isotherms.

Amino acid (pH 7)	**L-Phenylalanine**
Model: Langmuir	K = 0.11
	q_o = 0.02167
Model: Freundlich	k = 0.00215
	n = 1.282
Model: Henry's Law	b = 0.00164

3.4 Desorption from nano-sized magnetic particles

The desorption of L-phenylalanine from magnetic particles was carried out in acidic condition of pH 4. The adsorbed and desorbed quantities of L-phenylalanine at equilibrium are shown in Table-2. Desorption of 72% is achieved. The studies were also carried out at pH of 2 and 6 and the respective percentage of desorption were 65% and 80%.

Table-2. Desorption at different concentrations.

Conc. mM	**Amount adsorbed mM/mg of adsorbent**	**Amount desorbed mM/mg of adsorbent**	**% Desorption**
0	**0**	**0**	**0**
0.4	0.0034	0.00174	51.2
0.8	0.0061	0.00323	53
1.2	0.0072	0.00323	55
1.6	0.0084	0.00487	58
2.0	0.0090	0.00513	57
2.4	0.0111	0.00688	62
3.2	0.0131	0.0088	67.3
4.0	0.0156	0.0112	72

4. CONCLUSIONS

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 of the order of 10-15 nm. The Superparamagnetic properties of the magnetic particles are also verified by the magnetization curve measured by VSM.

In summary, the adsorptive behaviours of L-phenylalanine, on the nano-sized magnetic particles were studied under different pH conditions. From the adsorption data gathered and by fitting the experimental results to empirical models, the adsorption quantities between the investigated amino acid(s) and the magnetic particles were compared. Adsorption between aromatic amino acids such as L-phenylalanine should be oblivious to further changes in pH conditions if electrostatic attractions play the major role.

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