

Synthesis and Characterization of Bi-Functional Poly (Acrylic Acid-Co-2-hydroxyethylmethacrylate) Coated Iron Oxide Magnetic Composite Particles

Tania Tofaz¹, Dhananjay Chandra Mahanto¹, Shamima Akhter¹, Md. Mahbubor Rahman², M. Abdul Latif^{1,*}

¹Department of Chemistry, Begum Rokeya University, Rangpur, Bangladesh

²Department of Chemistry, University of Rajshahi, Rajshahi, Bangladesh

Email address:

latif503@brur.ac.bd (M. A. Latif)

*Corresponding author

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Abstract: This paper covers the targetable magnetic iron oxide core and biodegradable, cost-effective, eco-friendly polymer shell considering their versatile and extensive use in various fields. In this work, poly (acrylic acid-co-2-hydroxyethylmethacrylate) [P (AA-co-HEMA)] magnetic composite polymer particles were synthesized by the method of two-stage solution polymerization in aqueous media. At first synthesis, the Fe₃O₄ particles by a traditional co-precipitation method and in the second stage occurs the formation of the polymer using acrylic acid (AA) as monomer and 2-hydroxyethyl methacrylate (HEMA) as co-monomer. Finally, the synthesized iron oxide particles encapsulated by a polymer to modify the surface of composite particles. The modified composite particles were then characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffractometry (XRD), Dynamic Light Scattering (DLS), Thermo Gravimetric Analysis (TGA) and Vibrating Sample Magnetometry (VSM). The existence of carboxyl (-COOH) & hydroxyl (-OH) groups in the composite particles was confirmed by FTIR. XRD indicated the crystalline cubic spinel structure of magnetic composite particles. VSM results showed that the synthesized coated composite particles were paramagnetic in nature magnetic saturation is obtained 72.72 emu/g and 97.9 emu/g for bare Fe₃O₄ and coated magnetic composite particles respectively.

Keywords: Radical Copolymerization, AA, HEMA, MNPs

1. Introduction

Polymer microspheres are attracted much attention by the researchers because of their wide applications in biotechnology, paints and ink formulation, textile industry, electronics, and chromatography. These applications are attributed to their easy preparation [1, 2], clean and large specific surface area.

Various approaches to the synthesis of magnetic polymer particles have been investigated [3-8]. These include the co-precipitation of ferrous and ferric salts under alkaline conditions in presence of either polymers or surfactants,

cross-linking of functional polymers in an emulsifier-stabilized magnetic nanoparticle dispersion and layer-by-layer self-assembly of alternating layers of polyelectrolyte and magnetic nano-particles onto colloidal templates [9-11].

The fabrication of hybrid inorganic/organic polymer composites offers advantages especially when those applications depend on mechanical and surface properties. These inorganic-organic hybrid polymer particles find wide application potentials in catalysis, electrical, optical and electronic or photonic devices, biomaterials, flame-retardant and coatings [12-20]. There is an increasing interest in the synthesis of nano-sized metal oxides

because of their large surface area unusual adsorptive properties, surface defects, fast diffusivities and quantum size effects which are different from those of bulk materials [21-25]. Metal (oxide) composite particles 1 μ to several microns have received widespread interest recently because of their envisioned applications in electronics, optics, and magnetic storage devices. Among the various oxide materials, Fe₃O₄ is a very important magnetic material extensively used in catalysis, battery cathodes, gas sensors, electronic films, and magnetic materials [26-35]. These mechanical and physical properties, as well as application potentials, can be further improved by reducing the size and size distribution in the nano-range [36]. Despite the wide application potential of hybrid Fe₃O₄ composite polymer particles in different fields, only a few reports are available on the designing of such polymer particles.

2. Materials and Methods

2.1. Materials

Acrylic acid (AA) and 2-Hydroxy Ethyl Methacrylate (HEMA) purchased from Fluka, Germany, were distilled under reduced pressure to remove inhibitors and preserved in the refrigerator until use. Here acrylic acid was used as a monomer and a self-polymeric stabilizer due to having its exceptional behavior to iron oxide magnetic particles. HEMA was used as a co-monomer giving stability to the composite particles. Potassium persulfate (KPS) purchased from LOBA, India, was preserved in the refrigerator before use. KPS was used as a free radical initiator to the polymerization reaction. 25% NH₄OH purchased from Merck, Germany and other chemicals used were of analytical grade. Deionized water was distilled using a glass (Pyrex) distillation apparatus.

2.2. Preparation of Iron Oxide Magnetic (Fe₃O₄) Particles

As shown in Figure 1, iron oxide magnetic (Fe₃O₄) particles were prepared by co-precipitation method using FeCl₃ (0.9661g) and FeSO₄.7H₂O (0.834g) as 2:1 stoichiometric molar ratio in presence of 25% NH₄OH (14 mL pH > 10). FeCl₃ and FeSO₄.7H₂O salts were taken into two beakers each of which were 50 ml and then added 88mL of DD-H₂O as solvent. Then passed N₂ gas to remove oxygen about 10 minutes. After that the two solution mixed and further passed N₂ gas for inert medium. Then it was taken in a 500ml beaker which was already set at paraffin oil bath at 85°C and stirred at 900 rpm for 2 hours.

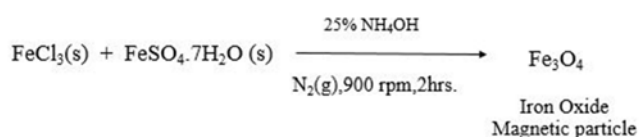


Figure 1. The reaction scheme for the synthesis of Fe₃O₄ magnetic particle.

Table 1. The preparation of iron oxide magnetic nanoparticles.

Ingredients	Amount(g)
FeCl ₃	0.9661
FeSO ₄ .7H ₂ O	0.834
25% NH ₄ OH	14 (ml) pH > 10
DD-H ₂ O	88

Reaction conditions: 85°C, 900 rpm, 2 hours, N₂ atmosphere.

2.3. Preparation of Poly (AA-co-HEMA)

Poly [AA-HEMA] was prepared by addition polymerization from acrylic acid with 2-Hydroxy Ethyl Methacrylate using potassium persulphate (KPS) as an initiator shown in Figure 2. Here acrylic acid (AA) was used as a promising and efficient stabilizer. 0.448 gm acrylic acid and 0.111 gm HEMA [4:1 weight content] were taken in a three necked round bottom glass reactor immersed in a thermo stated water bath as a monomer & co-monomer respectively. Then 0.016gm (2% weight content of AA-HEMA) KPS was mixed as initiator. Then the mixture was stirred at 70°C in presence N₂ atmosphere for 5 hours under mild stirring (about 120 revolutions per minutes). Polymerization conditions were shown in Table 2.

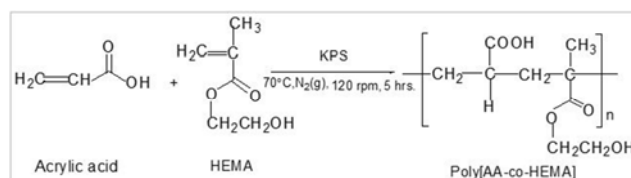


Figure 2. The reaction schemes for the synthesis of copolymer, poly (AA-HEMA) by free radical polymerization.

Table 2. The synthesis of copolymer, poly (AA-HEMA) by free radical polymerization.

Ingredients	Amount (gm)
AA	0.448
HEMA	0.111
KPS	0.016
DD-H ₂ O	49.216

Reaction conditions: 70°C, 120 rpm, 5 hours, N₂ atmosphere radical polymerization.

2.4. Preparation of Polymer-Coated Iron Oxide (Fe₃O₄) Magnetic Composite Particles

After preparation of iron oxide magnetic (Fe₃O₄) particles, 50% of these were separated for bare Fe₃O₄ and rest of them were added to a three-necked round bottom flask containing copolymer [AA-co-HEMA] immediately.

The solution was highly dispersed and turned to brownish from black. Then the mixture was stirred about 12 hours at 70°C in a thermostatic water bath. After 12 hours the polymer coated composite particles were washed from the dispersed solution by DD-H₂O using a magnet. This procedure was carried out about several times and finally, the particles were dried in an oven at about 60°C temperature.



Figure 3. Surface modification of iron oxide (Fe_3O_4) magnetic nano-particles with poly (AA-HEMA).

2.5. Characterization

The morphological images i.e., size and shape of the bare Fe_3O_4 particles were taken by SEM FEI, Quanta Inspect, made in the Czech Republic at 15 kV and Fe_3O_4 /PAA-HEMA composite particles were obtained by scanning electron microscopy (SEM) on a JEOL, model JSM 6490L, USA, operating at 20kV. The interaction (molecular structure) between the magnetic composite particles and the polymer i.e. presence of functional groups in the synthesized polymer coated magnetic composite particles were investigated by Fourier Transform Infrared spectroscopy (FTIR). The equipment used for the analysis of FTIR spectroscopy was carried out at the range of 10°C to 70°C . Thermal behavior of bare Fe_3O_4 and Fe_3O_4 /PAA-HEMA magnetic composite particles were recorded by TGA-50, Shimadzu, Japan. In this technique, samples were analyzed % weight vs. temperature from room temperature to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere. An X-ray diffract to meter of Rigaku brand, model Ultima IV, USA, operating at 40 kV, 17.5 mA, 200 V, equipped with copper tube ($\lambda=0.154$ nm) was used for the analysis of crystal structure of prepared composite particles. The hydrodynamic diameter of the polymer particles was measured by (DLS) NICOMP 380, USA. The magnetic property of Fe_3O_4 and Fe_3O_4 /PAA-HEMA composite particles were characterized by vibrating sample magnetometer namely microsense VSM.

2.6. Thermogravimetric Analysis (TGA) of Fe_3O_4 and Fe_3O_4 Coated with Poly (AA- co- HEMA) Particles

Thermal properties of the dried Fe_3O_4 and Fe_3O_4 coated with Poly [AA- co- HEMA] powder were measured by heating samples under flowing nitrogen atmosphere from 25°C to 600°C at a heating rate of $20^\circ\text{C}/\text{min}$ and the weight loss was recorded.

3. Results and Discussion

Figure 4 shows the SEM photographs of bare Fe_3O_4 and Fe_3O_4 /PAA-HEMA magnetite composite particles. From the

SEM photographs, it was found that microspheres of Fe_3O_4 / PAA-HEMA composites were spherical in shape, highly dispersed in solution but particles were agglomerated [Figure 4 (c) and (d)]. Therefore, the actual particle size was not confirmed by this test. On the other hand, due to lack of proper sampling size of bare Fe_3O_4 particles could not be measured. However, the particles supported good crystal surface.

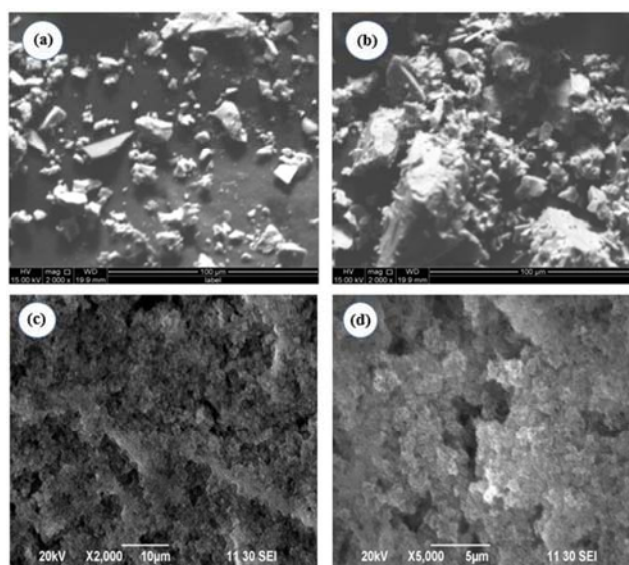


Figure 4. SEM photographs of Bare Fe_3O_4 (a), (b) and Fe_3O_4 /PAA-HEMA composite particles (c), (d).

Figure 5 represents the characteristics vibrational spectroscopy of bare Fe_3O_4 composite particles and poly-acrylic acid co 2-hydroxyl ethylmethacrylate coated iron oxide composite particles, respectively. The fingerprint of Fe_3O_4 occurs mainly at 480.28 cm^{-1} and 650.01 cm^{-1} where two medium sharp peaks correspond to the presence of Fe-O-Fe stretching bond in Fe_3O_4 magnetic particles [37]. Broad absorption above 3000 cm^{-1} typically stands for the stretching vibration of O-H bonds in hydroxyl group of a carboxylic acid which corresponds at 3477.66 cm^{-1} [38].

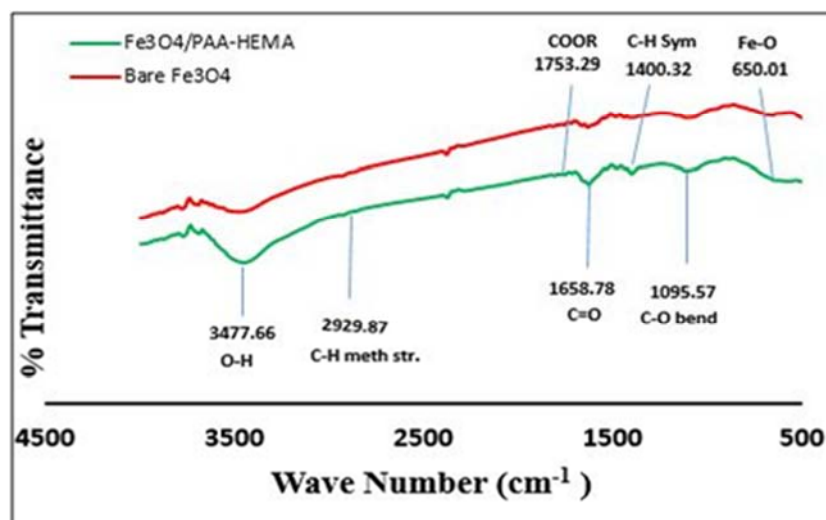


Figure 5. FTIR analysis of bare Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{PAA-HEMA}$ magnetic composite particles.

The two doublets at 1625.99 cm^{-1} and 1658.78 cm^{-1} represent the presence of carbonyl (C=O) group. Moreover, absorption at 1753.29 cm^{-1} and 1095.57 cm^{-1} correspond to stretching vibration of ester ($-\text{COOR}$) group and C-O bond [39], respectively. The absorption peak just below the 3000 cm^{-1} i.e., at 2929.87 cm^{-1} corresponds to stretching of the methyl group ($-\text{CH}_3$) [40] while two doublets at 1400.32 cm^{-1} and 1479.40 cm^{-1} signify the symmetric and asymmetric vibration of (C-H) bond in the resultant composite particles. All the above information indicates the polymer coated iron oxide composite particles [41].

The XRD pattern of Fe_3O_4 composite particles were prepared at room temperature is shown in Figure 6. The modified Fe_3O_4 particles exhibited main peaks at 2 theta (deg) of 30.5, 35.8, 43.3, 53.9, 57.4, 62.8, 74.5,

corresponding to the (220), (311), (400), (422), (511), (440), (533) reflection planes of the face-centered cubic crystal Fe_3O_4 [42]. The XRD data clearly confirmed the crystalline phase of magnetite (Fe_3O_4) to be very close to the JCPDS No. 89-4319. For the prepared Fe_3O_4 , the most intensive lines (311) and (440) were observed the diffraction peak indicated at $2\theta = 35.8$ and 62.8 . The XRD pattern showed the prepared composite particles were in a cubic structure of Fe_3O_4 . It could be seen that the sites and intensity of the diffraction peaks were consistent with the standard pattern for JCPDS Card No. 89-4319. The sample showed very broad peaks, indicating the ultra-fine nature and small crystalline size of the particles. The XRD pattern of the modified Fe_3O_4 NPs, indicating that a portion of the Fe_3O_4 NPs was successfully encapsulated by a copolymer (AA-co-HEMA).

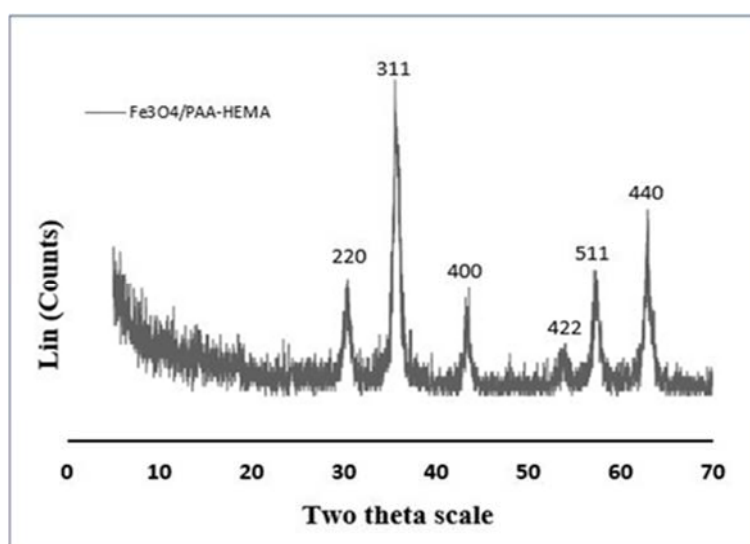


Figure 6. The XRD pattern of Fe_3O_4 composite particles at room temperature.

The TGA curve of Fe_3O_4 MNPs coated with Poly (AA-co-HEMA) is shown in Figure 7. There were five decomposition points in the curve which indicated the four mass losses of coated iron oxide magnetic nanoparticles with respect to

time. The observation was carried out at ambient temperature 29.03°C . The first decomposition point was at about 97.07°C , which was around the boiling or decomposition point of HEMA, and the percentage of mass loss was about

2.15%, which possibly due to the removal of free polyacrylic acid co- HEMA on the surface of Fe_3O_4 MNPs. The second point was at 270.70°C and the percentage of mass loss was about 4.18%, which confirmed that the percentage of mass loss was increased with increasing time and temperature. The third point was at 351.57°C, and the percentage of mass loss was about 10.02% which was attributed to the phase transition from Fe_3O_4 to FeO . The fourth point at 458.04°C,

related to a mass loss of 11.21%, possibly because of de-oxidation of FeO since the TGA analysis was achieved under the N_2 atmosphere [43]. The fifth decomposition point is about at 599.52°C and the percentage of mass loss was found as 11.40 %. Consequently, from Figure 7 the coating content of modified iron oxide nanoparticles was estimated to be about 11.40 %.

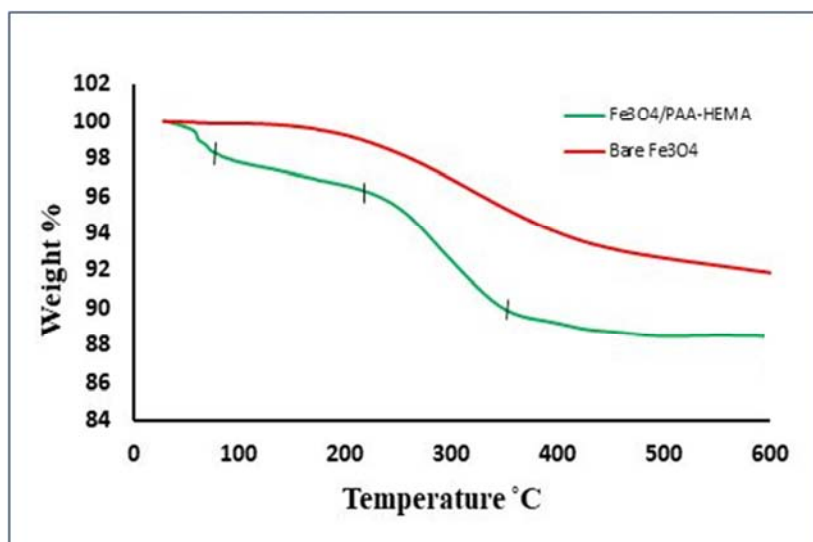


Figure 7. The TGA curve of Fe_3O_4 MNPs coated with Poly [AA- co- HEMA].

Figure 8 shows the measurement of the hydrodynamic diameter of washed Fe_3O_4 /PAA-HEMA composite polymer particles with pH 8 at room temperature. The obtained mean

diameter was 1426.8 nm where the coefficient of variation and the standard deviation was 0.689 and 983.042 nm respectively.

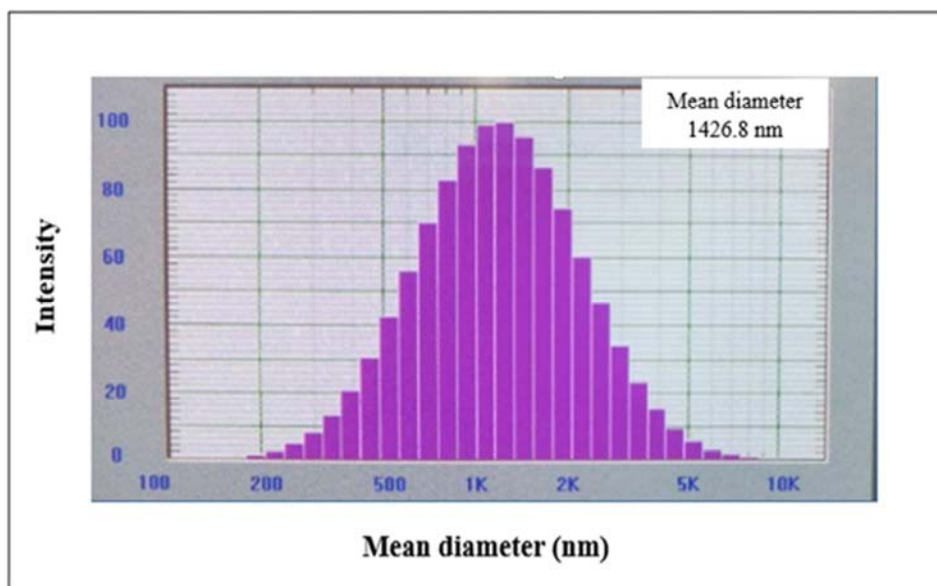


Figure 8. The size distribution of Fe_3O_4 /PAA-HEMA composite polymer particles obtained from DLS.

Figure 9 shows the presence of magnetic property in the composite particles coated with P(AA-co-HEMA) was characterized by the application of an external magnetic field [44]. The magnetic behavior of the iron oxide composite particles and the same composite particles coated with the polymer could be observed from the measurements of the

magnetization at room temperature. According to the magnetization curves, there was no hysteresis loop in the magnetization for both of samples, suggesting the magnetic particles possess typical super paramagnetic behavior. The saturation magnetization of the uncoated particles was 72.72 emu/g and the corresponding value, for the composite

particles coated with the polymer, was 97.9 emu/g [45]. The saturation magnetization values of P(AA-co-HEMA) coated Fe_3O_4 was higher than the value for the pure magnetite particles, therefore the saturation magnetization was increased after coating of acrylic acid and HEMA onto the surface of Fe_3O_4 magnetic particles. This could be explained

by the size and the broader distribution of the coated the composite particles, as well as, the fact that the composite particles uncoated when exposed to the environment, might undergo oxidation and consequently losing magnetism. The uncoated composite particles showed a smaller diameter and, consequently, smaller protection against oxidation [46].

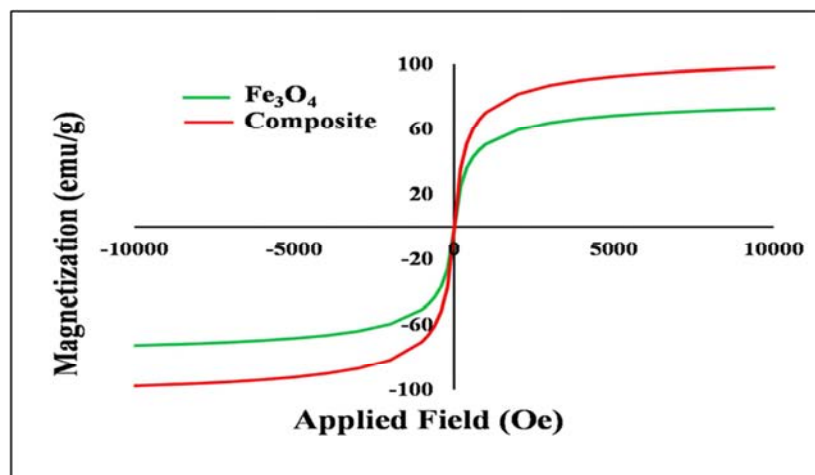


Figure 9. The VSM data curve for bare Fe_3O_4 and PAA-HEMA coated iron oxide nanoparticles.

4. Conclusion

Synthesis and characterization of bi-functional PAA-HEMA coated Fe_3O_4 magnetic composite particles were prepared with the aim of enhancing the surface modification of Fe_3O_4 . Magnetite composite particles were prepared by two-step preparation process. In the first step, magnetite particles were prepared by co-precipitation of Fe^{2+} and Fe^{3+} salts in presence of 25% ammonium hydroxide. In the second step, the produced magnetite particles were coated with a bi-functional polymer polyacrylic acid (AA) and 2-hydroxyethyl-methacrylate (HEMA) prepared by solution polymerization. The resulting samples of composite particles were analyzed utilizing SEM, FTIR, TGA, XRD, DLS, and VSM. SEM analysis showed that microspheres of Fe_3O_4 / PAA-HEMA composite were spherical in shape, highly dispersed in solution but particles were agglomerated. Therefore, the actual particle size was not confirmed by this test. Besides this finding, the average particle size of hydrodynamic diameter was confirmed by DLS analysis with the gradual ultra-sonication method. According to the FT-IR results, microsphere containing different amount of AA and HEMA in copolymer structure having carboxylic (-COOH) and hydroxyl (-OH) functional groups on the side chain of the copolymer was confirmed. The presence of Fe_3O_4 in the microsphere was also proved by FT-IR spectroscopy analysis and TGA analysis. From the TGA results the thermal behavior of prepared composite particles were confirmed by the degradation curve with respect to temperature vs. % of weight. It was also supported that the absorbed water molecules and bonding in the polymer were degraded as temperature increased to 600°C. The data obtained by particle size analysis indicated that the hydrodynamic mean diameter of microsphere was 1426.8 nm i.e. 1.42 μm approximately using DLS. VSM

analysis of the prepared Fe_3O_4 / PAA-HEMA composite particles showed abnormal behavior as there was noticed that the saturation magnetization increased after coating copolymer PAA-HEMA on the surface of bare Fe_3O_4 core. This is an interesting finding of this research. Moreover, in this work, no stabilizer was used separately as conventional emulsion, dispersion or solution polymerization method used. Due to special properties, AA supporting with HEMA was found as an efficient stabilizer in this work. Our findings may also open the possible way to prepare microsphere with Fe_3O_4 in the core by varying the amount of AA and HEMA. However, in each case, an increase in HEMA content in the composite polymer particles decreased the hydrophobic interaction between the surface of particles and biomolecules. Therefore, it can be concluded that the ratio of HEMA should be as low as possible to obtain high ratios of encapsulation. This study indicated that magnetically modified Fe_3O_4 /PAA-HEMA composite particles were successfully prepared and these particles may find applications in biomedical field.

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