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Preparation and Characterization of Iron Oxide Encapsulated In Starch Nanoparticles.

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ABSTRACT

Nano starch capsulated magnetic nanoparticles were produced by in situ chemical coprecipitation method. The formation of starch magnetic nanoparticles was confirmed by FTIR spectroscopy and thermogravimetric analysis (TGA). Transmission Electron Microscopy (TEM), and X-ray diffraction (XRD) were used for the determination of particle size and crystallinity of the resultant sample. The magnetic properties were studied by Vibrating Sample Magnometer (VSM). TEM image for the sample unstained showed that particle sizes are in the range 8-12.5 nm whereas that for stained with phosphotungstic acid are in 33.6 - 86.43 nm. VSM measurement showed that the prepared particles had a superparamagnetic behavior.

Keywords: iron oxide, starch, nanoparticles, superparamagnetic, FTIR.

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INTRODUCTION

Biocompatible super paramagnetic nanoparticles such as magnetite have been widely used for in vivo biomedical applications including magnetic resonance imaging contrast enhancement [1-5], tissue specific release of therapeutic agents [6,7], hyperthermia [8,9], and magnetic field assisted radionuclide therapy [10]. Conventional methods for preparing magnetic polymer microparticles can be divided into three classes: [1] the magnetic core materials are encapsulated by polymer coating; [2] the magnetic materials are evenly dispersed within the polymer matrix after polymerization; and [3] the magnetic Materials are filled in the pores of the pre-made polymer. By methods in the first class, the magnetic material core, typically comprised of iron oxide magnetic nanoparticles, is encapsulated by the polymer coating to form a core–shell structure of magnetic microspheres. The materials for coating on magnetic core include synthetic polymers such as polystyrene [11],

polyvinylbutyral [12], polyacrolein [13], and polyvinyl alcohol [14]. Natural polymers like dextran, agarose, cellulose, and albumin [15] are also widely used as the coating Materials. Magnetic polymer microspheres of core–shell type can also be made by a converse manner, i.e., forming a layer of magnetic material on polymer particles [16].

It is one of the naturally occurring polymers which is biocompatible, biodegradable and shows bio-adhesion property. Starch is a polysaccharide that contains amylose and amylopectin (17). Due to its biodegradability, abundance and low cost, starch has been widely used in various applications such as water-soluble pouches for insecticides [18], tissue engineering scaffolds [19], and drug delivery carriers [20].

The problem facing scientists to use starch for its application is that, the native starch has limited disadvantages such as poor solubility in cold water, tendency to retrograde and high viscosity once it is gelatinized. Therefore, nano-sized starch particles have attracted much attention due to their unique properties that are different significantly from their bulk Materials. Starch nanoparticles are usually obtained from acidic or enzymateric hydrolysis and consist mainly of small blocklets [21-23]. Once the starch structure is opened and dispersed by the application of alkali, acid and enzymes, the formation of the hydrogen bonds can be accelerated through which such nanoparticles can be formed [24,25]. In addition to acid hydrolysis, chemical or enzymatic agents others chemical methods such as miniemulsion cross-linking [26], nanoprecipitation [27-29], emulsion [30-31], and microemulsion [32-34] have been explored by researchers for synthesis of starch nanoparticles.

Previous studies have shown that some polysaccharides have the ability to interact with iron complexes, preventing the precipitation of iron hydroxide and enabling nanoparticles synthesis to occur under controlled conditions. For example, several workers have used a coprecipitation process in the presence of dextran [35-38]. Other biopolymers used include cyclodextrin [39] alginate [40,41], chitosan [41,42] starch-based coatings [41,43,44] and carrageenan [45, 46]. Formation of water-soluble compounds containing unexpectedly high number of iron(III) per repeating polymeric units has been observed and it has been concluded that the polysaccharide backbone unfolds as iron(III) is coordinated to them and nanometric size (subcolloidal) particles are formed [47-49].

This work aims to break down the starch molecules due to its incubation with iron salts then use the coprecipitation method to synthesis super paramagnetic nanoparticles encapsulated in starch nanoparticles that can be used in biological applications.

MATERIALS AND METHODS

All chemicals were of reagent grade and used without further purification. Starch soluble extrapure (Laboratory Rasayan) iron chloride hexahydrate (Riedel-deHaen), iron sulfate heptahydrate (fluka) and ammonium hydroxide 28 % (Edwek) were used in this experiment. Deionized water was deoxygenated by passing argon gas for 2 h before start. The Iron oxide particle was precipitated in a treated starch iron salts solution in alkaline media by using co- precipitation method [50]. Briefly, 10 ml of iron chloride hexahydrate was mixed with 10 ml iron sulfate heptahydrate with a molar ration 2 :1. Then mixed with 10 ml of 20 % starch solution for one hour and incubated for one month at 40° C. After that, starch iron salts solution was drop-wish to ammonium hydroxide solution with continuous stirring, immediately the solution colour became black then heated for 1 hour at 60 °C. The formed precipitate was separated with magnet and washed several

times with distilled water till reach to neutral pH. Native starch sample was prepared as described above without treatment with iron salts. The samples were dried under vacuum for the measurements. The Fourier transform infrared (FTIR) spectra of samples were recorded by Fourier transform infrared spectrometer Jasco 430 interfaced to a personal computer operating under windows-based Jasco software.

Thermal gravimetric analysis Shimadzu (Japan) N_2 Flow device was used to obtain TGA data of samples. Transmittance electron microscope image of samples were taken by JEOL JEM-2100 electron microscope. A drop of died samples dispersed in ethyl alcohol was loaded on a grid and left to dry before measurement. another one is stained with 1% phosphotingestic acid solution.

X Pert panalatical X-ray diffraction (XRD) device with CuKα 40kV/30mA was used for recording the X-ray diffraction pattern of the sample. Magnetic properties were measured through Vibrating Sample Magnomter (VSM) Lake shore 7410 USA.

RESULTS AND DISCUSSION

FTIR measurement:

The infrared spectra of native starch and starch Fe_3O_4 are given in Fig. (1). The characteristic bands of starch in FTIR spectra can be divided into four main regions. These regions are as follows: below 800 cm^{-1}, 800–1500 cm^{-1} (the fingerprint region), 2800–3000 cm^{-1} (C H stretching regions), and finally between 3000 and 3600 cm^{-1} (O H stretching region). The hydroxyl groups are the dominant functional groups in carbohydrates and they are involved in intra and inter-molecular hydrogen bonding with other hydroxyl groups [51]. The major peaks and their band assignments from the literature (Table 1) observed for starch were at 3446 cm^{-1} (O H stretching) 2925 cm^{-1} (C H_2 stretching), 1648 cm^{-1} (water bending), 1459 cm^{-1} (CH bending of CH_2), 1375 cm^{-1} (CH_2 twisting), 1160 cm^{-1} (C O and CH_2 stretching), 991 cm^{-1} (skeletal mode vibrations of -1,4 glycosidic linkage), 856 cm^{-1} (C(1) H, CH_2 deformation) and 709 cm^{-1} (skeletal mode of C C stretching). The broad band between 3000 and 3600 cm^{-1} was attributed by the vibrational stretching of hydroxyl groups amongst neighbouring molecules of starch [52].

Comparing the FTIR spectra of native starch with that of starch Fe_3O_4 Fig (1), it is observed that both spectra have absorption bands at 2925, 1429 and 929 cm^{-1} and there is distinctive changes in their other bands. The spectrum of native starch has absorption bands at 3446, 1648, 1460, 1161, 1083, 991 and 856 cm^{-1}. Starch Fe_3O_4 spectrum has absorption bands at 3414, 1635, 1153 and 1025 cm^{-1} and shoulders at 1375 and 1083 cm^{-1} and the absorption bands at 1460 and 991 cm^{-1} are absent. Also the appearance of the two characteristic bands of Fe_3O_4 at 583 and 443 cm^{-1} in starch Fe_3O_4 spectrum is recorded.

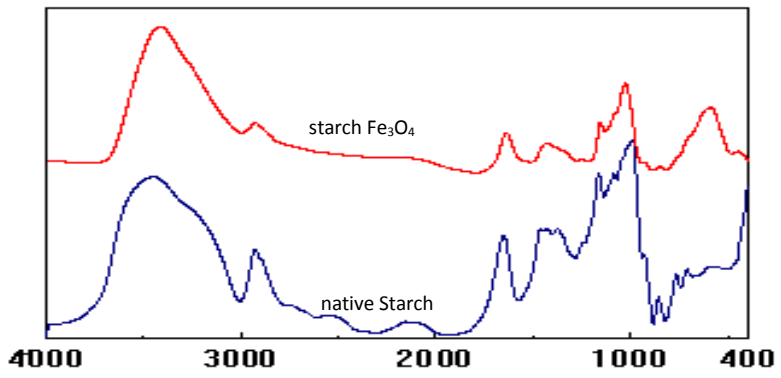


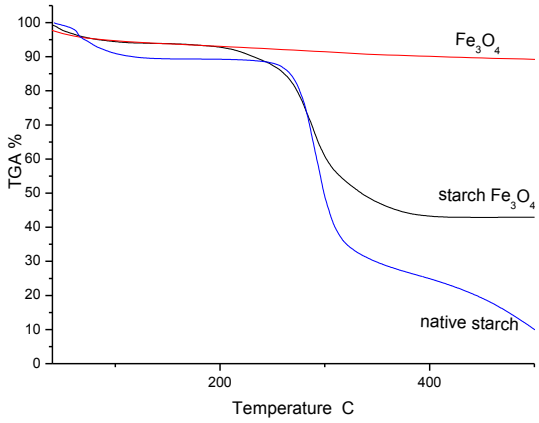
Fig (1): FTIR spectra of native starch and starch Fe_3O_4 nanoparticle

The spectral changes in the absorption peaks which are characteristic to H bonding to OH group and C-O-H group in the spectra of starch Fe_3O_4 indicated that the iron was ligated by the hydroxyl groups of starch. This result may be attributed to the fact that starch is a weak acid ion- exchanger. The OH- group of starch could dissociate protons into the aqueous phase. Consequently, the starch granule carries a negative charge

while the water phase carries a positive charge. The negative potential of starch granule attracts the cation and repels the anion [53]. Also the structure of the composite Materials formed between iron (III) and polysaccharides was described by two main approaches. The first assumes that iron (III) is bound through the binding sites of the saccharide moieties and forms spatially separated iron- (III) centers along the polymeric backbone (site binding model) [47-49]. Nonspecific interactions between the FeOOH precipitate and the polysaccharide are considered responsible for the high solubility of the metal hydroxide (colloidal model) [54, 55]. In the combination of these two mechanisms, the donor group of the polysaccharide act as nucleation sites for the metal ions, which then bind further to the metal ion through the formation of hydroxide bridges and a variety of nanostructures are formed in situ, with shape and size, that depend on the type of the polysaccharide and the properties of the solution [56].

TGA analysis:

Fig (2) illustrates the TGA curve for pure Fe_3O_4, native starch and starch Fe_3O_4 nanoparticles. It is noticed that there is no significant weight loss in the TGA curve of Fe_3O_4 nanoparticles. Whereas there are distinct weight loss in the TGA curves of native starch and starch Fe_3O_4 nanoparticles. The initial weight loss is 5.2 % for native starch that is observed from room temperature up to 73°C whereas that for starch Fe_3O_4 nanoparticles is 2.6% from room temperature up to 53 °C. This loss is due to the moisture content of both samples. The second weight losses are 5.3% (from 73 up to 170.7 °C) and 7. 6% (from 54 up to 235 °C) for native starch and starch Fe_3O_4 nanoparticles respectively. This weight loss is due to the dehydration reaction of –OH groups in starch molecules for both samples.



Starch Fe_3O_4 Native starch

Fig (2): the TGA curve for native starch, starch Fe_3O_4 nanoparticles and pure Fe_3O_4.

The third stage for weight loss started from 214 up to 358 °C for native starch and it is 60% while that for starch Fe_3O_4 nanoparticles started from 235 to 477 °C and it is 47%. This weight loss is referred to the decomposition of starch of the samples releasing CO_2 gas. It is noticed that the rate of weight loss for starch Fe_3O_4 nanoparticles sample is slower than that of native starch sample. This indicated that the more thermo stability for starch Fe_3O_4 nanoparticles sample that may be due to the coordination bond between iron and starch molecules. Then the TGA curve for starch Fe_3O_4 nanoparticles sample became steady with stable weight percentage up to 1000 °C which indicts that the remaining of Fe_3O_4 only and it is represent about 43% from the weight sample. The TGA curve of native starch has a forth weight loss at temperature between 358 to 602 °C and it is about 27%, then above 602 °C up to 1000 °C, the curve reach to steady weight about 2% from the total weight of starch sample, this result indicated that starch sample became ash.

TEM image:

Fig (3) shows TEM image of stained native starch (a), unstained starch Fe_3O_4 (b) and stained starch Fe_3O_4 (3c). It is observed from Fig (3a) that the particles size of stained native starch are in 120 to 250 nm.

While that stained one (3c) has particles in size 33.8 to 71.4 nm. Unstained starch Fe_3O_4 sample Fig. (3b) has particles size ranged from 8 - 12.5 nm. The decrease in the particles size of stained starch Fe_3O_4 sample as compared with that of stained native starch means that the native starch chains are degraded to smaller one this may be due to the incubation of starch with iron salts which have a low pH. This result is confirmed with that reported in literatures where it has been concluded that the polysaccharide backbone unfolds as iron(III) is coordinated to them and nanometric size (subcolloidal) particles are formed [47-48]. Also Yamada, et. al. 1997 [57] stated that the interaction of the polysaccharide κ-carrageenan with Fe(II) and Fe(III) ions facilitated depolymerization of that polysaccharide at room temperature Whereas the particles size of stained starch Fe_3O_4 are larger than that of unstained sample indicates that the starch capsulated the Fe_3O_4 particles.

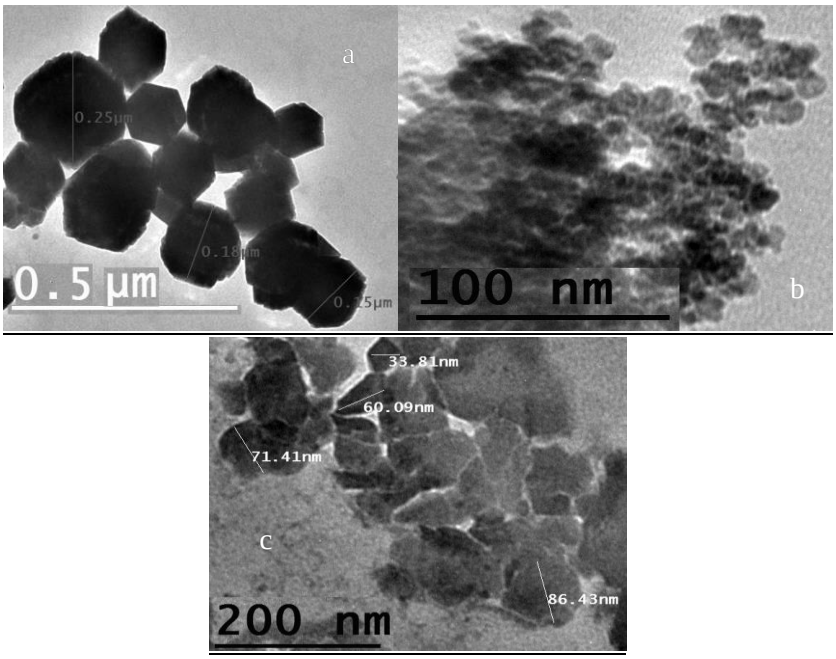


Fig (3): TEM images of stained native starch (a), unstained starch Fe_3O_4 (b) and stained starch Fe_3O_4(c).

X ray diffraction:

Fig (4) shows the XRD patterns of pure Fe_3O_4 and starch Fe_3O_4. It is apparent that the diffraction pattern of pure Fe_3O_4 nanoparticles is close to the standard pattern for crystalline magnetite (card no. 00-003-0863). It has the characteristic diffraction peaks at 2Θ = 30.2°, 35.5°, 43.2°, 53.6°, 57.2° and 62.8° which are matched well with that of standard Fe_3O_4 crystalline. Also the same diffraction peaks were observed in case of starch Fe_3O_4. These reveal that the starch has no effect on the crystallinity of Fe_3O_4

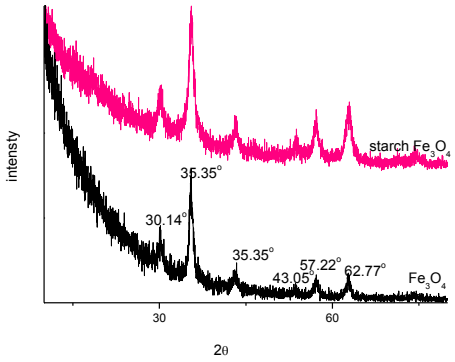


Fig (4): the XRD patterns of pure Fe_3O_4, starch Fe_3O_4.

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Magnetic properties:

The magnetic properties of prepared nanoparticles were measured by VSM. The hysteresis of starch Fe_3O_4 is representing in Fig. (5). The saturation magnetization for starch Fe_3O_4 particles is 20.5 emu g^{-1}; which is lower than that of bulk magnetite (98 emu g^{-1}) [58]. The lowering in saturation magnetization can be attributed to the reduction of the particles sizes and starch coated on the surface of Fe_3O_4 nanoparticles which acts as nonmagnetic layer. In addition the particles have a very low coercivity (2.8 G) and retentivity (38.273E-3 emu/g). These results indicate that these prepared particles are in nano sizes and have super paramagnetic behavior.

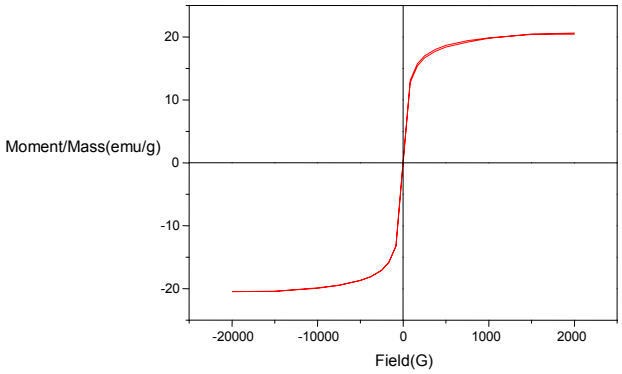

Fig (5): hysteresis curve of starch Fe_3O_4.

CONCLUSION

It can be concluded from the results of FTIR and TGA that the starch Fe_3O_4 composite was synthesized and a partial hydrolysis of starch is occurred when it was treated with the iron salts (this was indicated from TEM images). Also the obtained particles have a super paramagnetic behavior. Finally, these particles are suitable for many biological applications.

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