



Potentials of Starch Nanoparticles Jack Bean (*Canavalia ensiformis*) Coprecipitated with Iron (II, III) Oxide

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

Aim: The quest for unveiling the potentials of underutilized tropical starches as nanoparticle disintegrants in drug delivery system was the focus of this research work.

Place of Study: The analyses were carried out in the laboratory of Chemistry Department, University of Medical Sciences, Ondo, Nigeria.

Methodology: Native starch of jack bean (*Canavalia ensiformis*) was impregnated with iron (II, III) oxide via co-precipitation method, using glutaraldehyde as a crosslinker. The native starch and iron oxide starch nanoparticles were evaluated for swelling properties, FTIR patterns, morphologies and XRD patterns.

Results: The swelling powers of the native starch and the magnetic starch nanoparticles were affected altered between pH 2 and 12. O–H stretching appeared at 3242 cm⁻¹ and 3265.1 cm⁻¹; C–H stretching at 2926.7 cm⁻¹ and 2926.0 cm⁻¹ and C–O stretching at 1077.2 cm⁻¹ and 1077.2 cm⁻¹ absorption bands for native starch and starch nanoparticles respectively. C–O–C stretching of glycosidic bonds was observed at 1148 cm⁻¹ for both samples. The native starch had non-uniform shapes, appearing as a mix of oval, spherical and polygonal shapes while non-uniform rock-like granules with evidences of strata were obtained for starch nanoparticles. X-ray diffraction peaks of 24.04°, 18.32° and 33.95° 2θ were obtained for native starch while 24.00°, 18.24° and 57.36° 2θ for starch nanoparticles. The crystallinity indexes of the native starch and starch nanoparticles were 81.01% and 87.30% respectively. The same trend was obtained for their crystallite sizes.

Conclusion: The magnetic starch nanoparticles studied could be possible source of disintegrants for drug formulations and delivery. They could as well be applied in water treatment technology.

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Keywords: Starch nanoparticles; magnetic starch nanoparticles; crystallinity index; disintegrants.

1. INTRODUCTION

More than a decade, the synthesis and characterization of magnetic nanoparticles have been the quest for both research and technological applications. State-of-the-art applications such as magnetic fluids recording, catalysis, biotechnology/biomedicine, material sciences, electrochemical and bioelectrochemical sensing, microwave absorption, magnetic resonance imaging (MRI), medical diagnosis, data storage, environmental remediation, supercapacitors, lithium ion batteries (LIB) and magnetic inks for jet printing, have made magnetic nanomaterials to be popular [1-5].

Ferro fluids have been identified as the most widely known and extensively used magnetic nanoparticles, due their compatibility with living organisms, excellent *in vivo* stability and ability to migrate easily under magnetic fields [6]. Despite their worse magnetic properties, lower saturation magnetization and lower specific loss of power than the emerging Fe and Co nanoparticles, iron oxide-based nanoparticles stand out with better oxidative stability, compatibility in nonaqueous systems, and nontoxicity [7,8].

Of all the methods developed for preparing Fe₃O₄ magnetic nanoparticles, such as chemical co-precipitation, hydrolyzation, micro-emulsion, the chemical co-precipitation has been identified as the most promising one, because of its simplicity and productivity [9]. Co-precipitation method is a method of synthesis of Fe₃O₄ which is easy to do with the success rate from 96 to 99.9% with ferrous and ferric ions at the ratio of 1 to 2 in alkaline medium. Chemical co-precipitation can produce fine, stoichiometry particles of single and multi-component metal oxides [10,11].

Starch is a biocompatible, biodegradable, non-toxic polymer, which has gained increased attention in food and non-food applications due to a host of advantages, which include low density, cost effectiveness, abundant supply and environmental amity [12,13].

The growing interests and increasing demands for starch for both food and non-food applications have necessitated exploring alternative sources to the commercial starches from normal and waxy corn, rice and potato. Of prominence in the tropical region is an underutilized legume, jack

bean (*Canavalia ensiformis*), from which ozone-oxidized starch, hydroxypropylated starches and starch nanocrystals have been documented [14-16]. However, synthesizing and characterizing jack bean (*Canavalia ensiformis*) starch impregnated with iron oxide nanoparticles would be a novel contribution to knowledge, research and development.

Jack bean (*Canavalia ensiformis*) belongs to the family of the *Leguminosae*. It is native to the West Indies and Central America, but is now found scattered throughout the tropics and sub-tropics, having different native names. Presently in Nigeria, there are no farms where jack bean is commercially cultivated, but people plant jack bean as a flower around their homes while some grow wild [16].

The aim of this present study was to: (a) produce starch impregnated with iron oxide nanoparticles via copolymerization with glutaraldehyde as a crosslinking agent; and (b) investigate their selected properties such as swelling power, FTIR patterns, X-ray patterns and morphological properties with the view to proposing their possible applications. Glutaraldehyde is used in this study as a crosslinking agent, because of its hydrophilic ability, non-toxicity and biodegradability.

2. MATERIALS AND METHODS

2.1 Sources of Materials

Jack beans were harvested from a residential farm of Oladebeye Abraham Olasupo, Edo State, Nigeria. All the reagents used were commercially purchased and were of analar grade.

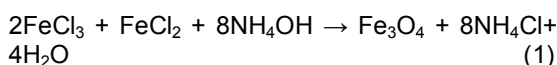
2.2 Isolation of Native Starch

The native starch of jack bean (*Canavalia ensiformis*) was extracted by according to the method described in previous work [16].

2.3 Synthesis of Starch-Iron Oxide Nanoparticles

Powdered jack bean starch (5.0 g) was weighed and dispersed in 20 mL of distilled water to form paste. Boiling water (40 mL) was added to obtain a clear solution. This was followed by the addition of iron solutions (16.25 g of FeCl₃ and 6.35 g of FeCl₂ in 200 mL of distilled H₂O). The

solution was mixed with vigorous stirring for 60 min at 30°C. Then, 2 M of NH₄OH solution was added to adjust the pH to 12. This was followed by addition of 5 ml of 25% glutaraldehyde to the solution and the crosslinking reaction was allowed to proceed at 70°C for 5 h. The particles obtained were washed successfully with toluene and acetone. The particles were dried in an oven at 60°C to obtain magnetic starch nanoparticles and were stored in polythene bag prior to analysis [6]. The proposed mechanism for the synthesis of magnetic starch nanoparticles is given in Fig. 1.



2.4 Swelling Power

Sample (0.1 g) was weighed into six different beakers. 10 mL of distilled water was added to each sample and the pH was adjusted to 2, 4, 6, 8, 10 and 12 with HCl and NaOH. The resulting slurries were heated at 90°C for 30 min in a water bath followed by cooling at 28±2°C and centrifuged at 2500 rpm for 15 min and the supernatant was removed.

$$\text{Swelling Power (g/g)} = \frac{W_t}{W_o} \quad (2)$$

where, W_o and W_t are the weight of dry and swollen nanoparticles at o and time, t respectively.

2.5 FTIR Spectroscopy

Fourier Transform Infra-red (FTIR) spectra of the sample were obtained with a Nicolet AVATAR 360 Fourier Infra-red spectrometer using KBR disks. 1.0 mg of the sample was dispersed in a matrix of KBR (100 mg) and pressed to form packet. The spectral was measured at a resolution of 4 cm⁻¹ and 32 scans were recorded per sample.

2.6 X-ray Diffractometry

Native starch and magnetic nanoparticle samples were equilibrated above distilled water in a desiccator for three days. The hydrated starch powders were packed in tightly sealed glass dishes and patterns were obtained with Ni-filtered Cu-Kα radiation of wavelength 0.1542 nm using a diffractometer (D-5000 Siemens, Madison, WI, USA) by exposing the samples to the X-ray beam from an X-ray generator running at 40 kV and 60 mA. The scanning regions of the diffraction angle 2θ were 1.5 – 60°. The scanning region of the diffraction angle (2θ) was from 1.5 to 60° at 0.05 step size with a count time of 3 s. From the resulting X-ray patterns, peak positions were identified using the instrument's software and these peak positions were used to determine the crystalline nature [17]. The crystallinity index and crystallite size were deduced as follows:

$$\text{Crystallinity Index, } I_c = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (3)$$

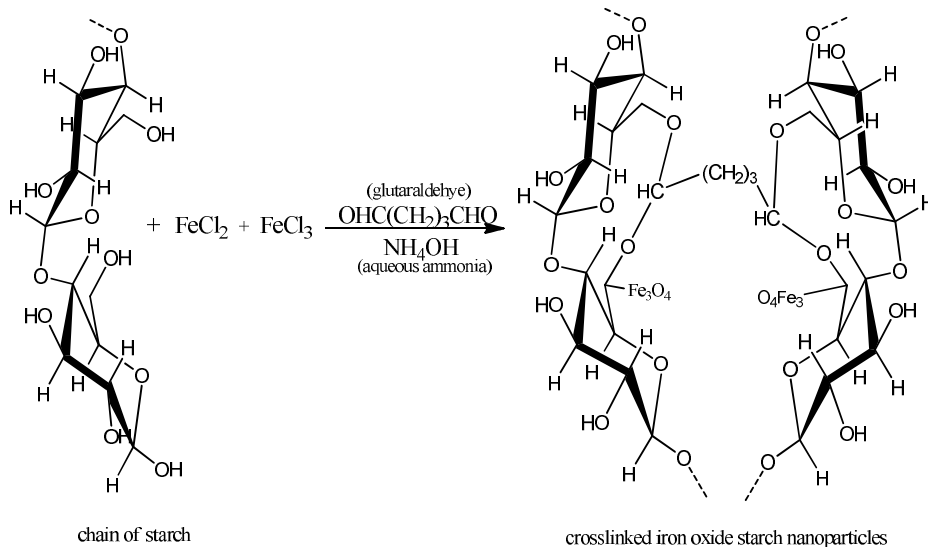


Fig. 1. Mechanism of synthesis of magnetic starch nanoparticles

where, I_{002} is the intensity of the 002 diffraction peak at 2θ angle close to 24° , representing the crystalline region of the material, and I_{am} is the intensity of the peak at 2θ angle close to 18° .

$$\text{Crystallite size, } D_{(hkl)} = \frac{k\lambda}{B_{(hkl)}\cos\theta} \quad (4)$$

where, k = Scherrer constant (0.84), λ = 0.154 nm, $B_{(hkl)}$ (FWHM – Full Width Half Maximum), and θ = corresponding Bragg's angle to FWHM).

2.7 Morphology

The starch granules were sprinkled onto the aluminium specimen stubs with double-sided adhesive tape while the non-sticking portion was blown off. The granules were coated with a 30 nm layer of gold using a sputter coater [Polaron (Fisons) SC 515 VG Microtech, Sussex, UK]. The coated starch granules were observed using a Scanning Electron Microscope (SEM-FEI model Q250, FEI Netherlands). Images were captured at different magnifications of 150 K, 500 K and 1000 K for morphological studies [14].

3. RESULTS AND DISCUSSION

3.1 Swelling Power

Swelling powers of the native starch range from 9.20 to 18.90 g/g within the pH 2 – 12. Similarly, the magnetic starch nanoparticles exhibit swelling powers between 4.20 and 14.00 g/g

within the same pH values (Fig. 2). From the figure, it is clear that pH affects the swelling behaviours of both the native starch and the starch nanoparticles. It is worthy of note that between pH 2 and 8, the swelling powers of the native starch increase with a drop at pH 10 and final elevation at pH 12. A slightly different trend is obtained for the nanoparticles; the swelling powers increase between pH 2 and 8, followed by a drop at pH 10 and subsequent elevation at pH 12.

The swelling behaviour of polymeric nanoparticles depends on the nature of the solvent and polymer. The swelling properties of nanoparticles affect their usability as a biomaterial in medicine pharmacy and veterinary practices. Since starch is non-ionic in nature, the change in pH of the swelling medium does affect the charge profiles of the iron oxide nanoparticles in an aqueous medium which eventually influences the water sorption capacity of the nanocomposite. It has been observed that as the pH of the medium increases, the existing repulsion forces goes on decreasing, which consequently produces a decreasing swelling of the nanoparticles [6]. It is noted from this study that the iron oxide impregnated starch nanoparticles attain the highest swelling power at pH 6, after which recovery to high swelling behavior is impossible. The reason may be adduced to the insufficient protonation of acidic Fe^{2+} ions, which could counteract the effect of change in pH of the medium above 7.

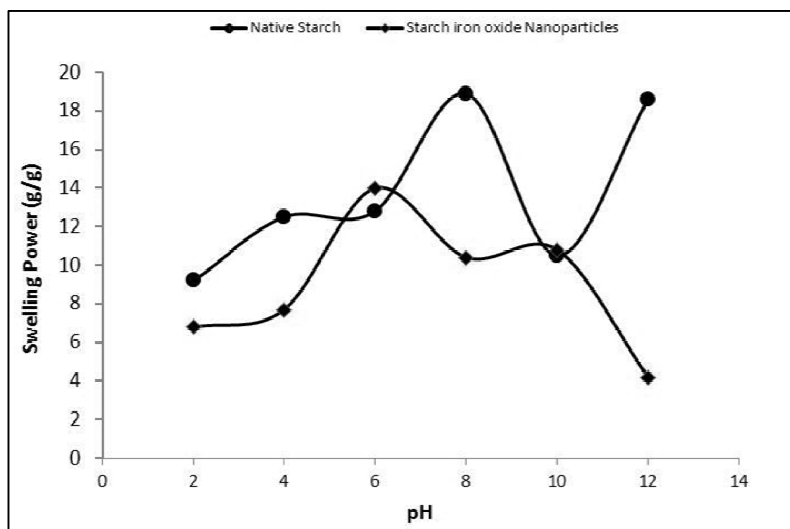


Fig. 2. Effect of pH on swelling power of native starch and magnetic starch nanoparticles

The differences in the extent of swelling indicate structural differences among starches. The swelling power of starches is of great significance in tablet and capsule formulations, as it is believed that disintegrants work through a swelling and wicking action [18,19]. As a result, starches with higher swelling power would be expected to release the active pharmaceutical ingredient from its compacts at a faster rate, where starch acts as a disintegrant.

3.2 FTIR Patterns

The FTIR spectra of the native starch and the magnetic starch nanoparticles are displayed in Fig. 3. At 3242 cm^{-1} absorption band, O–H stretching appears at the expense of starch hydroxyl groups. The bands appear at a lower frequency than the native starch (3265.1 cm^{-1}). A characteristic C–H stretching is observed at 2926.7 cm^{-1} for native starch and 2926.0 cm^{-1} for magnetite starch nanoparticles, indicating a higher energy of activation for the nanoparticles than the corresponding native starch. This may imply the increased activity of the granules of the starch as their architectural network is converted to nano scale.

Also, C–O stretching is observed at 1077.2 cm^{-1} for native starch and 1077.2 cm^{-1} for magnetite starch nanoparticles, although at higher frequency. This can equally account for possible low susceptibility of nanoparticles to corrosion. C–O–C stretching of glycosidic bonds, typical of starch is observed at 1148 cm^{-1} for both samples. In addition, peaks between 700 and 861 cm^{-1} may be indications of magnetite in the nanoparticles. 526–418 cm^{-1} indicative peaks for iron oxide in the starch matrix have also reported [6].

3.3 XRD Patterns

X-ray diffraction peaks for the native jack bean starch appear at 24.04°, 18.32° and 33.95° 2 θ , corresponding to interplanar d-spacing of 3.70 Å, 4.84 Å and 2.64 Å (Table 1). Likewise, the iron oxide impregnated starch nanoparticles exhibit X-ray diffraction peaks, which appear at 24.00°,

18.24° and 57.36° 2 θ , corresponding to interplanar d-spacing of 3.71 Å, 4.86 Å and 1.61 Å (Table 2). Diffraction peak of 57.36° 2 θ is similar to 57.215° 2 θ , which has been identified as one of the crystal planes for pure Fe₃O₄ [20, 21]. Noticeably, the intensity counts of the peaks increase in the nanoparticle derivative, which may arise from the impregnation of magnetite (Fe₃O₄) in the matrix of the nanoparticles.

The amorphous and crystalline nature of the magnetite starch nanoparticles were determined by degree of crystallinity. The degree of crystallinity of native starch is 81.01% while for iron oxide impregnated starch nanoparticles is 87.30%. Lower values of 43.8% and 67.5% have been reported as percent crystallinity for native starch and iron oxide impregnated starch nanoparticles [22]. The results obtained are obviously appropriate, because a single matrix of starch, being an amorphous polymer, is expected to exhibit less crystalline nature than its composite material containing iron oxide. The results obtained in this present study are in league with those reported, where the starch nanoparticles exhibited higher crystallinity index more than their corresponding native starch [6]. The estimated average crystalline size of the native jack bean starch is 0.71 nm while that of the starch nanoparticles is 1.09 nm. These data may be a true reflection of direct proportionality between the crystallite size and crystallinity index of a material.

3.4 Morphology

The micrographs of the native starch show non-uniform shape of the granules (Fig. 4). They appear as a mix of shapes, which are predominantly oval. There are scant granules that are spherical and polygonal. Such mixes classify them as irregular or non-uniform granules. Magnetic starch nanoparticles are known to have non-uniform shapes [22]. From the surface outlook of the granules, there is so single pore, indicating that the method of isolating starch from jack bean (*Canavalia ensiformis*) does not distort or disrupt the architectural network of the granules.

Table 1. Major peak characteristics of native jack bean starch and magnetic starch nanoparticles

Sample	Peak I				Peak II				Peak III			
	I	2 θ	D	RI	I	2 θ	D	RI	I	2 θ	D	RI
Native Starch	756	24.04	3.70	100	143	18.32	4.84	19	79	33.95	2.64	10
Nanoparticles	1147	24.00	3.71	100	143	18.24	4.86	12	99	57.36	1.61	9

I = Intensity (counts); *2 θ* = Bragg's angle; *d* = d-spacing; *RI* = relative intensity

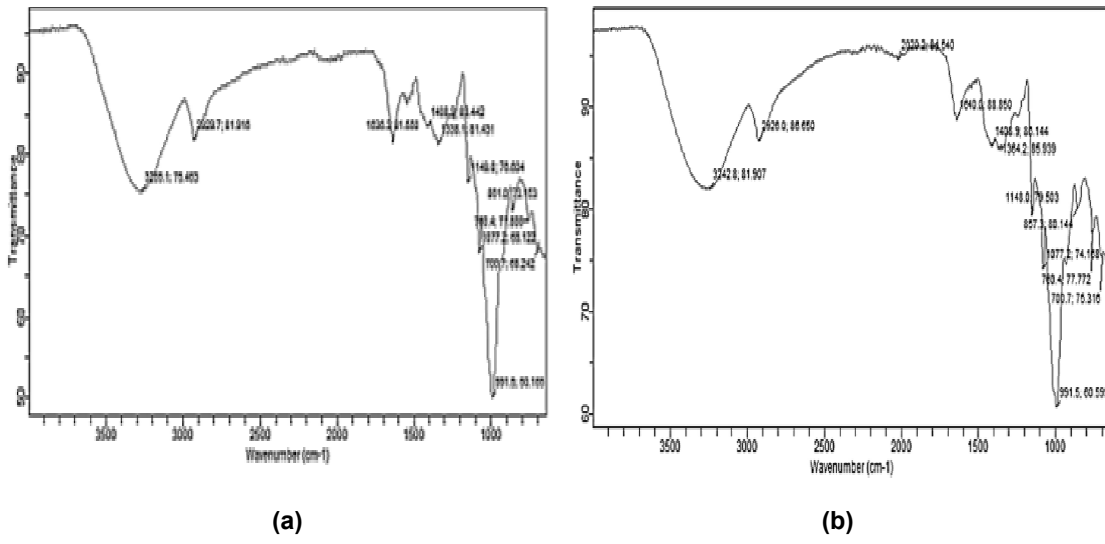


Fig. 3. FTIR spectra of: (a) native starch and (b) magnetic starch nanoparticles

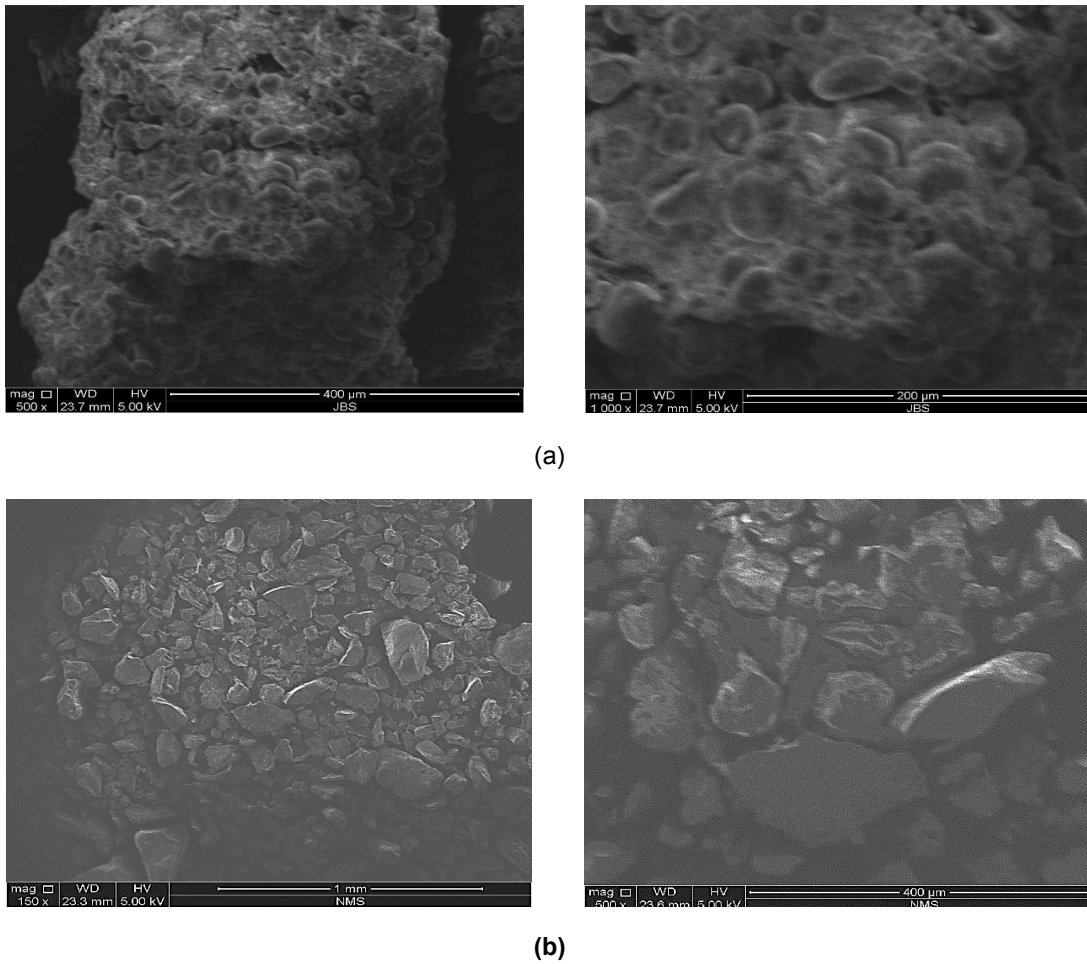


Fig. 4. SEM images of: (a) native jack bean starch and (b) magnetic starch nanoparticles

Table 2. Crystallinity indexes and crystallite sizes of native jack bean starch and magnetic starch nanoparticles

Sample	$B_{(hkl)}$	θ ($2\theta^0$)	Degree of crystallinity I_c	Crystallite Size, $D_{(hkl)}$ (nm)
Native Starch	0.20	24.09	81.01	0.71
Nanoparticle	0.13	24.06	87.53	1.09

$B_{(hkl)}$ = FWHM (Full Width Half Maximum), θ (corresponding Bragg's angle to FWHM); $I_c = \frac{I_{002} - I_{am}}{I_{002}} \times 100$;

$$D_{(hkl)} = \frac{k\lambda}{B_{(hkl)} \cos\theta}$$

The micrographs of the magnetite starch nanoparticles, taken at different magnifications, show rock-like granules without uniform shape, but with evidences of strata (Fig. 4). The micrographs confirm that nanoparticles tend to be aggregate rather than discreet individual granules. Aggregation of magnetic starch nanoparticles may be attributed to the fact that there is a hydrophilic biopolymer and may show a tendency to get adsorbed onto the surfaces of the magnetic starch nanoparticles.

4. CONCLUSION

Synthesis of magnetic starch nanoparticles from the co-precipitation of the native starch matrix of jack bean (*Canavalia ensiformis*) and iron salts, using glutaraldehyde as a crosslinking agent is possible. The swelling powers of both the native starch and the magnetic nanoparticles are affected by pH. Peaks between 700 and 861 cm^{-1} may be indications of iron oxide in the matrix of the starch nanoparticles. The degree of crystallinity of native starch is 81.01% while for iron oxide impregnated starch nanoparticles is 87.30% while the estimated crystalline sizes of the native jack bean starch and the starch nanoparticles are 0.71 nm and 1.09 nm respectively. Their morphologies of the native starch show a mix of shapes, which are predominantly oval while the nanoparticles appear rock-like granules without uniform shape, but with evidences of strata. The magnetic starch nanoparticles in this present study could be a possible alternative source of recipe for drug formulations and delivery. They can also be used in water treatment nanotechnology.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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