

Green Synthesis of pH Sensitive Polymer Hydrogel-Silver Nanocomposites and its Applications as Body Water Retainers and Stomach Bulking Agents

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ABSTRACT:Hydrogels are macromolecular networks able to absorb and release water in response to specific environmental stimuli. Such stimuli sensitive behavior of hydrogels prompted to synthesize biodegradable super absorbent polymeric hydrogel based on cross-linked poly (acrylamide) prepared through an optimized rapid redox solution polymerization with N,N'-methylenebisacrylamide (MBA) in presence of carboxymethylcellulose (CMC). Silver nanoparticles have been obtained within hydrogel networks as nanoreactors via insitu reduction of silver nitrate using AzadirachtaIndica (neem) plant extract under atmospheric conditions. The synthesized hydrogel-silver nanocomposites were characterized by UV, XRD, EDX, SEM and TEM. Effect of pH on swelling capabilities was investigated. Results indicate that pH response of hydrogel-silver nanocomposites in acidic and basic environments made it suitable for body water retainers and stomach bulking agents.

KEYWORDS: Hydrogel, silver nanoparticles, environment friendly, pH sensitive, swelling agent.

I. INTRODUCTION

Hydrogel nanocomposites (HN) include the incorporation of inorganic nanoparticles inside three-dimensional polymeric networks. Hydrogels possess hydrophilic character and have potential for biocompatibility. Hydrogels can swell and absorb water without dissolving, provided that chemical or physical crosslinks exist among the macromolecular chains. The polymer network resulting from the crosslinks swells in the aqueous solvent, until the thermodynamic force of swelling is totally counterbalanced by the elastic, retroactive force exerted by the crosslinks. The amount of water retained by the mesh of the hydrogel network depends on the structure of the polymer network itself and on the environmental conditions, such as the temperature, pH and ionic strength of the water solution in contact with the polymer [1].

Hydrogels are potentially useful for the development of a variety of smart devices, such as valves, artificial muscles and substrates for controlled drug release [2-5]. Since the first hydrogels based on poly(hydroxyethylmethacrylate) (PHEMA) developed by Otto Wichterle in the 1950s and later patented for use as soft contact lenses [6], great steps have been taken by researchers towards obtaining novel hydrogels, based on synthetic, natural or hybrid polymers, which possess given swelling properties, biocompatibility. Innovative hydrogel products have thus been developed either as water absorbents for specific applications (e.g., personal hygiene products, underwater devices, water reservoirs for dry soils) [7-10] or as biomedical devices, including soft contact lenses, lubricating surface coatings, phantoms for ultrasound-based imaging, controlled drug release devices, wound healing dressings, cell immobilization islets, three-dimensional cell culture substrates, and bioactive scaffolds for regenerative medicine [4,5,11-16].

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Recently, silver nanoparticles have been widely utilized in hydrogel networks due to remarkable improvement in some properties of hydrogel such as mechanical toughness, large deformability, high swelling/deswelling rates, excellent electrical conductivity, antimicrobial effects, and optical properties, and high transparency.

This research work deals with the synthesis of biodegradable super absorbent polymeric hydrogel, based on cross-linked poly (acrylamide) prepared through an optimized rapid redox solution polymerization with N,N'-Methylenebisacrylamide (MBA) in presence of Carboxymethylcellulose (CMC). Silver nanoparticles have been obtained within hydrogel networks as nanoreactors via in situ reduction of silver nitrate (AgNO_3) using Azadirachta Indica (Neem) plant extract under atmospheric conditions satisfies the world's firm decision for environmental protection and potentially support the idea of partially/totally replacing the synthetics by "greener" alternatives [17].

II. MATERIALS AND METHODS

A. Materials

Acrylamide (AM), Carboxymethylcellulose (CMC), Ammonium persulphate (APS), Silver- nitrate (AgNO_3), N, N'-Methylenebisacrylamide (MBA), N, N, N', N' Tetramethylethylene-diamine (TEMED), were supplied by S.D. Fine Chemicals (Mumbai, India) and used without further purification and double distilled water procured locally.

B. Preparation

Hydrogel was prepared by polymerizing 1 g of AM dissolved in 6 ml of distilled water with 0.10 g of CMC in presence of a cross-linker MBA (0.01 g), initiating system APS (0.005 g) and TEMED (0.02 ml). Polymerization was performed in 100 ml beaker at room temperature. The polymerization reaction results in the formation of gel within 20 minutes of reaction time and was equilibrated with water for 3 days and then transferred to another beaker containing 50 ml of 0.005 M AgNO_3 aqueous solution, allowed to equilibrate for 1 day. These silver salt loaded hydrogel was finally transferred into a beaker containing 50 ml of neem plant extract and allowed for 2 hours to reduce the silver ions into silver nanoparticles. The colorless gel changed to brown shows the reduction of silver ions to silver nanoparticles known as hydrogel - silver nanocomposite (HSN) as shown in Fig. 1.

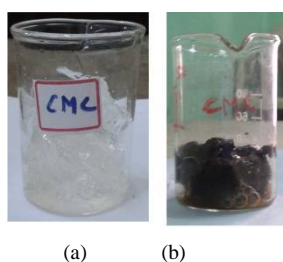


Fig.1.(a) Hydrogel (colourless); (b) HSN Brown

C. Mechanism of HSN formation

The advanced feature of this methodology is that the nanoparticles simply prepared at room temperature in presence of green stabilizers. In these experiments, the hydrogel was allowed to swell in the AgNO_3 solution and reduced with neem plant extract throughout the gel networks. In detail, the PAM cross-linked networks act as reservoir for metal ions uptake and the ions are anchored through carboxylic, amide, and hydroxyl groups of carbohydrate polymer (CMC) and thereby holds large amounts of metal ions in their network and facilitate the reducing process as well as helps in stabilization. The carbohydrate polymer (CMC) in hydrogel networks arrests the agglomeration of silver nanoparticles.

III. CHARACTERIZATION

A. UV-vis spectra

The existence of silver nanoparticles in the gel networks is confirmed by absorption peak for HSN at 420 nm

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Vol. 5, Special Issue 1, March 2016

wavelength in UV–vis spectra assigned to silver nanoparticles which arose from the surface Plasmon resonance (SPR) as shown in Fig. 2.

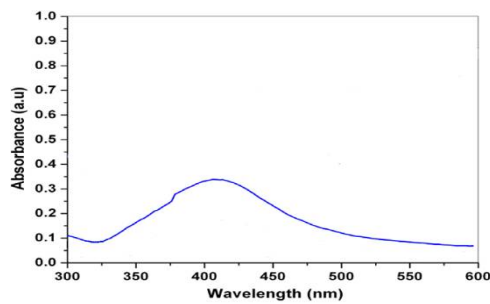


Fig.2.UV-visible spectra of HSN

B. SEM Analysis

The SEM micrographs of HSN showed that silver nanoparticles are spherical shaped, well distributed without aggregation with an average size of about 20-50 nm as shown in Fig.3.

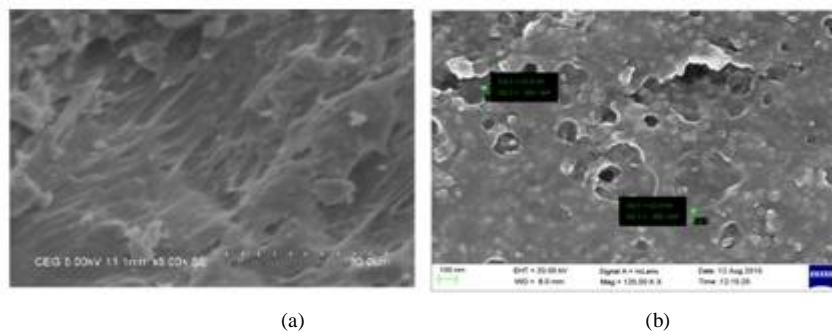


Fig.3.SEM images of (a) Hydrogel (b) HSN

C. Energy dispersive X – ray Spectrum (EDX) Analysis

The EDX analysis of HSN synthesised by insitu process using neem plant extract reveals the silver content of about 19.28 wt% shown in Fig.4

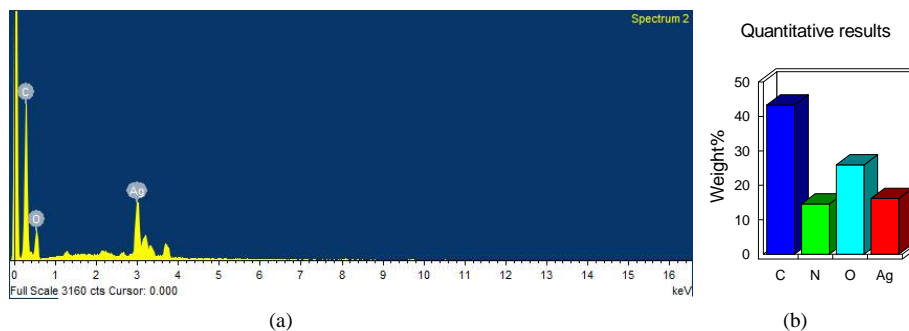


Fig.4.(a) EDX Spectrum of HSN (b) Quantitative Results

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

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D. XRD Analysis

Fig.5 illustrates the X ray diffraction Pattern of HSN. A common broad diffraction peak 2θ seen below 20° is due to the amorphous nature of polymeric hydrogel. The diffractions at 2θ values of about $38^\circ, 44^\circ, 65^\circ, 78^\circ$ are due to the Bragg reflections of (111), (200), (220) and (311) plane of face centered cubic (fcc) structure of silver nanoparticles. Sharp intense peaks represent the highly crystalline silver nanostructures formed in HSN.

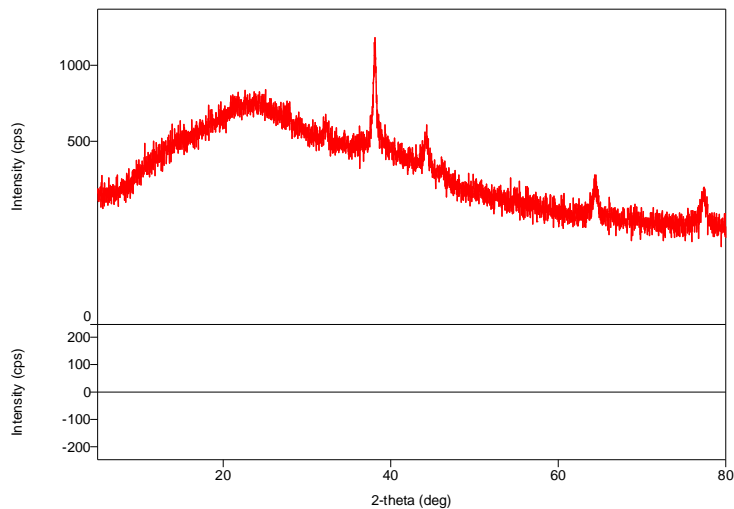


Fig.5.XRD Spectrum of HSN

E. TEM Analysis

The TEM image in Fig. 6 showed spherical shaped silver nanoparticles in the biopolymer matrix, with an approximate size of 10-40 nm.

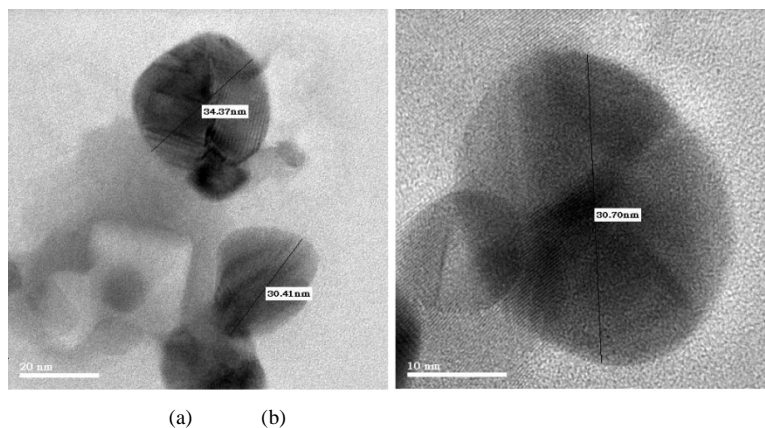


Fig.6.(a) and (b)TEM images of HSN

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

IV. SWELLING STUDIES

Dried sample (Hydrogel, Hydrogel-Ag⁺, HSN) of known weights were put in separate tea bags (i.e., a 100 mesh nylon screen) and immersed in 100 mL of DDW or solutions with different pHs at 37°C. After the specific time interval the tea bags were taken out and hung up for 5 min in order to remove the excess solution and weighed. The swelling ratio (Q) of the Hydrogel, Hydrogel-Ag⁺, HSN were calculated from equation

$$Q = W_e / W_d, \text{ where } W_e \text{ is the weight of swollen hydrogel and } W_d \text{ is the weight of dry hydrogel.}$$

A. Swelling capacity of Hydrogel, Hydrogel-Ag⁺, HSN

In Fig. 7, the swelling capacities of Hydrogel is because of hydrophilic polymeric chains were entrapped in the hydrogel networks to improve swelling characteristic of gel systems. It was known that polar head groups of polymeric chains such as hydroxyl, thiol, amine, and nitrile groups have a high affinity for salts [18 -20]. After treating the Hydrogel with silver salts, the silver ions loaded through the gel networks are responsible to cause repulsion of networks, ultimately leads to an improved swelling behaviour of hydrogel systems. Further increase in swelling capacity was recognized after addition of reducing agent (neem plant extract) to silver ions loaded hydrogel. This pattern of swelling is reasonable because once the silver nanoparticles are formed inside the network/throughout the gel networks overall porosity of system increased which allow for more number of water molecules inside the gel. The other reason can be that the formed particles have different sizes and different surface charges in the gel networks that cause absolute expansion of the networks.

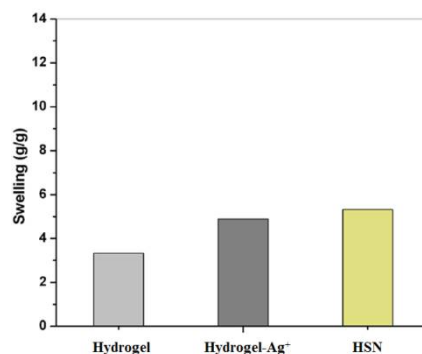


Fig.7. Bar diagram of swelling capacities of Hydrogel, Hydrogel-Ag⁺ and HSN

B. Effect of PH on swelling capacity of HSN

In Fig.8, the swelling increases with rising pH up to 8 and then it decreases at pH = 10. It has been observed that maximum degree of swelling was observed at pH 8. The anion-anion repulsive forces between the groups (for example, carboxylate groups) in the networks of the hydrogel are the main reason for the swelling at pH 8. In high basic solutions, the hydroxyl groups on the CMC can ionize to reactive alkoxy anions which subsequently can react with carboxylic acid (or carboxylate) groups of the hydrogel to make an ester moiety. This reaction can make more networks in the hydrogel which is responsible for the lower swelling of the hydrogel at pH 10. This ester moiety formation can also decrease the hydrophilicity of the whole network.

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Vol. 5, Special Issue 1, March 2016

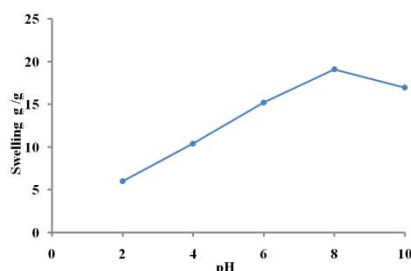


Fig.8.Effect of pH on swelling capacity of HSN

C. Effect of pH reversibility on swelling capacity of HSN

A known weight of HSN was put in pH 2 and pH 8 solutions alternatively at every 30 minutes interval and swelling ratio was recorded. Fig. 9 shows the reversible swelling-deswelling behavior of HSN in solutions with pH 2 and 8. At pH 8 the hydrogel swells due to anion-anion repulsive electrostatic forces, while at pH 2, it shrinks within a few minutes due to protonation of the carboxylate anions. This swelling-deswelling behavior of the hydrogel makes HSN as a suitable option for stomach bulking agent and body water retainers.

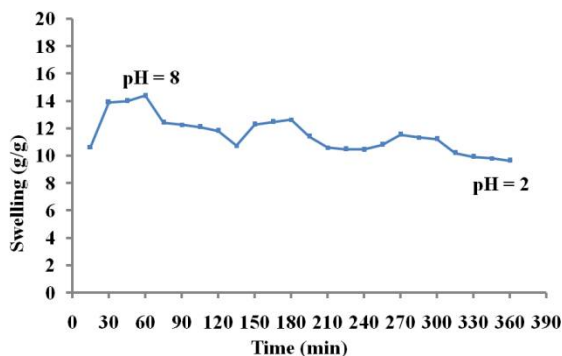


Fig.9.Swelling capacity of HSN in pH 2 and pH 8 solutions alternatively for every 30 minutes

V. APPLICATIONS

A. Body Water Retainers

Due to the intrinsic biocompatibility of carboxymethylcellulose together with versatile properties displayed by hydrogels in biomedical applications, cellulose-based hydrogels are appealing materials for a number of applications *in vivo*. For example, hydrogels hold promise as devices for the removal of excess water from the body, in the treatment of some pathological conditions, such as renal failure and diuretic-resistant oedemas. The HSN in powder form can be administered orally and absorb water in its passage through the intestine, where the pH is about 6-7, without previously swelling in the acid environment of the stomach. The HSN is then expelled through the faecal way, thus performing its function without interfering with body functions.

B. Stomach Bulking Agents

Obesity and overweight represent the second cause of death after smoking, as major risk factors for several chronic diseases, such as type 2 diabetes, cardiovascular disease, sleep apnea, hypertension, stroke, and certain forms of cancer. The treatment of overweight and obesity usually consists of a supervised diet, often combined with adequate physical exercise. In the most serious cases, surgical procedures, that involve essentially gastric restriction, or particular drug

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Special Issue 1, March 2016

treatments, may be required. However, in the recent years, a number of dietary supplements and meal replacements have been developed and sold as over-the-counter slimming aids. Dietary supplements are claimed to act either by binding fats and so reducing fat absorption, as reported for chitosan-based products, or by directly reducing the appetite, as for different natural fibres and herbal products, that seem to absorb liquids and swell inside the stomach, thus giving a sense of fullness [21, 22].

The basic idea is that HSN-based pill can be administered orally before each meal, and that the HSN powder swells, once in the stomach. In such a way, the space available for food intake is reduced, giving a feeling of fullness. The swollen hydrogel is then eliminated from the body by faecal way. In this perspective, the hydrogel is envisaged to pass through the gastrointestinal tract, thus it is supposed to encounter the different pH environments of the stomach and the intestine. Thus pH-sensitive water retention capacity of HSN renders its use as stomach Bulking agent.

VI. CONCLUSION

Controlled sized silver nanoparticles were synthesized using neem plant extract as reducing agent inside the hydrogel templates that containing biocompatible CMC polymeric networks. Under the UV-Visible wavelength, silver nanoparticles shown quiet good surface plasmon resonance behaviour. SEM image, TEM image of HSN shown well defined silver nanoparticles of size 20- 50nm. In XRD of HSN broad peak below 20° confirmed the polymeric hydrogel and sharp peaks at 38°, 44°, 65° and 78° confirmed crystalline silver nanoparticles and EDX analysis confirmed the formation 19.28wt% of silver nanoparticles. Incorporation of silver nanoparticles increased the swelling capacity of hydrogel. The swelling response of the prepared HSN against pH made its suitable as body water retainers and Stomach bulking agents.

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