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Research Paper

Nanocomposites based on chitosan/silver/clay for durable multi-functional properties of cotton fabrics

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ABSTRACT

The present work addresses an innovative approach for benign development of environmentally synthesis of chitosan-based nanocomposite. The synthesis involves the inclusion via interaction of AgNPs and clay with chitosan (Cs) giving rise to Cs/AgNPs and Cs/AgNPs/clay nanocomposites which when applied independently induce super functionalities. Comparison is made among the two nanocomposites with respect to their intimate association with the in depth cotton fibre-fabric surfaces and the onset of this on the multi-functionalization of cotton fabrics. It is as well to emphasize that Cs/AgNPs/clay nanocomposites prove unequivocally that its use in one–step treatment process for cotton fabrics results in imparting very appreciable good technical properties which, in turn, are reflected on all the gained functionalities of cotton fabrics. Of these functional performance properties, mention is made of cotton fabrics which exhibit high strength, uniform morphology, increased thermal stability, successful deposition of the composite on the surface of cotton fabrics, high water absorption, antimicrobial activity, flame retardant, controlled release of fragrance and UV protection. The obtained data indicate that the treatment for cotton fabrics with these nanocomposite is stable against washing even after 20 washing cycles. Based on encourage data, the environmental benign synthesis of Cs/AgNPs/clay nanocomposites is considered as a promising nanocomposite for the multifunctional finishing textiles.

1. Introduction

Textiles development arises greatly in clothing, firefighter uniform, military garments and medicinal coating in order to make our lives harmless and relaxed (Kuklane, 2000). By virtue of its features of softness, breathability, and capability to absorb moisture (Jiang et al., 2015), cotton fabric is extensively used to harvest apparel, home furnishings and varies industrial products. Conversely, a vital drawback of cotton fabric is related to the cost effect for its chemical finishing. Additionally, the high sensitivity regarding flammability and infections of untreated cotton fabrics detract from their use (Nguyen et al., 2013). This, indeed, calls for the necessity of finishing cotton fabrics for its application in medicinal and military garments with new chemicals particularly that have many multifunctional properties (Ristić et al., 2011) and cost effective as substitutes for the conventional high cost materials (Sanchez, Belleville, Popall, & Nicole, 2011).

In common practice, nowadays the application of inorganic nanoparticles on textiles is considered to be a good alternative to conventional materials and as a consequence they provide a new opportunity for the multi- functional modification of fibers (Sanchez et al., 2011). For the sake of achieving this purpose, a great deal of studies was conducted aiming at coating nanoparticles on cotton using different methods. Of these methods mention is made of the following; (a) treatment with dispersion of nano-oxides (El-Naggar, Shaheen, Zaghloul, El-Rafie, & Hebeish, 2016; El-Naggar, Hassabo, Mohamed, & Shaheen, 2017; Mohamed, El-Naggar, Shaheen, & Hassabo, 2016, 2017; Shaheen, El-Naggar, Abdelgawad, & Hebeish, 2016). (b) grafting of particles (Ye et al., 2005); (c) pre-treatment of fibers with corona discharge (Ryu, Wakida, & Takagishi, 1991; Ye et al., 2005); (d) gamma irradiation (Nair & Laurencin, 2007), (e) UV irradiation (Shameli et al., 2010), (f) ultrasound vibration (Montazer & Seifollahzadeh, 2011); (g) plasma process to enhance coating of nano-particles (Shi et al., 2011); (h) functionalization by inorganic sol–gel coating (Shi et al., 2011) and (i) layer-by-layer deposition method (Dotzauer, Dai, Sun, & Bruening, 2006; Pastoriza-Santos et al., 2000). In current investigation, emphasis is placed on the use of a three – component nanocomposite, namely chitosan/AgNPs/clay in a single step process for finishing of cotton fabrics. Existence of chitosan is a must as it acts as stabilizer and reducing agent for conversion of the Ag^{+} to Ag^{0} which forms ultimately silver nanoparticles (AgNPs). The as prepared AgNPs are responsible for conferring

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on cotton fabrics the antimicrobial and enhance the dyeing properties. On the other hand, the function of clay is to accentuate the flame retardant and thermal stability of the untreated flammable cotton fabrics.

Intensive research efforts have been made for the green synthesis of ex situ and in situ metal (Yan, Abdelgawad, El-Naggar, & Rojas, 2016) and metal oxide nanoparticles (El-Naggar et al., 2016; Shaheen et al., 2016) for finishing cellulosic based textiles (Emam, Rehan, Mashaly, & Ahmed, 2016; Rehan et al., 2017; Rehan, Mashaly, Mowafi, El-Kheir, & Emam, 2015; Shameli et al., 2010). It is well established that the green environmental synthesis includes three main steps: selection of solvent medium, reducing agent, and nontoxic compound for stabilization of these metal nanoparticles. Also, required is an economic, commercially viable, and environmentally green route for the synthesis of metal nanoparticles (Khan et al., 2016; Shameli et al., 2010; Vigneshwaran, Nachane, Balasubramanya, & Varadarajan, 2006). There are several methods which are used for the preparation of metal nanoparticles; these methods comprise chemical reduction (El-Rafie et al., 2011; Guzmán, Dille, & Godet, 2009; Hebeish et al., 2011; Hebeish, El-Rafie, EL-Sheikh, Seleem, & El-Naggar, 2014), chemical vapor deposition (Swihart, 2003), electrochemical (Yin, Ma, Wang, & Chen, 2003), microorganism reduction (Shahverdi, Minaeian, Shahverdi, Jamalifar, & Nohi, 2007) and photo-reduction by UV radiation (Jia, Zeng, Song, An, & Zhao, 2006; Xu, Qiao, Qiu, & Chen, 2008).

With the above need in mind, silver nanoparticles (AgNPs) can be synthesized using a variety of green irradiation methods in aqueous solution in the presence of environmental benign carbohydrate polymer; viz. chitosan (Cs) as stabilizing agent for the prepared AgNPs. Experiments are designed to use the photochemical reduction method for producing silver nanoparticles (AgNPs) because it is more convenient and environmental friendly than either chemical or physical methods. The synthesis is undertaken in the presence of chitosan (Cs) as stabilizing agent. Cs has been submitted to extensive investigation as a natural polysaccharide biopolymer derived from naturally occurring chitin.

The presence of active amino and hydroxyl groups renders chitosan (Cs) to be a unique polycationic chelating agent (Kong, Chen, Xing, & Park, 2010). Cs is widely used in various fields including medicine, textile finishing, medical and agricultures (Lim & Hudson, 2003). It is also reported that Cs/AgNPs composite has been used as finishing agent for antibacterial. In addition to the flammability and lack of the thermal stability of cotton fabrics, there is an urgent need to modify the surface of cotton fabrics with flame retardant materials. It was reported that there are some compounds such as halogenated additives and boron containing additives are used before in flame retardancy of cotton fabrics (H. Yang, Wang, Lei, Fei, & Xin, 2012). The drawbacks for using these compounds mainly focusing on that halogenated compound release the gas that is harmful to human bodies and the environment (Tai et al., 2012)and the boron containing flame retardant restricted due to its lack of durability (Martin, Ronda, & Cadiz, 2006). Hence, there is a necessity need to develop an environmentally friendly and effective approach to flame retardant finishing of cotton fabrics. Clays are natural and environmentally benign materials with high specific surface area (Shahidi & Ghoranneviss, 2014) and they are widely applied in many fields because of its good mechanical properties, thermal stability and flame retardant properties. Sodium Montmorillonite (Na-MMT) is inorganic mineral clay. The flame retardant study of MMT applied to textile fiber has attracted much attention in recent years, it has not any adverse effects in animals or humans (Cao et al., 2014). In most of prior arts silver nanoparticles (AgNPs) or chitosan (Cs) had a single use as antibacterial agent. In our current study, the target is to prepare multipurpose nanocomposite based on Cs, AgNPs and clay for antibacterial, UV protection, thermal stability and flame retardant applications.

The novelty in this research work is to compare the effect of Cs/AgNPs and Cs/AgNPs/clay nanocomposites on the cotton fabrics. In addition, the work was prolonged to characterize these treated fabrics to be multifunctional fabrics.

Therefore, In the present work, experiments are designed for multifunctionalization of cotton fabrics through conducting the following intensive studies:

(1) Green synthesis and characterization of chitosan/AgNPs/clay nanocomposite under UV radiation for different times (1, 2 and 4 h); The particle size and spherical shape of AgNPs was evaluated by using UV–vis and TEM techniques.
(2) Application of the two as synthesized nanocomposites independently to the cotton fabric.
(3) Comparison among the two nanocomposites with respect to their intimate association with the in depth cotton fibre – fabric surfaces and the onset of this on multi-functionalization of cotton.
(4) Characterization of the cotton fabrics before and after multi-functionalization using Fourier transform infrared analysis (FTIR), filed emission scanning electron microscopy (FE-SEM), X-Ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA).
(5) The work was extended to evaluate the controlled release of fragrance, antimicrobial activities, flame retardant and UV protection of the treated cotton fabrics.

2. Materials and methods

2.1. Materials

All reagents used in this work were of analytic grade and employed as received without further purification. $AgNO_3$ (99.98%) was used as the silver precursor, and obtained from Merck (Darmstadt, Germany). Chitosan (Cs) with Low molecular weight (Mw = 30 KDa and 97% degree of deacetylation. was obtained from VansonTR Company (USA).) Glacial acetic acid (HAC, 99%) were obtained from Sigma-Aldrich (St. Louis, Mo, USA). Sodium Montmorillonite (Na-MMT) clay was purchased from Sigma Co. (USA). All the aqueous solutions were used with deionized water.

2.2. Methods

2.2.1. Preparation of AgNPs under the reducing action of UV-radiation

For the synthesis of Cs/AgNPs composite, Cs solution was prepared by dissolving 2 g in 100 mL of 1.0 wt% acetic acid under constant magnetic stirring for overnight. After complete dissolution, 100 mg/l of silver nitrate ($AgNO_3$) was added to Cs solution under continuous stirring. At the end of addition, the dissolved mixture of Cs/AgNO3 was irradiated using the UV range (320–400 nm) with a UV lamp at λ = 350 nm, photon energy 2.26–3.94 eV emitting 668 μW cm^{-2} at a distance of 5 cm. The Cs/AgNO3 composite was subjected for different irradiation time (1, 2 and 4 h). At the end of irradiation, the color of prepared samples at different UV- irradiation times gradually changed from colorless to yellow color, indicating the formation of AgNPs surrounded by Cs molecules. The formation of AgNPs was followed by measuring the surface plasmon resonance bands of Cs/AgNPs suspensions at wavelengths in the range of 300–600 nm.

2.2.2. Preparation of Cs/AgNPs/clay nanocomposite

Clay solution (1%) was prepared by dissolving 1 g of clay in 100 mL deionized water under magnetic stirring for 1 h then sonicated for another 1 h. The Cs/Ag^+ composite was prepared using the same concentrations of $AgNO_3$ and Cs that is mentioned in the previous paragraph followed by adding clay suspension and the mixture was further vigorously stirred for 4 h at room temperature. The homogenous solution was nominated as CS/AgNPs/clay solution and irradiated using the UV for 2 h. The color of prepared sample was gradually changed from colorless to light gray, then to gray and finally to dark gray.