Inclusion complexes of β-cyclodextrıne with Fe_3O_4@HA@Ag Part II: Their use in the production of PVP nanowebs

DOI: 10.35530/IT.074.06.2022140

RIZA ATAV
AHMET ÖZGÜR AĞIRGAN
AYLIN YILDIZ
DERMAN VATANSEVER BAYRAMOL
UĞUR ERGÜNAY

ABSTRACT – REZUMAT

Inclusion complexes of β-cyclodextrıne with Fe_3O_4@HA@Ag Part II: Their use in the production of PVP nanowebs

Humic acid is a material formed as a result of the degradation of animal and plant wastes, it cleans heavy metals which are industrial wastes that threaten both the environment and human health. In part I of this study, the Fe_3O_4@HA@Ag compound was synthesized, its inclusion complex with β-cyclodextrin was prepared by using the kneading technique and obtained inclusion complexes were characterized. In this study, part II, nanowebs were formed from the inclusion of complex-containing polymer solution via the electrospinning method. The electrospinning solution consisted of β-CD:Fe_3O_4@HA@Ag inclusion complexes at the rate of 5%, 7.5% and 10% by weight and the polyvinylpyrrolidone (PVP) polymer as the carrier. The obtained nanoweb material was characterized by instrumental methods such as SEM, FTIR, XRD, and TGA. The results obtained from FTIR, XRD and TGA revealed that β-CD:Fe_3O_4@HA@Ag inclusion complexes containing nanowebs were successfully produced. The uniform fibre formation was detected from SEM images. The average fibre diameter of 5%, 7.5% and 10% β-CD:Fe_3O_4@HA@Ag inclusion complex containing nanowebs were measured to be 612.5 nm, 610.8 nm and 431.2 nm, respectively.

Keywords: *β-cyclodextrin, Fe_3O_4@HA@Ag, inclusion complex, electrospinning, nanoweb*

Complecși de incluziune ai β-ciclodextrinei cu Fe_3O_4@HA@Ag Partea a II-a: Utilizarea acestora în producția de nanovăluri PVP

Acidul humic este un material format ca urmare a degradării deșeurilor animale și vegetale și curăță metalele grele care sunt deșeuri industriale ce amenință atât mediul, cât și sănătatea umană. În partea I a acestui studiu, compusul Fe_3O_4@HA@Ag a fost sintetizat, complexul său de incluziune cu β-ciclodextrină a fost preparat prin utilizarea tehnicii de malaxare, iar complecșii de incluziune obținuți au fost caracterizați. În partea a II-a a acestui studiu, nanovălurile au fost obținute din soluția de polimer care conține complex de incluziune, prin metoda de electrofilare. Soluția de electrofilare a constat din complecși de incluziune β-CD:Fe_3O_4@HA@ la o rată de 5%, 7,5% și 10% în greutate și polimerul polivinilpirolidona (PVP) ca purtător. Materialul de nanoväl obținut a fost caracterizat prin metode instrumentale precum SEM, FTIR, XRD, TGA. Rezultatele obținute din FTIR, XRD și TGA au evidenţiat că au fost produși cu succes complecși de incluziune β-CD:Fe_3O_4@HA@Ag, care conțin nanovăluri. Formarea uniformă a fibrelor a fost detectată din imaginile SEM. Diametrul mediu al fibrei de 5%, 7,5% și 10% pentru complexul de incluziune β-CD:Fe_3O_4@HA@Ag, care conține nanovăluri a fost măsurat la 612,5 nm, 610,8 nm și, respectiv, 431,2 nm.

Cuvinte-cheie*: β-ciclodextrină, Fe_3O_4@HA@Ag, complex de incluziune, electrofilare, nanoväl*

INTRODUCTION

This article is the second part of the study, on the production and characterization of the β-CD:Fe_3O_4 @HA@Ag inclusion complex and this part includes electrospinning of nanowebs of β-CD:Fe_3O_4@HA@Ag inclusion complex with polyvinylpyrrolidone (PVP), as the carrier polymer [1]. Magnetic nano-materials such as Ferrite (Fe_3O_4) have attracted the attention of researchers in recent years due to their electrical, magnetic and optical properties, and these materials have found use in many different fields [2].

Humic acid (HA) is an organic macromolecule substance that emerges as a result of the degradation of animal and plant wastes in nature. It is among the materials that have the capacity to clean heavy metals, as a result of forming a complex with heavy metals, which occur as industrial waste and threaten both the environment and human health by passing into the soil [3]. HA has strong complexing ability with metal ions because it consists of large amounts of carboxyl, phenolic hydroxyl and carbonyl groups [4–7]. Today, active groups and other compounds in HA are used to prepare polymer composite materials that are insoluble in water and have good adsorption properties. In recent years, the materials used for the modification of HA are mostly carbon-based materials, metal oxides and synthetic polymer materials [8–11]. Compared with other materials, natural polymer

materials have a wide variety, diversity of resources, and low cost. Natural polymer materials can reduce the solubility of HA and increase the adsorption capacity of HA when they react through cross-linking. Therefore, natural polymer-modified HA materials as metal ions adsorbents have greater potential than other materials [4, 12–13].

Silver has been used safely in many areas for centuries as a broad-spectrum antimicrobial agent with antibacterial, antifungal and antiviral properties. Silver has been used for many years in the forms of metallic silver, silver nitrate and silver sulfadiazine for the treatment of burns, wounds and numerous bacterial infections. This is because silver is a very broad-spectrum antibiotic, there is virtually no bacterial resistance to silver, and it is non-toxic at low concentrations [14].

PVP was synthesized by Reppe in 1938 as a result of the polymerization reaction of N-vinylpyrrolidone monomer produced by acetylene chemistry. In the literature, hydrogels have found wide use in wound dressings, and scaffolds, in the development of drug and gene delivery systems, and in biomedical treatments [15]. The importance of PVP has been demonstrated by the commercialization of homopolymers, copolymers and crosslinked structures. Its amphilicity is due to the polar lactam group in the hydrophilic pyrrolidone and the non-polar methylene part, which offers lipophilicity [16]. It has found wide use in biomedical applications due to its chemical stability, non-toxicity and biocompatibility. PVP is widely used in the development of nanofibers, scaffolds, drug and gene delivery systems [17, 18]. The main working principle of the electrospinning technique is the application of electrostatic forces on a polymer liquid mixture to produce nanofibers or nano scaffolds. It is a simple conventional method for the production of different biodegradable materials and composites [19]. Electrospinning involves the injection of a charged polymer solution through a metallic needle (spinneret) by forming a Taylor cone at the needle tip and a jet of polymer solution, into a counter-charged collector [20, 21].

Magnetic nanocomposites containing Fe_3O_4, HA and silver (Ag) were synthesized by Amir et al. [2]. In another study, the Fe_3O_4@HA@Ag complex was directly doped into PVP, but it was stated that homogeneous distribution could not be achieved in the carrier polymer due to solubility problems [22].

Furthermore, Yildiz et al. produced Fe_3O_4@Cs@Ag in their previous study [23]. However, since this nanocomposite contains chitosan in its structure and its cost is high, HA recovered from waste was used instead of chitosan in this study, and thus a more environmentally friendly and inexpensive complex nanocomposite was obtained. In the first part of this article, which was previously published, the Fe_3O_4@HA@Ag compound was synthesized, the inclusion complex of Fe_3O_4@HA@Ag with β-cyclodextrin prepared by mass kneading technique, and characterized by performing various instrumental analyzes [1]. In this study, nanoweb containing β-CD:Fe_3O_4@HA@Ag inclusion complex was obtained by electrospinning method from solution by using PVP as the carrier polymer. The prepared nanoweb was characterized by SEM, FTIR, XRD and TGA.

MATERIAL AND METHOD

The substances used in the β-CD:Fe_3O_4@HA@Ag inclusion complex were $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, $C_{187}H_{186}O_{89}N_9S_1$ (HA), $AgNO_3$, $NaBH_4$, NH_3 and they were obtained from Merck, while polyvinylpyrrolidone ((C_6H_9NO) X, MW = 1.300.000), N, N-dimethylformamide (DMF), ethanol (solvent) were obtained from Sigma ALDRICH companies.

PVP (10% w/v) solution was prepared using pure ethanol. Since it was concluded in our previous work that the 1:2 inclusion complex of β-CD with Fe3O4@HA@Ag prepared by kneading technique was found to have better results [1], in this nanoweb production part of the work, 1:2 β-CD:Fe_3O_4@HA @Ag was used in different weight ratios (5%, 7.5% and 10% by weight). Inclusion complexes were dissolved in DMF (10 ml), by vigorously stirring at 50°C for 6 hours. Then, the PVP solution and the solution containing β-CD:Fe_3O_4@HA@Ag were mixed to prepare the electrospinning solution. The prepared electrospinning solution was placed in a 10 mL syringe and placed in a single-needle electrospinning device with an inner needle diameter of 0.7 mm for nanoweb production. The nanoweb material was obtained by setting the device parameters at a 0.5 mL/h feed rate, 17 kV voltage and a 15 cm collection distance. Fourier transform infrared (FTIR) spectra of the nanoweb material were recorded in transmission mode with the BRUKER, VERTEX 70 ATR spectrometer. The FTIR spectrums of the samples were taken in the wavenumber range of 4000–400 cm^{-1}. X-ray diffraction measurements (XRD) of the crystal structure of the samples were analysed with a Bruker AXS diffractometer and the surface morphology was analysed with a Quanta FEG 250 scanning electron microscope (SEM) (FEI, Netherlands).

Thermogravimetric analysis (TGA) of the samples was characterized by a Perkin Elmer Instruments brand TGA device. 6 mg of sample in powder form was inserted into the equipment. The analysis was carried out under a nitrogen atmosphere with a heating rate of 10°C/min. The temperature ranged from room temperature to 900°C.

RESULTS AND DISCUSSION

FTIR results

The surface chemistry of the nanoweb containing different amounts of β-CD:Fe_3O_4@HA@Ag inclusion complex (5%, 7.5% and 10%) was investigated using the FTIR spectrum (figure 2). In the spectrum of β-CD:Fe_3O_4@HA@Ag/PVP nanowebs, peaks at ~1650 cm^{-1} and ~1415 cm^{-1} correspond to -COO

groups, while peaks at 2980 cm^{-1} and 2870 cm^{-1} correspond to -CH_2, -CH_3. The PVP polymer has a peak at 3420 cm^{-1} showing the O-H stretch band. The peaks at 2953 cm^{-1} and 1656 cm^{-1} indicate asymmetric stretching of CH_2 and C-O stretching, respectively [24]. Therefore, FTIR results confirmed that the obtained nanowebs contain β-CD:Fe_3O_4 @HAAg in the structure (figure 1).

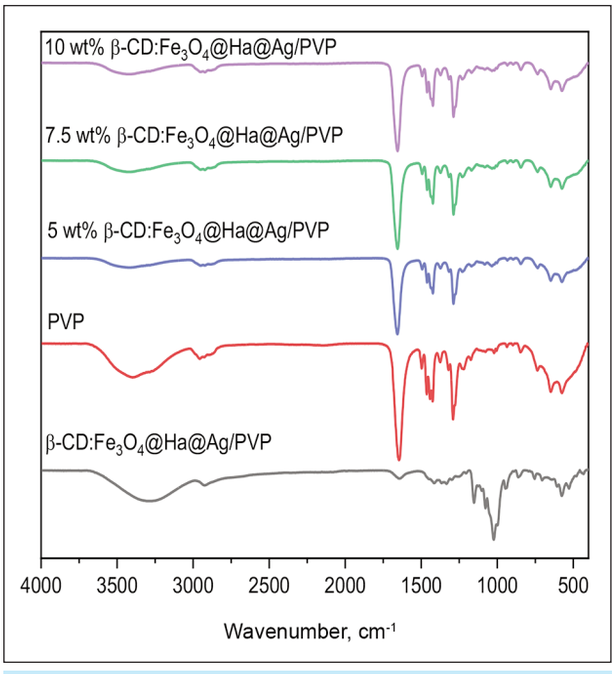

Fig. 1. FTIR spectra of produced nanowebs

SEM results

SEM images of produced nanowebs containing 5%, 7.5% and 10% by weight inclusion complex are presented in figure 2. In the SEM images, it was seen that no beads were formed and composite nanowebs were produced successfully. The uniform fibre formation was detected from SEM images. The fibre diameter distribution and mean fibre diameter of 5%, 7.5% and 10% β-CD:Fe_3O_4@HA@Ag inclusion complex containing nanowebs were measured. The data was plotted in histograms and given in figure 2. The mean fibre diameter was found to be 612.5 nm, 610.8 nm and 431.2 nm for 5%, 7.5% and 10% β-CD:Fe_3O_4 @HA@Ag inclusion complex-containing nanowebs, respectively.

XRD results

Produced nanowebs were analyzed by XRD for the determination of their crystal structures. The XRD patterns of nanowebs with three different ratios (5%, 7.5% and 10% by weight) of β-CD:Fe_3O_4@HA @Ag/PVP inclusion complex are shown in figure 3. The presence of both Fe_3O_4 ((220), (311)) (JCPDS No.75-0033)) and Ag (111) (JCPDS No.87-0720) was observed in samples which contained 7.5wt% and 10wt% Fe_3O_4@HA@Ag [2,25]. In the 5wt% β-CD:Fe_3O_4@HA@Ag/PVP nanoweb sample, a peak of Fe_3O_4 was observed, but the Ag peak was weak since the amount of Ag was relatively low as compared to others.

TGA results

Thermograms of TG analysis of β-CD:Fe_3O_4@HA @Ag magnetic nanowebs are shown in figure 4. The 10% weight loss observed in the range of 25–200 °C was associated with the removal of water vapour and volatiles of the H_2O absorbed by the starting materials and solvents used in solution preparation, such as DMF, and ethanol. Weight losses between 200 and 400°C refer to the decomposition of metallic precursors and degradation of beta-cyclodextrin. It was seen that the degradation of PVP started at an onset temperature of 400°C and ended at an offset temperature of ~500°C. When the TGA thermograms of β-CD:Fe_3O_4@HA@Ag/PVP nanowebs are examined, it is seen that there is a weight loss compatible with the amount of β-CD:Fe_3O_4@HA@Ag.
Examining the total weight losses at 600°C, it was seen that the amount of β-CD:Fe_3O_4@HA@Ag in the structure and the weight loss exhibited an inversely proportional attitude as expected.

CONCLUSION

In this study, humic acid recovered from the waste was used instead of the chitosan used in the previous study, and a homogeneous distribution in the PVP matrix was achieved by preparing an inclusion complex with β-CD. Nanowebs, containing 5%, 7.5% and 10% by weight β-CD: Fe_3O_4@HA@Ag inclusion complex into 10% PVP polymer solution, was produced by using the electrospinning method. Considering the SEM images and the fibre diameter measurements, the average fibre diameter of 5%, 7.5% and 10% β-CD:Fe_3O_4@HA@Ag inclusion complex containing nanowebs were found to be 612.5 nm, 610.8 nm and 431.2 nm, respectively, which revealed successful production of nanowebs. Fe-O bonds were visible in the FTIR results of nanowebs containing the inclusion complex at different weight ratios, and the peaks displayed in the XRD patterns supported the FTIR results. In all three samples, both Fe_3O_4 and Ag were seen according to the XRD result, and the intensity of the respective peaks differed only by the amount of β-CD:Fe_3O_4@HA@Ag (5%, 7.5% and 10%). Therefore, in nanowebs containing 5% β-CD:Fe_3O_4@HA@Ag, the peak associated with Ag, belonging to the (111) crystal plane, was found to be quite weak. In TGA thermograms, it was seen that the use of inclusion complex in the β-CD structure increased the degradation temperature and revealed a stable structure.
In the study, the inclusion of the structure in the form of an inclusion complex, which was added to the Fe_3O_4@HA@Ag structure and prepared with HA and β-CD obtained from the waste, increased the homogeneity and formed a stable structure. Although the antibacterial properties of the active substance

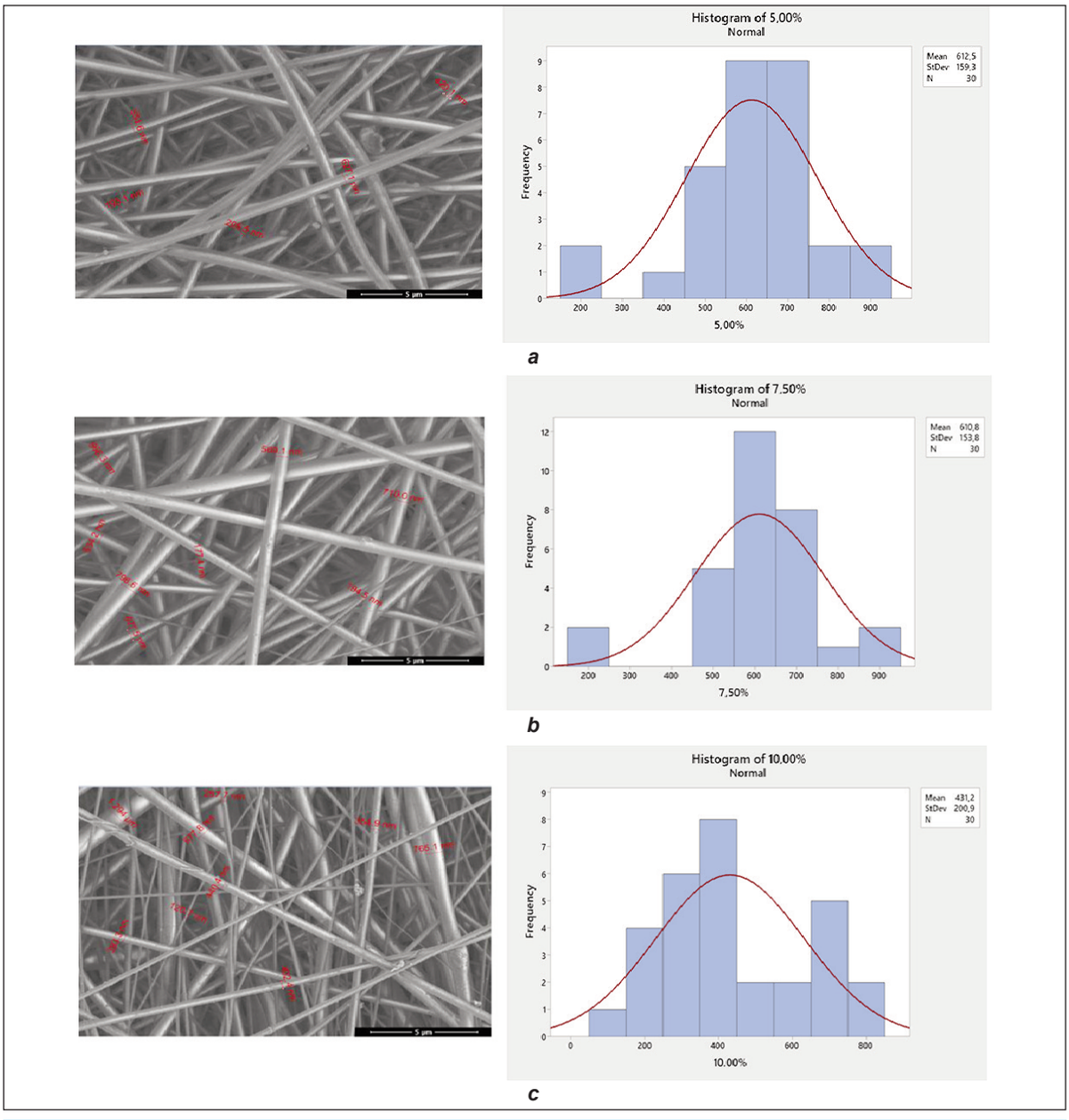

Fig. 2. SEM images and fibre diameter distribution of produced nanowebs: *a* – 5wt% β-CD:Fe_3O_4@HA@Ag/PVP; *b* – 7.5wt% β-CD:Fe_3O_4@HA@Ag/PVP nanoweb; *c* – 10wt% β-CD:Fe_3O_4@HA@Ag/PVP)

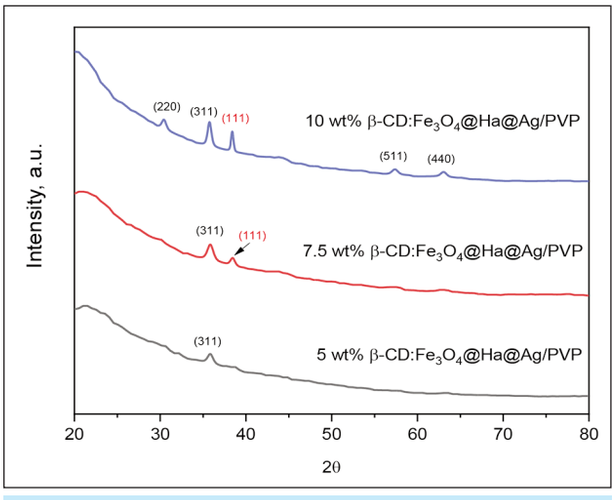

Fig. 3. X-Ray powder diffraction pattern of produced nanowebs

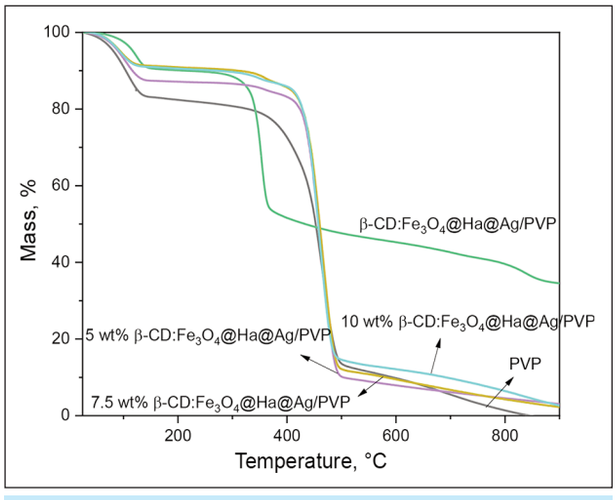

Fig. 4. TGA thermograms of produced nanowebs

Fe_3O_4@Ag were examined and positive results were obtained in previous studies [22, 23], to clarify the usability of the nano-surfaces produced in this study in the medical field, it was considered to perform antibacterial, cytotoxicity and histological tests in the future studies.

REFERENCES

[1] Atav, R., Yıldız, A., Vatansever Bayramol, D., Agirgan, A.Ö., *Inclusion Complexes of β-Cyclodextrine with Fe3O4@HA@Ag Part I: Preparation and Characterization*, In: Industria Textila, 2019, 70, 3, 255–258, https://doi.org/10.35530/IT.070.03.1548

[2] Amir, Md., Güner, A., Yıldız, A., Baykal, A., *Magneto-optical and catalytic properties of Fe_3O_4@HA@Ag magnetic nanocomposite,* In: Journal of Magnetism and Magnetic Materials, 2017, 421, 462–471

[3] Stevenson, F.J., Humus Chemistry: *Genesis, Composition, Reactions*, John Wiley & Sons., ISBN: 978-0-471-59474-1, 1994

[4] Basu, H., Saha, S., Mahadevan, I.A., Pimple, M.V., Singhal, R.K., *Humic acid coated cellulose derived from rice husk: a novel biosorbent for the removal of Ni and C*r, In: Journal of Water Process Engineering, 2019, 32, 100892, https://doi.org/10.1016/j. jwpe.2019.100892

[5] Bai, H., Wei, S., Jiang, Z., He, M., Ye, B., Liu, G., *Pb (II) bioavailability to algae (chlorella pyrenoidosa) in relation to its complexation with humic acids of different molecular weight*, In: Ecotoxicology and Environmental Safety, 2019, 167, 1–9

[6] Klucakova, M., Kalina, M., Smilek, J., Lastuvkova, M., *The transport of metal ions in hydrogels containing humic acids as active complexation agent*, In: Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2018, 557, 116–122

[7] Wang, J., Tian, H., Ji, Y., *Adsorption behavior and mechanism of humic acid on aminated magnetic nanoadsorbent*, In: Separation Science and Technology, 2015, 50, 9, 1285–1293

[8] Jin, X., Zheng, M., Sarkar, B., Naidu, R., Chen, Z., *Characterization of bentonite modi ed with humic acid for the removal of Cu(II) and 2,4-dichlorophenol from aqueous solution*, In: Applied Clay Science, 2016, 134, 2, 89–94

[9] Yang, T., Hodson, M.E., *Investigating the potential of synthetic humic-like acid to remove metal ions from contaminated water*, In: Science of The Total Environment, 2018, 635, 1036–1046

[10] Singhal, P., Jha, S.K., Pandey, S.P., Neogy, S., *Rapid extraction of uranium from sea water using Fe3O4 and humic acid coated Fe3O4 nanoparticles*, In: Journal of Hazardous Materials, 2017, 335, 152–161

[11] Basu, H., Saha, S., Pimple, M.V., Singhal, R.K., *Novel hybrid material humic acid impregnated magnetic chitosan nano particles for decontamination of uranium from aquatic environment*, In: Journal of Environmental Chemical Engineering, 2019, 7, 3, 103110

[12] Zhang, W., Luo, J., Huang, Y., Zhang, C., Du, L., Guo, J., Wu, J., Zhang, X., Zhu, J., Zhang, G., *Synthesis of a novel dispersant with topological structure by using humic acid as raw material and its application in coal water slurry preparation*, In: Fuel, 2020, 262, 116576

[13] Su, X., Hu, J., Zhang, J., Liu, H., Yan, C., Xu, J., Ma, Y., Song, J., *Investigating the adsorption behavior and mechanisms of insoluble Humic acid/starch composite microspheres for metal ions from water*, In: Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2021, 641, 125672

[14] Rai, M., Yadav, A., Gade, A., *Silver Nanoparticles as a new generation of antimicrobials*, In: Biotechnology Advances, 2009, 27, 1, 76–83

[15] Liu, X., Xu, Y., Wu, Z., Chen, H., *Poly(N-vinylpyrrolidone)-Modified surfaces for biomedical applications*, In: Macromolecular Bioscience, 2013, 13, 147–154

[16] Koczkur, K.M., Mourdikoudis, S., Polavarapu, L., Skrabalak, S.E., *Polyvinylpyrrolidone (PVP) in nanoparticle synthesis*, In: Dalton Transactions, 2015, 44, 17883–17905

[17] Teodorescu, M., Bercea, M., *Poly(vinylpyrrolidone) A Versatile Polymer for Biomedical and Beyond Medical Applications*, In: Polymer-Plastics Technology and Engineering, 2015, 54, 9, 923–943

[18] Kurakula, M., Koteswara, *R.G.S.N., Moving polyvinyl pyrrolidone electrospun nanofibers and bioprinted scaffolds toward multidisciplinary biomedical applications*, In: European Polymer Journal, 2020, 136, 109919, https://doi.org/10.1016/j.eurpolymj.2020.109919

[19] Sridhar, R., Lakshminarayanan, R., Madhaiyan, K., Barathi, V.A., Lim, K.H.C., Ramakrishna, S., *Electrosprayed nanoparticles and electrospun nanofibers based on natural materials: Applications in tissue regeneration, drug delivery and pharmaceuticals*, In: Chemical Society Reviews, 2015, 44, 3, 790–814

[20] Wang, C., Wang, J., Zeng, L., Qiao, Z., Liu, X., Liu, H., Zhang, J., Ding, J., *Fabrication of electrospun polymer nanofibers with diverse morphologies*, In: Molecules, 2019, 24, 5, 834

[21] Shahriar, S.M.S., Mondal, J., Hasan, M.N., Revuri, V., Lee, D.Y., Lee, Y.K., *Electrospinning nanofibers for therapeutics delivery*, In: Nanomaterials, 2019, 9, 4, 532

[22] Demir, C., *Fe3O4@HA@Ag Sentezi, Yapısının İncelenmesi ve Tekstilde Kullanımı*, Tekirdağ Namık Kemal Üniversitesi Fen Bilimleri Enstitüsü Tekstil Mühendisliği Anabilim Dalı, Master Thesis, Tekirdağ, 2018

[23] Yildiz, A., Vatansever Bayramol, D., Atav, R., Agirgan, A.Ö., Aydin Kurç, M., Ergünay, U., Mayer, C., Hadimani, R.L., *Synthesis and characterization of Fe3O4@Cs@Ag nanocomposite and its use in the production of magnetic and antibacterial nanofibrous membranes*, In: Applied Surface Science, 2020, 521, 146332

[24] Sriyanti, I., Edikresnha, D., Rahma, A., Munir, M.M., Rachmawati, H., Khairurrijal, K., *Correlation between structures and antioxidant activities of polyvinylpyrrolidone/Garcinia mangostana L. extract composite nanofiber mats prepared using electrospinning*, In: Journal of Nanomaterials, 2017, 9687896

[25] Kurtan, U., Topkaya, R., Baykal, A., Toprak, M., *Temperature dependent magnetic properties of CoFe2O4/CTAB nanocomposite synthesized by sol–gel auto-combustion technique*, In: Ceramics International, 2013, 39, 6, 6551–6558

Authors:

RIZA ATAV[1], AHMET ÖZGÜR AĞIRGAN[1], AYLIN YILDIZ[1], DERMAN VATANSEVER BAYRAMOL[2], UĞUR ERGÜNAY[1]

[1]Namık Kemal University, Çorlu Engineering Faculty, Department of Textile Engineering, 59860, Tekirdağ, Türkiye

[2]Department of Metallurgical and Materials Engineering, Alanya Alaaddin Keykubat University, Alanya-Antalya, Türkiye

Corresponding author:

AYLIN YILDIZ
e-mail: ayildiz@nku.edu.tr